
Organic Redox Materials for High Performance Lithium Batteries

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Thesis submitted in fulfillment of
the degree of Doctor of Sciences

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À mes grand-mères et mes parents...

"*Exactly!*" said Deep Thought.
"So once you do know what the
question actually is, you'll
know what the answer means."

*The Hitchhiker's Guide to the
Galaxy, Douglas Adams*

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¹On m'a prétendu qu'en vérité les moules ont des dents, mais je n'ai pas trouvé de référence sur le sujet.

tourné vers l'avenir quand je pense à ceux qui étaient mes colocataires de Mont-Saint-Guibert et qui sont devenus des amis sincères. Malgré le master à Louvain-la-Neuve, je nourrissais encore des aprioris sur les gens du BW au début de mon doctorat. Si mon avis est entériné à propos de ceux qui portent des pantalons chino couleur menthe à l'eau ou framboise (peut-être chuper chympas mais difficilement fréquentables), il faut leur laisser qu'ils ont de très bonnes raisons pour se tirer à Knokke. A ce sujet, je suis reconnaissant envers cette sympathique bande d'ex-colocs et ceux qui gravitent autour d'avoir fait de moi un Belge plus accompli. En effet, il n'est jamais trop tard pour apprendre à déguster son premier moules-frites. Nul doute que cela continuera à m'aider à me fondre dans la masse.

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Prenez un mot, prenez-en deux, qu'il vous faut lier sans œufs. Prenez un grand bout de sens et une pointe de confidences. Faites chauffer à petit feu. Sur le petit feu chimique, façonnez le produit physique. Afin que tout se dévoile, servez et puis mettez les voiles. Mais où voulez-vous en venir ? A vous qui venez de me lire, à vous remercier. Vraiment ! A vous remercier !

ABSTRACT

The ever-growing global economy implies a steadily increasing demand for more portable energy sources, currently relying mostly on Li-ion technology. In this context, the market is continuously asking for improved performances from Li-ion batteries (LIBs). Furthermore, not only the consumer needs are driving the research toward higher standards but also the global energy demand growth, evermore pressing the need of a cleaner and more sustainable energy supply chain. Yet LIBs are well-optimized devices and going beyond what is the current state-of-the-art in the battery field entails to explore new materials and components. The quest for better batteries has shed light on materials and technologies promising improved levels of sustainability, cost-effectiveness, power density and/or energy density. In that respect, significant efforts are devoted to new organic positive electrode materials that could supersede their inorganic counterparts at all levels mentioned beforehand.

The goal of this thesis is to develop new concepts to allow a successful implementation of redox organics as positive electrode materials without any trade-off over their current inorganic counterparts. To that end, we explored different strategies based on: (i) the design of hybrid materials with near-ideal dispersion properties thanks to the covalent grafting of our nitroxide-bearing polymers on conductive carbon nanotubes, (ii) the design of a cross-hybrid structure merging the conducting properties of polyaniline with the high specific capacity of quinone redox moieties, (iii) the modulation of electrode potentials driven by changes of electrolyte composition to increase the battery voltage output.

FOREWORD

This manuscript constitutes the accomplishment of several years of research and takes the form of a dissertation that aims at rationalizing the author's thoughts and findings regarding his doctoral project. By doing so, the present work supports his candidature for the academic degree of Doctor of Sciences.

For those purposes, this original contribution has been divided into six parts, each of them structured into chapters. The structure of these parts is the following:

1. *Introductory background*, providing the context and reviewing the current research art. Intrinsically, the research project is multidisciplinary and hence might attract the attention of scientists from diverse respective fields such as polymer sciences, electrochemistry, material chemistry etc. According to his personal background, each reader may be interested to go through one or more of the three chapters of this part.

2. *Objectives and strategy*, setting the goals and methodology as well as explaining the novelty of the present research work. In so doing, this part provides a road-map for the research project and justifies the analysis and development efforts.

3. *Results and discussion*, constituting the substance of the research project. This part is shedding light on data collected throughout the developments efforts and critically discuss the related findings.

4. *Concluding remarks*, summarizing and completing the dissertation. This part is highlighting the breakthroughs and provide a scope for future works. In that extent, this part presents the author's opinion on directions to follow toward more advanced developments but also on potential impacts resulting from this thesis work.

In addition to the heart of the matter of this thesis work unveiled beforehand, two appendices are also provided. These appendices are featuring discussions dedicated to readers willing to get a broader knowledge on materials and electrochemical techniques that are closely related to the main research topics.

5. *Appendix A*, featuring a discussion on the use of supramolecular interactions to prepare organic redox hybrid materials. These materials have been developed by the Laboratory of Polymeric and Composite Materials (LPCM, UMONS) with the author's contribution focusing mostly on electrochemical characterization and their implementation. This appendix details the aims, strategies and result discussions on nitroxide-bearing (co)polymers designed to display non-covalent interactions with carbon nanotubes. In that respect, such designs could be regarded as competing with the materials that we developed via covalent approaches for the purpose of the thesis work. A comparison between these non-covalent approaches and their covalent counterparts is then featured at the end of the appendix.

6. *Appendix B*, hosting a review on electrochemical cell configurations, testing methods, and characterization techniques. The concepts described in this part are frequently encountered in our experimental developments and were commonly implemented for evaluations of materials, components and systems throughout the research work.

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LIST OF SYMBOLS

C_P	practical capacity
C_T	theoretical capacity
D_{OX}	degree of oxidation
E	electric potential
E°	electric potential in standard conditions
$E_{1/2}$	half-wave potential
E_{eq}	equilibrium potential
F	Faraday constant
K	equilibrium constant
M_n	average molar mass in number
M_w	average molar mass in weight
P	power
Q	gravimetric capacity
R	resistance
R	universal gas constant
V	voltage
W_{max}	maximum possible work that can be extracted
W_{rev}	reversible work
ΔG	Gibbs free energy
ΔG°	Gibbs free energy in standard conditions
δ	chemical shift
η	overpotential

γ	lithium ion occupancy
λ_{max}	maximum of absorbance
ν	wavenumber
a	activity coefficient
i	net current
k	rate constant
n	number of moles
q	electrical charge in coulomb
v	reaction rate
$\bar{D}$	dispersity
C	rate of charge or discharge
Ox	oxidizing agent
Red	reducing agent

LIST OF ACRONYMS

^1H -NMR	proton nuclear magnetic resonance
^{13}C -NMR	carbon nuclear magnetic resonance
AE	adsorption energy
AGET	activator generated by electron transfer
ATR	attenuated total reflectance
ATRP	atom transfer radical polymerization
AzPMA	3-azidopropyl methacrylate
Bipy	2,2'-bipyridine
BMA	butyl methacrylate
BMPBTS	(trichlorosilyl)butyl 2-bromo-2-methylpropanate
BMS	battery management system
BnBiB	benzyl 2-bromoisobutyrate
BP	biphenyl
BQ	1,4-benzoquinone
C_{60}	buckminsterfullerene
CCV	closed circuit voltage
CDF	cylindrical distribution function
CE	counter-electrode
CEI	cathode electrolyte interphase
CMC	carboxymethyl cellulose
CNT	carbon nanotube
CRP	controlled radical polymerization

CTA	chain transfer agent
CuAAC	2-hydroxyethyl bromosisobutyrate
CV	cyclic voltammetry
DABQ	2,5-diamino-1,4-benzoquinone
DAE	density of adsorption energy
DCM	CH ₂ Cl ₂
DEC	diethyl carbonate
DFT	density functional theory
DMC	dimethyl carbonate
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DOSY	diffusion-ordered spectroscopy
DP	degree of polymerization
dppp	1,3-bis(diphenylphosphino)propane
EBiB	ethyl- α -bromoisobutyrate
EC	ethylene carbonate
EDLC	electrical double layer capacitor
EDTA	ethylenediaminetetraacetic acid disodium salt dihydrate
EMC	ethyl methyl carbonate
emf	electromotive force
EmIm ⁺	1-ethyl-3-methylimidazolium
ESI	electrospray ionization
EV	electric vehicle
Fc	ferrocene
FRP	free radical polymerization
FT-IR	Fourier transform infrared
GPE	gel polymer electrolyte
GTP	group-transfer polymerization
HEBB	2-hydroxyethyl bromosisobutyrate
HFP	hexafluoropropylene
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
HOMO	highest occupied molecular orbital
Ini	initiator
IPA	isopropanol
KCTP	Kumada catalyst-transfer polycondensation

LCO	LiCoO ₂
LFP	LiFePO ₄
LIB	lithium-ion battery
LiBOB	LiB(C ₂ O ₄) ₂
LiFSI	Li(FSO ₂) ₂
LiTFSI	Li(CF ₃ SO ₂)N
LMO	LiMn ₂ O ₄
LTO	Li ₄ Ti ₅ 12
LUMO	lowest unoccupied molecular orbital
MALDI-ToF	matrix assisted laser desorption ionization - time of flight
MCMB	mesophase carbon microbeads
mCPBA	3-chloroperoxybenzoic acid
MD	molecular dynamic
Me ₆ TREN	tris(2-dimethylaminoethyl)-amine
MS	mass spectroscopy
MWCNT	multi-walled carbon nanotube
NCA	lithium nickel cobalt aluminum oxide
NCM	lithium nickel cobalt manganese oxide
NiMH	nickel-metal hydride
NMP	<i>N</i> -methyl-2-pyrrolidone
NMP	nitroxide-mediated polymerization
OCP	open circuit potential
OCV	open circuit voltage
ORB	organic radical battery
P3HT	poly(3-hexylthiophene)
PANi	polyaniline
PC	propylene carbonate
PCM	protective circuit module
PDHA	poly(2,5-dihydroxyaniline)
PDMA	poly(2,5-dimethoxyaniline)
PE	polyethylene
PEO	poly(ethylene oxide)
PMDETA	<i>N,N,N',N'',N'''</i> -pentamethyldiethylenetriamine
PMMA	poly(methyl methacrylate)
PP	polypropylene

PPy	polypyrrole
PS	polystyrene
PTC	positive temperature coefficient
PTFE	poly(tetrafluoroethylene)
PTh	polythiophene
PTMA	poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate)
PTVE	poly(2,2,6,6-tetramethylpiperidine- <i>N</i> -oxyl-4-vinyl ether)
PVDF	polyvinylidene fluoride
Pyr	pyrene
Pyr ₁₄ ⁺	1-butyl-1-methylpyrrolidinium
PyrM	pyrene methyl methacrylate
RAFT	reversible addition-fragmentation chain-transfer polymerization
RE	reference electrode
rGO	reduced graphene oxide
RRS	reference redox system
RTIL	room temperature ionic liquid
SARA	supplemental activation reducing agent
SBR	styrene-butadiene rubber
SEC	steric exclusion chromatography
SEI	solid electrolyte interphase
SEM	scanning electron microscopy
SET-LRP	single electron transfer-living radical polymerization
SHE	standard hydrogen electrode
SI-ATRP	surface-initiated ATRP
SI-CRP	surface-initiated CRP
SOC	state of charge
SPE	solid polymer electrolyte
SS	stainless steel
SWCNT	single-walled carbon nanotubes
TBAF	tetrabutylammonium fluoride
TBP	tributyl phosphate
TBTA	tris(benzyltriazolylmethyl)amine
TEM	transmission electron microscopy

TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TEMPO- <i>t</i> Bu	2,2,6,6-tetramethyl-piperidineoxy <i>tert</i> -butyrate
TEP	triethyl phosphate
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMP	trimethyl phosphate
TMPM	2,2,6,6-tetramethylpiperidine methacrylate
TMPO _x	trimethylphosphine oxide
TMThP	trimethyl thiophosphate
VC	vinylene carbonate
WE	working electrode
XPS	X-ray photoelectron spectroscopy

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Part I

Introductory background

CHAPTER 1

BATTERY CHARACTERISTICS, COMPONENTS AND ELECTROCHEMICAL TESTING METHODS

Abstract

The purpose of the present chapter is to unveil the working principles, materials, metrics, performance factors, evaluation methods, and manufacturing processes of batteries. The focus is set in particular on lithium-ion batteries (LIBs) which are considered as the current state-of-the-art. Thanks to their wide market penetration, various designs and solutions have been explored with the aim at gaining competitive advantages. Since their first appearance almost three decades ago, the journey has pushed the boundaries as physics, engineering and chemistry have contributed to increase our knowledge on this topic that stirred an ever-increasing community of researchers. The perspective depicted in this first introduction chapter will mostly focus on the chemical aspects, in particular those related to electrochemistry, as this will be of particular relevance for the understanding of the result part disclosed afterwards.

1.1 General context

The world population and its demand for new and advanced technologies is still steadily increasing. Coupled to that, the release of carbon dioxide and other greenhouse gases induced by human activity are responsible for climate change and acidification of the oceans. Left uncontrolled the growth of greenhouse gases emissions could lead to a global temperature average increase of up to 4°C by the year 2100.^[1]

The transition from fossil energies to renewable and cleaner sources is evermore a point of attention and is most likely one of the main challenges of our third millennium. Although abundant and even in excess energy can be harvested from natural sources such as solar radiation and wind, their practical use is still hindered as they only deliver energy in an intermittent fashion. Storage systems are a necessary solution to decouple production *vs.* consumption patterns, smoothing out the variations and deliver energy when needed.^[2] Here step in Li-ion batteries (LIB), for instance, to improve the quality of the energy supply chain from the renewable sources to the final applications.^[3]

LIBs have already a widespread use in portable electronic devices of our everyday life but have also the potential to go beyond this current field of applications. Compared to other rechargeable batteries, LIBs proved their versatility with respect to possible applications, both in terms of power and autonomy requirements,^[3] but they also display long-life capability and have improved significantly their cost-performance effectiveness over the years. Therefore, the attractiveness of LIB technology is explaining why it is currently piercing the field of transportation and finding its way in small to medium grid applications.

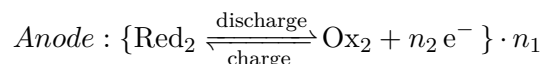
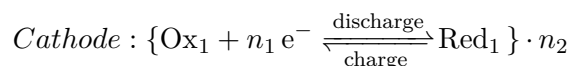
1.2 Definitions and characteristics

1.2.1 Working principle

Batteries are devices coupling electrochemical reactions and converting the chemical energy thereof into readily usable electrical energy at the terminals.^[4] The simplest unit of a battery is the electrochemical cell. Batteries can be typically constituted of several units connected

electrically either in series or in parallel. The cell is typically comprising two electrodes, usually composed of materials of different chemical nature (Figure 1.1). The electromotive force is obtained thanks to the electrochemical potential difference between the two electrodes which serves as a driving force for the redox reactions happening at the electrode level during the discharge of the cell.

The net discharge reaction taking place in an electrochemical cell is the result of coupling two electrochemical reactions, a reduction and an oxidation, happening at the positive electrode (cathode) and the negative electrode (anode), respectively. During the process, an oxidizing agent (Ox_1) gains electrons to generate a reduced species (Red_1) at the cathode, while at the anode a reducing agent (Red_2) loses electrons to generate an oxidized species (Ox_2).



The discharge process is therefore the spontaneous process happening when the electrodes are connected through the external electrical circuit. The consequence is the generation of an electrical current that can be used to power external devices. The capacity of the system is determined by the electrode materials and the amount of ions that they can store.

To close the loop composed by the electrodes and the external circuit, an ionic conductor, namely the electrolyte, has the purpose of maintaining charge neutrality; as electrons are extracted from the anode to enter the cathode during the discharge process, the charge balance needs to be compensated with ions from the electrolyte drawn to the electrodes. Additionally a separator is often found between the electrodes so that electrodes are physically isolated to prevent short-circuits. When the cell is fully discharged, an electrochemical equilibrium is reached, and the charge neutrality is ensured by the electrolyte.

As opposed to primary batteries which are used once and disposed, a cell that can be charged and discharged multiple times is called a secondary or rechargeable battery. In a secondary battery, the whole

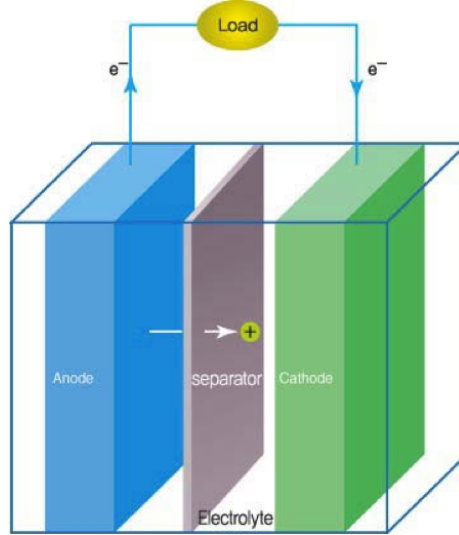


Figure 1.1 – Schematic representation of an electrochemical cell under discharge. ^[4]

discharge process can be reversed under certain conditions by applying a suitable voltage at the terminals. This external driving force charges the batteries as current is applied in the opposite direction of the discharge process. During the charge process, the positive electrode is being oxidized and hence acts now as a cathode, while the negative electrode is being reduced and acts as an anode. However, in the field of batteries, these conventions are often not applied and the names remain the same.

1.2.2 Electrochemical reactions and electric potential

Considering the electrochemical reaction, $pA + qB \rightleftharpoons rC + sD$, one can express the Gibbs free energy (ΔG ; $\text{kJ}\cdot\text{mol}^{-1}$) relationship with respect to its value in the standard conditions (ΔG^0) and the activity coefficients a as follows:

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^r a_D^s}{a_A^p a_B^q}$$

The maximum possible electric energy that can be recovered from the system (W_{max}) is the reversible work (W_{rev}) that would be obtained

at equilibrium state, which can be expressed as,

$$W_{rev} = W_{max} = -\Delta G$$

Furthermore, as the electric energy is related to the charge (q ; expressed in coulomb, C) and the electric potential (E ; volts, V) as follows,

$$-W_{max} = qE$$

This expression can be rearranged as, with n being the number of moles of electrons exchanged by the reaction and F being the Faraday constant (96,485 C·mol⁻¹),

$$-W_{max} = -nFE = \Delta G$$

This later equation leads also to the following expression in the standard conditions (1 bar, 273.15 K),

$$\Delta G^\circ = -nFE^\circ$$

Therefore comes the Nernst equation, which correlates the difference in electric potential with the concentrations of the reactants and products involved in an electrochemical reaction,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^r a_D^s}{a_A^p a_B^q}$$

1.2.3 Electrical characteristics and performance factors

1.2.3.1 Voltage

The electric potential difference, or electromotive force (emf, E , volts), is the driving force of the electrochemical reaction. When it is expressed in standard conditions (1 bar, 273.15 K, 1 M) under equilibrium conditions, it sets the standard electric potential. The electric standard potential can be correlated to the standard potential of each electrode,

$$\Delta E_{reaction}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$

Or in non-standard conditions,

$$\Delta E_{reaction} = E_{cathode} - E_{anode}$$

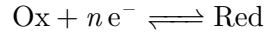
In a galvanic cell, as it is the case for a LIB during discharge, the reaction is spontaneous and the electric potential is positive. When the reaction is non-spontaneous, an external driving force is required and the electric potential is negative.

Regarding the equilibrium conditions, they define the maximum electric energy according to thermodynamics. In these conditions, there is no current flow per definition. The voltage is then obtained without electrical load. This is setting the definition of the open circuit voltage (OCV) or open circuit potential (OCP). Measuring OCP can provide information on the voltage of electrode materials, the occurrence of internal short-circuits, and initial interfacial reactions.^[4]

The definition of closed circuit voltage (CCV) is opposed to the definition of OCV. When current is flowing spontaneously, the system is connected to an external circuit. The system is then evolving outside of thermodynamic equilibrium conditions, and several phenomena contribute to decrease the operating voltage. Conversely, during the charge process, the operating voltage is higher than the OCV, accounting for the same phenomena as for the discharge process, which are defined as polarization, which is discussed in further details later at the end of this section.

1.2.3.2 Current

Current is defined as the flow of electric charges. Considering the case of an electrochemical process happening at an electrode, it can be defined by the following set of equations,



$$v_f = k_f C_{Ox}(x, t) = \frac{i_c}{nFA}$$

$$v_b = k_b C_{Red}(x, t) = \frac{i_a}{nFA}$$

Where v_f and v_b are the rates of forward and backward reactions, respectively, while k_f and k_b are the respective rate constants. $C_{Ox}(x, t)$ and $C_{Red}(x, t)$ denote the concentrations of the electrochemical species at a distance x of the electrode at a certain time t . Regarding currents i_c and i_a , they are related to the electrochemical process considered. In the present case, i_c and i_a are referring to the reduction process and the oxidation process, respectively (regardless if it is a cathode or an anode). Lastly, A is the electrode surface area.

Based on the equations developed beforehand, one can obtain the net reaction (v_{net}) rate as a function of the net current (i),

$$v_{net} = v_f - v_b = \frac{i}{nFA}$$

When forward and backward reaction rates are equal, both the net current and the net reaction rate are equal to zero. Consequently, the system is at equilibrium.

1.2.3.3 Capacity

The capacity is the total amount of charge that a cell can deliver when discharged from a full-charge state to the cut-off voltage (minimum allowed potential). The theoretical capacity (C_T) is defined by the total amount of active material and can be defined per the following equation,

$$C_T = xF$$

Where x is the number of moles of electrons.

A practical and more realistic capacity (C_P) is also defined. This practical capacity is always inferior to C_T because full material utilization is never achieved. This may be due to side-reactions but also to polarization of the system. As polarization is scaling up with the rate of charge or discharge process, C_P will be most affected at higher rates.

For this reason, C_P is usually defined by manufacturers with reference to a discharge rate. The battery capacity can also be expressed in terms

of charge/discharge current,

$$h = \frac{C_P}{i}$$

In this equation, the current (i) drawn from the charge or discharge process is defined in ampere (A) and h is the time (hours) required to reach the cut-off voltage. The capacity is then defined in Ah (1 Ah = 3600 C).

The capacity can be expressed using gravimetric capacity ($\text{Ah}\cdot\text{kg}^{-1}$, $\text{mAh}\cdot\text{g}^{-1}$) or volumetric capacity ($\text{Ah}\cdot\text{L}^{-1}$, $\text{mAh}\cdot\text{cm}^{-3}$). The theoretical gravimetric capacity Q ($\text{mAh}\cdot\text{g}^{-1}$) is calculated as per the following equation, where M ($\text{kg}\cdot\text{mol}^{-1}$) is the molar mass of the active material,

$$Q = \frac{nF}{3600M}$$

Manufacturers are often specifying the nominal or rated capacity, which is the practical capacity that can be reached upon full discharge under properly defined conditions such as initial voltage, cut-off voltage, current, temperature, cycle number, etc.

1.2.3.4 C-rate

The C-rate is a common way of expressing the rate at which a cell or electrode is discharged (or charged).^[5] This concept is often defined by the manufacturers as the value of current with respect to the value of its nominal or theoretical capacity.¹ Considering a battery rated at 1 Ah, a current of 1 A will discharge (or charge) the battery within one hour and this current would be expressed as 1C rate, while the same battery at 5C rate, full discharge (or charge) will be achieved in 5 hours at 0.2 A.

¹For consistency, all values presented in this manuscript are considered with respect to the theoretical capacity of the active material.

1.2.3.5 Cycle life

Cycle life is the number of charge – discharge cycles that a battery can achieve under operation over its whole lifetime. This is typically related to the structural and chemical stability of the system, in particular with respect to the electrode materials.

Irreversible capacity is the amount of electrical charges lost during the charge – discharge process. In the first cycles of the battery life, an irreversible capacity loss is usually observed and is notably related to new layer formation at the electrolyte – electrode interphase. In the case of traditional secondary LIBs, this phenomenon must be controlled to provide a passivation layer at the anode, the so-called solid electrolyte interphase (SEI), which is tightly related to successful application of the electrochemical processes within this class of systems.

The irreversible capacity loss can be accounted via the coulombic efficiency, which is defined as the efficiency ratio (%) of the amount of electrons that are extracted over the amount that have entered the system.

To cumulate the effect of coulombic efficiency over the cycles, the capacity retention can be defined. Starting from the first cycle with a certain capacity C_1 and the remaining capacity C_n , the capacity retention is expressed as C_n/C_1 (%).

Manufacturers are often benchmarking batteries based on the cycle index which lays at 50% or 80% of the nominal value. Yet, the cycle life remains dependent on other performance specifications, such as power and energy density, which have consequences on the magnitude of degradation mechanisms. In portable electronics applications the cycle life requirements are often around a thousand of cycles, but up to 3000 cycles can be requested for typical high-energy applications such as electric vehicles (EVs).^[6]

1.2.3.6 Energy

The energy of a cell can be derived from the discharge current (i_{dis}) over a certain period of time (Δt) with a certain output voltage ($V(t)$). Using the definition of current, $i_{dis} = dq/dt$, one can express the energy

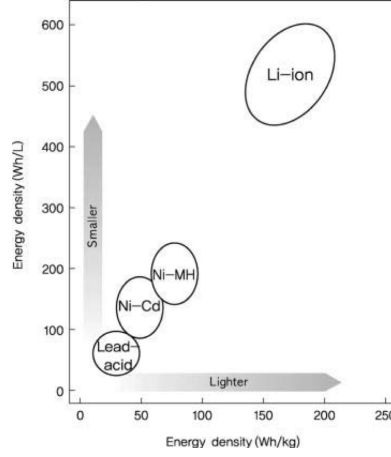


Figure 1.2 – Comparison of different battery technologies in terms of volumetric and gravimetric energy density. ^[4]

of a system as follows, ^[7]

$$Energy = \int_0^{\Delta t} i_{dis} V(t) dt = \int_0^Q V(q) dq$$

Consequently, of two active materials with same capacity, the one displaying the higher voltage can deliver more energy.

Based on this definition, the energy density is one of the key performance factors of batteries. It can be expressed as the amount of energy per unit mass or volume, with respective units such as $\text{Wh}\cdot\text{kg}^{-1}$ and $\text{Wh}\cdot\text{L}^{-1}$. Plotting the energy density per unit volume *vs.* unit mass highlights the capability of different technologies for compact or lightweight designs (Figure 1.2).

1.2.3.7 Power

Power (P) is the energy that can be delivered per unit time, or in other words is a measure of the current flowing (i) at a certain electric potential (E) which can be expressed as follows,

$$P = i.E$$

Similarly to battery capacity and energy, a specific power can be

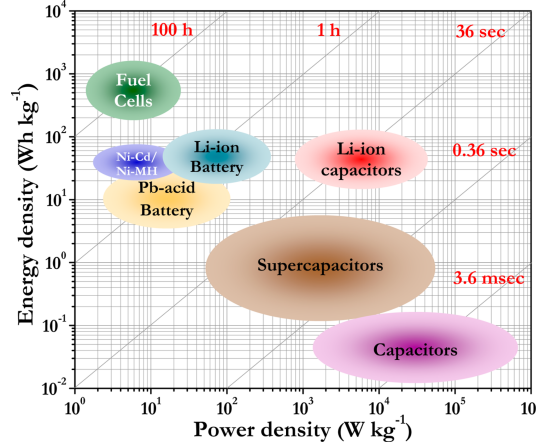


Figure 1.3 – Ragone plot of different electrochemical storage technologies.^[9]

defined as the power per unit mass or volume, respectively in $\text{W}\cdot\text{kg}^{-1}$ and $\text{W}\cdot\text{L}^{-1}$ for instance. A chart frequently encountered in the literature is the Ragone plot.^[8] Such kind of plot represents the energy density *vs.* the power density, both in log scales. This allows comparing different electrochemical technologies (Figure 1.3). The comparison is not only provided in terms of specific power or energy, but also in terms of typical time-scale for the discharge process. This is made possible by drawing iso curves (constant delivery time) with unity slope.

1.2.3.8 Polarization

Polarization is related to the loss of energy due to voltage difference with respect to the equilibrium potential.^[5] For a spontaneous process to be happening at a finite rate, it is observed as a lack of voltage at the cell terminals. On the other hand, in the case of a non-spontaneous process, an excess of voltage is required.

This observed phenomenon is referred as overpotential (η), and is characterizing the polarization. The relationship between actual potential (E) and equilibrium potential (E_{eq}) can be expressed as follows,

$$\eta = E - E_{eq}$$

The overpotential is affecting the rate capability of the cell and can be

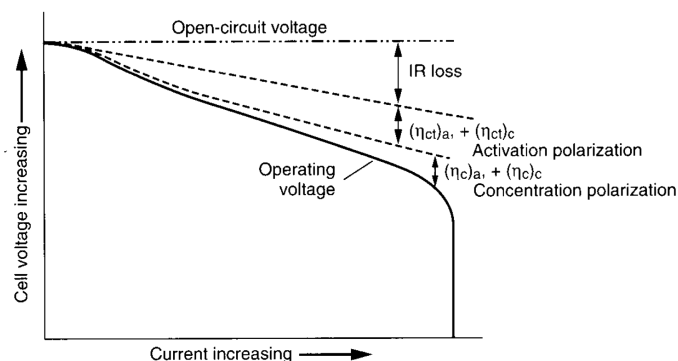


Figure 1.4 – Cell polarization as function of operating current. The scheme depicts the contributors to the overpotential, namely iR loss, activation polarization and concentration polarization. ^[5]

broken down into different contributions: ohmic polarization, activation polarization, and concentration polarization (Figure 1.4).

The ohmic polarization is due to the internal impedance (R) of the cell. It is referred as iR drop as it decreases the voltage proportionally to the drawn current under discharge (the opposite effect is observed during the charge process). The total impedance of the cell is the sum of ionic resistance of the electrolyte, as well as electronic resistances of active mass, current collectors and electrical tabs of both electrodes plus contact resistances at electrode – active mass interfaces. In usual applications of LIBs, iR drop is primarily associated with the electrolyte resistance (instead of resistance from electrode reactions).

The activation polarization is what drives the reaction within the electrode materials. Such polarization is intimately related to the characteristics of redox-active materials. These characteristics are determining the kinetics of electron transfer reactions which display a strong dependence with temperature.

Concentration polarization is originating from the concentration gradients of reactants at the active materials surface and in the bulk, and therefore is a result of mass transport limitations.

These polarization effects consume the useful energy and dissipate it as wasted heat. In practical applications, it is however difficult to determine the values of the respective contributors because of the complicated

physical structure of the electrodes.

1.3 Overview of battery technologies

1.3.1 Primary batteries

The first described cell was invented by Volta in 1800. It consists in a stack of two series of discs with different metal nature. Typically the stack was composed of copper (or silver) disc cathodes alternating with zinc disc anodes. These electrodes were separated by cloth or cardboard soaked in brine as electrolyte.

In 1865 the first widely used primary battery was developed by Leclanché. The Leclanché (or manganese) cell consists in a zinc anode and a manganese dioxide (MnO_2) cathode, in an acidic aqueous electrolyte containing ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2). This cell yields an emf of ca. 1.5 V and was later adapted as a dry cell (1.4 V), where the electrolyte is a paste with no free liquid, but yet containing enough liquid to reach useful conductivity. The Leclanché cells enabled to develop a wide variety of applications and were the forerunners of modern zinc-carbon dry cells.

Later, the acid electrolyte of the Leclanché cell was substituted by an alkaline one, which is then named the alkaline battery, with improved capacity and discharge performances.

Many other battery technologies have been developed since then such as zinc-air (1.4 V) and silver oxide (1.5 V). An important step was made in the 1970s with the commercialization of 3 V class primary batteries using lithium metal as anode, which stand apart from other batteries in their high energy density.

1.3.2 Secondary batteries

The earliest secondary battery is the lead-acid battery invented by Planté in 1859. The design, basically unchanged since then, involves a lead-peroxide anode, a lead cathode and sulfuric acid as electrolyte. With its 2 V per cell, it is still widely used nowadays as storage battery.^[4,5] Despite their low energy density, lead-acid batteries remained

attractive compared to newer technologies thanks to their low cost of ownership. In addition, their ability to deliver high instantaneous (surge) currents makes them attractive as storage batteries for automotive, to provide the high power required by the starter, but also as backup power supply.

In 1984, nickel-cadmium (NiCd, 1.2 V) stepped up in the market and became widely adopted, replacing primary batteries in small electric appliances. Due to the harmful effects on the environment related to cadmium extraction and recycling, this technology was superseded by the more eco-friendly and better performing nickel-metal hydride (NiMH, 1.2 V) in the early 1990s.^[4]

The early 1990s saw also the dawn of completely new generation of secondary batteries, owing more compact and lightweight designs, namely the 3 V LIBs. Their high energy density contributed tremendously to the emergence of portable electronics, a booming market that they dominated so far, with applications such as cell phones, laptops, camcorders etc.^[4]

1.4 Lithium-ion batteries

1.4.1 Historical developments of LIBs

For many years Sony and other companies have been trying to develop a secondary battery based on the lithium metal battery design already applied as a primary battery. Their efforts have been plagued with safety issues resulting in short-circuits that have the potential of dramatic consequences such as explosion of the device. Nonetheless, their work with lithium led to define process and material requirements which turned helpful to design Li-ion present systems.

While Sony was the first to manufacture a commercial LIB, numerous studies paved the way for this successful technology. Its working principle, was first reported by Armand and formalized in the late 1970s. In this seminal publication, two intercalations materials with different redox potentials are used as active components, and lithium ions are moving reversibly between the negative and positive electrodes.^[10] This back and forth movement of ions during charge and discharge is often referred

as the rocking-chair mechanism. A key concept in its implementation is the discovering in 1973 by Stanley Whittingham of intercalation electrode materials, such as titanium disulfide.^[11] This rocking-chair mechanism was then applied by Scrosati and Lazzari, combining electrodes of lithiated tungsten dioxide and titanium disulfide.^[12] The output voltage was still modest with respect to subsequent developments.

An important step was achieved by the Goodenough laboratory with the discovery that compounds from the family of NaFeO_2 -like structures are enabling intercalation – deintercalation of lithium ions at relatively high potentials.^[13] Many other structures based on Ni and Co but also Mn, Al, and Fe were found subsequently to hold the same capabilities. Later, the LiCoO_2 (LCO) patented material formed the active cathode component of Sony's LIB.

Finding suitable anode materials turned out to be a more complicated journey than for cathode materials. Despite early work demonstrating Li^+ intercalation capability from graphite and other carbonaceous materials,^[14,15] some challenges were hindering practical applications.

A major milestone was then reached by Yoshino and coworkers from Asahi Kasei (Japanese battery suppliers of separators and electrolytes) as they described in their patent the advantage of low temperature coke (intermediate crystallinity) over graphite.^[16] In this first patented generation of LIB almost all the major categories of components found in modern batteries are already disclosed: microporous polyolefin separator (such as polyethylene), carbonate-based lithium salt solution (such as LiPF_6 , LiBF_4 or LiClO_4 in propylene carbonate), binders (such as polymethylmethacrylate, polyvinylidene fluoride or various elastomers) etc. In this respect, Yoshino *et al.* are regarded as the inventors of the modern LIB.^[16] Recognizing their considerable contribution to the creation of a rechargeable world, the Nobel Prize in Chemistry 2019 was awarded together to three scientists who laid down the foundations of all current LIBs: S. Whittingham, J. Goodenough and A. Yoshino.

Retrospectively, the hopes for a more advanced technology than the nickel-based one was great as this later technology was suffering from many drawbacks, notably the memory effect,² their relatively limited

²It describes the situation in which NiCd batteries gradually lose their maximum capacity on shallow cycling, i.e. if they are repeatedly recharged after being only partially discharged. The battery appears to "remember" the smaller capacity.

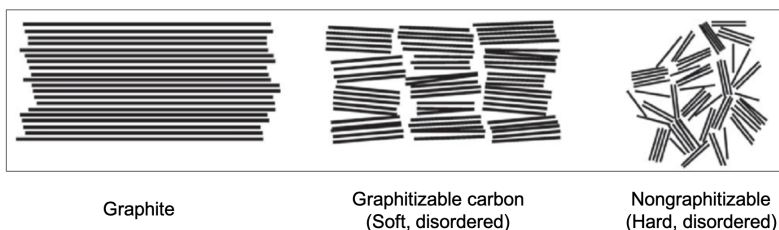


Figure 1.5 – Schematic representations of different carbon particle structures used in LIBs.^[18] Petroleum coke is an example of soft carbon found in the early LIBs. Later came nongraphitizable hard carbon, with its highly disordered structure allowing a smooth expansion upon lithiation. In modern LIBs, graphite is ubiquitous, and is found as both natural or synthetic graphite, with a noticeable example of the latter being mesophase carbon microbeads (MCMB).^[19]

energy density, poor charge retention and environmental concerns related to cadmium.^[5] Yet a few critical steps were still required for LIBs to become a truly successful commercial technology, outperforming the newly discovered NiMH batteries.

A major obstacle to overcome was to increase the anode energy density, for the coke of the first generation was known to hold only half of the theoretical capacity of graphite ($180 \text{ mAh}\cdot\text{g}^{-1}$ *vs.* $372 \text{ mAh}\cdot\text{g}^{-1}$).^[17]

Indeed higher crystallinity is desirable to promote higher capacities via favorable expansion during lithiation.^[18] This mechanism is disfavored in coke as its disordered structure tends to block the shifting of the stacking layer due to cross-linking. At the time, full capacity of carbon remained elusive as the surface of graphite is highly reactive and leads to solvent decomposition, a particularly problematic phenomenon when PC is adopted.^[17] Figure 1.5 displays different drawings of carbon structures typically found in LIB anodes.

Special preparation methods of hard carbon together with the implementation of new electrolyte formulations based on ethylene carbonate were key factors that contributed to raise the anode capacity close to the one of pure graphite.^[17] It is recognized that nongraphitizable carbon, called hard carbon, consists of small crystallites with several layers that are oriented randomly.^[18] In contrast to soft carbon (graphitizable) such as coke, hard carbon is called nongraphitizable to refer to the fact that it cannot be graphitized under heat treatment ($>2500^\circ\text{C}$).^[4] The highly disordered structure of hard carbon is favorable to lithiation

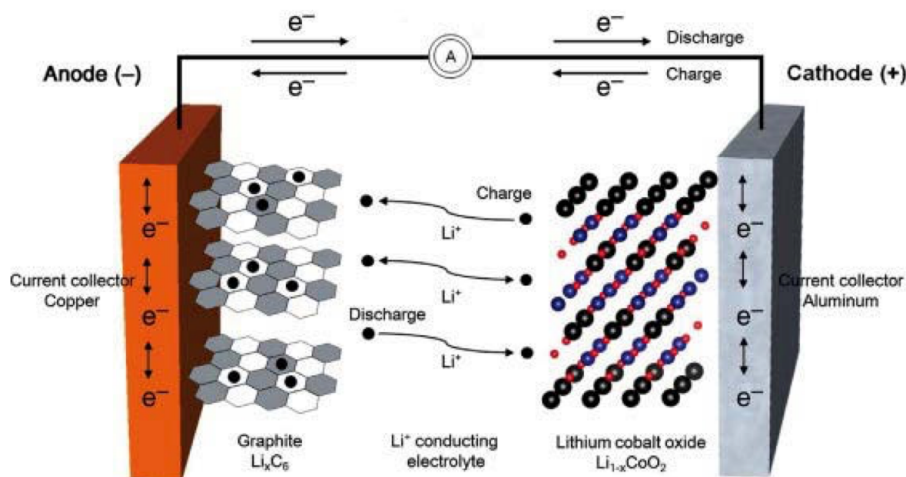


Figure 1.6 – Movement of Li^+ in an electrolyte and insertion/extraction of Li^+ within electrodes in a lithium-ion secondary battery. ^[4]

as it can be smoothly doped without expansion.^[18] Nevertheless, the fate of graphite carbon was not settled as carefully designed preparation methods afforded the now commonly used mesophase carbon microbeads (MCMB). MCMB is composed of nearly spherical particles – yielding the most favorable aspect ratio to minimize side-reactions with the electrolyte – with high degree of graphitization, thus delivering a still higher specific capacity.^[17]

1.4.2 Working principle and components of LIBs

In a secondary battery, over the repeated charge-discharge cycles, the materials should be kept stable during insertion / extraction of ions within the electrode structure. As lithium ions are extracted from one electrode to be inserted in the opposite one, the electrolyte of a LIB only serves as an ion transfer medium, allowing the shuttle mechanism. The back and forward movement repeated over the cycles led to its definition as rocking chair mechanism. This working principle as well as typical components of LIBs is illustrated in figure 1.6.

In LIBs, the electrons are traveling through the external circuit and collide with active material reactive centers undergoing redox reactions, while the ions traveling through the electrolyte are meeting the redox centers to achieve charge neutrality. Upon charging of the device, this

mechanism effectively uses the electrode materials as media to store electric energy. Therefore the types of ions and materials are the main components that determine the specific energy of the system.

Lithium is the lightest of all metals and has one of the lowest reduction potential ($-3\text{ V vs. H}_2/\text{H}^+$ in standard conditions, standard hydrogen electrode, SHE), which are very desirable properties to achieve high energy densities using lithium-based anode materials.

Table 1.1 lists the key components usually found in secondary LIBs. The selection criteria for suitable active electrode material formulations for LIBs are: (i) reversible capacity, (ii) good ionic and electrical conductivity, (iii) long cycle life, (iv) high rate of lithium diffusion into the active material, (v) low cost, availability and ecocompatibility of the components. In addition the device should meet the requirements of high power and energy density, optimizing the choice and implementation of the components listed in table 1.1.

As exposed beforehand in this section, modern LIBs are generally based on a carbon anode and a transition metal cathode to generate a working voltage higher than 3.0 V . Such large potential differences are desirable to maximize the energy density of the cell. Therefore, the design of a LIB often considers to choose a negative electrode material displaying a redox potential as low as possible together with a positive electrode material displaying a redox potential as high as possible. Nevertheless, the resulting working potentials of electrode materials typically used in LIBs are mostly laying beyond the lower and higher limits the electrochemical stability of water, that would undergo decomposition in such conditions. In the canonical LIB systems, this is dismissing water as electrolyte carrier candidate and organic electrolytes should be used instead. The electrolyte is most often composed of a solution of lithium hexafluorophosphate (LiPF_6) in organic solvents such as mix of ethylene carbonate (EC) and diethyl carbonate (DEC). This electrolyte solution soaks a separator, which prevents contact between the electrodes and subsequent short-circuits. Since the ionic conductivity of the electrolyte is much lower than the electronic conductivity of the electrodes, batteries are composed of large-area electrodes to ease the access of the electrolyte and a thin electrolyte interlayer is preferred to decrease the diffusion distance.^[7]

Table 1.1 – Overview of secondary LIB typical components and related characteristics.^[4]

	Component	Material / characteristics	Example
Electrode	Cathode active material	Transition metal oxide / capacity	LiCoO ₂ , LiMn ₂ O ₄ , LiNiO ₂ , LiFePO ₄
	Anode active material	Carbon, noncarbon alloy, transition metal oxide / capacity	Graphite, Li, Si, Sn, lithium alloy, Li ₄ Ti ₅ Si ₁₂
Electrolyte	Conductive agent	Carbon / electron conductivity	Acetylene black
	Binder	Polymer / bonding property	Polyvinylidene fluoride (PVDF), styrene-butadiene rubber (SBR), carboxymethyl cellulose (CMC)
	Current collector	Metal film / formation of pole plates	Cu (-), Al (+)
	Separator	Polymer / separation of cathode and anode, prevention of short circuits	Polyethylene (PE), polypropylene (PP), PVDF
Others	Lithium salt	Organic and inorganic lithium compounds / ion conduction	LiPF ₆ , LiBF ₄ , LiAsF ₆ , LiClO ₄ , Li(CF ₃ SO ₂)N (LiTFSI), Li(FSO ₂) ₂ (LiFSI)
	Electrolyte solvent	Nonaqueous organic solvent / dissolution of lithium salt	Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC)
	Additive	Organic compounds / SEI formation and overcharging protection	Vinylene carbonate (VC), biphenyl (BP)
Others	Tab	Metal / pole socket	Ni (-), Al (+)
	Outer casing	Cell protection and casing	Stainless steel, aluminum pouch
	Safety component	Overcharge and overdischarge protection, safety device	Safety vent, positive temperature coefficient (PTC) thermistor, protective circuit module (PCM)

1.4.3 Anode materials for LIBs

As detailed in subsection 1.4.1, to date, most developments towards current LIBs have been relying on graphite as anode electroactive material, which represents the state of the art. The reasons are its excellent features fulfilling prerequisites for active materials as presented in previous subsection 1.4.2. This allowed graphite to become the most used anode material in modern LIBs.^[20] This material also advantageously displays a relatively flat (and low) working potential *vs.* Li/Li⁺, allowing effective utilization of the stored energy at constant rate and power in a tight voltage window, furthermore simplifying the designed application.

Due to some shortcomings of carbon-based materials, other alternative materials have been explored to achieve notably higher capacities as the one of graphite is relatively moderate (372 mAh·g⁻¹). The capacity of graphite is limited stoichiometry wise as only one lithium can be intercalated per six carbon atoms. In addition the rate of lithium ions diffusion (10⁻⁹ cm²·s⁻¹ – 10⁻⁷ cm²·s⁻¹) is also a limiting factor in terms of power density for LIBs.^[21,22]

As defined earlier in this chapter, the capacity of electrode materials is only one of the factors defining energy density of LIBs. Another main factor is the voltage which is arising from potential differences between both electrodes. To achieve high energy density, the anode should have a potential as low as possible and cathode a potential as high as possible. Yet, the lowest redox potential that can be practically achieved in a LIB should still be higher than the reduction potential of Li/Li⁺, otherwise plating of lithium metal at the anode would occur, with a possible dramatic outcome.

Lithium metal has one of the highest capacity of LIB anode materials (3860 mAh·g⁻¹).^[23] Before the first steps and implementation of carbon-based materials as LIB anode, extensive research has been carried out to make practical implementation of lithium metal as an anode material for secondary batteries. These efforts on lithium metal batteries have been plagued by the poor reversibility of the plating process and the same safety concerns encountered with carbon materials when the system undergoes adventitious lithium plating. Safety hazards are intimately related to the growth of dendrites during plating, that can pierce the separator or even a solid state electrolyte, possibly resulting in catastrophic failures such as short-circuit or thermal runaway. There-

fore, setting new performance standards consists in designing new anode materials with enhanced capacity, good ionic diffusion in the anode, good cycling life and free of safety concerns.

Many efforts have been devoted to both carbon and non-carbon materials in order to develop better performing anodes. The main categories of materials are the following: (i) intercalation / de-intercalation materials, (ii) alloy / de-alloy materials, and (iii) conversion materials. The first category, insertion / de-insertion materials, is mainly represented by carbon based hosts such as the famous graphite. These materials are characterized by the intercalation of ions within a layered structure. The second category, i.e. alloys compounds, is characterized by the ability of some metals and semi-metals to solubilize lithium metal in an alloy phase. The third category, i.e. conversion materials, reacts with lithium to form lithium compounds while undergoing reduction of transition metal centers.^[23]

Among **intercalation compound** alternatives to graphite, titanium based oxides have attracted significant interest as they allow practical application with only minor safety concerns. Although the most appropriate titanium based oxide, namely the spinel material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), possesses only half of the capacity ($175 \text{ mAh}\cdot\text{g}^{-1}$) of graphite, this material offers several other benefits such as low price, low toxicity, low volume change ($2\% - 3\%$) under cycling, and excellent cycle life (up to 9000 cycles).^[24,25] The stability and high safety of LTO is explained by its redox activity exhibited at a relatively high voltage of $1.55 \text{ V vs. Li/Li}^+$ allowing passivation layer and dendrite formation to be mitigated.^[26]

Lithium alloys with materials such as silicon, tin, germanium, silicon oxide or tin oxide are also under intensive investigation.^[23] As highlighted in figure 1.7, these materials are fulfilling the requirement of higher capacity as they are displaying typically high values, silicon being even able to deliver a capacity of $4211 \text{ mAh}\cdot\text{g}^{-1}$ ($9786 \text{ mAh}\cdot\text{cm}^{-3}$),^[23,27] that is a ten fold improvement compared to graphite. In addition, silicon displays a discharge (lithiation) potential almost close to graphite i.e. $0.4 \text{ V vs. Li/Li}^+$, and is the second most abundant element on earth. Yet a major drawback shared among such high capacity battery materials is the huge expansion coefficients upon lithiation. In the case of alloying materials this results in poor cycle life. The stress experienced upon volume change can provoke pulverization of the material leading to

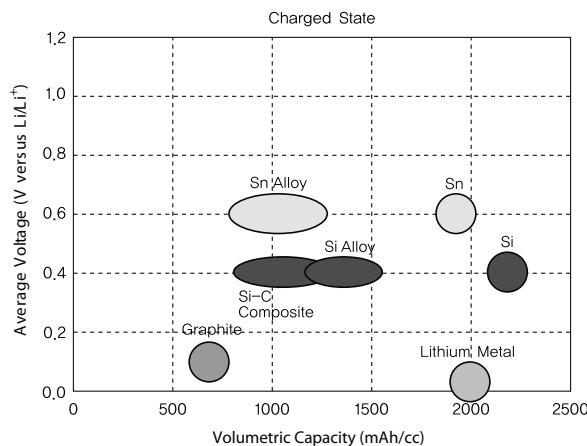
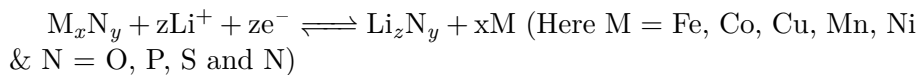


Figure 1.7 – Voltage and capacity of metal elements that form alloys with lithium compared to graphite and lithium metal. ^[4]

a loss of cohesion and contact in the electrode in addition to irreversible processes triggered by the repeated renewal of the interphase with the electrolyte. To tackle these issues, different strategies have been developed to limit the effect of expansion stresses: downsizing the materials as nanoparticles,^[28,29] buffering the expansion using composites with inactive material,^[30,31] buffering via introduction of free volume^[32,33] etc.

Conversion materials such as oxides, phosphides, sulphides or nitrides have been proposed as high capacity anode materials.^[23] During the charge process the transition metal compound (M_xN_y , where $M = \text{Fe, Co, Mn or Ni}$) undergoes decomposition while lithium compounds are generated (Li_zN_y , where $N = \text{O, P, N or S}$) are generated. The high capacity of such systems ($500 \text{ mAh}\cdot\text{g}^{-1} - 1000 \text{ mAh}\cdot\text{g}^{-1}$) is owed to the participation of a high number of electrons.^[34] The electrochemical reaction can be written as follows,



Conversion materials based on iron oxides such as $\alpha\text{-Fe}_2\text{O}_3$ and magnetite (Fe_xO_4) have been extensively studied because of their low cost, high availability and low toxicity. However as most conversion materials, iron oxides exhibit poor cycling performances due to the high volume changes and dramatically changed structure and chemistry under oper-

ation.

While progress is still currently made towards anode with higher specific capacities, it is worth to mention that for capacities above $1200 \text{ mAh}\cdot\text{g}^{-1}$, the specific capacity gain of the overall battery owed to a higher capacity anode will level off, unless capacity improvements are made on the cathode material as well.

1.4.4 Cathode materials for LIBs

In addition to the prerequisites detailed in subsection 1.4.2, to be of practical use, cathode materials should display a redox activity at redox potential as high as possible *vs.* Li/Li^+ . Although high capacity anode materials are receiving much attention, the capacity of current cathode materials is relatively limited in comparison. This ultimately limits the perspectives of any performance improvement regarding the overall capacity of the system.

The three main classes of common inorganic electrode materials are (i) layered materials (LiMO_2), (ii) spinel materials (LiM_2O_4), and (iii) polyanionic materials which are mainly represented by lithium transition metal phosphates (LiMPO_4) such as olivine LiFePO_4 (LFP). In the chemical formula of each class, M stands for a transition metal, usually Ni, Co, Mn or Fe. Further developments within these classes are relying mostly on mixing, surface coating and compounds formation of materials.^[4]

The transition metal in these materials is suitably a $3d$ transition metal, affording advantageously higher specific capacity and higher redox potentials than heavier $4d$ and $5d$ transition metals. Chalcogens, especially oxygen, are more suitable as anions than halogens in terms of structural stability.^[4] Lithium ions are intercalated / de-intercalated to maintain charge neutrality. Materials displaying minimal changes in the crystal structure are desirable as it could otherwise limit lithium ion diffusion and so charge – discharge performances.

In LiMO_2 structures of layered materials, the transition metals are usually Co, Mn, or Ni, and their combination or substitution. Within the structure, lithium ions intercalate in sites between slabs (layers) of octahedral metal oxides (MO_2). A representation of the crystal structure of a layered material is provided in figure 1.8a.^[35–37] A typical

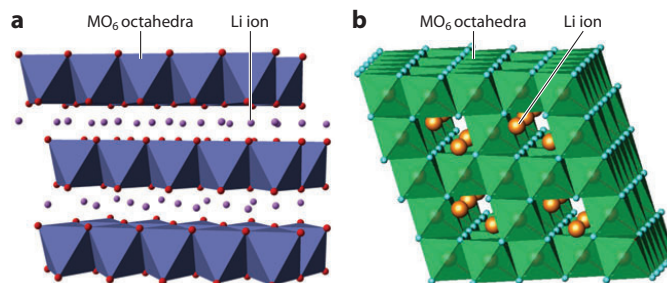


Figure 1.8 – Crystal structures of typical lithium metal oxide cathode materials. (a) LiMO_2 . (b) LiM_2O_4 .^[35]

example of layered materials is LiCoO_2 (Average potential *vs.* $\text{Li}/\text{Li}^+ = 3.9\text{ V}$), which is a component of the commercial LIB.^[4] However, the practical capacity ($145\text{ mAh}\cdot\text{g}^{-1}$) of this material is relatively limited and is only about half of its theoretical value ($274\text{ mAh}\cdot\text{g}^{-1}$) since only half delithiation can be reached without structural instability issues that would result in irreversible capacity loss.^[4] Moreover cobalt is relatively expensive, not very abundant and raises environmental concerns related to its toxicity.^[38]

To address LiCoO_2 limitations, the emphasis has been set on less costly and more environmental friendly nickel, manganese and aluminum to replace – fully or partially – cobalt in the LiMO_2 material structure. The capacities and voltages achieved with such systems are bringing slightly higher values. Yet, LiNiO_2 and LiMnO_2 (LMO) have been proven to be more challenging to synthesize and rather unstable thermodynamically. The synthesis of mixed oxides ($\text{LiNi}_x\text{M}_{1-x}\text{O}_2$) in which Ni is partially replaced by other transition metals (M) is another alternative. Some encouraging results have been obtained through these investigations – high cycle-rate capability and improved thermal stability, notably. Some materials have proven to be commercially viable solutions nowadays, such as lithium nickel cobalt aluminum oxide (NCA, commonly $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) or lithium nickel cobalt manganese oxide (NCM, often $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ or $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$).^[38] However, thermal stability and cycle life still need to be improved.^[25,35,36]

In LiM_2O_4 spinel structures, the oxygen anion lattice is the same as in LiMO_2 , and the transition metal cations also occupy the octahedral site, but one fourth of them are located in the lithium layer, leaving one fourth of the sites in the transition metal layer vacant. Lithium

ions occupy the tetrahedral sites in lithium layers that share faces with the empty octahedral sites in the transition metal layer (Figure 1.8b). The vacancies in the transition metal layer result in the formation of tunnel structures. This ensures the three-dimensional facile diffusion of lithium ions, associated to good rate capability. The spinel LiM_2O_4 in particular displays good structural stability for reversible lithium ion intercalation. It is also a safe cathode material due to the chemical stability of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. However, LiM_2O_4 experiences capacity fading. This has been attributed to the destabilization of Mn^{3+} due to Jahn-Teller distortion but also the dissolution in the electrolyte of Mn^{2+} , generated by the disproportionation reaction of Mn^{3+} into Mn^{4+} and Mn^{2+} .

$\text{Li}_x\text{M}_y(\text{XO}_4)_z$ (M = metal; X = P, S, Si, Mo, W, etc.) are considered to be very promising for the design of the next generation of Li-ion batteries powering electric vehicles. In particular, the olivine LiFePO_4 has drawn attention due to its low cost, its high safety, the high abundance of iron and phosphate, and the clean nature of phosphate ions, combined to good thermal stability and reasonable theoretical specific capacity ($170 \text{ mAh}\cdot\text{g}^{-1}$). Nevertheless, its lower energy density (14% of that of LCO) and poor electronic conduction limit the potential of this material. Other phosphate olivines can be obtained by substituting Fe by Mn, Co or Ni, giving LiMnPO_4 , LiCoPO_4 , and LiNiPO_4 . These compounds are currently under investigation and have higher operating voltages (4.1 V, 4.7 V and 5.1 V respectively) enabling higher energy densities. In any case, those densities are inferior to the values obtained for lithium metal oxides, which have a higher packing density and are thus more adapted for applications that require small-sized batteries.^[35–37]

The cathode materials described above are all inorganic. Their production involves ecologically and energetically unfriendly processes as well as the exploitation of finite resources. In addition to this, inorganic intercalation compounds are reaching their intrinsic limitations, and alternative paths need to be explored. In that respect, some organic compounds are showing promise for utilization as cathode material, but also anode materials, in lithium batteries.^[37,39,40] This topic will be covered in the next chapter.

1.4.5 Electrolytes for LIBs

1.4.5.1 General characteristics

Electrolytes directly affect the performances of LIBs as they are the medium where the ions shuffle between the two electrodes; Solvation, diffusion and interfacial properties are thus paramount to the lithium ion transport characteristics. In addition to their role on ion transport, the reaction of electrolytes with the highly reactive electrodes of typical LIBs must be carefully controlled to ensure that the battery operates well over a long cycle life.

The main characteristics that must be fulfilled by the electrolyte are the following,^[4]

- High ionic conductivity at room temperature ($> 10^{-1} \text{ mS}\cdot\text{cm}^{-1}$),^[41]
- Electrochemical stability toward electrodes over a broad potential range,
- Chemical stability toward the various components such as metal (current collectors notably) and polymers (such as binder and separator),
- High level of safety. As typical organic solvents in LIBs are volatile and flammable, they may cause fire and explosion when batteries are exposed to temperatures, or experience failures and short-circuits. Therefore components with high flash points and ignition points are preferred.
- Aforementioned characteristics over a broad temperature range (-20°C to 60°C),
- Low cost, low toxicity and sustainable production.

The common LIB electrolyte comprises a lithium salt in an organic based solvent as discussed next.

1.4.5.2 Lithium salts

Typical LIB electrolytes are relying on the dissolution of lithium salts in a carbonate solvent. The salt in a typical LIB electrolyte is almost exclusively LiPF_6 .^[41] This salt allows to fulfill almost all the above-mentioned requirements because its solution in polar aprotic solvents, either cyclic or linear carbonates, displays high ionic conductivity,

good electrochemical stability and protects aluminum current collector from corrosion.^[42] Yet this salt possesses several drawbacks. First, it has limited thermal stability above 55°C that can generate highly toxic species^[43] and initiate polymerization of solvents^[44] that produces thicker and more resistive films at the interphases.^[45] LiPF₆ is moreover extremely moisture sensitive, yielding byproducts such as HF and PF₃O that can degrade the passivation layer at the anode.^[42,46]

These limitations have motivated research on alternative salts. Some of them are not practical; LiAlF₆ and LiClO₄ are toxic and explosive, respectively. Many other anions have been considered with different central atoms including N, C or B.^[42] Examples of related salts are lithium bis(trifluoromethanesulfonyl)imide LiN(SO₂(CF₃)₂) (LiTFSI),^[47,48] lithium bis(fluorosulfonyl)imide LiN(SO₂F)₂ (LiFSI),^[49] or lithium bis(oxalato)borate LiB(C₂O₄)₂ (LiBOB).^[50–52]

LiTFSI is the best alternative candidate: excellent ion-pair dissociation, solubility and thermal stability. Unfortunately LiTFSI is responsible of severe corrosion of aluminum current collectors above 3.6 V *vs.* Li/Li⁺ due to the solubility of Al(TFSI)₃ in alkyl carbonates.^[53] To overcome this issue, LiTFSI can be mixed with another salt to combine advantages of different components. Blending LiTFSI with LiBOB has been proven to be a successful strategy,^[54] that not only suppresses Al corrosion but also provides improved thermal stability and better tolerance to water than LiPF₆.

1.4.5.3 Solvents

Regarding the solvent characteristics, they should allow to meet the electrolyte general requirements. More specifically, the solvent should display a high dielectric constant (ϵ) to allow favorable dissolution of the lithium salt; the other electrolyte requirements can be directly applied to the solvent selection. To qualify as an electrolyte solvent and dissolve the salt, non-aqueous compounds must possess polar groups such as carbonate, carbonyl, nitrile, sulfonyl, ether or ester. Most of the solvents investigated fall into the categories of carbonate, ester and ether. Figure 1.9b compares the electrochemical stability window of different solvent categories. It is worth to mention that non-aqueous is a term often used in the literature, but aprotic would be a more precise term. For instance, anhydrous ethanol is non-aqueous but does not qualify as sol-

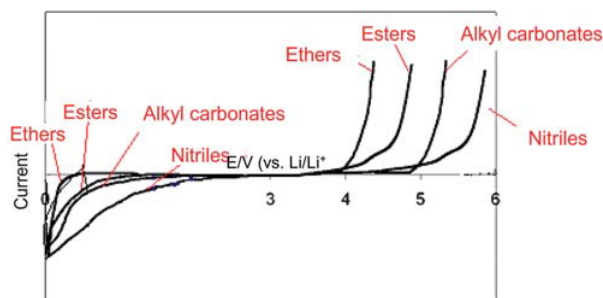


Figure 1.9 – Schematic presentation of the electrochemical windows of LiPF_6 salt solutions in various solvent families.^[24]

vent for LIBs because of its reactivity due to its active protons.^[55] Protic solvents are ruled out because the reduction of their protons and/or the oxidation of the corresponding anions generally occurs within 2.0 V to 4.0 V *vs.* Li/Li^+ .^[56]

To date, no suitable single solvent is readily available that possesses simultaneously high dielectric constant and low viscosity while still meeting satisfyingly all other requirements. To circumvent this situation, the compromise for LIBs is to rely on a mix of solvents, each either providing high dielectric constant or low viscosity.^[57] The now indispensable ethylene carbonate (EC) provides the former in almost all commercial LIB electrolytes.^[57] As for the latter, modern systems rely on a series of acyclic carbonates or carboxylic esters, most often dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethyl methyl carbonate (EMC). Such mix of solvents are the state-of-the-art of aprotic solvent systems, with conductivity reaching $5 \text{ mS}\cdot\text{cm}^{-1}$ to $10 \text{ mS}\cdot\text{cm}^{-1}$ at ambient temperature and supporting routine operations in the range of -30°C to 60°C .^[57] A representative set of common carbonates solvents is depicted in figure 1.10.

As it is the case for lithium salts, many alternative solvents have been proposed to cope with the challenges newly brought with the evolution of research topics on lithium batteries, in particular with respect to their electrode materials. The main categories of alternative solvents are the following:^[57] Fluorine-containing solvents, whether derived from carbonates or other chemistries; phosphorous-containing solvents such as phosphates, phosphites and phosphazenes; sulfur-containing solvents such as sulfones and sulfoxides; nitriles; and esters. Most of these sol-

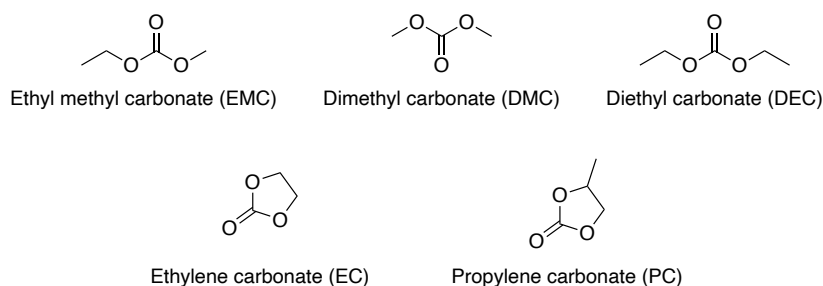


Figure 1.10 – Selection of alkyl carbonates solvents for Li-ion batteries.^[24]

vents are bringing improvements either in terms of reduced flammability (those containing fluorine phosphorous atoms) or improved stability toward high potential cathode materials (> 4.3 V).

As LIBs are now considered fit to power systems such as electric vehicles and energy storage systems,^[58] much attention has been set on the safety issues of LIBs. Different approaches have been proposed.^[20] Some of these are flame retardants (co-)solvents, room temperature ionic liquids (RTILs),^[57,59,60] gel polymer electrolyte (GPE, polymer swollen matrix encompassing a liquid solution of an electrolyte salt),^[55] or solid polymer electrolyte (SPE, ion conducting polymer matrix encompassing an electrolyte salt),^[57,61,62]. Yet these approaches are usually meeting difficulties application wise, in particular regarding charge-discharge rate capability, and reliability of the system.

Alkyl phosphates and related compounds as non-flammable components are well known and have practically been used as fire-retardant additives for polymers.^[63,64] As alternative electrolyte (co-)solvent for LIBs, they also share similar physico-chemical properties with carbonates such as wide range of operating temperature, good solubility of lithium salts, relatively wide electrochemical stability window. The fire-retardant properties of phosphates are attributed to the decomposition products of phosphates that act as radical scavenger of hydrogen radicals, the main carrier of oxidative chain reaction.^[64] Since the pioneering work of Wang *et al.*^[64] the most commonly used phosphate is trimethyl phosphate (TMP), which as additive can be totally mixed with standard carbonate electrolyte solutions.

1.4.5.4 Phosphorous-based compounds as electrolyte (co-)solvents and additives

While some phosphates have demonstrated good performances with standard cathode materials such as LCO and LMO,^[64–68] they are prone to undergo irreversible reactions on graphite at low redox potentials as they are not yielding a stable and compact passivation layer.^[69] To cope with this behavior, additives have been proposed such as vinylene carbonate (VC) to aid in the formation of the passivation layer,^[70] or the addition of $\text{Ca}(\text{TFSI})_2$ that affects the solvation structure so that the compatibility of TMP with the anode is improved.^[71,72] This latter effect is due to the higher complexation ability of phosphates than carbonates. The presence of Ca^{2+} , which is preferably solvated than Li^+ , would reduce the presence of TMP in the solvation shell of Li^+ . In that respect, Matsumoto *et al.* have also found that optimization based on higher Li^+ salt concentration ($> 2\text{ M}$) can have a positive impact on the cathodic stability of TMP as this is owed to changes in the solvation number of Li^+ .^[68] Combined with anode film preformation on graphite, they demonstrated that they can obtain safe and high performance LIBs. Overall these optimizations on solvation structure and interfacial properties can render non-flammable formulations viable for practical applications.^[67,68,70–72]

1.4.5.5 RTIL electrolyte formulations

Room temperature ionic liquids (RTILs) as electrolytes are in a class of their own. Ionic liquids or molten salts are liquids that contain only ionic species. By definition, these salts are liquid below 100°C but in the context of LIBs, they are already liquid at room temperature, hence RTILs, are best suitable. These liquids are composed of a "onium" unsymmetrical cation³, such as 1-ethyl-3-methylimidazolium (EmIm^+) or 1-butyl-1-methylpyrrolidinium (Pyr_{14}^+) (Figure 1.11a and b), and a delocalized anion, most often FSI^- or TFSI^- (Figure 1.11c and d). These RTILs can afford good conductivities ($> 1\text{ mS}\cdot\text{cm}^{-1}$)^[73] and can efficiently dissolve lithium salts (LiTFSI or LiFSI). In turn such formulations are affording transport of Li^+ which can represent 20% to 30% of

³In the context of RTILs, onium are cations that would result from the substitution of an hydrogen atom by another moiety.

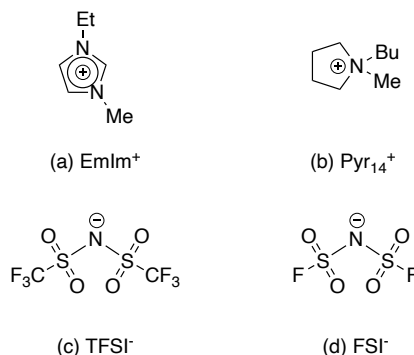


Figure 1.11 – Typical structures of ions in RTILs: cations (a) and (b); anions (c) and (d).

the total conductivity. RTILs are less flammable and non-volatile but at the expense of their high cost and high viscosity.^[42,73] This later drawback is not only posing manufacturing challenges when cells are vacuum filled with electrolyte but also affects transport properties. In that respect, transport is further affected by the poor wetting characteristics of RTILs with some electrode materials and separators.^[74] In addition they display stability issues at low potential which are attributed to the cation and are often requiring special salts and additives formulations to efficiently passivate the anode surface.^[42,59]

1.4.5.6 Semi-solid and solid polymer-based electrolytes

As electrolyte stands as the only compartment being liquid in the cell, trading it for a solid media would be a major step toward a completely solid system, with potential benefits such as higher level of mechanical strength and safety. Potential solutions are found as GPEs and SPEs. The demarcation between these two categories is however not always unambiguous as plasticizers of low molecular weight can be part of the formulations.

GPEs are a mature and commercially available technology offered in systems which are often referred as lithium-polymer batteries.^[55] In GPEs, polymers are found at the additive level. The entanglement of their long chains along with their miscibility with the electrolyte solvent provides a semi-solid behavior at the macroscale while at the microscale Li^+ behaves as in a liquid phase. This allows conductivity $>1 \text{ mS}\cdot\text{cm}^{-1}$

and electrochemical stability within the potential window of most 4.0 V class batteries. The major material used in commercial systems is a copolymer of vinylidene fluoride and hexafluoropropylene (PVdF-*co*-HFP).^[55,75,76] Some other systems have also been proposed such as the poly(ethylene oxide) (PEO) / PVDF / poly(methyl methacrylate) (PMMA) blend reported by Song *et al.*^[77] GPEs are reducing the risks associated with corrosive products leakage. Yet a trade-off is made in terms of rate capability and capacity utilization.^[57] However the risks are not completely addressed as the carbonate content remains a concern with respect to the flammability hazards. This further stimulates the development of GPEs containing non-flammable components such as RTILs^[78–81] or alkyl phosphates.^[82]

Regarding SPEs, polyether as polymeric architecture is so far the most effective at dissolving lithium salts and is acknowledged as the main conductive matrix since the first report by Wright *et al.*^[61,83] Its application to LIB system then followed Armand's suggestion from four decades ago.^[84] The main challenges hindering SPE implementation are their low ionic conductivity ($<1 \text{ mS}\cdot\text{cm}^{-1}$), their contacts at electrode-electrolyte interphase and their relatively limited electrochemical stability window.^[57] PEO are notably facing as main-obstacle the break-down of ether functions at potentials below 4.0 V vs. Li/Li⁺.^[55] Currently SPEs are only considered for batteries operation at higher temperatures where their conductivity is in the range for practical applications.^[4]

1.4.5.7 Electrolyte additives

Most commercial batteries are containing small quantities of additives to enhance their ionic conductivity, battery life and safety.^[55] It is however difficult to know the actual composition of formulations proposed by the few major companies active on this market. A few representative examples of electrolyte additives are depicted in figure 1.12. The main categories can be described as follows,

- SEI formation additives: The most common one is vinylene carbonate (VC)^[85] which is added to enhance battery life. VC aids to passivate the surface and limit graphite exfoliation by forming a stable layer through ring opening reactions at the anode surface.
- Overcharge inhibitors: These are acting as an internal safety feature that is meant to suppress uncontrolled reactions.^[86] The redox

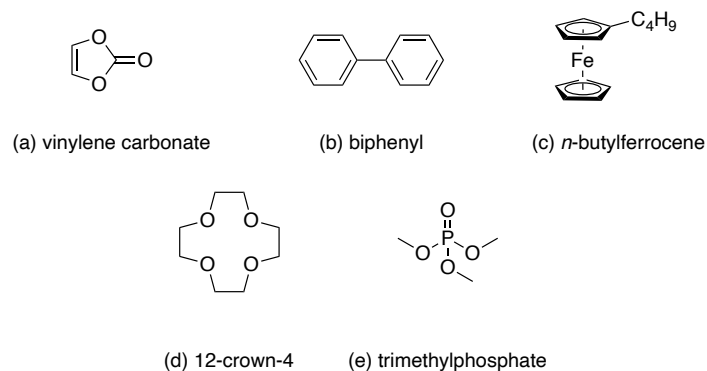


Figure 1.12 – Representative examples of electrolyte additives: (a) for anode SEI formation, (b) cathode layer forming overcharge protector, (c) redox-shuttle overcharge protector, (d) cation acceptor conductivity enhancer and (e) flame-retardant additive.

shuttle type restricts high voltage by dissipating the excess of energy.^[87,88] The cathode layer forming type is generating a thick layer which is both ionic and electric insulating.^[89] The former type is effective at low excess of charge, the latter is meant to be more effective at larger ones. Examples of structures of such additives are depicted in figure 1.12.

- Ionic conductivity enhancers: They improve the salt dissociation. The two main categories are the cation receptors such as crown ethers,^[90,91] and the anion receptors such as those based on boron chemistry.^[92,93]
- Flame retardants: The lithium salt itself can be partly assuming that role, a practical example being LiPF_6 . In GPEs, polyacrylonitrile can be considered as displaying flame-retardancy characteristics.^[4] Yet for liquid electrolytes, achieving flame-retardancy is still difficult and as already explained earlier in this section, this is then motivating research on other additives such as phosphorous-based and fluorinated compounds .

1.4.6 Passivation layers at the electrode – electrolyte interphases

Even if their working principle is quite simple, LIBs possess complex components which consequently make their aging process and related

chemistry even more complicated. The very broad potential operating window of LIBs induces electrochemical processes to occur not only with the active components in the bulk of electrode materials but also at their interphases with the electrolyte component which are usually facing redox potentials outside the electrochemical stability windows.^[94] This adds a further level of complexity to the system as cathode and anode interphases redox processes differ significantly; at the anode, electrolyte components undergo reductive reactions, while electrolyte oxidative processes are taking place at the cathode. The electrode – electrolyte interphase reactions in a LIB can play major roles in the decrease of performance in terms of rate capability, cycle stability, irreversible capacity loss, exfoliation of graphite and safety notably.^[95] It is then imperative to master these interphases phenomena.

The key characteristics of a well-performing SEI are the following,^[55]

- Electronic insulating behavior, otherwise electron tunneling can induce continuous electrolyte decomposition.
- High ionic conductivity, lithium ions must easily access the bulk of active materials for the redox process to occur.
- Uniform morphology and chemical composition, required to obtain homogeneous current distribution.
- Good adhesion to the electrode material.
- Good mechanical strength and flexibility, since most of the active materials are undergoing expansion/contraction upon cycling.
- Low solubility in the electrolyte, to avoid continuous removal and formation of the passivation layer.

Since the origins of LIBs, interfaces are a topic of vivid research interest,^[96–102] with the coined solid electrolyte interphase (SEI) term being introduced to describe the passivation layer at the anode surface. Due to the implementation of graphite, the research intensified due to the critical role of SEI in preventing the graphite anode from exfoliation, which is owed to its susceptible nature of solvent co-intercalation. Therefore specific and controlled reactions must happen for the SEI to fulfill its roles (Figure 1.13). The onset and the extent of electrolyte reactions at electrode surfaces are varying significantly with the components. Different values are found in the literature, from 0.8 V to 2.0 V.^[55,96,97,103] The value of 0.8 V, which is close to the first intercalation of lithium into graphite, is the most commonly acknowledged

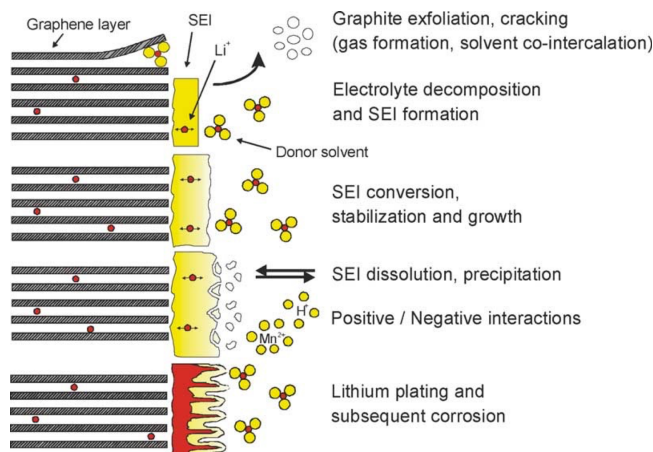


Figure 1.13 – Changes at graphite/electrolyte interphase. ^[110]

one.^[104,105] At such low values, liquid electrolytes undergo reduction to generate a plethora of negative and/or radical species,^[99] subsequently giving rise to a solid lithiated layer (around 40 nm to 70 nm thick) of mostly mixed organic and inorganic (semi-)carbonates.^[106,107] In the process other components are generated: carboxylates (such as oxalate and succinate), alkoxides,^[108] oligomeric products^[57,109] or gaseous products (CO_2 , alkenes).^[57] This overall process goes along with irreversible depletion of lithium ions from the electrolyte, decaying coulombic efficiency and battery performances.^[110] Under controlled conditions, this SEI is electrically insulating but possesses ionic conductivity and is not allowing solvent diffusion.

Regarding reactions at the cathode, decomposition of the electrolyte yields thinner passivation films (around 10 nm) which are also less resistive. Furthermore this decomposition takes place at a relatively high potential (>4.3 V vs. Li/Li^+).^[4,55,111] As usually LIBs are not exceeding 4.2 V, they do not depart too much from the electrolyte oxidation limit.^[55] The interfacial reactions at the cathode are then of less practical consequences, which induced scarcer studies on the topic. Some of studies even questioned the existence or the protective role of a SEI at the cathode.^[112,113] Yet over long-term cycling, the surface layer at the cathode, namely the cathode electrolyte interphase (CEI), tends to grow at a faster pace than at the anode and can take over the role of the most resistive component at a certain point.^[113] Also salts and solvent decomposition products as those generated at the anode have been

found at the cathode; their generation mechanism differs as cathode interfacial reaction are triggered by the lithium rich surface chemistry of the cathode material.^[95]

1.4.7 Manufacturing and design of LIBs

The design optimization of LIBs is constrained by practical considerations. For instance, the optimization of one electrode may be limited by geometrical and performance factors affecting the other electrode. The overall fraction of active material must allow a decent energy density, i.e. there is a limited amount of fillers that can be acceptable, and in systems where SEI forms, increase of the specific area of an electrode can lead to undesirable side reactions.^[114] Most often, the optimization of one property is done at the expense of others. An example is the dichotomy of high energy density *vs.* high power cells.

The main objective for designing high power cells is to decrease transport resistance. With respect to both material properties and structural aspects, this is requiring to optimize the following characteristics:

- solid-state ion diffusivity in the electrodes (maximize)
- electrical conductivity (maximize)
- solid-state path lengths for ion transport (minimize)
- path length for ion transport in the electrolytes (minimize)
- electrode/electrolyte contact area (maximize)

Maximizing the power density leads to consider an increase of the amount of fillers, a decrease in the thickness, or an increase of the porosity of the materials spread on current collectors, which all consequently decrease the energy density. Besides material choices, performance requirements are thus tied down by design, processing and manufacturing parameters which are all part of the LIB value chain.

The value chain (Figure 1.14) of LIB production process has as first step the manufacturing of three different types of foils: anode, cathode, and separator. Within this first step, the electrode coating is a core element of the fabrication. The main goal is the fabrication of continuous, homogeneous and smooth electrodes (overall deviation of thickness <1.5%) without compromising production costs.^[115]

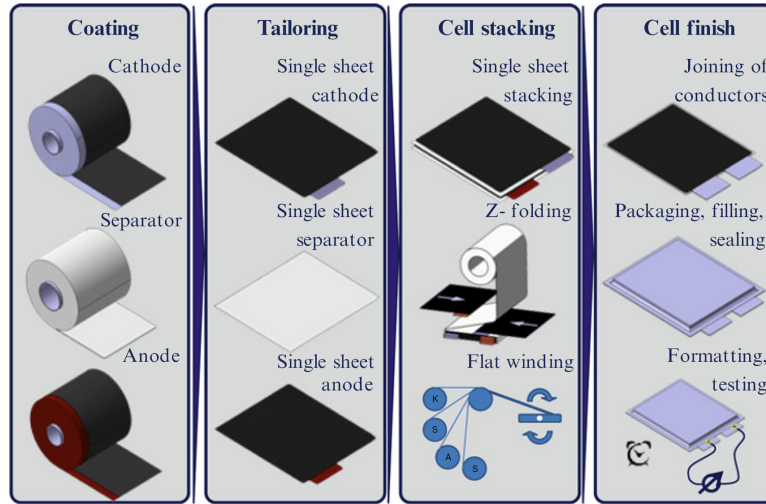


Figure 1.14 – Value chain for the conventional production of Lithium-ion cells.^[115]

Although most of the manufacturing processes are sharing these very similar steps, many different shapes and requirements are influencing their engineering. The common forms that the cells can take are cylindrical laptop batteries, prismatic cells for portable devices, single-cell coin-shaped batteries, and pouch-shaped cells cased in aluminum plastic composites (Figure 1.15).^[116]

The common practice of electrode material preparation involves the preparation of a slurry of active materials, polymer binder, conducting agents, solvents and additives with controlled parameters such as density, composition, pH, rheology etc.^[117] This slurry is subsequently coated on current collector sheets with carefully defined thickness: typically 50 μm on a 10 μm thick current collector; a thicker coating decreases the conductivity; too thin and the collector to active material ratio is less favorable (Figure 1.16).^[118] The mixing method and parameters of the slurry are notably influencing its properties.^[119,120] Among the methods, twin-screw continuous mixing, ultrasonification, dry power blending or ball-milling are the most common ones. Different coating methods are frequently found: slit coating, die coating, tape casting, and blade casting.^[115,120,121] Other monitored parameters are controlled on the resulting film: porosity, adhesion, coating ability, manufacturability etc.^[117,119]

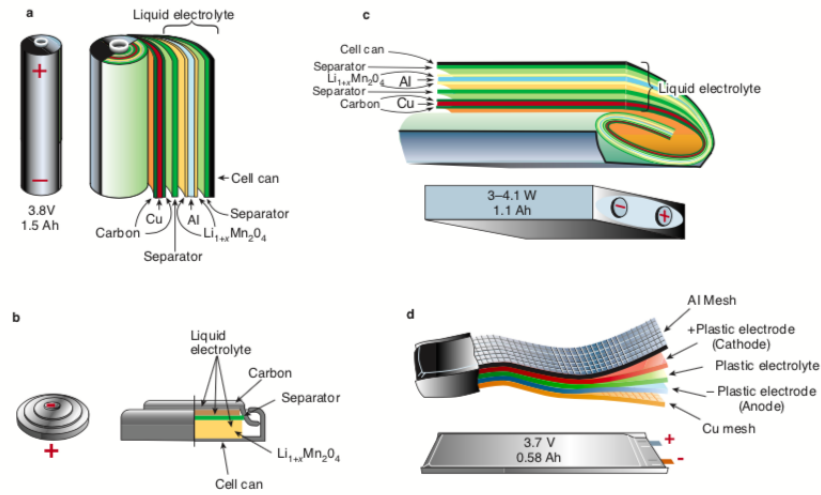


Figure 1.15 – Different shapes of lithium secondary batteries: (a) cylindrical, (b) coin, (c) prismatic, (d) pouch. ^[116]

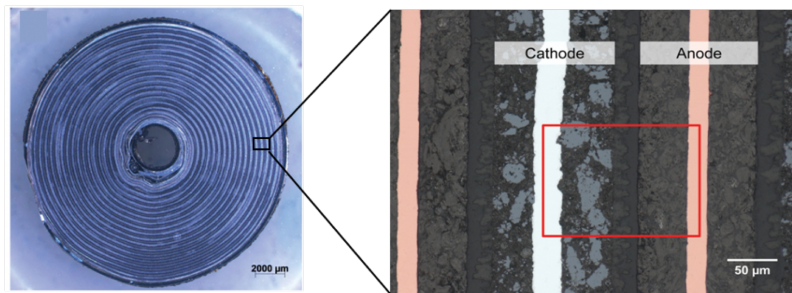


Figure 1.16 – Cross-section of a Li-ion 18650 cell: low magnification and high magnification highlighting the compact and dense structure with well-defined interfaces. The red square contains a complete unit cell of the battery. ^[122,123]

Once the film is obtained, the solvent – often *N*-methyl-2-pyrrolidone,^[120] but water can be used for anodes instead – is evaporated and then compressed, usually via calendaring.^[115,117] The drying time and temperature are critical parameters as they affect porosity, adhesion and micromechanical properties.^[115] The calendaring is increasing the coating density and reduces the surface roughness with effects on cell safety and cycle stability. By reinforcing particle-to-particle contact, calendaring also affects the intra-electrode conductivity and thus power performances. Yet some porosity must be kept to allow enough lithium ion transport.

After coating, the cells are assembled by stacking anode-separator-cathode units. This can be done following different patterns: z-folding, flat winding, stacking of single sheets, or cylindrical rolling according to the resulting shape.^[4,115,124] As for the cell assembly finalization, the joining of the conductor lugs – most often done by ultrasonic welding – holds a peculiar attention since this step can influence durability and performance via the electric resistance and the leak tightness of the device, respectively. Lastly the battery is filled with electrolyte and sealed.

The sealed cells are undergoing a SEI formation step that can last from a few days to a few weeks.^[117,125,126] This step consists in the cycling of the cell at very low rates (C/5 down to C/20)^[118,126] to form a compact SEI layer. After the first charge-discharge cycle, the formation cycling goes on at different rates and or temperatures to build quality SEI layers.

The final product testing via external measurements is used not only to be correlated with production parameters but also to assess the operating characteristics of the resulting battery. Basic characteristics are measured such as open circuit voltage, resistance and capacity. More advanced evaluation protocols can be also carried out such as thermal performance, cold start, pulse power, self-discharge etc.^[117] In addition, abusive tests can be effectuated on a fraction of the production to describe risk situations such as: short-circuit, overload, overheating and so on.

The extreme quality requirements are thus implying consequent developments efforts from design to manufacturing. The development phase is involving up to thousands of cells with as many testing mea-

surements over the years. These efforts are commensurate with the production volume that can amount to millions of cells.

1.5 Conclusion

All in all, LIBs are characterized by a very rich, complex and well-optimized chemistry inside. Bringing further improvements is proven to be difficult as all subcomponents are part of a intricate system. In this context, developments are often only incremental changes. On the other hand, changing completely the chemistry of a single component is often seen as a disruptive change that affects the whole system. In this later case, it holds even more true that progresses on the components require to redesign and re-optimize the other parts of the system. Sometimes these other components can also require further developments to avoid becoming limiting factors, canceling out any progress made elsewhere. Hence, setting new standard of performances requires first to combine efforts at the system sub-level. Once the evaluation work on a single component is done, an upscaling process can start with the implementation in a full cell device to assess the compatibility with the other cell components. Moving forward into the upscaling process, a subsequent step will be to carefully evaluate how this new component is compatible with existing manufacturing tools and techniques. Overall, as there is a wide variety of emerging alternatives to the current materials and technologies, this explains how broad is the community of researchers working for the next generation of batteries.

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CHAPTER 2

SECONDARY BATTERIES BASED ON ORGANIC ELECTRODE MATERIALS

Abstract

It is now well admitted in the battery research community that the next generation of batteries following this lithium-ion battery era should enable more sustainability with respect to energy storage. The heavy metal extraction and life cycle is one of the key problems that makes the current technology one of the least green components of battery-powered devices. The path leading to more sustainability could trade the current heavy metal-based compounds for more abundant and eco-friendly elements, to make for instance organic-based electrodes. The aim of this chapter is to provide a comprehensive overview of active materials for all-organic and organic hybrid batteries. Although there are many other electrode related applications where they could shine, the categories that will be highlighted in this chapter, namely conjugated polymers, carbonyl compounds and organic radical polymers, will be mostly portrayed in the context of battery related applications. In this context, not only the benefits of such approaches but also the challenges and limitations currently at play will be presented since this is where the research should focus its efforts in order to bring them to the fore. This chapter will serve to provide the required picture for the motivations behind the result part of this research work.

2.1 General properties

Regarding our future energy economy, the trend toward more sustainable development is not only affecting the energy production and its consumption but also every system found in between, such as portable energy sources. Cleaner energy storage solutions should be developed with the aim to minimize CO₂ release during their production. In addition, their design as well as their components should be revisited to rely on renewable raw materials.

Current LIB technologies are mostly relying on the use of electroactive components (e.g. LiCoO₂, LiNiO₂) that could hardly be considered as green, their production and recycling being responsible of significantly high CO₂ releases.^[1] The renewability of natural resources is another point of concern as they are relatively scarce, which would render their production even more energy-intensive in the future.

In this context, electroactive organic materials may offer intrinsic advantages over their inorganic counterparts,^[1] as their syntheses can generally be carried out at lower temperatures, but also they are based on more abundant elements (C, H, O, N, S in particular), that can be potentially generated via CO₂ capture or from renewable resources such as biomass (Figure 2.1). Additionally, owed to their organic nature and the absence of heavy metals, their end-of-life disposal can be facilitated by combustion for instance.

As other advantages, there are numerous accessible chemical combinations, some of them being multi-electron reaction materials. Furthermore, the variety of accessible structures allows to tailor their redox properties via the introduction of chemical groups. This can advantageously provide either low or high potential materials without altering the underlying chemistry and enables tuning of the resulting battery voltage. As for their performances, high rates are often achievable thanks to the simple redox reactions in contrast, for instance, to complex mechanisms of intercalation compounds.^[2] Regarding processing, organic materials of polymeric nature are potentially flexible and compatible with efficient industrial processing such as roll-to-roll techniques.

Yet in order to raise their competitiveness, some of their characteristics are posing challenges that need to be overcome, either via the use of original strategies or the development of new materials with more

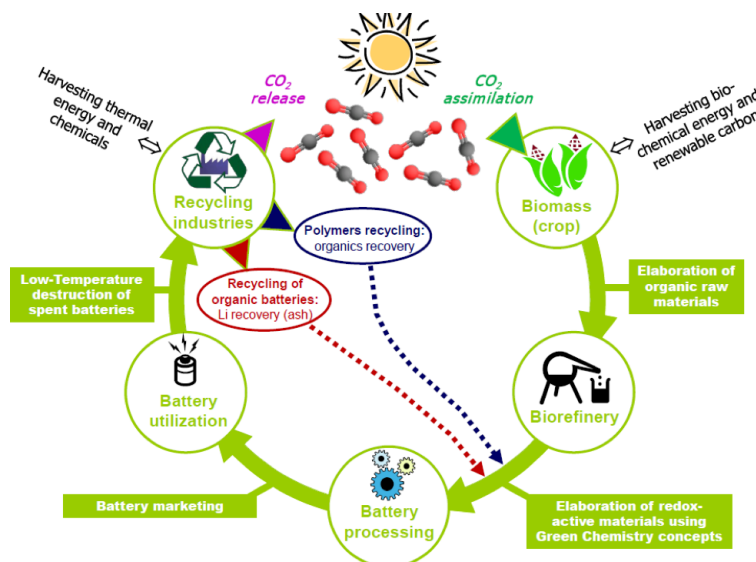


Figure 2.1 – Schematic of an idealized life cycle of a lithium organic battery, supposing that no additional carbon dioxide is generated. Nevertheless, CO₂ capture must be involved. Also some process energy is required for this cycle but could rely on renewable sources.^[1]

desirable properties. Among the challenges to face up, organic materials are usually displaying lower thermal stability and lower volumetric energy density. Additionally they are often displaying a finite solubility in common battery electrolytes for LIBs. This latter drawback is frequently sought to be mitigated via new electrolyte formulation, or the incorporation of electrochemical moieties in polymer and organic salts.

Regarding the electroactive compound nature, all organic molecules that undergo reversible redox reactions are in principle suitable candidates for electrode materials. Because of the large assortment and variety of these materials, different classifications can be applied. They can notably be classified according to their chemical functionality or structure but also according to redox reaction directions, i.e. oxidation and/or reduction, that are accessible to the electroactive base material. The former classification will be used in this chapter to provide an overview of a selection of materials. The latter classification is defined here because of the consequences related to the material class properties with respect to its implementation in an actual battery. In this classification (Figure 2.2) three categories of materials are distinguished: p-type

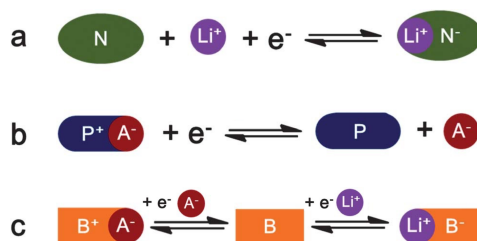


Figure 2.2 – The redox reaction of three types of electroactive organics: (a) n-type; (b) p-type; (c) bipolar. A^- stands for an anion of the electrolyte. Li^+ can be replaced by other alkali ions.^[3]

organics (P^+/P) yield cations upon oxidation, whereas n-type organics (N/N^-) yield anions upon reduction, and b-type organics ($\text{B}^+/\text{B}/\text{B}^-$) can be both oxidized and reduced.^[3]

Organic compounds have mostly their redox potentials ranging roughly between 2 V and 4 V, which makes them usually more suitable as cathode than anode.^[4] Materials of every class can be theoretically used at the positive or the negative electrode but as a general rule of thumb, p-type organics displays higher redox potentials than n-type ones. Whether the active compounds behave as a positive or negative electrode material depends on its redox potential and on that of the particular counter electrode. As a large potential difference is commonly desirable, it influences the choice of respective materials to be implemented within the set of electrodes.

Most of the electroactive organics are processed in the uncharged state. As for n-type materials, they are potentially Li^+ exchanging materials. Yet $\text{Li}^+ \text{N}^-$ is most often unstable in an ambient atmosphere because of the spontaneous hydrolysis reaction and oxidation reaction, especially when the N/N^- redox potential is lower than 2.5 V *vs.* Li/Li^+ .^[3] Therefore, for implementation with conventional LIB materials, the oxidized uncharged form is more suitable as negative electrode material, otherwise as positive electrode material they need to be processed in the reduced state, which may require a pretreatment.^[5]

P-type materials in their reduced state are intrinsically compatible with traditional LIB negative materials. Yet the positive electrode is not exchanging Li^+ cations. In the present case the mechanism of operation involves both ions from the electrolyte, thus the cell is per definition a dual-ion cell. There lies a major difference with LIBs which are based on

the rocking chair principle. Additionally the resulting hybrid batteries are better called lithium batteries, or lithium metal batteries when the negative electrode is lithium metal. Since the electrolyte is not just an ion transferring medium, a practical consequence is that salt concentration is decreasing upon charging. Because of the charge compensation, this may affect performances of the system under operation and requires an excess of lithium salt that has a non-negligible impact on the volumetric capacity of the cell.^[6]

In the case of all-organic cells, p-type are matching well with n-type materials, as positive and negative electrode material respectively, provided they are processed in the same state of charge. If both electrode are from the same type, cell assembly is then carried out so that one electrode material is in the oxidized state while the other is in the reduced state. This is a common strategy in the case of all-organic cells.

2.2 Conjugated conducting polymers

By definition, conjugated conducting polymers possess an extended π -conjugation along their backbone. However, this basic criterion is not enough to bring conductivity alone. In fact, the electrons move within discrete energy states called bands. These bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can provide electron mobility. Owing to the presence of partially filled energy bands, metals have high conductivities, but most conventional polymers have full valence bands and empty conduction bands.

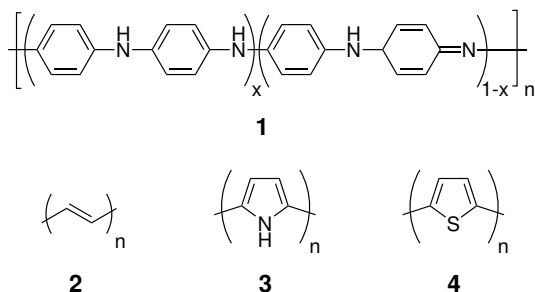


Figure 2.3 – Examples of conducting polymers: 1. Polyaniline, 2. polyacetylene, 3. polypyrrole, 4. polythiophene.

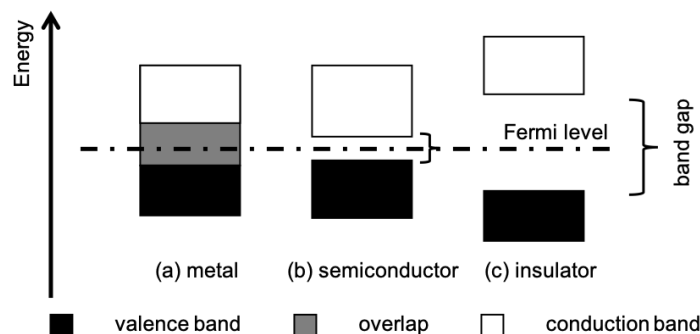


Figure 2.4 – Schematic representation of electron energy gaps in (a) metals; (b) semiconductors; (c) insulators.

Conjugated polymers have relatively narrow band gaps (Figure 2.4c) analogous to inorganic semiconductors.^[7] Many of these materials, such as polyacetylene, polythiophene (PTh), polypyrrole (PPy), and polyaniline (PANi) (Figure 2.3) can have their band structures altered, allowing to reach conductivities exceeding $100 \text{ S}\cdot\text{cm}^{-1}$.^[8] This can be achieved by withdrawing electrons, resulting in a net positive charge on the polymer backbone (p-doping). At higher levels of oxidation, a delocalized polymer segment known as a bipolaron with two electronic charges is formed at a higher energy level. The mobile polarons and bipolarons can move down the polymer chain, and constitute the primary charge transport mechanism in this class of polymers. At the higher levels of oxidation, the bipolaron states form energy bands of substantial width.^[9] In some cases, electrons can be injected^[10] into the polymer, resulting in a net negative charge (n-doping). Both n- and p-doping are then per definition associated with an intercalation of counterions from solution, but also are providing conductivity to the polymer otherwise non-conducting in the undoped state. Consequently, when used as redox active electrode material, the conductivity of the polymer changes with the state of charge (oxidation state). It should be noted that functional groups have an influence on the ability and extent of either p-doping or n-doping of conjugated structures.^[10]

The main conducting polymers can be produced by anodic or chemical oxidation of the corresponding monomer. In both cases, low molar mass material is sometimes solvent-extracted from the polymers produced. However, conducting polymers are most often obtained by elec-

tropolymerization which yields films of the electroactive material.

The electrodeposition can be carried out via different techniques, using mainly potentiostatic, potential-sweep or galvanostatic methods,^[5] yielding films that may grow to thicknesses of several millimeters.^[5] Electropolymerization is the preferred procedure because of the process easiness along with the excellent structural and electrical properties of the polymer films. The deposited polymer is normally obtained as a highly conducting film, and the oxidized material may subsequently be returned to a neutral state by electrochemical cycling. Moderate chain lengths (10 to 1,000 repeating units) have been observed in these materials. The electropolymerization is carried out at potentials chosen to prevent decomposition of the polymer film and the electrolyte. The process optimization may involve other parameters such as the solvent and the electrolyte nature and composition. The high doping level of electrodeposited films is enforced by the electrochemical synthesis and its related stoichiometry of coulombic charges per repeating unit together with the favored growth of the polymer in regions of higher conductance.

On the other hand, the preparation of polymers via chemical oxidation is not allowing a precise control of their doping level and state of charge. The polymers obtained via this method are always pristinely in the oxidized, p-doped (charged) state, and hence contain the anions required (or desired) for charge compensation.

Although their intrinsic conductivity is a desirable property, there is a trade-off inherent to the connection of the redox centers; as they are not separated electronically from each other, the redox potentials of conjugated polymers depend on the doping level and gradually change upon charging/discharging. This results in a sloping cell voltage, which limits the range of application.

Another limitation is related to achievable doping levels. While one charge per repeating unit would be ideal from a conductivity standpoint, conjugated polymers are typically restricted to doping levels of 0.3 to 0.5 at most, reducing the practical capacity.^[11] Higher doping levels tend to destabilize the polymer structure through undesired interchains interactions and/or lead to the destruction of polymer chains. Highly charged species also react more likely with electrolyte components and/or oxygen.^[12,13] Further shortcomings are a limited postsynthesis processability due to their poor solubility, infusibility, and mechanical brittleness.^[4]

Nevertheless all these drawbacks are balanced by the high rate performances that can be delivered, which make conjugated polymers as suitable candidates for high power applications such as high power batteries and supercapacitors, as shown next.^[4]

2.2.1 Polypyrrole

PPy is one of the most studied conjugated polymer in the field of energy storage. Several synthetic methods have been developed including chemical,^[14–16] potentiostatic and potential sweep,^[17,18] as well as galvanostatic^[19] methods.

With respect to battery applications, a cell with PPy as both cathode and anode in acetonitrile electrolyte was already reported in 1986.^[20] Nevertheless, PPy has been mostly studied as a positive electrode material as it cannot be reversibly n-doped. The redox response is typically observed between 3.0 V and 4.0 V *vs.* Li/Li⁺ depending on the doping level, which has a commonly accepted value of maximum 0.33. This latter value determines the theoretical capacity (136 mAh·g^{−1}).^[3] However, the practical capacity without considering the contribution of the counter anion is usually significantly lower.

Despite this specific capacity drawback, PPy-based electrochemical systems still enjoyed a large success owed to their high power performances, simple synthesis and cycling stability. Developments went through composites with enhanced conductivity,^[21] paper-based batteries,^[22] aqueous lithium hybrid batteries,^[23] and so on.

2.2.2 Polythiophene

PTh and its derivatives have been of interest for electrochemists for decades. Such conjugated polymers can be produced by both chemical and electrochemical methods.^[10,24,25] Typical electrochemical methods are set in galvanostatic mode in nonaqueous solvents such as acetonitrile or propylene carbonate, affording doping levels comparable to PPy ($x_{\text{max}}=0.3$). In contrast to PPy, the preparation of good quality films must be carried out in dry conditions and PTh is able to undergo both p-doping and n-doping, although the latter is unstable – particularly in air – and is not fulfilling high doping level requirements.^[5,9]

Regarding battery applications, the first cell with PTh as active material was described in 1983.^[4] Recently, poly(3'-styryl-4,4''-didecyloxy-terthiophene) with a maximum capacity of $45 \text{ mAh}\cdot\text{g}^{-1}$ and poly(4,4''-didecyloxyterthiophene) with maximum capacity of $95 \text{ mAh}\cdot\text{g}^{-1}$ were used as anode material in combination with a PPy cathode.^[26]

The redox response of PTh is usually observed between between 3.0 V and 4.0 V.^[3] Based on the maximum doping level of 0.3 electron per monomer unit, the theoretical capacity equals to $100 \text{ mAh}\cdot\text{g}^{-1}$ for PTh derivatives depending on the molecular structure. Again, the practical capacity is frequently much lower, and values around $50 \text{ mAh}\cdot\text{g}^{-1}$ are typically reported. The greatest strength of conducting polymers such as PPy and PTh being their high electronic conductivity, the most appropriate application for energy storage is then as a cathode for supercapacitors^[11,27] or as a conductive additive in composite cathode materials.^[28–30]

2.2.3 Polyaniline

Among all intrinsically conducting polymers, polyaniline (PANi) has the longest history as it is known in its aniline black form for more than a century.^[31] It has been extensively studied over the past three decades, in particular for its conducting and redox properties, and has found numerous and diverse applications, notably in rechargeable batteries.^[32]

The redox reactions of PANi are more complex than those of PPy and PTh as it features several redox states. The three main states are depicted in figure 2.5. The proportion of benzenoid and quinoid rings varies with the oxidation state. The fully reduced state is called leucoemeraldine ($x=1$), while the fully oxidized state is pernigraniline ($x=0$). Emeraldine, which is 50% oxidized ($x=0.5$), is situated in between.^[31] Some of these states are also displaying protonation - deprotonation equilibria further complicating its chemistry.

The conductivity of PANi depends on two factors: its oxidation state and the degree of protonation of the N atoms (p-doping).^[33] The mechanism of this protonic acid doping is illustrated in figure 2.6. Unlike most polyaromatics, the fully oxidized form of this polymer, pernigraniline, is not conducting. Instead, the partially oxidized states of polyaniline, and in particular emeraldine, become conducting when the N atoms are

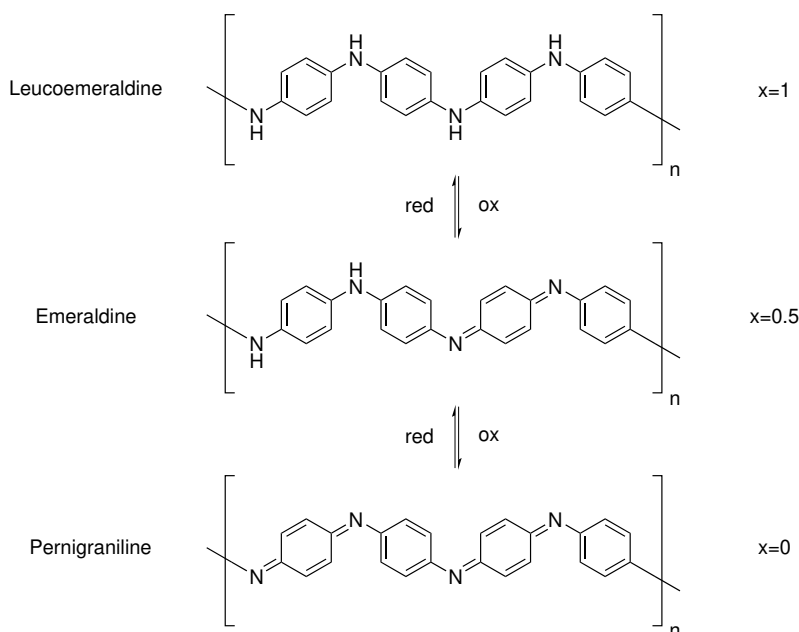


Figure 2.5 – Main redox states of polyaniline.

protonated and charge carriers are thus created.

The electropolymerization of aniline can be carried out potentiostatically,^[34,35] galvanostatically,^[36,37] or through potential-sweep^[35,36,38] at the anode substrate. This deposition is usually achieved in acidic aqueous medium, although other solvent such as acetonitrile or propylene carbonate have been reported, and afford first a compact globular structure with later formation of a porous fibrous structure.^[38,39] As for the chemical synthesis methods, they are carried out in acidic medium to afford the protonated partially oxidized form of the polymer.^[40] This form can be converted into the corresponding base by treatment with an alkali solution.^[41]

Regarding processing of PANi powder materials, the fact that it can afford a viscous liquid in *N*-methyl-2-pyrrolidone has been used to prepare coatings via the doctor blade method.^[5] To improve the conductivity as well as the mechanical stability of the electrodes, carbon additives and binder are frequently used to allow the formation of film with satisfying thicknesses and electrical properties.

The average discharge voltage for PANi is generally found at around

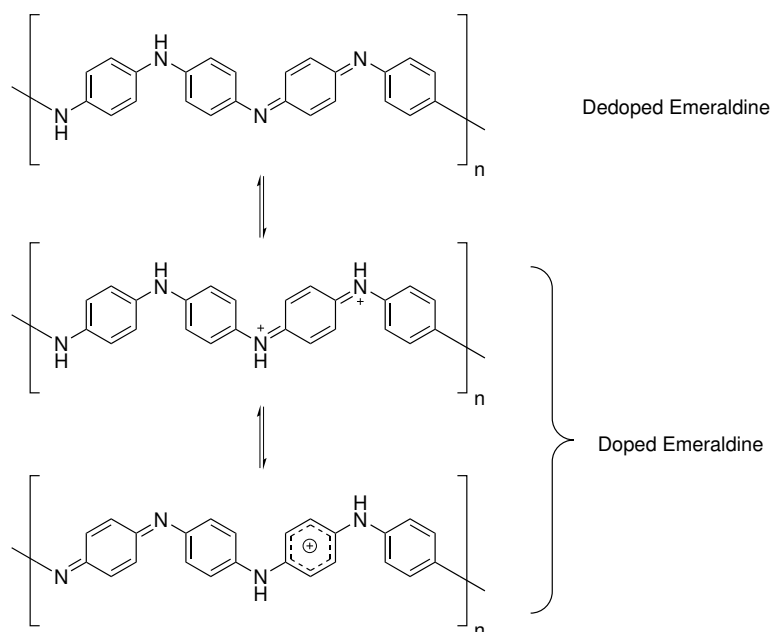


Figure 2.6 – Protonic acid doping of emeraldine.

3.65 V *vs.* Li/Li⁺. While the theoretical capacity is 295 mAh·g⁻¹, the typical specific charge in liquid electrolyte can reach values of about 150 mAh·g⁻¹.^[9] This specific charge can be observed to increase over the first few tenth of cycles, which is believed to be related to electrolyte penetration into the polymer structure enhancing the doping level.^[5] There is a general observation of long cycle lifetimes with the best being approximately 500 charge-discharge cycles.^[9]

Nevertheless, it holds true for PANi as for the other conjugated polymer systems that cycling stability and lifetime of conjugated polymer electrodes must be increased to compete with other existing electrode materials. By fusing the key benefits of nonconjugated redox-active compounds with the conductivity of conjugated polymers, a new class of high-performance materials may emerge in future battery research.

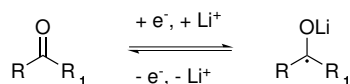


Figure 2.7 – Redox mechanism involving a carbonyl function.

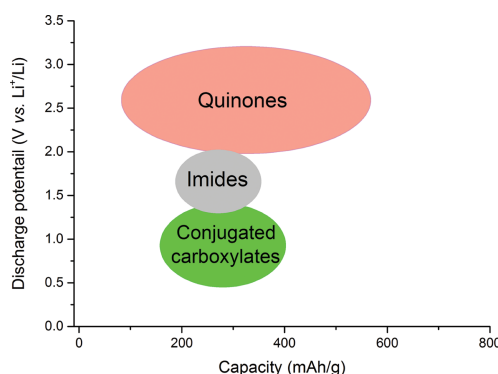


Figure 2.8 – Representation of theoretical capacities and discharge cell potentials *vs.* Li/Li^+ of the three main categories of chemistry used in carbonyl-based electroactive materials.^[42]

2.3 Carbonyl compounds

Almost all carbonyl-based materials are n-type as they are forming anions upon reduction (Figure 2.7). They are therefore mostly used at the positive electrode. Usually the redox active units are displaying two or more carbonyl groups connected via conjugated bonds.^[6] Examples of such carbonyl compounds can be based on imide, conjugated carboxylate and/or quinone chemistry.^[6,42] This latter chemistry is the most promising in terms of battery potential and specific capacity, and is therefore also more investigated to provide high capacity candidates as alternatives to traditional inorganic positive electrode materials for lithium batteries (Figure 2.8).

The stabilization mechanism of the anion can bring another classification of carbonyl materials into three groups (Figure 2.9) as follows,^[42]

- Group I involves vicinal carbonyls – for instance 1,2-diones – providing enolates upon reduction. The enolates functions can be further stabilized by neighboring aromatic systems as in phenanthraquinones.

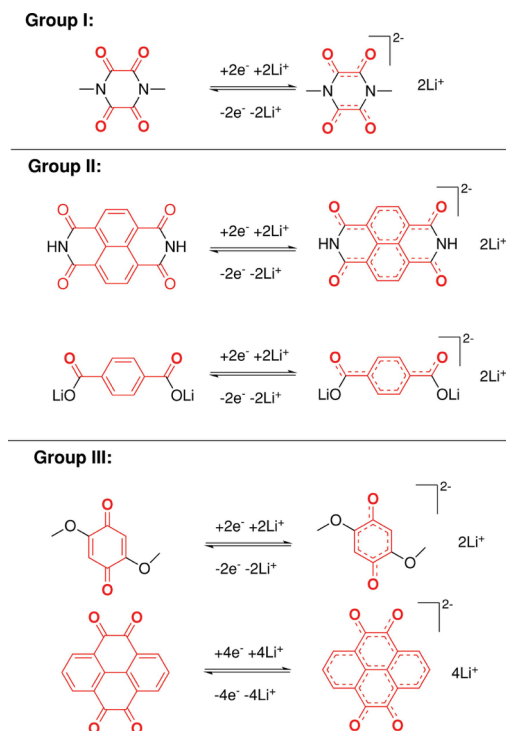


Figure 2.9 – Representative structures of carbonyl-based active electrode materials of the three groups (I,II,III).^[42]

- Group II consists of compounds that are aromatic carbonyl derivatives. The carbonyl groups are directly connected to an aromatic core, dispersing the negative charge by delocalization.
- Group III is composed of well-known quinone moieties that can share some characteristics with group I and II compounds, but having their main stabilizing force lying in the formation of an additional aromatic core upon reduction.

Although the class of carbonyl materials has been studied sporadically in the 1970s and 1980s, it is only a couple of decades ago that it really started to shine in the research on organic materials. Since then many different structures have then been proposed as variations within these three groups. The library has also been further expanded by the introduction of functional groups on the redox units in order to tune the potential of the redox activity. This can be achieved by means of electron-withdrawing or electron-donating groups, that will lower or

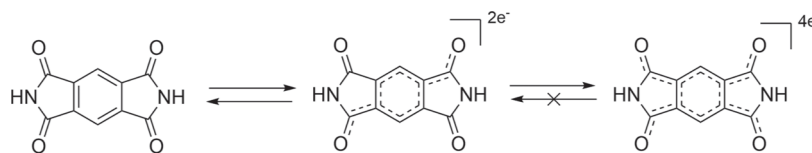


Figure 2.10 – Representation of the redox reaction of phthalimides.^[42]

raise the redox potential of the system, respectively. Yet such approach with functional groups that are redox inactive is realized at the expense of the specific capacity.

2.3.1 Imides derivatives

The aromatic imide moieties can undergo electrochemical redox reactions delivering up to two electrons over two subsequent steps, where only the first one is reversible. The second reduction is irreversible and leads to the destruction of the redox system (Figure 2.10).

Aromatic imides enable high theoretical specific capacity when two imide groups are substituted on a single aromatic core, taking only the first reversible redox process into account (up to $248 \text{ mAh}\cdot\text{g}^{-1}$). One of the simplest compound of this class is dilithium pyrromellitic diimide (Figure 2.11), which was studied as positive electrode material. This compound yields a two-stage redox process affording charge/discharge plateaus centered at 1.81 V and 1.62 V *vs.* Li/Li⁺, each of them corresponding to a one-electron redox reaction per diimide molecule.^[43] Another representative example is naphthalenediimide (Figure 2.11) which is displaying a broad redox activity between 2.4 V and 2.6 V but is characterized by a lower theoretical capacity of $201 \text{ mAh}\cdot\text{g}^{-1}$.^[44]

The cycling stability of these structures is limited by their solubility in the electrolyte. Although the formation of lithium salts lowers their solubility, they cannot afford high cycling stability. Another approach to cope with this issue is the incorporation of aromatic imide moieties into polymeric materials.

Polyimides are well-known as specialty polymers offering high thermal stability together with good mechanical properties. They are synthesized via polycondensation of dianhydrides with diamines. An example is the polymer prepared by reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with 1,2-ethanediamine (Figure 2.11).^[45] The re-

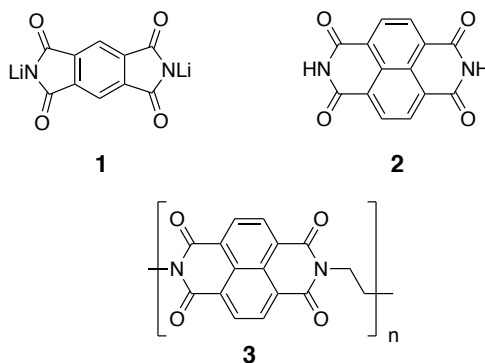


Figure 2.11 – Examples of imide-based electroactive compounds: 1. dilithium pyrromellitic diimide, 2. naphthalenediimide, 3. polyimide based on 1,4,5,8-naphthalenetetracarboxylic dianhydride and 1,2-ethanediamine.

dox process of polyimides process is similar to low molar mass na(phtalimides) compounds, only the first redox stage per imide moiety is practically attainable.

As for their electrochemical performances, the smaller the aromatic unit, the lower the redox potential (1.9 V to 2.6 V) and the higher the theoretical capacity ($100 \text{ mAh}\cdot\text{g}^{-1}$ to $230 \text{ mAh}\cdot\text{g}^{-1}$).^[42] Besides this, the linker has negligible influence performance wise. Too densely cross-linked networks obtained with polyfunctional amines tend however to lower the rate performances. Furthermore, even with high ratios of conductive carbon, rate performances are still limited, as high material activity at rates around 0.5 C typically requires up to 30 wt% of carbon, detrimental to the specific capacity of the electrode. Also, their application to lithium hybrid batteries is hindered by their relatively low voltage and the fact that polyimide systems are not protected against deep discharge.

2.3.2 Carboxylate derivatives

Organic conjugated carboxylates can undergo a reversible two-electrons redox process, relying on the stabilization of the dianions by a conjugated, preferably aromatic, system (Figure 2.12). In comparison to other redox organics, the redox reaction has its potential brought down to very low values due to the loss of resonance in the process.

The first study within this class of materials was initiated by Ar-

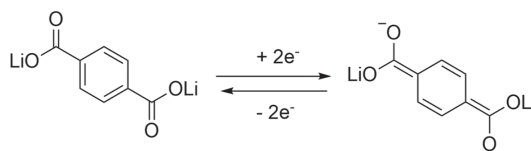


Figure 2.12 – Representation of the redox reaction of an aromatic dicarboxylate.^[42]

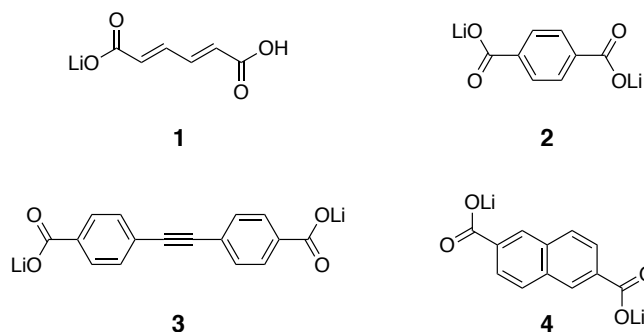


Figure 2.13 – Examples of carboxylate-based electroactive compounds: 1. dilithium-*trans-trans*-muconate, 2. dilithium terephthalate, 3. 4,4'-tolane-dicarboxylate, 4.2,6-naphtalene dicarboxylate.

mand *et al.* with the investigation on dilithium-*trans-trans*-muconate (Figure 2.13), exhibiting a specific capacity of $205 \text{ mAh}\cdot\text{g}^{-1}$ (59% of the theoretical capacity) at an average potential of 1.45 V.^[46]

Higher material utilization was achieved later when aromatic systems were examined. In that respect terephthalic acid represents a very interesting candidate, as it can be produced sustainably from oxidative metabolism of *p*-xylene, or by recycling polyethylene terephthalate.^[46] Electrodes based on dilithium terephthalate (Figure 2.13) demonstrated full material utilization during the first discharge cycle at a potential of 0.8 V *vs.* Li/Li⁺. Yet the capacity retention could be improved as it was only about 78% after 50 cycles.

To improve the cyclability, a common strategy consists in the extension of the conjugated system to enable π -stacking. This was successfully applied with 4,4'-tolane-dicarboxylate (Figure 2.13) exhibiting 89% capacity retention (initial capacity of $192 \text{ mAh}\cdot\text{g}^{-1}$) at a potential of 0.65 V *vs.* Li/Li⁺.^[47]

Owed to their low redox potential and their n-type behavior, carboxylate compounds as synthesized in their oxidized form should be

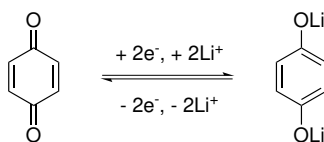


Figure 2.14 – Redox mechanism of 1,4-benzoquinone in a lithium-based electrolyte.

well suited as negative electrode materials. A successful practical example has been brought in the literature as a 3.9 V organic LIB applying 2,6-naphthalene dicarboxylate (Figure 2.13) in a metal-organic framework as anode and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a cathode, both as laminated electrodes.^[48]

2.3.3 Quinones derivatives

Quinones are advantageously displaying a low molar mass per unit combined with the theoretical ability of a two-electrons redox process (Figure 2.14). For instance 1,4-benzoquinone, one of the simplest structures, has a theoretical capacity of about $500 \text{ mAh}\cdot\text{g}^{-1}$.^[49] However, strategies must be developed to circumvent the main drawback of most quinone derivatives, that is their solubility in common organic electrolytes.

In the late 1980s, a first milestone in terms of cyclability has been reached with the introduction of nonylbenzohexaquinone as cathode material, its large planar structure preventing dissolution (Figure 2.15). Despite its high theoretical capacity of $489 \text{ mAh}\cdot\text{g}^{-1}$, only a fourth was practically attained owed to irreversible loss in discharge capacity. This is partly due to the low potential to be reached for complete reduction of the quinones units where decomposition of the electrolyte also occurs, but also to an irreversible redox process where three of the twelve electrons are lost in the formation of radical anions.^[50]

Thanks to the low molar mass per unit and their two-electron redox reaction, quinones are of particular interest as active material for secondary batteries. Depending on the structural design, this material class displays its redox activity between 1.8 V and 3.0 V *vs.* Li/Li^+ , making them more suitable as positive electrode material.^[42]

Many different approaches have been developed in the literature to

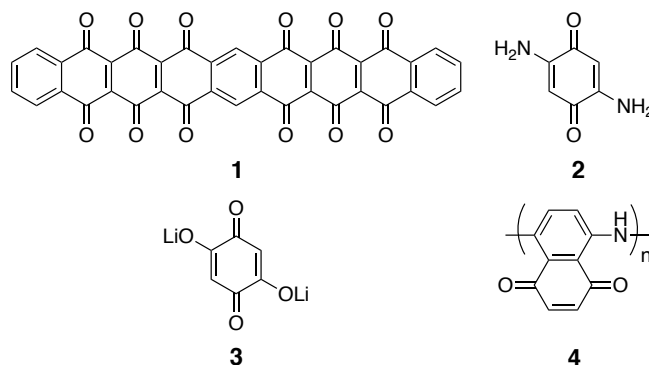


Figure 2.15 – Examples of quinone-based structures: 1. nonylbenzoehexaquinone, 2. 2,5-diamino-1,4-benzoquinone (DABQ), 3. dilithiated 2,5-dihydroxy-1,4-benzoquinone, and 4. polymeric quinone with NH linkage.

cope with their solubility in common battery electrolytes. Nevertheless most of them were not without any drawback. A straightforward strategy consists in enhancing their polarities via salt formation, notably by lithiation. Besides, this salt formation can advantageously result in the formation of a metal-organic framework. Sun *et al.* studied the dilithiated form of 2,5-dihydroxy-1,4-benzoquinone coordinated with lithium ions (Figure 2.15).^[51] However, there was a noticeable voltage gap of 0.6 V between charge (2.35 V) and discharge voltage (1.75 V), indicating a strong polarization of the electrode. Also, from the examples applying this strategy, a significant drop of the working potential is generally observed.^[6]

Promising approaches are found in the use of non-covalent interactions such as $\pi - \pi$ stacking or hydrogen bonds. The former was applied to anchor the active compounds on carbon nanotubes, a strategy limited in terms of loading ability and restricting the access to high specific capacities. The latter, i.e. intermolecular interactions via H-bonds, was recently developed by Sieuw *et al.* who examined the redox behavior of 2,5-diamino-1,4-benzoquinone (DABQ, figure 2.15). This compound possesses a high theoretical capacity of $388 \text{ Mah} \cdot \text{g}^{-1}$ at an average voltage of 2.4 V.^[52] Results provided on the electrolyte formulation would require further optimizations to improve the cycling stability and opportunities could be found in the use of H-bond interacting binders and/or conductive carbon networks.

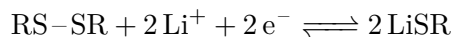
Another strategy is the utilization of quasi-solid state or polymer-gel electrolytes, in which the active material is insoluble, but these materials suffer from low ion conductivity and led to a poor rate performance.^[53]

Probably the most promising approach is the incorporation of quinone structures in or on a polymeric backbone. Among the examples, poly(5-amino-1,4-naphthoquinone) (Figure 2.15) was polymerized chemically and electrochemically affording a quinone redox activity at 2.6 V with a specific capacity of 286 mAh·g⁻¹. This polymer is displaying a polyaniline backbone which is redox active as well, but because its redox activity is occurring at a higher potential, it does not interfere in the redox chemistry of the quinone system.^[54]

Globally, such approaches possess their own challenges because the design of the polymerization technique is constrained by the redox active units that can be acting as radical scavenging species as well as electrophilic and/or nucleophilic moieties. Nevertheless results have been reported via different polymerization techniques, such as polymer-analogous reactions, polycondensations, and polyaddition reactions while allowing to aim for satisfying stability at more than a hundred of cycles.^[42]

2.4 Organosulfur compounds

Organosulfur compounds made their first entrance as electroactive material with a report from Viasco *et al.* on the use of small molecules bearing disulfide bonds for high temperature batteries.^[55] The redox process of these small molecules is based on the reversible scission / reformation as per the following equation,



Cyclic voltammetry showed a very broad separation between the cathodic and anodic peak potentials ($\Delta E_p = 1.25\text{ V} - 1.63\text{ V}$), indicating very poor kinetics of the redox reaction, and the the material utilization was very poor. Nevertheless this work demonstrated the feasibility of positive electrode materials based on organosulfurs. Among the various material reported after this first attempt, different categories can be distinguished, notably main-chain organosulfur polymers, side-chain polymers, and p-type organosulfur polymers.

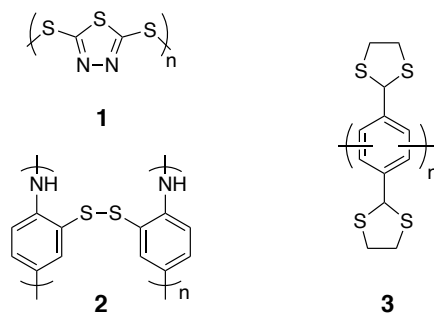
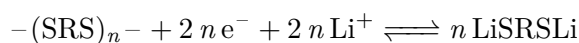


Figure 2.16 – Examples of organosulfur-based structures: 1. main-chain type, poly(2,5-dimercapto-1,3,4-thiadiazole); 2. side-chain type, poly(2,2'-dithiodianiline) and 3. p-type, poly[1,4-di(1,3-dithiolan-2-yl)benzene].

2.4.1 Main-chain organosulfur polymers

As the name suggests, they contain disulfide bonds in the main chain. The scission / reformation results in the cleavage of the polymer backbone into smaller segments as follows,



Polymers based on this redox couple are offering high energy density (50% higher than LiCoO_2) but suffers from low redox rates at room temperature. However, electrocatalysts such as polyaniline can be used to accelerate the cleavage kinetics of the disulfide bonds by lowering the separation between the cathodic and anodic peaks ($\Delta E_p = 0.5 \text{ V}$).^[56] An early example of this design is the blend reported by Sotomura *et al.* which is incorporating PANi and a polymer based on 2,5-dimercapto-1,3,4-thiadiazole (Figure 2.16, theoretical capacity of $362 \text{ mAh}\cdot\text{g}^{-1}$). This system displays a single discharge plateau at 3.4 V corresponding to the electron transfer through PANi to reduce disulfides moieties. Charging of the electrode at 4.5 V deactivates PANi which is subsequently reactivated by the oxidative polymerization of thiolate species. Thanks to improved kinetics, such systems are then allowing the cell to operate at room temperature but only with limited rate capabilities.

Nevertheless, the main caveat of main-chain architectures is dissolution and diffusion issues of thiolate fragments through the electrolyte solution, resulting in low recombination efficiency and poor capacity re-

tention.^[6] For these reasons, only solid-state or gel polymer electrolytes can be used with these systems.

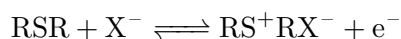
2.4.2 Side-chain organosulfur polymers

Side-chain organosulfur polymers can be considered as the second generation of organosulfur compounds. They feature a confined structure where disulfide bonds are installed in the side-chain, thus avoiding the scission of the main chain during the redox process. This strategy efficiently avoids fragment diffusion and hence allow to access better capacity retention than the main-chain type polymers.

An interesting example is poly(2,2'-dithiodianiline), a polymer designed by Naoi *et al.* which is hybridizing a PANi structure with the disulfide moiety (Figure 2.16).^[57] This polymer delivered a flat discharge plateau at 2.5 V *vs.* Li/Li⁺ with a capacity of 270 mAh·g⁻¹; this high capacity value is evidencing that redox processes of both disulfide moieties and the PANi backbone are accessible as the overall theoretical capacity considering these two is about 330 mAh·g⁻¹ (assuming a doping level x=0.5).

2.4.3 P-type organosulfur polymers

Thanks to the absence of bond destruction in the redox, this category allows to get round both diffusion issues of active material species but also the sluggish reaction kinetics of disulfide bonds and the related low rate capabilities. The organosulfur chemistry here is not involving thiolate / disulfide redox couples but thioethers that can undergo reversible electron-extraction to form stable cationic radical species as follows,



Although this concept is relatively new, many structures derived from the concept of these p-type polymers have been proposed since the first attempts in the late 2000s. Among others, conducting structures seems to have hold the attention of researchers. An example is poly[1,4-di(1,3-dithiolan-2-yl)benzene] (Figure 2.16), a thioether proposed by Zhang *et al.* which displays four redox sites per unit, allowing to obtain a theoretical capacity of 374 mAh·g⁻¹ while displaying a discharge potential

of about 2.2 V *vs.* Li/Li⁺), both being just comparable to that of disulfides.^[58]

2.5 Organic radical compounds

Many organic compounds are involving radical species in their redox states, and examples have already been introduced in the two past sections: p-type organosulfurs and conducting polymers. The purpose of the present section however is to focus on some oxygen-centered radical compounds, and more specifically those involving nitroxide functional groups.

2.5.1 Main characteristics

Nitroxide-based polymers are widely acknowledged as the most studied radical compounds for electrode applications. Nitroxides are potentially able to undergo reversible reduction to a n-doped aminoxy anion and/or a reversible oxidation to a p-doped oxoammonium cation (Figure 2.17). To allow stability of the nitroxide group, bulky substituents such as alkyl groups are usually surrounding the radical. The most representative example of stable nitroxides as a small molecule is 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) which has found numerous applications as a probe for biological systems, a radical trap, a catalyst in inorganic oxidation reactions, a mediating species for controlled radical polymerization etc.^[59–64]

Studies on nitroxides for energy applications kicked off in 2002 with the first report on their use as positive electrode material by Nakahara *et al.*, which employed poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA). PTMA is bearing TEMPO units as redox active side-groups (Figure 2.18).^[65] This compound displays a theoretical capacity of 111 mAh·g^{−1} and affords flat charge/discharge plateaus cen-

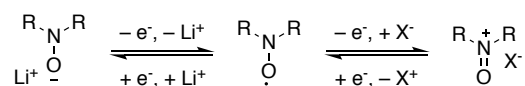


Figure 2.17 – N- and p-doping mechanism of nitroxide compounds in presence of a lithium-based electrolyte.

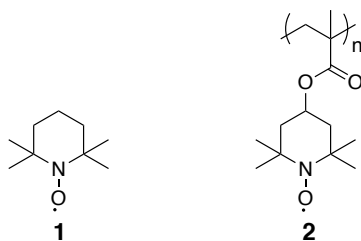


Figure 2.18 – Chemical structures of two main representatives of nitroxide radicals: 1. TEMPO, and 2. PTMA.

tered at 3.6 V *vs.* Li/Li⁺. In their report, the group synthesized PTMA starting from its amine precursor, obtained via free-radical polymerization of 2,2,6,6-tetramethylpiperidine methacrylate monomer (TMPM), subsequently oxidized with 3-chloroperoxybenzoic acid into the redox active form. PTMA later became one of the most studied of its class and many other groups reported their own synthesis strategies, relying on techniques as various as atom transfer radical polymerization (ATRP),^[66–68] reversible addition-fragmentation chain-transfer polymerization (RAFT),^[68] group-transfer polymerization (GTP),^[69] single electron transfer-living radical polymerization (SET-LRP),^[70] nitroxide-mediated polymerization (NMP)^[68] etc. These polymerization techniques will be detailed in the next chapter.

One of the most distinctive features of such nitroxide compounds with respect to other electroactive materials, whether they are organic or inorganic, is the high-rate capability. Kinetic studies have evidenced very fast reaction rates with electron transfer rate constants of about 10^{–1} cm²·s^{–1},^[71] surpassing the value of ferrocene 10^{–2} cm²·s^{–1},^[6] a well-known internal calibrator in electrochemistry. Such high kinetics can be explained by structural aspects; the nitroxide radical hybridized orbital was found to exhibit a character in-between pure *sp*² and *sp*³ of oxoammonium cation and amine, respectively. The structure is thus experiencing minimal structural changes upon oxidation in addition to the absence of bond cleavage/formation, both being beneficial for the reaction rates.

As for the electron transfer within a radical polymer composite, 5 processes are potentially rate determining steps:^[6]

- the interfacial charge transfer between the current collector and the conductive filler,

- the electric conduction in the conductive filler network,
- the heterogeneous charge transfer at the conductive filler / polymer interface,
- the charge transfer within the bulk polymer layer,
- the diffusion of electrolyte counter-ions throughout the composite.

As the first two processes are usually smooth, research is more focusing on the last three factors. As for the charge transfer in such non-conjugated polymers, it relies on a different mechanism than for conjugated polymers presented earlier in this chapter. Here the mechanism involves localized redox sites and is referred as a hopping mechanism.^[72] In this mechanism, the charge transfer occurs through electron self-exchange between redox sites and progresses along the redox gradient among these close radical units. The resulting semi-conductive behavior (conductivity around $1.5 \text{ mS}\cdot\text{cm}^{-1}$)^[73] is regarded as sufficiently fast when distances are limited (such as in thin films) but is regarded as sluggish when thicker layers of polymer are involved.^[2] In this latter case, the charge transfer can be the rate limiting step to the propagation of the redox process within the bulk polymer. Therefore the electrodes are typically incorporating conductive fillers – as much as 70 wt% in the earlier reports – to support the redox process,^[2,65] especially at the very high rates that the nitroxide redox kinetics can potentially deliver.

The last electron transfer process, the counter-ion diffusion is another limiting parameter at very high current densities and hence can prevent full material utilization. It is worth noting that from that standpoint the charge process can be slightly less efficient than the discharge process because the concentration of the electrolyte salt drop to minimum at the fully discharged state.^[6]

As for the cyclability of nitroxide-based polymer electrodes, the redox species are regarded as offering good long-term cycling stability (> 1000 cycles). Nevertheless, even high molecular weight polymers of this class are usually soluble in standard organic solutions,^[69,74] leading to so-called shuttle effect – and related self-discharge issues – as well as considerable initial irreversible capacity loss. In that respect, conductive carbon additives are generally serving an additional purpose to their charge collection enhancement role, that is, adsorbing soluble species and hence retarding the effects of the slow dissolution of active materials.^[75]

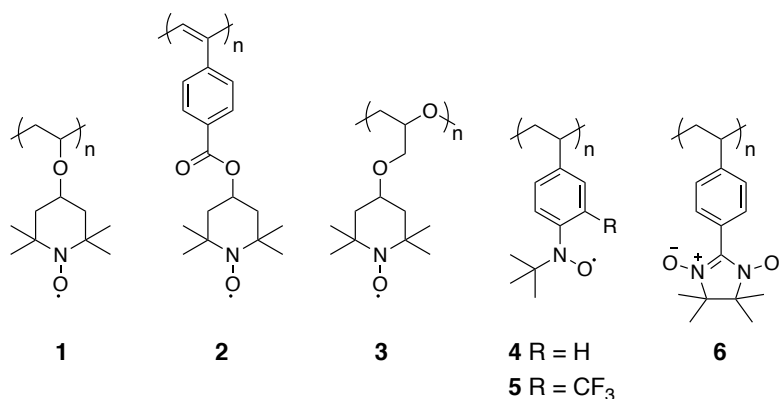


Figure 2.19 – Chemical structure variations of nitroxide-based polymers: 1. poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE), 2. polyacetylene derivative, 3. polyether derivative, 4. and 5. poly(nitroxystyrene) derivatives, and 6. poly(nitronylnitroxide) derivative.

2.5.2 Variations of nitroxide polymer structures and their related properties

Thanks to their many promising properties, nitroxides have enjoyed a vivid interest as evidenced by the many different related structures proposed in the literature. Some of them were designed to cope with the relatively low theoretical capacity of PTMA ($111 \text{ mAh}\cdot\text{g}^{-1}$) in comparison with common inorganic electrode materials ($140 \text{ mAh}\cdot\text{g}^{-1}$ to $170 \text{ mAh}\cdot\text{g}^{-1}$). This value drops to $70 \text{ mAh}\cdot\text{g}^{-1}$ when the weight of the counter-anion is considered (assuming it to be PF_6^-).

Some of these variations have been designed to simplify the polymer motif, or to increase the redox active group over molecular weight ratio (per repeating unit). An example of such structure with a higher theoretical capacity is poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (Figure 2.19, PTVE, $135 \text{ mAh}\cdot\text{g}^{-1}$).^[76,77]

Other attempts have also been made to improve the rate capabilities. For instance, a conjugated backbone is expected to exhibit semi-conductivity and enhance charge transport properties. This strategy has been applied with the design of polyacetylene derivatives such as the one displayed in figure 2.19.^[78,79] Another example is the polyether derivative (Figure 2.19) displaying a flexible and ionophoric backbone obtained from an epoxide functionalized TEMPO monomer.^[80]

Structural variations have also been brought to modulate the potential of the redox groups. As for the p-type doping, the tuning can only be achieved over a limited potential window (3.5 V to 3.8 V *vs.* Li/Li⁺).^[6] The potential of the n-type is more interesting from an application standpoint as it can bring nitroxides to be implemented as negative electrode materials. Furthermore, there is the possibility to assemble an all-polymer cell thanks to a reasonable potential difference (around 1.0 V) accessible with variations of poly(nitroxystyrenes): one using a structure displaying its p-doping redox activity at a higher redox potential (positive electrode) and second with a structure bearing trifluoromethyl groups optimized for its n-doping process at lower potential (negative electrode) (Figure 2.19).^[81] Another point of interest regarding n-doping is the design of structures that can be both reversibly n-doped and p-doped such as the poly(nitronylnitroxide) reported by Suga *et al.* (Figure 2.19), which displays its redox activity at 2.33 V *vs.* Li/Li⁺ (n-doped) and 3.60 V *vs.* Li/Li⁺ (p-doped). This n-doping process is then of practical interest for positive electrode applications thanks to its higher overall theoretical capacity of 206 mAh·g⁻¹ considering both redox processes.^[82]

2.5.3 Nanostructures in nitroxide polymer electrodes

As evidenced beforehand in this section, a suitable radical polymer electrode should be insoluble in the electrolyte and rely on a minimal amount of conductive additive to achieve the best balance between specific capacity and power performances. Polymers such as PTMA are only partially fulfilling these requirements.

To cope with the slow dissolution in the electrolyte, the traditional solutions are to increase the molar mass or to cross-link the electroactive polymer. A less traditional approach was realized by Lin *et al.* who grafted the electroactive polymer on silica nanoparticles using surface-initiated ATRP (SI-ATRP).^[83]

Two other strategies were developed by Hauffman *et al.* (Figure 2.20), both based on block copolymer self-assembling properties.^[67,84] Their strategies relied on the synthesis by ATRP of diblock copolymers combining a PTMA block linked to an insoluble polystyrene (PS) block (PS-*b*-PTMA). In the first strategy they aimed at the obtaining of copolymer micelles that were incorporated in a relatively classical composite

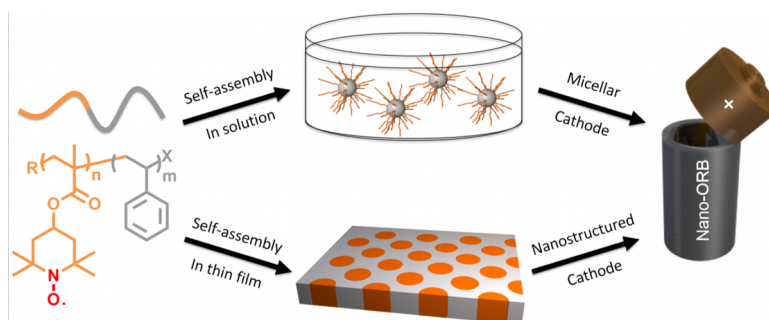


Figure 2.20 – Schematic representation of nanostructured organic radical cathodes by self-assembling block copolymers in solution and in bulk with the aim of their application in organic radical batteries (ORBs).^[67,84]

electrode by blending them with conductive carbon and a binder. In their second report, they used similar block copolymers to realize self-assembled monolayers with phase segregation of PTMA cylindrical domains in a PS matrix. The resulting nanostructured thin film prepared on indium tin oxide demonstrated high rate performances when tested as electrode in an acetonitrile-based electrolyte.

Another interesting strategy to prepare thin films electrodes was disclosed by Choi *et al.*^[85] In their report they describe a method to individualize single-walled carbon nanotubes (SWCNTs) and wrap them with PTMA at the molecular level. The favorable dispersion and the thin film structure (<200 nm) of this composite material also allowed to reach high rate performances with a very low dead-weight content (4wt% of SWCNT) in an acetonitrile-based electrolyte.

Nevertheless, in all the above-mentioned systems, there is a significant dead-weight in the resulting material and/or the rate performances are demonstrated at the very favorable level of thin films. Furthermore, at the exception of polymer-wrapped SWCNTs, these strategies are not addressing the main downside of traditional approaches which is related to the conductive agent incorporation after all synthetic steps, hence preventing to achieve the formation of an ideal composite structure at the nanoscale.

A straightforward approach to circumvent this issue was proposed by Vlad *et al.*^[86] The solution that has been adopted consists in incorporating the conductive charge directly during the synthesis of the polymer (*in situ*). To this end, all reagents (monomer, radical initiator

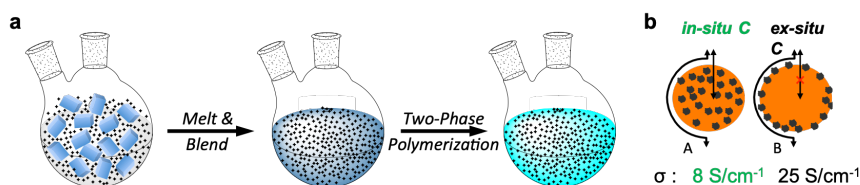


Figure 2.21 – (a) Schematic representation of the solvent-free melt-polymerization to synthesize PTMA with *in situ* incorporated carbon.

The monomer is melted and blended in presence of SC45 prior to polymerization. (b) schematic of various PTMA/C composite morphologies: *left*, carbon is uniformly dispersed within the polymer matrix as it is better obtained via its incorporation during the polymerization; *right*, carbon primarily coats the surface of polymer particles as usually obtained when incorporation is carried out after all synthetic steps.^[86]

and cross-linking agent) are ground and blended together in the solid state in presence of the SC45 conductive nanocarbon agent. Afterwards the reaction mixture is heated up above the monomer melting point in the reactor to form first a slurry where the polymerization process is taking place upon further heating (Figure 2.21a).

This melt polymerization process possesses the further advantages that it is solvent-free, and that it can potentially be scaled up, as demonstrated by successful preparations at the 100 g scale. Comparisons made with *ex situ* incorporation of carbon after all synthetic steps showed that although conductivity is lower for *in situ* carbon incorporation, the rate performances are higher thanks to the texture of the composite material which is more favorable to the electrochemical reaction propagation upon cycling (Figure 2.21b). In their study they evidenced that their composites are enabling long-term cycling (>1200 cycles) but also that PTMA with 30 wt% of carbon can deliver more than half of its nominal capacity at impressive C-rates higher than 20C.

2.5.4 Hybrid pseudocapacitors based on nitroxide polymers

Batteries and supercapacitors both rely on electrochemical processes that are determining the power and energy performance metrics. Whereas batteries are relying on bulk reaction properties, supercapacitors, also known as electrical double layer capacitors (EDLCs) are involving sur-

face charge storage. Although significant progresses have been made to provide higher power density batteries and higher capacity density supercapacitors, the research is also focusing on electrode materials that combine the best of both worlds. Recognizing that certain electrode materials can display EDLC-like power performances while featuring redox processes that bring their capacity closer to traditional LIB materials, a new classification was proposed for them as pseudocapacitive materials.^[87]

A noticeable example of pseudocapacitive materials is PTMA. Nevertheless, for all the reasons presented in their dedicated section in this chapter, there is still a gap between nitroxide-based polymer electrode and LIB materials regarding the specific energy density. A straightforward approach to reach higher capacity for such pseudocapacitive materials would be to combine different energy storage materials within a single device. Such hybrid systems have already been explored with the combination of LIB and EDLC materials,^[88] but components are only contributing to the performances in proportional relationship with their composition. Furthermore, power and energy are decoupled.

An elegant solution has been provided by Vlad *et al.*, which makes synergistic use of pseudocapacitive and battery components.^[89] In their publication, they showed that enhanced battery-capacitor hybrids offering more than the sum of their components can be realized by careful choice of the supercapacitive and battery materials. This idea is exemplified by the choice of LiFePO_4 and PTMA as battery and pseudocapacitive materials, respectively.

The key design principle of this concept is the rapid electrochemical response in combination with higher working potential of PTMA (Figure 2.22). This allows, at equilibrium, the preferential charging of LiFePO_4 at the expense of PTMA. Nonetheless, PTMA is the faster discharge component. Using an appropriate pulse charge sequence, the rapid response of PTMA will ensure the fast charge. During the subsequent relaxation, PTMA will charge the LiFePO_4 component. Overall, this hybrid system was evidenced to provide high energy and power capacity, over-polarization protection, as well as fast and stable recharge over more than 1500 cycles. Additionally, its unique power leveling capability could be of particular relevance in solar conversion-storage units.

Applying the same rational, Dolphijn *et al.* designed a system based

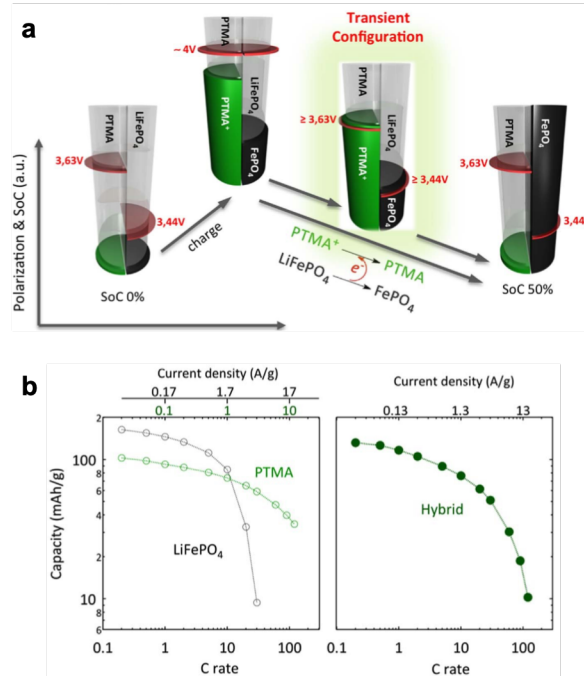


Figure 2.22 – (a) Representation of the fast charge/relaxation process. The green and black half-cylinders are indicative of the stored charge in PTMA and LiFePO₄, respectively. The relative position of the red disk indicates the polarization of the constituents in the hybrid electrode. Except during the charge, the polarization is the equilibrium OCP for each component. Fast charging leads to a thermodynamically unstable configuration, with evanescent co-existence of high potential PTMA⁺ with low potential LiFePO₄ species forcing an internal charge transfer equilibration. The depicted situation is representative of 50% SOC, i.e. at equilibrium only the LiFePO₄ component will be charged, (b) capacity function of C-rate and applied current density (symmetrical charge/discharge conditions) for LiFePO₄, PTMA and hybrid electrode. 1C corresponds to 100 mA·g⁻¹, 170 mA·g⁻¹ and 130 mA·g⁻¹ for PTMA, LiFePO₄, and hybrid electrode respectively. [89]

on the coupling of PTMA with a higher voltage material (LiMn_2O_4).^[90] The aim here is to obtain hybrid electrodes with enhanced power delivery characteristics, as oxidized PTMA^+ will be both the favored and the best rate capable redox species – hence acting as a power buffer.

2.6 Conclusion

Different organic-based electrode materials can be envisioned as promising candidates to overcome current limitations of conventional LIB electrode materials: cost, toxicity, power and energy density performances. To date, many materials with various redox-centers have been identified: conducting polymers, organosulfurs, nitroxides radicals or carbonyl compounds. Each of these classes possesses its own advantages and drawbacks. Research has achieved significant progresses to address their major common issues: dissolution in the electrolyte and electrical resistivity. Nonetheless, further improvements are required to reach practical feasibility and replace current inorganic materials. This must be achieved by realizing the combination of properties that would allow to match or exceed current performance standards imposed by the current inorganic LIB chemistry.

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CHAPTER 3

CARBON NANOTUBE SURFACE MODIFICATIONS

Abstract

Thanks to their unique structure and related physical properties, CNTs have been envisioned for a wide variety of applications, both in materials and life science. This chapter starts with an introduction to their properties. From an application standpoint, functionalization is regarded as extremely important to improve CNT processability and combine their unique properties with those of other classes of materials. Functionalization is then portrayed with an emphasis on covalent methods. Among the chemical methods, functionalization with polymers holds great interest to maximize the loading and functionality in the resulting hybrid material. Therefore a selection of synthetic methods allowing control over the synthesis of well-defined functional polymers is also presented. Lastly, this chapter is unveiling the use of such kind of methods for direct polymerization from surfaces.

3.1 Carbon nanotubes

3.1.1 Historical perspective, properties and interest

In 1985, Kroto, Smalley *et al.*^[1] discovered a new allotrope of carbon, the buckminsterfullerene (C_{60}). The C_{60} is a molecule that resembles a soccer-ball with carbon rings fused together in a cage-like structure. The cage structure is composed of 32 faces (20 hexagons and 12 pentagons) with 60 carbon atoms at the vertices. The discovery of this structure contributed to raise the interest of the research on carbon-based cage structures.^[2]

In 1991, another allotrope of elemental carbon, namely carbon nanotubes (CNTs), was reported by Sumio Iijima.^[3,4] The reported CNTs were multi-walled carbon nanotubes (MWCNTs) which were incidentally synthesized during fullerene synthesis experiments via arc-discharge evaporation method. Two years later, Iijima *et al.*^[5] and simultaneously Bethune *et al.*^[6] discovered the synthesis of single-walled carbon nanotubes (SWCNTs) while aiming at synthesizing MWCNTs filled with transition metals. SWCNTs can be represented as a single sheet of carbon atoms which has been rolled up. This sheet is typically an hexagonal lattice in which one atom forms each vertex. The structures of MWCNTs and SWCNTs can be considered as an intermediate between the buckyballs (closed shells) and another allotropic form of carbon, graphene (flat sheets, single layer of atoms in a 2D hexagonal lattice). This latter allotrope was isolated and characterized in 2004 by Geim and Novoselov who were awarded the Nobel Prize in Physics 2010 for their "groundbreaking experiments regarding the two-dimensional material graphene". Figure 3.1 is displaying graphical representations of a graphene sheet, a SWCNT and a MWCNT. In all these different forms, the carbon atoms are found in the sp^2 -hybridization state, and are thus essentially structures fusing aromatic rings together, the result being an extended polyaromatic system.

SWCNTs are composed of a graphene layer rolled up as a cylinder with diameter typically within the range from 0.7 nm to 2 nm and exhibiting half-spheres similar to a half-fullerene on both ends. MWCNTs are consisting in concentric layers on nested nanotubes (2 to 50), with an interlayer spacing around 3.4 Å, an external diameter up to 100 nm, an internal diameter (hollow space) between 1 nm to 10 nm and a length

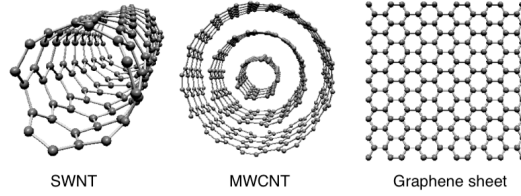


Figure 3.1 – Graphical representations using a structural model: SWCNT, MWCNT and a graphene sheet.^[7]

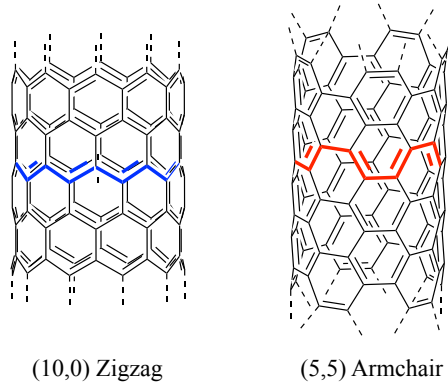


Figure 3.2 – Two particular configurations found among others in CNT particles; on the left a (10,0) CNT displaying a zigzag pattern, on the right a (5,5) displaying an armchair pattern.

of a few micrometers. As SWCNTs, pristine MWCNTs are equally exhibiting half-fullerene at their ends.

A SWCNT can be metallic or semiconducting depending on the chirality of the structure. Some CNTs are characterized by a structure displaying a closed zigzag path along the circumference of the CNT. If the tube is instead encircled by a closed armchair path, the structure is called armchair type (Figure 3.2). Besides the zigzag and armchair configurations, some other structures can be exhibited by CNTs.

To describe them, one should imagine to cut the CNT along its axis and lay it down flat on an imaginary sheet of graphene. The two halves of the atom C will end up on opposite edges of the strip, over two atoms C and C' of the graphene (Figure 3.3). The line from C to C' will correspond to the circumference of the cylinder that went through the atom A , and will be perpendicular to the edges of the strip. In the graphene lattice, the atoms can be sorted in two classes, depending on

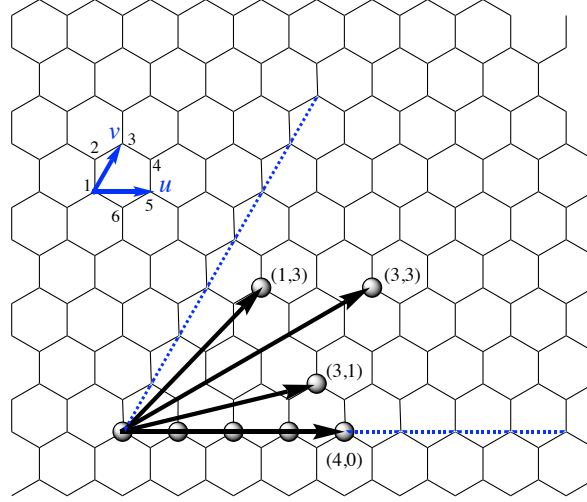


Figure 3.3 – This scheme presents the four types of vectors associated to non-isomorphic nanotubes: the armchair $(3,3)$, the zigzag $(3,0)$, and the chiral types (m,n) with $0 < m < n$; $(1,3)$ is the mirror image of the $(3,1)$ type.

their bond orientations. Half of the atoms have their bonds oriented in the same way, the other one displaying bonds oriented at 180 degrees from the other. Atoms C and C' must belong to the same class.

Considering an atom of the graphene lattice, one can define two linearly independent vectors u and v that connect this atom to its nearest neighbors with the same bond orientations (Figure 3.3). Numbering the consecutive carbon atoms from 1 to 6, u is the vector from C_1 to C_3 , and v is the vector from C_1 to C_5 (blue arrows). Hence, for two atoms belonging to the same class, the vector connecting them can be defined as a linear combination $nu + mv$, where n and m are integers. If the mathematical operation is applied to a strip which is then rolled up into a cylinder to bring the points C (origin of the vector) and C' (end of the vector) together, the result is a SWCNT characterized by the vector (n,m) . When the result of the construction is a pair $(n,0)$, the SWCNT is a zigzag nanotube, with a closed zigzag of $2n$ atoms. When the result of the construction is a pair (n,n) , the SWCNT is a zigzag nanotube, with a closed zigzag of $4n$ atoms. It should be noted that the pair $(-2m, n+m)$ corresponds to a rotation of the strip of 60 degrees in the plane defined by vectors (u,v) and hence the structure of the resulting SWCNT is unchanged.

Some properties of carbon nanotube are notably influenced by their spatial configurations, and can be described by the pair (n, m) , also called the chiral index or just chirality. A nanotube is chiral if $m \geq 0$ and $m \neq n$. Its enantiomer is then characterized by the pair (m, n) which corresponds to a 30 degrees clockwise rotation of the strip from the direction of the vector u . Consequently, the only achiral nanotubes are the zigzag $(n, 0)$ and the armchair (n, n) types.

Regarding the electrical properties, carbon nanotubes are exhibiting different conductivity along their tubular axis depending on their chirality: when $n = m$, the nanotube is characterized as metallic; when $n - m$ is a multiple of 3, $n \neq m$ and $nm \neq 0$, then the nanotube is quasi-metallic with a limited band-gap; otherwise the nanotube is a moderate semi-conductor. Individual metallic carbon nanotubes can display electric current density up to $2 \times 10^7 \text{ S}\cdot\text{m}^{-1}$,^[8] that is the same order of magnitude than the electrical conductivity of metals such as copper ($6 \times 10^7 \text{ S}\cdot\text{m}^{-1}$).^[9] Nevertheless several limitations are at play, such as the presence of more resistive CNT-to-CNT junctions and impurities. Moreover, no control of chirality is currently achieved, a broad set of chirality being found in a same batch of CNTs and as for MWCNTs, each layer can potentially display a different chirality. Altogether these limitations results in conductivity of the macroscopic nanotubes being lowered by several orders of magnitude with respect to the conductivity of individual nanotubes.

When it comes to nanotubes as electrically conducting charge, the addition of a small amount of conductive CNTs to an otherwise low-conducting or non-conducting matrix results in nanocomposites with highly enhanced conductivity. Therefore, the composite is exhibiting a conductivity threshold as function of CNT concentration (Figure 3.4). The onset of this conductivity increase is named the percolation threshold. In optimized polymer composite systems, the onset is found with amounts of CNTs as low as a few percents. Yet, many factors are affecting the phenomenon, such as CNT type, synthesis method, composite preparation method, polymer structure and composition, CNT surface modification etc. Furthermore, since the best dispersion is usually implying the formation of a polymer layer around each CNT, the most homogeneous dispersion does not necessarily afford the highest conductivity. Above the percolation threshold, the conductivity of the composite (σ) is displaying a power law behavior as function of the maximum

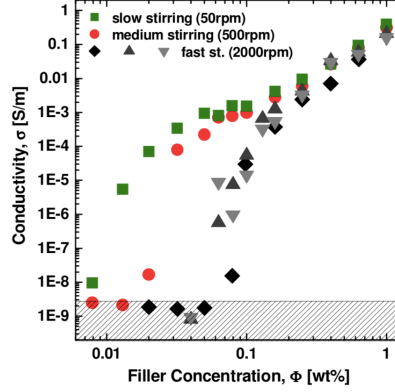


Figure 3.4 – Comparative log-log plot of a nanocomposite (MWCNT/epoxy) conductivity as a function of the nanotube weight fraction for the three different sample preparation methods: slow (50 rpm), medium (500 rpm), and fast (2000 rpm) stirring of the dispersion for 5 min at elevated temperature (80°C) prior to curing.^[10]

conductivity (σ_0) and the filler composition (Φ): $\sigma \approx \sigma_0 \Phi^t$. The power-law exponent is a result of plotting experimental results and fits yield values in the range 1.3 to 4.^[10]

Resulting from their all sp^2 hybridized structure, CNTs are extremely stables, both chemically and thermally. They are thermally stable to temperatures up to 2800°C under vacuum^[11] and up to 750°C under air. CNTs are also displaying excellent thermal conductivity at room temperature ($3500 \text{ Wm}^{-1}\text{K}^{-1}$, axial direction),^[12] exceeding the value of diamond ($3000 \text{ Wm}^{-1}\text{K}^{-1}$)^[13], and exceeding 6 times the value of silver ($429 \text{ Wm}^{-1}\text{K}^{-1}$), the most conductive metal.^[14] Mechanically, the CNT geometry induces different properties in axial and radial directions. With respect to the axial direction, CNT is considered as one of the stiffest and strongest materials discovered to date, with reported values of Young modulus in the range of 270 GPa to 950 GPa and tensile strength in the range of 11 GPa to 63 GPa.^[15]

Yet, CNTs are not as strong under compression because of their hollow structure and they are significantly softer in the radial direction (Young modulus in the GPa range).^[16] These properties are of particular relevance for CNT-based composites as these embedded fillers may experience large deformation and/or compression in the traverse direction under applied load on the composite.

Owing to their outstanding physico-chemical and mechanical properties, numerous technological applications have been envisioned for CNTs^[17], such as microelectronic devices (field-effect transistors, rectifying diodes and other logic circuits elements)^[18,19], catalyst supports^[20], gas storage applications^[21], reinforced composites^[11] etc.

3.1.2 CNT functionalization

CNT functionalization still stirs the attention of many research groups in the interdisciplinary fields of nanoscience, nanotechnology and bio-engineering. Owing to their inert nature, CNT functionalization presents many challenges to achieve an enhancement or addition of desirable properties without a significant trade-off of others. Indeed CNTs do not disperse well in most of the common solvents, they hold an important chemical stability and they do not present a significant amount of surface chemical functions intrinsically. Designing the best surface chemistry approaches while circumventing these limitations promises to extent the field of applications by: improvement of the solubility and compatibility of CNTs in solvents and matrices, tailoring the structure and properties of CNTs and preparation of novel CNT-based devices, composites, biocomplexes and adducts.

Surface functionalization methods are classified in two major categories: covalent or non-covalent. As for the non-covalent approach, the strategies rely on physisorption. Physisorption is an adsorption mechanism involving physical interactions, therefore relying on electrostatic, van der Waals or hydrogen bond interactions. As for the covalent approach (also called grafting), the strategies rely on chemisorption, that is the creation of chemical bonds as the reactant molecules are modifying the surface of the substrate.

3.1.2.1 Non-covalent functionalization of CNTs

Thanks to their non-invasive nature, non-covalent approaches are allowing to preserve the properties of the surface to modify. Non-covalent approaches are exhibiting another selling point from a process standpoint, as the design of compounds of interest and the functionalization procedures are usually more straightforward, requiring less synthetic steps and more easily allowing convergent strategies.

Many different interactions can theoretically be used to modify a surface (Table 3.1). Most of them are generally weaker than covalent ones, which possess a dissociation energy between $150\text{ kJ}\cdot\text{mol}^{-1}$ and $450\text{ kJ}\cdot\text{mol}^{-1}$ for a single bond. On the other side, non-covalent interactions values are ranging from a few $\text{kJ}\cdot\text{mol}^{-1}$ for London dispersive forces to $300\text{ kJ}\cdot\text{mol}^{-1}$ for ion-ion pairs. These interactions can be used in a cooperative manner to obtain structures with a greater stability.

In the case of CNT modification, non-covalent strategies are dictated by the particle properties. CNT surface being hydrophobic by essence, amphiphilic molecules are a simple, yet relatively efficient manner to cover nanotube walls and achieve surface modification. This is thanks to the strong hydrophobic attraction between the CNT and the tail group of the surfactant species. Such method are popular to improve the dispersability and other properties of CNTs.^[22]

Another non-covalent strategy is relying on polymer wrapping (Figure 3.5). This method consists in the adsorption of a single layer of polymer around mostly individualized CNTs. The polymer tends to adopt a (multi-)helical structure owed by Van der Waals or stronger interactions, and the rotation around the backbone bonds, resulting in an extensive coverage of the surface.^[22–24]

As CNTs are exhibiting an extended π network, non-covalent approaches are also often based on π -interactions which are classified into three categories: (i) cation- π , (ii) anion- π , and (iii) π - π .

Cation- π interactions are commonly used in transition metal catalysts such as metallocenes. In such complexes the binding is strong enough to reconsider their classification as covalent interactions. Additionally this interaction is originating from overlapping of partially occupied metal orbitals with the aromatic system. Nevertheless, weaker interactions are usually observed with other cations such as alkali metals, alkaline earth metals, organic cations etc.^[25]

Anion- π interactions are intuitively disfavored due to the electrostatic repulsion between the π electronic system and an anion. Nevertheless, the possibility for an electrostatic attraction exists due to charge difference between anions and overall neutral aromatic rings. Such interactions are found more favorable for smaller anions such as halides, but remain typically weaker than cation- π and π - π interactions.^[25]

π - π interactions are known to afford different interaction geometries

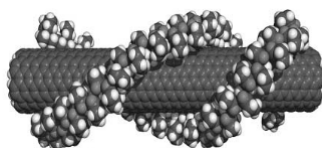
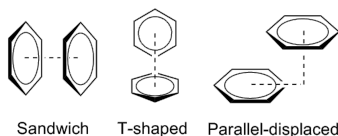
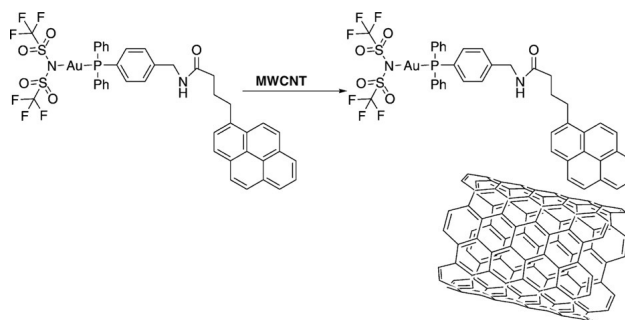
(Figure 3.6). In the simplest case displayed by the interaction between two benzene rings, the overlap is not happening between the π -orbitals of the two aromatic systems but between electrons from the π -system of each aromatic system and positive σ -orbitals from the other interacting species. This is then mostly an electrostatic interaction. Furthermore, these interactions are dictating the geometry of the complex, that is a parallel displaced configuration, also described as an offset stack. Other configurations are possible such as T-shaped and sandwich – the latter being the less stable of the three – where substituent effects are affecting the strength and relative populations of these complexes.^[25] Although face-to-face interactions are not favorable in the case of two simple interacting species such as benzene, they may be promoted when one of the interacting species is an electron-rich π -system for instance. These systems have their electron density increased by the presence of electron donating groups (alkoxy, amino etc.). On the other hand, interactions may also be promoted when one of the two interacting species is an electron-deficient π -system, which can be obtained by the presence of electron withdrawing groups (cyano, nitro etc.) as substituents on the aromatic core. The most favorable conditions are then met by the interactions of an electron-rich π -system and an electro-deficient π -system thanks to their electrostatic complementarity. This combination is also identified as an arene-arene interaction, where arene refers to a substituted aromatic system. Lastly, further extension of the π -system of the two interacting species is also a mean to reinforce the overall interaction.

Systems based on π -interactions can rely on pyrene or imidazolium moieties for instance.^[26,27] Tagging molecules of interest with such moieties allows then to bring additional functionality through their adsorption (Figure 3.7). Related strategies have been reported to bring a broad variety of properties to CNT-based materials: catalytic activity,^[20] biomolecule immobilization,^[27] surface functionalization for improved dispersability in a polymer matrix etc.^[26]

Although the adsorption is favorable and providing a relatively strong molecular anchor, the robustness of this functionalization method is usually inferior to designs based on covalent approaches. These covalent approaches are illustrated in the next section through examples focused on the specific case of polymer grafting.

Table 3.1 – Summary of intermolecular interaction and properties thereof. ^[25]

Interaction	Binding energy [kJ·mol ⁻¹]	Example
ion-ion	100–350	tetrabutylammonium chloride
ion-dipole	50–200	[Na(15-crown-5)] ⁺
dipole-dipole	5–50	acetone
H bond	4–120	water
cation- π	5–80	K ⁺ in benzene
π - π	0–50	pyrene and graphite
van der Waals	<5	argon
solvophobic	solvent dependent	-

**Figure 3.5** – Non-covalent CNT functionalization through polymer wrapping. ^[28]**Figure 3.6** – Structures of complexes based $\pi - \pi$ stacking interactions.**Figure 3.7** – Incorporation of a pyrene-tagged gold complex catalyst onto a MWCNT. ^[20]

3.1.2.2 Covalent functionalization of CNTs

Compared to non-covalent approaches, covalent ones are usually considered as providing more robust functionalization with higher loading. As CNTs are extremely stable chemically, very reactive treatments are required to attack their vast π -system. Predominantly, the most reactive sites are found at the tips (increased curvature-induced strain) and at the defect sites (non-hexagonal rings such as vacancies, and pentagon-heptagon pairs).^[27] While the functionalization can bring desirable properties, the local disruption of the π -system via the introduction of sp^3 carbon sites on the side-walls can alter the CNT conduction properties.

Among surface functionalization techniques, oxidation of CNTs is probably the most widely used. Liquid-phase oxidation mainly involves acidic etching by hot nitric acid or sulfuric/nitric acid mixtures.^[29] During this process, a plethora of oxidized functions are generated, notably carbonyls, carboxylates, alcohols and nitro groups which are spread in an heterogeneous manner over the tube length. Usually care must be taken to avoid overoxidation of the tubes leading to their shortening and exfoliation. This method has been proved to be an effective way to remove catalyst particles used in the CNT synthesis process, with an additional benefit being the enhanced dispersability of CNTs in aqueous or polar media.^[29]

As for functional CNT-based materials, the oxidative treatment is also a popular pathway for further modification of carbon nanotubes, notably via the carboxylic acid functions. These acids groups can react with alcohols or amines to generate ester or peptide bonds using methods derived from traditional solution chemistry such as carbodiimide coupling, or acyl chloride formation with thionyl chloride.^[27]

The functionalization of SWCNTs is not limited to the chemistry of carboxylic acid. More elaborate methods have been developed to attach organic moieties directly onto the nanotube sidewalls: radical additions through the use of xanthates^[30] or diazonium salts,^[31] adduct formations using Diels-Alder reaction or nitrene cycloaddition,^[31] nucleophilic additions such as Bingel reaction^[27] or addition of organolithium compounds^[32,33] etc. Examples of such reactions are depicted in figure 3.8.

These various methods can also be regarded as an intermediate step or just a component of a bigger leap forward in the direction of bioconju-

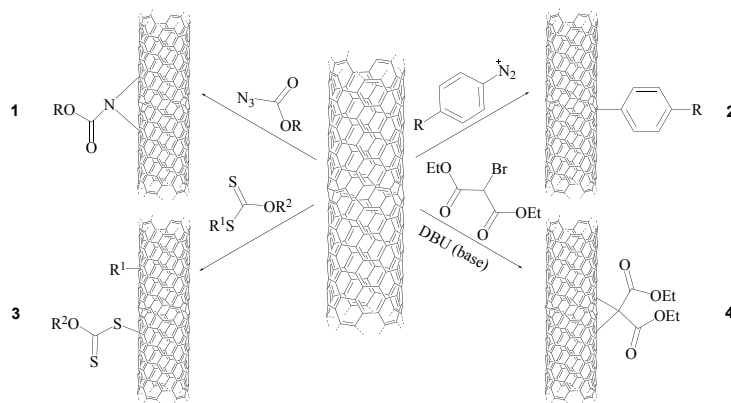


Figure 3.8 – Covalent CNT functionalization through addition of (1) nitrene, (2) diazonium salt, (3) xanthate or (4) diethyl bromomalonate.

gates, catalyst supports, photosensitive compounds or polymer grafted composites etc. [27,31]

3.2 Surface functionalization with polymers

Surface functionalizations with polymers has become a powerful tool to tailor physico-chemical properties at the interface, prepare smart coatings, or composites with enhanced properties. This has given rise to great advances in surface and interface engineering as well as the emergence of novel applications such as catalysis, electronics, nanomaterial synthesis, and biosensing. Modifications of surface have been explored on a broad range of materials, whether they are flat surfaces such as metal oxides, silicon, silicon nitride, carbon, gold, clay etc., or whether they are porous or particle surfaces such as natural fibers, polymer nanofibers, mesoporous materials, graphene, viruses and protein nanoparticles etc. Although the strategies to modify the surfaces of such diverse materials may differ from a chemical standpoint, general concepts have been laid out that provide guidelines when it come to the elaboration of a preparation strategy.

In order to modify a surface with polymers, there are two general categories of strategies that can be applied (Figure 3.9): physisorption and chemisorption, the latter can be obtained either via grafting onto or grafting from. When the grafting density becomes high, the steric

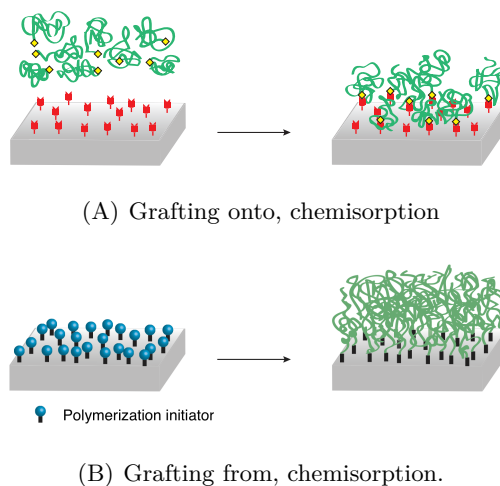


Figure 3.9 – (A) Grafting onto, chemisorption relying on functional groups, which display a suitable reactivity towards the surface to graft. In many cases, the surface has to be pre-functionalized in order to be provided with the right surface chemistry, (B) Grafting from approach, growth of polymer brushes that has been initiated directly from the surface.

repulsion between the chains on the surfaces may induce a stretching of the polymer backbone that can lead to a brush conformation. When lower grafting densities are achieved, other conformations are allowed, which can be referred as pancake or mushroom.^[34–37]

Grafting onto strategies are relying on the synthesis of pre-synthesized chains in order to anchor them on the surface by chemisorption.^[38–45] The polymer displays functional groups that can undergo a chemical reaction with reactive sites on the surface. Via the grafting from strategy, the polymer chains are growing directly on the surface in presence of monomers.^[34,46–51]

3.2.1 Grafting onto

The grafting onto consists in the tethering of polymer on a surface by mean of a chemical reaction between a reactive functional group belonging to the polymer and a reactive site on the surface to graft. The covalent bond formed between surface and polymer chain makes the bond robust and resistant to common chemical environmental conditions.

From a reactivity standpoint, the grafting is possible as long as the surface chemical sites can interact with the polymer functional groups. Macromolecular chains must diffuse through the existing polymer film to reach the reactive sites on the surface.^[34] When the covering of the surface is increasing, the access to residual sites by the subsequent chains to graft becomes hindered. Additionally, the grafted chains may be coiled or even collapsed on the surface, masking neighboring reactive sites.

Therefore, to achieve a dense and homogeneous grafting of a polymer, the density of reactive sites on the surface and a proper polymer functionalization are important parameters to master as they are determining process efficiency. This latter parameter can benefit substantially from the use of controlled polymerization techniques that allow to control precisely the composition of the synthesized polymer chains. Such techniques are the topic of a subsequent section of this chapter.

Although the grafting densities and polymer loadings of grafting onto techniques are usually higher than those relying on physisorption, high values are still difficult to achieve. This holds even more true as the molecular weight of the polymer and the typical thickness that can be reached via chemisorption are in the range of 1 nm to 5 nm.^[52]

3.2.2 Grafting from

Grafting from processes are typically realized in two steps as depicted in figure 3.10. The first step consists in the functionalization of the surface with a polymerization initiator.^[34] Usually the tethering of initiator moieties is carried out on reactive site generated or already present at the surface. The second step is the polymerization carried *in situ* in order to obtain the chain growth.

During a grafting from process, the polymerization of the brushes implies the diffusion of the monomer. It turns out that this diffusion of small molecules is an advantage in comparison to the grafting onto situation where the diffusion process toward the surface involves polymer chains. Consequently, the grafting from allows to aim at higher loading and grafting density.^[34,53,54]

Nevertheless, some considerations regarding steric hindrance are still relevant. In the case of free radical polymerization (FRP), it has been

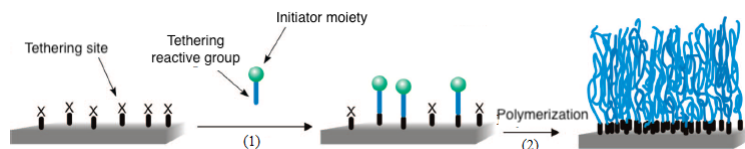


Figure 3.10 – Chain growth through grafting from. Step 1 is the functionalization of reactive sites at the surface to tether a polymerization initiator. Step 2 is the subsequent polymerization from the surface.

evidenced that the initiator efficiency is significantly reduced due to its tethering in comparison to its soluble counterpart. This difference could be due to the confinement of the initiator at the surface.^[54] Even in the case where the initiator is bound to the surface through a long alkyl chain, its diffusion outside the solvation shell and toward the monomers is hindered. This results in a decrease of the initiator efficiency and possible deactivation of propagating radicals.

Furthermore, a decrease of the efficiency is related to the kinetics characterizing every FRP, which are by definition uncontrolled.^[54] Such polymerization processes are usually exhibiting a slow initiation step with respect to propagation. As all the chains are not initiated at the same time, some early growing chains are already long enough to hinder the diffusion of monomers toward later initiating sites. This phenomenon is even more pronounced as chains are becoming longer and spread on the surface.

To circumvent such issues, controlled radical polymerization techniques (CRPs) can be advantageously applied. In a CRP process, the transfer and termination reactions are decreased so that the initiation is fast with respect to propagation. This lowers the dispersity ($\bar{D}$) of the growing chains, which benefits the grafting density. The general characteristics of CRPs are developed in the next section.

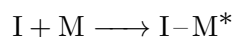
3.3 Controlled radical polymerizations

Techniques allowing a precise control over functionality, architecture and composition of polymer chains have attracted a vivid interest over the past decades. The origin of this attraction lays in the discovery of the anionic polymerization of styrene by Szwarc in 1956.^[55] Szwarc

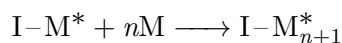
defined the concept of living polymerization as the absence of transfer and termination reactions. His work is often acknowledged as a seminal work for the modern polymer chemistry.

Ionic and radical polymerizations are belonging to the chain-growth mechanism category. As for the general case of chain-growth polymerization, three main kinds of reactions can be distinguished,^[56]

- Initiation: This step is characterized by the reaction of the initiator with a first monomer unit, generating a reactive species. The initiator (I) is typically an anion, a cation or a free radical. This leads to the following classification as anionic, cationic, or radical polymerization, respectively. The initiators are strong bases, strong acids or free radicals etc. This step can be represented by the following equation,



- Propagation: Following the initiation, this step consists in the addition of subsequent monomer units (M) on the propagating centers which is then transferred to added unit. This sequence is repeated n times during the growth of the polymer chain, as per the following equation,



- Termination: This step consists in the lost of a propagating center that can be related to different processes such as recombination, dismutation in the case of free radicals, transfer without any possible reactivation, adventitious or desired side-reactions (impurities or terminating agents, respectively). An overview of these termination processes is represented in figure 3.11

The term living has been introduced to define the ability of polymer chains to undergo further chain-growth after complete depletion of the initial monomer feed. Living polymerizations are also defined by a fast initiation rate in comparison to the propagation.^[57] Initiation is then happening almost simultaneously for all polymer chains, and the number of growing centers is almost constant throughout the polymerization. The combination of these characteristics yields therefore to polymers with controlled molar mass, and narrow size distribution (or

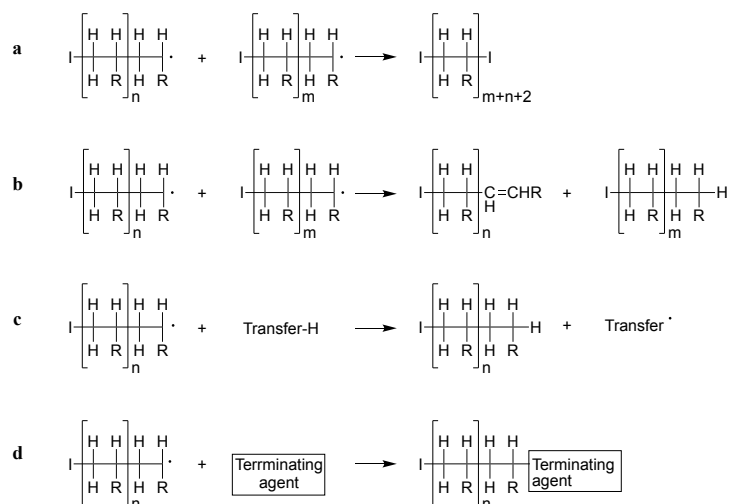


Figure 3.11 – Overview of the termination processes that can apply to chain-growth polymerizations: (a) Recombination of propagating macroradicals, (b) dismutation of macroradicals, (c) hydrogen atom transfer, (d) reaction with a terminating agent.

dispersity).^[56] This dispersity ($\mathcal{D}$) is defined as the ratio of the average molar mass in weight (M_w) over the average molar weight in number (M_n), as per the following equation,

$$\mathcal{D} = \frac{M_w}{M_n}$$

A chain-growth polymerization exhibits a narrow dispersity when $\mathcal{D}$ is close to 1. In the case of a living polymerization, the dispersity can also be expressed as a function of the polymerization degree (DP_n), which is related to the conversion (Conv.), the initial concentrations of the monomer and initiator ($[M]_0$ and $[I]_0$, respectively). These relations can be expressed by the two following equations,

$$\mathcal{D} = 1 + \frac{1}{\text{DP}_n}$$

$$\text{DP}_n = \text{Conv.} \cdot \frac{[M]_0}{[I]_0}$$

In 1956 the anionic polymerization was the first one to demonstrate a living behavior. The cationic ring opening polymerization followed next

in 1982.^[56] In comparison to such techniques, FRPs that were already known by then are presenting several advantages, such as:^[56]

- a broader portfolio of monomer chemistries are potentially suitable thanks to a better tolerance of radical species toward various functional groups (acids, hydroxyles, amines etc.),
- their implementation can be carried out in less drastic conditions,
- their tolerance toward water and impurities in contrast to ionic polymerizations that are requiring tedious purification procedures.

Limitations are affecting radical processes as unwanted side-reactions are inherent to such systems. Although transfer can be limited with appropriate conditions, terminations such as dismutation and recombination are harder to avoid using radical species. Yet bimolecular termination rates can be significantly reduced by decreasing the radical species concentration to very low levels (from ppb to ppm). On this basis, many different controlled radical processes have been developed since the early 1990s.¹

CRPs are in a way similar to living polymerizations as both are displaying a fast initiation rate with respect to propagation, in combination to a low termination rate.^[58] Therefore the following characteristics are expected from CRPs,

- $\ln[M]_0/[M]$ displays a linear relationship with time,
- $\bar{D}$ is well-defined with values typically lower than 1.3,
- the theoretical molar masses can be related to the ratio of initial concentrations of initiator over monomer, $[M]_0/[I]_0$,
- the aforementioned properties are still applicable after a subsequent addition of monomer to the reacting medium.

Living and controlled polymerizations are additionally allowing the possibility to synthesize polymers with well-defined topology (linear, star-like, comb-like, dendrimer, or gels), functionality (side functional groups, chain ends), and composition (statistic, block, periodic or gradient copolymers) as depicted in figure 3.12. A noticeable feature shared

¹CRPs are never strictly living. For this reason, IUPAC recommends to use the term *controlled* rather than *living* when it comes to CRPs.

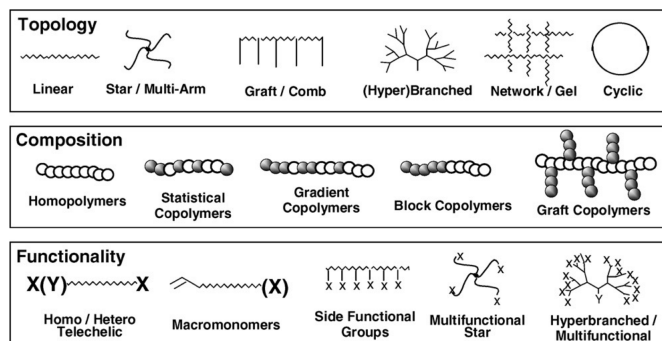


Figure 3.12 – Illustration of polymers with controlled topology, composition, and functionality.^[58]

by CRPs is the dynamic equilibrium set between a very low concentration of propagating species (typically $\ll 1\%$) and a much larger proportion of deactivated species (dormant chains). A key parameter is the activation-deactivation that must allow a fast interconversion between these two populations of species. Then all the chains are enjoying a similar propagation time and the dispersity will consequently be narrow.

The three main categories of CRPs that are the most represented in the literature are the following,^[58,59]

- Nitroxide mediated polymerization (NMP), which involves nitroxide radicals as mediating species,
- Atom transfer radical polymerizations (ATRP), which are involving metal halide catalyst species as control agents,
- Reversible addition-fragmentation chain transfer (RAFT), which is based on a degenerative chain transfer process. This process is reversible and controlled by a chain transfer agent (CTA).

NMP and copper catalyzed polymerizations are techniques based on persistent radical effect, which is a kinetic characteristic leading the system to order itself in time.^[60] In the early stages of the polymerization, a large amount of the propagation radicals are undergoing bimolecular termination, either with another propagating radical or a mediating species. Any termination with another propagating radical will lead to an irreversible accumulation of mediating species, and a decrease of the amount of propagating radicals. The latter will ultimately be displaying a much lower concentration than the mediating species. When

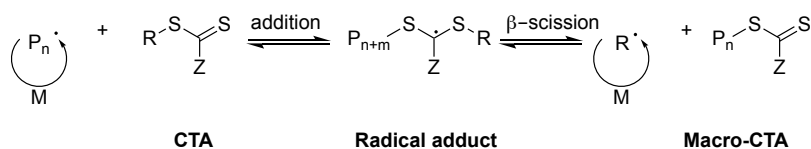


Figure 3.13 – RAFT reaction mechanism.

the persistent radical effect is set, the dormant chains are also present in the medium in higher concentration than the propagating radicals. The deactivation of the radicals is then happening less favorably with other growing species than by reaction with the more available dormant chains (generating back another propagating radical in this activation-deactivation reaction). This deactivation being reversible and the concentration of propagating radicals being very low, a quasi steady-state of growing species is then reached.

In contrast, RAFT polymerizations are not based on the persistent radical effect but on a degenerative chain transfer process,^[58] and then display some features that are more related to classical FRPs, namely a slow initiation step and a fast termination. CTA can be regarded as a deactivated species and its concentration is usually far higher than the initial initiator concentration. The monomer conversion is progressing thanks to a radical concentration set purposely at a very low value. These radicals can undergo an irreversible termination or a degenerative chain transfer with CTAs or macro-CTAs present in the medium. Typical CTAs are thiocarbonylthio compounds or similar. The transfer agent is the key ingredient to set the equilibrium between the deactivated species and the propagating ones. The polymerization mechanism is depicted in figure 3.13. During the polymerization process, radicals are reacting with the thiocarbonyl group to form a radical adduct. This adduct can later undergo a β scission that will either generate back the radical, or release a propagating radical corresponding to the R group.

The first reports regarding ATRP are dating back to 1995.^[61,62] ATRP as defined in these earlier reports involves a transition metal catalyst displaying at least two distinct redox states which are differentiated by one electron (Mt^n/Mt^{n+1}), and able to expand its solvation shell.^[58] This catalyst is accommodating complexing agents (L) and one or more counter-ions (X) in its solvation shell. Such transition metal complex (Mt^nY/L) is able to homolytically cleave alkyl-halide bonds to generate the corresponding oxidized complex ($Mt^{n+1}Y/L$) and a rad-

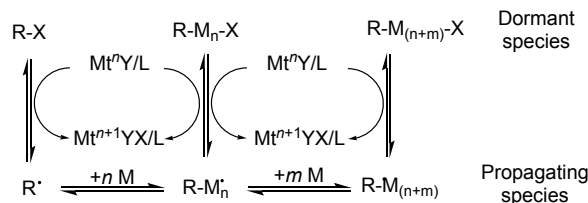


Figure 3.14 – ATRP reaction mechanism.

ical species ($R^\bullet$). The radical can then proceed with propagation by addition of vinylic monomer units or be reversibly deactivated by the oxidized complex, generating back an end-chain halogenated dormant species. Similarly to nitroxides in NMP, the transition metal complex is the deactivating species. Combined with the persistent radical effect, the equilibrium is strongly shifted toward dormant species. The overall reaction mechanism is depicted in figure 3.14.

ATRP kinetics are function of the activation and deactivation processes (k_{act} and k_{deact}), corresponding to radical generation and alkyl-halide formation, respectively. The equilibrium ($K_{\text{ATRP}} = k_{\text{act}}/k_{\text{deact}}$) between these two processes is determining the radical concentration in the medium, and thus the propagation and termination rates, as well as the dispersity. k_{act} and k_{deact} must ideally be high enough to allow a good control over the polymerization while affording a reasonably high polymerization rate. Disregarding all termination processes, the ATRP reaction rate can be represented by the following equation,

$$v_p = k_p K_{\text{ATRP}} [M] [I]_0 \frac{[Mt^n Y/L]}{[Mt^{n+1} YX/L]}$$

This equation highlights that the propagation rate is directly related to the ratio between of activating over deactivating species concentrations.^[58]

As for the dispersity, the equation is similar to the one presented for living polymerizations, but incorporating an additional term. The expression can then be written as follows:

$$D = 1 + \frac{1}{DP_n} + \frac{k_p [I]_0}{k_{\text{deact}} [Mt^{n+1} YX/L]} \left(\frac{2}{\text{Conv.}} - 1 \right)$$

This revised equation highlights that the polymerization control de-

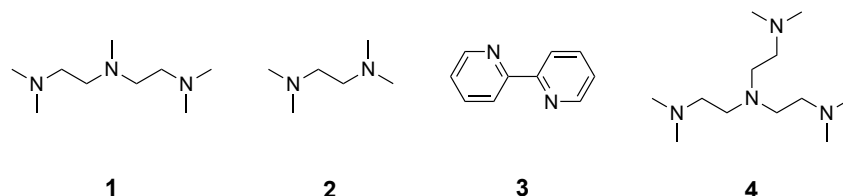


Figure 3.15 – Ligands used for copper complexation in ATRP: 1. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), 2. *N,N,N',N'*-tetramethylethylenediamine (TMEDA), 3. 2,2'-bipyridine (Bipy), and 4. tris(2-dimethylaminoethyl)-amine (Me₆TREN).

depends only on the deactivating species concentration, which then must have an appreciable and adequate concentration. Nevertheless, as the conversion progress, dispersity is increasing. Additionally, above a certain range of molar masses – which are different for every polymerization procedure – transfer, termination and other side-reactions are no longer negligible. The conversion is then often wisely limited at reasonable conversion values (between 30% and 50%) on purpose in order to keep a good control.

ATRP catalysts are often copper complexes.^[63] Other transition metals have also been successfully used (Mo, Fe, Ru, Os etc.) but copper has turned to be the most efficient to control the polymerization of a broad range of monomers in a large set of media.^[59] The main roles of complexing agents are to provide stability and solubility to the catalyst species. This complex stability is particularly important when it comes to the polymerization of monomers (pyridine, amide, amine etc.) that can display affinity toward the catalyst.^[64] Furthermore, by varying the nature of the complexing agents, the redox potential of the catalyst can be tuned to allow appropriate polymerization and atom transfer kinetics. In the case of copper catalyzed ATRP, complexing agents are often amine derivatives. A few examples of ligand structures are depicted in figure 3.15. The activating ability of the resulting complex can be rationalized according to the ligand structures as follows,

tetradentate, bridged > tetradentate, branched > tetradentate, unbridged cycle > tetradentate, linear > tridentate > bidentate

pyridine ≥ aliphatic amine > imine

In comparison to other CRPs, ATRP was proven to be more versatile with respect to the variety of polymerizable monomers than NMP, which is notably unable to polymerize methacrylates for instance.^[65] Additionally, ATRP and related techniques are enjoying the advantage of commercial availability of numerous polymerization reactants (catalysts, ligands, initiators).^[59] Yet there are a few drawbacks, such as traces of metal catalysts that can be difficult to remove, or limitations for the polymerization of complexing monomers. Over the years, several methods derived from ATRP have been developed to refine the concept: (i) reverse ATRP using a conventional FRP initiator to generate Cu^{I} at the expense of Cu^{II} ,^[66] (ii) eATRP using electric current converting a base stock of Cu^{II} into Cu^{I} ,^[67] (iii) activator generated by electron transfer ATRP (AGET ATRP) where the $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ catalytic system activity is regulated through electrochemical reactions.^[68,69] These systems have the main advantage to be less sensitive to air contamination and sometimes are allowing to decrease the catalyst concentration to a few ppm. A last variant of ATRP consists in the use of a $\text{Cu}^0/\text{Cu}^{\text{II}}$ mix as catalytic system. The mechanism is relying on comproportionation - disproportionation equilibrium involving Cu^0 , Cu^{I} , and Cu^{II} . The exact mechanism is however still matter to debate. The discussion is mainly focused on whether Cu^{I} or Cu^0 is the main contributor to the activation process. The supporters of the former or the latter are defining it as supplemental activation reducing agent (SARA-ATRP)^[70–72] or single-electron transfer living radical polymerization (SET-LRP),^[73,74] respectively.

3.4 Surface grafting using ATRP processes

Building on the foregoing section, CRPs appear to be techniques of choice to enable control over the grafting from flat surfaces and particles. Depending on the surface to graft, different control systems can be chosen. Nevertheless the most represented technique is ATRP. The first publication regarding grafting from a flat surface using ATRP, or surface-initiated ATRP (SI-ATRP) was reported in 1997.^[75]

SI-ATRP is still displaying most of the advantages that contributed to the success of solution ATRP.^[39] In comparison to other techniques (SI-NMP, SI-RAFT) SI-ATRP has access to a broader set of surface-bound initiators, some of them being ready-to-use and commercially available

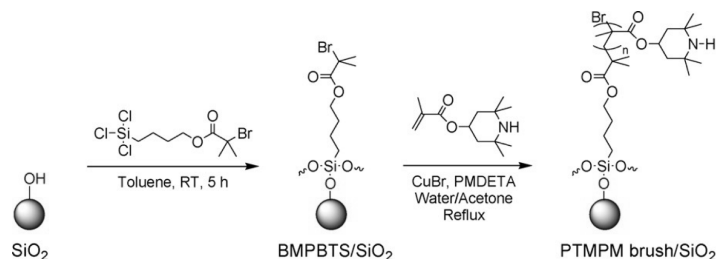


Figure 3.16 – Synthesis of PTMPM brushes on silica nanoparticles.^[51]

products.^[39] Furthermore, SI-ATRP is compatible with a broad set of monomer classes: styrenics,^[40,47,76,77] acrylates,^[47,78,79] acrylamides,^[75,80] or methacrylates.^[76,77,81,82] The chain-end functionality retention of this technique allows to use the as-synthesized chains as macro-initiators for the chemical functionalization of polymers, providing access to complex macromolecular architectures such as block copolymer brushes.

An example of grafting from nanoparticles is depicted in figure 3.16.^[51] The method involves an initiator, (Trichlorosilyl)butyl 2-bromo-2-methylpropanoate (BMPBTS), bearing a trichlorosilane on one end and a α -haloisopropionate moiety on the other end. This initiator fragment is similar to those typically used for the solution synthesis of polymethacrylate derivatives. Prior to the polymerization, a prefunctionalization of silica nanoparticles is carried out by reaction of the trichlorosilane end together with silanol surface groups. Subsequently, the grafting from is obtained by SI-ATRP of the monomers, TPM in the present case.

In order to achieve an efficient control, specific adjustments to the protocol are required to deal with the persistent radical effect. Otherwise the deactivating species concentration – which would be generated by the sole surface-bound initiators – would be too low to perform its mediating role. This is explained both by the relatively low amount of surface-bound initiator groups and confinement effects. Without these adjustments molecular masses are lower than theoretically expected and initiator efficiency is reduced. To cope with these effects, two strategies have been developed, first the addition of a sacrificial initiator,^[83] and second the direct addition of the deactivating species (such as Cu^{II}) to the medium.^[47] In both cases, they allow to greatly improve the initiator efficiency and allow a good control of the polymerization.

3.5 Conclusion

Functional properties of CNTs hold great interest for their implementation in technological devices. This leads to continuous efforts to develop dispersion and functionalization techniques. Surface chemistry has long been used to modify solid surfaces and particles. Over the past two decades, the advent of CRPs has allowed to design functional hybrid materials and particles with precise control over their architecture, composition and properties. This should open up the field of applications for nano-hybrid materials, and for CNT-based materials among others, and should bring their components to benefit from their mutual properties.

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Part II

Objectives and strategy

CHAPTER 4

OBJECTIVES AND STRATEGIES

Abstract

Among positive electrode materials for the next generation of batteries, nitroxide and quinone derivatives are showing great promises thanks to some of their properties that outperform current inorganic materials. Yet, their competitiveness on other levels must be increased for such organic materials to be considered as viable alternatives. The goal of the present thesis is to address the specific points that could bring them to the fore.

4.1 Context and motivation

The development of the next-generation of batteries has not only to address the fact that LIBs are facing limitations to their further energy and density optimization, but also has to fulfill the pressing need of mankind to develop clean and renewable energy sources and storage solutions. Therefore, the axes of development could benefit from organic redox materials to set new performance standards while alleviating or mitigating the limitations of current materials in terms of cost, toxicity and performances.

In this perspective, materials belonging to the classes of radical polymers and quinone derivatives are promising applicants as positive electrode materials for the next generation of electrochemical energy storage solutions. The former class is particularly attractive for its power performances owed to its ultrafast redox kinetics.^[1] The latter class holds great interest thanks to its high theoretical capacity at decent voltages *vs.* Li/Li⁺.^[2] Both of them on their respective turfs have the potential to outperform current inorganic LIB materials.

Nevertheless, progresses have still to be achieved for these material classes to be considered as mature enough to reach practical applications. Notably both classes are facing issues due to their dissolution in common battery electrolytes.^[1] Additionally, there is still room for improvements regarding their performance metrics as their processing since electrode materials requires the incorporation of redox inactive fillers in high content.

4.2 Aims of the project

This project proposes several distinct solutions all based on macromolecular organic architectures to cope with their present limitations. In a nutshell, the main targets are to improve power density, energy density, and cyclability of nitroxide and quinone derivatives.

Although those goals lead to significantly different strategies, this thesis presents original approaches to address the common limitations of both type of materials by rational design applied to macromolecular chemistry. The related design principles are here targeting improve-

ments of specific capacity, power density and cyclability of organic-based electrode materials by preventing dissolution and improving charge transfer.

The incorporation of redox centers into macromolecules inherently presents the advantage of decreasing issues related to the solubility of redox species into standard non-aqueous electrolytes. Yet, to be efficient, such approaches are usually making use of crosslinked polymers. Generally, the electrode formulation based on low conductivity organic macromolecules is thus performed after all synthetic steps, leading to difficulties to obtain a nanoscale homogeneous conducting network. As a consequence, crosslinking is an obstacle that prevents to reach the highest degree of homogeneity. This is where rational design can help by targeting structures that would permit the combination of facilitated charge transfer and improved robustness.

From an application standpoint, an improved charge transfer allowed by advanced macromolecular architectures would bring improvements either in terms of power density or energy density. When it comes to organic electrodes with high carbon content, it is particularly true that these two density parameters can be addressed by a common strategy. For instance, a facilitated charge transfer allows higher power performances at a given carbon content. Conversely, same power performances can be expected at a lower carbon content, which is therefore benefiting to the energy density. The first proposition would then influence the design of systems requiring to further optimize power performances. On the other hand, the second proposition would be applied to systems where the energy density is a stronger prerequisite.

A last axis of research is investigated in parallel to the elaboration of such robust electrode materials with improved charge transfer. In the specific case of nitroxide-based polymers such as poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate (PTMA), even minimal conductive carbon content would always result in material with specific capacity ($111 \text{ mAh}\cdot\text{g}^{-1}$) lower than inorganic counterparts ($140 \text{ mAh}\cdot\text{g}^{-1}$ for LiCoO_2). Since the redox potentials of most p-type nitroxide compounds are found in a relatively limited window (from 3.5 V to 3.8 V *vs.* Li/Li^+),^[3] the quest for higher energy density for such systems would ultimately benefit from a raise in voltage once no further improvement could be reached by decreasing the filler content. This is an axis of development explored in parallel to the elaboration of macromolecular

architectures mentioned beforehand, but that can be brought in addition to them in a common device.

This thesis is then an interdisciplinary project at the crossroads of applied electrochemistry, polymer synthesis, macromolecular engineering, nanomaterial science and supramolecular chemistry to which are combined electrochemical, molecular and structural characterizations.

4.3 Design and strategies

4.3.1 Nitroxide-bearing (co)polymers

Among redox organics, PTMA displays all the characteristics allowing nitroxides derivatives to come to the fore as candidates for high power density electrodes: chemical stability, ultrafast redox kinetics, suitable redox potential for cathode applications (3.6 V *vs.* Li/Li⁺) etc. Thanks to its features and the convenience of its synthesis, PTMA is the most representative polymer of its class. For the same reasons, PTMA has then been selected for all strategies and development on radical polymers within this research work.

To cope with its solubilization issues, this project proposes to rely on surface chemistry as a mean to provide a chemical anchor on the conductive support while promoting charge transport. The conductive charge being multi-walled carbon nanotubes (MWCNTs), their high specific area is beneficial for all surface interactions and/or modifications. The advanced polymer architectures that are targeted are making an extensive use of controlled radical polymerization (CRP) for their syntheses. CRP techniques are allowing to prepare well-defined architectures, notably in terms of functionality. Functionality is critically important in the frame of this project since this is the key to promote an efficient covalent anchoring of the redox active polymer.

In parallel to the research work carried in the frame of this PhD project, other competitive strategies are explored thanks to a collaboration with the Laboratory of Polymeric and Composite Materials (LPCM, UMons). This collaboration is taking place within the HYB2HYB project funded by the Walloon Region and aims at the development of hybrid materials based on PTMA (co)polymers and MWCNTs using non-covalent functionalization strategies. Such strategies have the potential

to offer a straightforward route toward comparable materials without altering the sp^2 chemical structure of MWCNTs. This is thus allowing to preserve their intrinsic conductivity, and more specifically the conductivity relative to the MWCNT outer wall. Non-covalent functionalization could then benefit from better charge transfer at the polymer to CNT interface, and exploit the conductivity of the outer wall of the MWCNT. This could be done without requiring an electronic transfer from the outer to the inner layers of the MWCNT, the radial transfer mechanism being disfavored due to distance between concentric walls in comparison to the axial conduction pathway in a chemically preserved sp^2 structure. A part dedicated to the development based on these non-covalent strategies can be found in the present manuscript (Appendix A).

4.3.1.1 Covalent MWCNT functionalizations

Grafting polymerization strategies such as grafting onto and grafting from are involving the creation of a chemical bond between the surface and the polymer chain. In the case of CNTs, this bond is obtained by reaction at the surface with highly reactive species which often are causing alterations of the sp^2 network, altering the tube conductivity. Nevertheless, the consequences on the conductivity are mitigated by the presence of several layers in the case of MWCNTs. Since the network disruption is mostly limited to the area of the tube in direct contact with the reaction medium, inner tubes can have their conductivity preserved.

In this thesis work, both categories of grafting polymerization techniques, i.e. grafting onto and grafting from, are explored to anchor PTMA chains on MWCNTs. With respect to prior art, at the time when the strategies detailed in this work were reported, only one similar example was published in the literature. This earlier report was dealing with nitroxide functionalized polynorbornenes derivatives on MWCNTs both via grafting onto and grafting from.^[4] However, polymer loading was limited to typical values of nitroxide polymer derivatives (<30 wt%) and the synthesis is requiring expensive ruthenium based catalysts (Grubb's 2nd generation catalyst). Also noteworthy, the authors showed the electrochemical performances in thin film conditions with an acetonitrile-based electrolyte. Although these conditions are allowing ultrafast charge-discharge rates, they are far from representative of

typical battery conditions in a conventional LIB electrolyte over a prolonged period of time, which is precisely one of the aims of this thesis work.

The **grafting from** strategy developed in this project is based on a procedure frequently found for the functionalization of CNT with small organic molecules. This strategy is then transferred to the functionalization of CNTs with ATRP initiator moieties in order to prepare polymer brushes through grafting from.^[5] Because PTMA is a nitroxide radical polymer, the direct polymerization from its corresponding monomer via SI-ATRP is not possible as it would interfere with the CRP process. Therefore, MWCNTs grafted with a precursor polymer, namely poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM), must be synthesized first (MWCNT-*g*-PTMPM) and then subsequently oxidized into the electroactive brushes (MWCNT-*g*-PTMA). Such intermediate step involving the PTMPM precursor polymer is typical of CRP processes applied to the preparation of nitroxide radical polymers. Compared to non-covalent and grafting onto strategies, higher polymer loading is expected while still ensuring an intimate contact between all chains and a CNT wall. This should possibly be the preferred approach while aiming for the higher PTMA loading range (>30 wt%).

Regarding the **grafting onto** strategy, loading is expected to be lower than what is achievable through grafting from. Therefore, the aim is reasonably set at loadings at least comparable to values typical of PTMA - MWCNT composites obtained via a traditional blending method (active material around 30 wt%). In this project, it is proposed to synthesize copolymers embedding a minimal amount of reactive functions. These reactive functions should be handling the coupling of the polymer chains with CNTs. Again, CRP methods are well suited for the task of producing these PTMA derivatives thanks to their control over functionality. An advantage of the grafting onto over the grafting from is that this strategy can afford more convergent synthetic pathways, and thus possibly a more efficient overall process. Moreover, in contrast to grafting from that had to first go through the grafting of a PTMPM precursor, it should be possible to directly graft PTMA derivatives, which should also contribute to raise the process efficiency. This is also bringing another advantage since it allows a full and comprehensive characterization of the polymer prior grafting. This strategy should yield a composite material with a robustness comparable to grafting

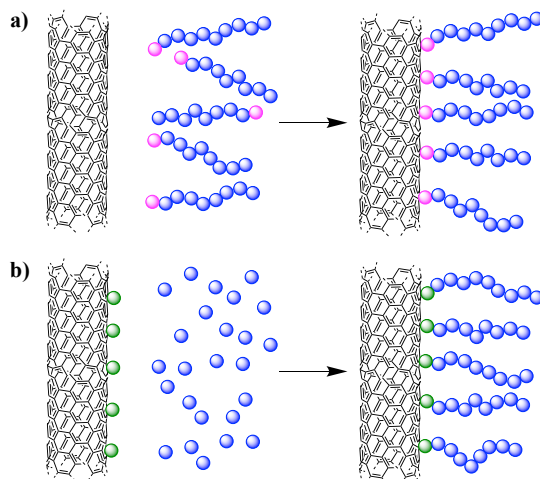


Figure 4.1 – Illustration of two covalent grafting strategies to chemically anchor polymers on a CNT surface: (a) grafting onto, (b) grafting from.

from, but should be better suitable when higher power performances need to be exhibited.

4.3.2 Quinone polymers

Whereas organic redox centers such as nitroxide are showing great promises to set new power performance standards, other organic redox small molecules or moieties are holding great interest for their high specific capacity metrics. Among these, the carbonyl reversible redox process has been intensely studied over the past years, with the quinone – hydroquinone based molecular structures being the most representative example.^[2,6,7] This low molar mass couple undergoes a reversible two-electron exchange process at a relatively high potential (average of 2.6 V *vs.* Li/Li⁺) resulting in very appealing characteristics: theoretical specific capacity of 495 mAh·g⁻¹ corresponding to an energy density above 1.2 kWh·kg⁻¹, that could supersede the metrics of current inorganic materials.

However, the solubility of benzoquinone in battery electrolytes is cause for major concerns. Different strategies have been proposed in the past to overcome this disadvantage, either by avoiding the use of a liquid electrolyte within a solid-state cell configuration^[8] or by limiting the solubility of the material. As part of the second option, surface

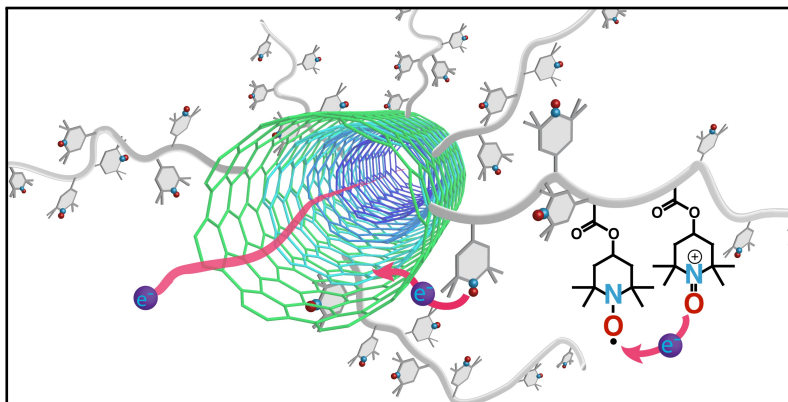


Figure 4.2 – Schematic representation of a MWCNT-*g*-PTMA hybrid structure and the associated redox process and electrical conduction phenomenon. The depicted structure displays polymer brushes tethered at the surface and extending from the CNT wall into the solution.

grafting methods have been explored for benzoquinone units,^[9–11] while others used benzoquinone derivatives (for instance, dicarboxylates) with intrinsic limited solubility.^[12,13] The drawback of the latter is the increased molar mass leading to lower theoretical capacities. The third, and probably the most promising route to reduce the solubility is the use of polymeric quinones.^[14–18]

Although the incorporation of benzoquinone units within a polymeric architectures is offering a solution to address the solubility issues and consequent poor cyclability of their low molar mass counterparts, underestimated performances were observed.^[19,20] This is probably due to the limited conductivity of these polymeric architectures leading to partial material utilization.

To address this specific point, the solution that we are exploring in this thesis is to merge the key benefits of non-conjugated redox active materials (such as a high capacity) with the conductivity of conjugated polymers. To confer conjugation to a polyquinone derivative, the proposed strategy relies on linking the monomers with amino groups. Due to its chemical design, the resulting polymer – namely poly(2,5-dihydroxyaniline) (PDHA) in its acid-doped state – hybridizes the redox properties of quinone groups, which are part of the polymer backbone, with the electrical conduction of π -conjugation in polyaniline (Figure 4.3).

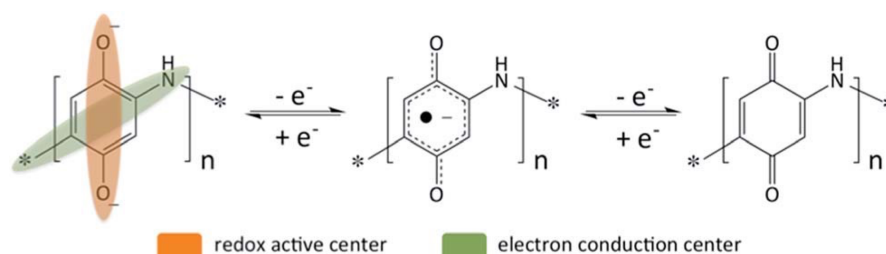


Figure 4.3 – Molecular formula of poly(2,5-dihydroxyaniline) and the redox mechanism based for a two-electron per monomer unit process. Thanks to its chemical design, PDHA hybridizes the redox properties of quinone groups, which are part of the polymer backbone, with the electrical conduction of p-conjugation in polyaniline.

With respect to prior art, while resembling structures have been proposed in the past, there are major conceptual differences with our approach.^[14,21] Indeed, by using a naphthoquinone-based polymer, both functions were molecularly decoupled and the molar mass increased.^[15] A naphthalene-dicarboximide-bithiophene based redox conducting polymer was also proposed and shown to support fast electrode kinetics.^[16] Interestingly, in an analogous study, the quinone redox kinetics in thin films of electropolymerized poly(pyrrol-3-ylhydroquinone) was found to be the limiting step, rather than the electron transport through the polypyrrole conducting backbone.^[22]

More specifically, the synthesis and characterization of PDHA has been the object of only a few studies.^[23,24] In these studies, only the electrochemical synthesis has been explored and the quinone functionality of these polymers remained limited. The novelty of the present research work is two-fold: First, to propose an all-chemical route toward PDHA that would provide benefits (over the electrochemical pathway) such as enabling gram-scale synthesis along with higher quinone functionality incorporation; second, this new synthetic strategy should provide a useful material with enhanced properties for its battery electrode implementation, that has yet to be demonstrated.

4.3.3 Voltage

As already illustrated by the objectives and strategies related to the two classes of organic materials developed in the frame of this thesis

work, the energy density is a major point of attention for the development of new organic-based batteries and electrode materials. Currently most of the work is focusing on optimizing existing electrode material formulations and the design of new organic structures based on already-known chemistries. In this latter case, this work often consists in increasing the redox potential of organic positive electrode material or decreasing its molar mass per redox unit.

The application of rational design in molecular engineering led to a broad variety of newly proposed structures. Some of them can be considered as minimalist structures for high specific capacity (low molar mass per exchanged electron).^[25] Some others have been designed following approaches based on the introduction of moieties that are selected to effectively tune the redox potential of the electroactive centers, as exemplified by the categories of carbonyls,^[2] or nitroxides compounds.^[3]

Although the effects of number, position and nature of those moieties on the potential can even be predicted by theoretical approaches such as density functional theory (DFT)^[26] – hence assisting in the selection of compounds of interest – actual breakthroughs are difficult to achieve. This may be explained by the fact that current compounds have been already selected based on voltage and capacity considerations and that considerable synthetic efforts are often required to find an efficient pathway toward new compounds. Furthermore, new structural design developments are also prevented by requirements that must be met in terms of stability and absence of unwanted irreversible side reactions during electrochemical processes.

Therefore, we propose to explore a radically different approach to increase the energy density by tuning the operating voltage, not by changing any of the electrode material components but by modification of the electrolyte chemistry. The electrolyte composition is an important focus point of any modern battery development. In liquid electrolytes, chemical considerations about this medium are encountered from the standpoints of dissolution of ions, ion conductivity, stability toward the electrodes etc. Regarding the chemical description of these aspects, they are frequently benefiting from a description of the coordination behavior of the solvent toward the electrolyte ions.

Yet, another solvent property is seldom studied in the literature of lithium-based batteries such as Li-ion and is particularly relevant in this

thesis work. Precisely thanks to the solvent coordination properties, the behavior of the electrolyte can have a profound effect on the redox potential of the electrodes.

In the specific case of Li-ion cells, such effects are often overlooked because the solvent is affecting redox potential of both negative and positive electrodes symmetrically, hence – as it can be drawn from an overall Nernst equation – canceling out each other with no effect on the operating voltage. Nevertheless, this is no longer holding true in the case of lithium hybrid cells where the set of electrodes can be charge-balanced by different species of the electrolyte ion pair during operation. Consequently, solvent effects on the ion coordination behavior can be expected to be different at both electrodes, so that both electrode redox potentials are differently affected as well. By carefully selecting the solvent, one can affect advantageously the redox potential of the electrodes in order to increase their potential difference, and thus the energy density of the cell.

In the frame of this project we are aiming at, first providing a selection of suitable solvents as well as studying their electrochemical properties, and secondly, delivering a proof of concept by carrying the implementation in a lithium hybrid battery. Regarding this latter objective, the properties of the electrodes that we selected have been defined to allow a successful implementation. Of particular relevance, both electrodes are possessing different doping mechanism in order to avoid symmetrical solvents at the negative and positive electrode side. Regarding the negative electrode, we intend to select a lithiated material (n-doped). As for the positive side, a p-doped material is required and we then selected PTMA for this task.

With respect to the selection of suitable solvents, it is well-known in coordination chemistry that solvents can significantly affect the potential of redox centers.^[27,28] Such solvent effects are well detailed for transition metal catalysts, but data are more scarce when it comes to redox couples based on alkaline elements and ions. Yet, during our literature survey carried out for our research on PTMA, we came across a patent with intriguing data by Nakahara *et al.* on the effect of organophosphates on the voltage difference observed between nitroxide/oxoammonium and Li/Li⁺ redox couples.^[29] In this patent the voltage was reported to increase upon addition of organophosphates. Nevertheless the authors ascribed this effect to interactions between the electrolyte and the ni-

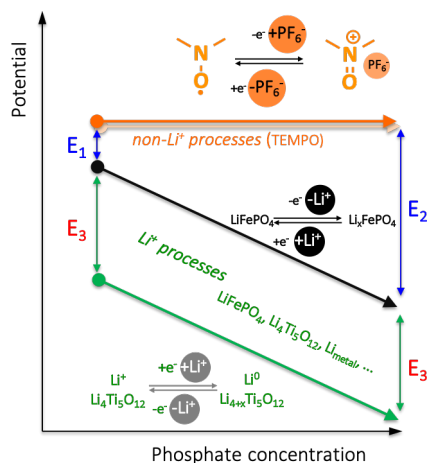


Figure 4.4 – Schematic describing solvent effects in the lithium hybrid cell design of the present project. For comparison, in a Li-ion cell, as it could be represented here by LFP and LTO redox couples, both electrodes are affected symmetrically, and thus no net effect is observed on the voltage (E_3 remains E_3). In a hybrid cell using a PTMA positive electrode and LTO as negative electrode, the solvent has little or no effect on TEMPO redox potential, while the value of potential of the lithiated electrode is shifted in the negative direction; this results in an increase of the output voltage from E_1 to E_2 .

troxyl compound without a proper demonstration, and evidence of a possible implementation remained limited to single charge-discharges curves. Motivated by these findings, we decided to carry a more extensive review of the literature to explore the possibilities that can be brought by the modification of solvent properties.

This literature survey led us next to a couple of references from Gritzner *et al.* providing useful data regarding the Li/Li^+ reduction potential.^[27,28] These values have been recorded in a broad set of solvents and are featuring variations by as much as 0.78 V. Among the tested solvents, trimethyl phosphate (TMP) is worth particular attention since this compound is already present in the literature of Li-ion batteries as a flame retardant. The attractiveness of this compound is also justified by its properties that are reasonably close to state-of-the-art LIB formulations based on carbonates (electrochemical stability window, ability to dissolve lithium salts, viscosity etc.). More importantly, the effects of TMP (or other similar organophosphates) on a lithiated electrode could affect its redox potential by as much as 0.4 V in the negative direction

compared to carbonate-based formulations. On the other hand, PTMA should remain relatively unaffected by such solvent changes due to the bulkiness of methyl groups surrounding the nitroxide redox centers, preventing interactions with solvent molecules (Figure 4.4).

To sum up, we will target the implementation of trimethyl phosphate or other related solvents in a cell combining a negative lithiated electrode with PTMA as positive electrode. This cell could possibly deliver an output voltage raised by 0.4 V; that is, from 10% to 20% increase in energy density for a lithium hybrid cell based on PTMA. These percentages are depending on the nature of the negative electrode, whether it is graphite or LTO for instance, and are provided in comparison to a standard implementation relying on commonly used carbonate formulations (PTMA *vs.* Li/Li⁺ in EC:DEC 1/1 v:v, 1 M LiPF₆). While pursuing this goal, we will also investigate the effects of the solvent change on other electrochemical properties – both at the electrode and electrolyte level – which are of practical consequences with respect to the application.

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Part III

Results and discussion

CHAPTER 5

MWCNT-G-PTMA, GRAFTING FROM APPROACH FOR RADICAL CATHODES WITH HIGHER ENERGY DENSITY

Abstract

In this chapter we expose an original strategy towards dense grafting of electrochemically active nitroxide-bearing polymer brushes on multi-walled carbon nanotubes (MWCNTs). Our strategy involves the surface initiated polymerization of 2,2,6,6-tetramethylpiperidin-4-yl methacrylate (TMPPM) through atom transfer radical polymerization (ATRP) from the high-density initiator-functionalized MWCNT surface and the oxidation of accordingly obtained PTMPPM into poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate) (PTMA), yielding MWCNT-g-PTMA composites. Extended chemical and morphological analysis confirmed the compact core-shell morphology with a high active material mass loading of 60 wt%. The electrodes made out of these MWCNT-g-PTMA composites display good cycling stability (87% of capacity retention after 200 cycles), good rate capabilities and an excellent specific capacity (85% of the theoretical capacity). The success of this strategy offers new opportunities to overcome the issue of PTMA solubilization through an electrolyte and minimal utilization of conductive carbon species.

5.1 Introduction

The strategy we have explored in the present chapter consists in the grafting PTMA on multi-wall carbon nanotubes (MWCNTs). In such a design, MWCNTs act both as the structural support and conducting agent. The strategy that we developed and the related results have been the topic of a dedicated publication in Journal of Materials Chemistry Part A.^[1] Although a similar strategy for a polynorbornene derivative bearing nitroxide radicals has been reported earlier, the amount of active material grafted on MWCNTs remained low, with the maximum content reported to be less than 30 wt%.^[2] To overcome this limitation, we propose here a grafting strategy based on SI-CRP, a class of grafting techniques that is well known to allow polymer grafted MWCNTs with a high loading of an anchored material.^[3,4]

5.2 Initiator-functionalized MWCNTs

The grafting of polymers via SI-ATRP from MWCNTs necessitates the presence of specific moieties able to initiate polymerization.^[5] To successfully graft polymers via a controlled polymerization method and to yield high polymer content onto MWCNTs, the surface of the nanotubes requires a high density of initiating groups. Since the targeted redox polymer belongs to the polymethacrylate family, we selected the bromoisobutyrate group as the initiating moiety. The selected synthetic procedure is inspired by previous studies concerning SI-ATRP^[4,6,7] and is summarized in figure 5.1. The first step consists of introducing functionality on the MWCNT surface via chemical oxidation, leading, among others, to carboxylic acid functions. Next, the carboxylic acid functions are activated with SOCl₂. The accordingly generated acyl chloride subsequently reacts with the alcohol group of 2-hydroxyethyl bromoisobutyrate, affording the MWCNT-initiator for subsequent SI-ATRP.

Thermogravimetric (TGA) measurements allowed us to monitor the functionalization procedure at each step. The plots for pristine MWCNTs, oxidized MWCNTs and MWCNT-initiator are displayed in figure 5.2. The curves obtained for all samples are typical of such systems.^[3,4] The curve for oxidized MWCNTs displays a 4.1% weight loss between 200 °C and 450 °C. In the same range of temperature the pristine nanotubes display a 0.7% weight loss. The increased weight loss is due to the oxidized functions introduced on the MWCNT outer surface. In the case of MWCNT-initiator, TGA leads to a weight loss of 10% between 200 °C and 450 °C. The difference in weight loss (5.9%) between the oxidized MWCNT and the functionalized MWCNT is attributed to the decomposition of the initiator groups bound to the nanotubes. Calculation based on the initiator fragment molar mass ($210 \text{ g}\cdot\text{mol}^{-1}$) leads to a value of 4 initiating groups per 1000 carbon atoms which is in agreement with previously reported values.^[7,8]

X-ray photoelectron spectroscopy (XPS) analyses were carried out to further assess the suitable functionalization of the MWCNTs. XPS evidences the presence of organic bromide in the MWCNT-initiator samples considering the position of the peak (70 eV) (Br_{3d} narrow scan is depicted in figure 5.3. Integration of the signal yields an atomic ratio of 2 bromides per 1000 carbon atoms. The relatively low value of this signal and the inherent experimental errors associated with both TGA and XPS measurements could explain the difference between the values obtained with these two techniques. Nevertheless, both techniques confirm the proper functionalization of the MWCNTs with the SI-ATRP initiator.

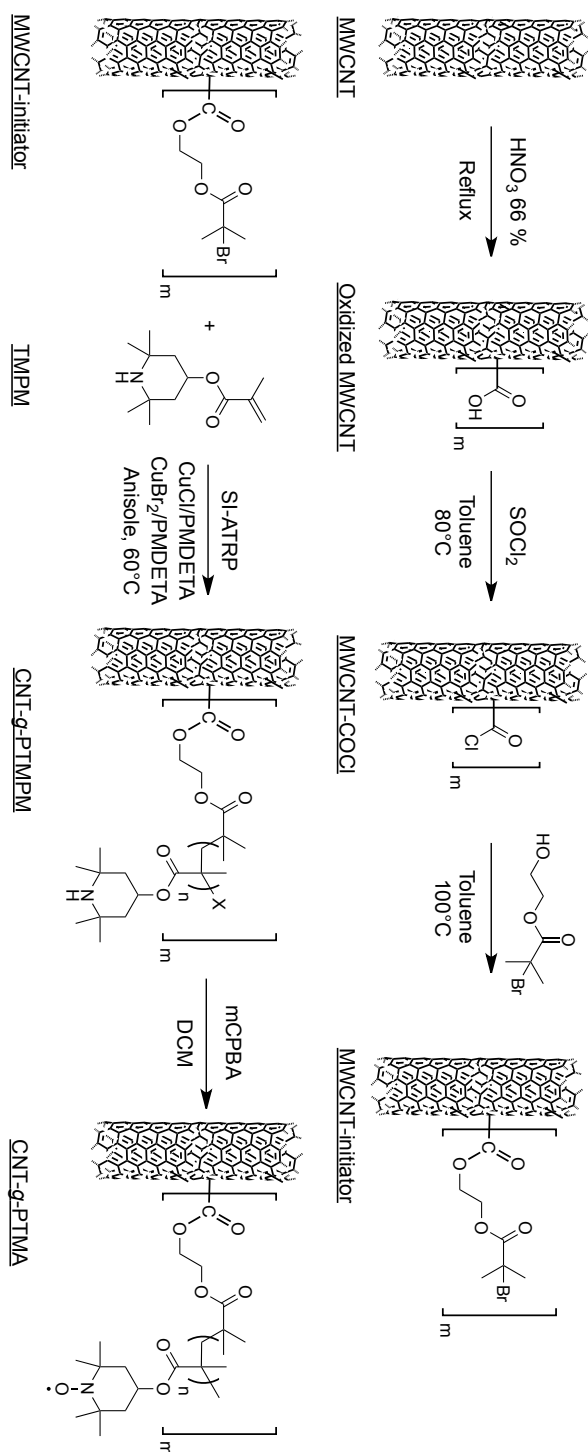


Figure 5.1 – Strategy for the “grafting from” synthesis of PTMA covalently anchored on MWCNTs (MWCNT-*g*-PTMA).

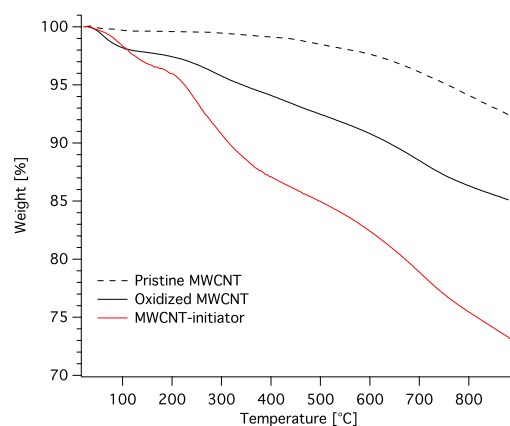


Figure 5.2 – TGA thermograms of pristine MWCNTs, oxidized MWCNTs and MWCNTs functionalized with the ATRP initiator (MWCNT-initiator).

The weight losses between 200°C and 450°C are 0.7%, 4.1% and 10%, respectively.

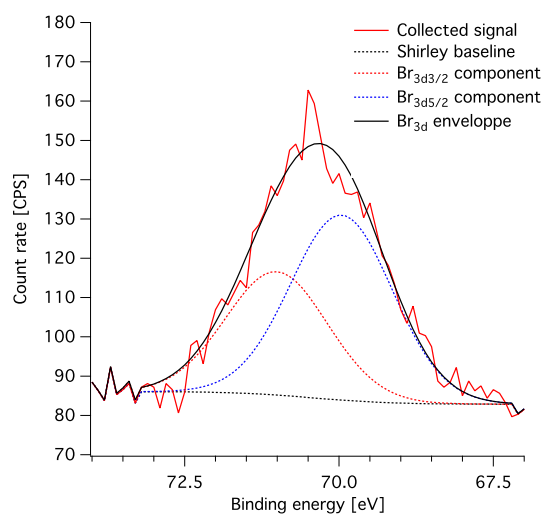


Figure 5.3 – Br_{3d} narrow scan of MWCNT-initiator.

5.3 PTMPM grafting from MWCNT-initiator

SI-ATRP was selected for SI-CRP since the controlled polymerization of the PTMA precursor polymer, i.e. poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM) was previously successfully demonstrated by Hauffman et al.^[9] Once grafting from MWCNTs of PTMPM is achieved (yielding MWCNT-*g*-PTMPM), the latter is chemically oxidized into PTMA, producing the composite cathode material (MWCNT-*g*-PTMA).

The control of the SI-ATRP process is usually achieved either by means of the addition of Cu(II) in the medium or by means of addition of a sacrificial initiator.^[5] To circumvent issues related to a possible physisorption of the growing chains onto the MWCNTs in the sacrificial approach, the polymerization was carried out by the addition of Cu(II) to the medium.¹ The SI-ATRP set up has been adapted from previous work of our group concerning synthesis of PTMPM.^[9] The polymerization is carried out overnight at 60 °C with the MWCNT-initiator (8×10^{-3} mmol of initiator groups) suspended in a PTMPM solution (120 eq with respect to CuCl; 70 wt% of anisole) and CuCl / CuBr₂ / PDMETA (1/0.1/2.42 eq/eq/eq) as a catalytic system.

The absence of self-initiated unbound polymers in the reaction mixture was verified by means of proton nuclear magnetic resonance (¹H-NMR). An aliquot of the polymerization mixture is successively passed through a poly(tetrafluoroethylene) (PTFE) 0.22 μm filter and further diluted with CDCl₃. The analysis of this sample reveals no characteristic signals of PTMPM or other adventitious reactions.

The polymer grafted MWCNTs are highly dispersible in PTMPM compatible solvents. For example, as depicted in figure 5.4, a MWCNT-*g*-PTMPM suspension in CH₂Cl₂ remains stable for more than 24 h with no sign of sedimentation while the MWCNT-initiator suspension sediments within 5 min. This experiment further emphasizes that the surface

¹The sacrificial initiator approach was tried with similar grafting conditions, with polymer loading in the resulting composite amounting to comparable percentages. Yet the electrodes failed to deliver satisfactory results as the capacity showed a massive drop during the first few cycles which further faded in a significant manner over the electrode life. The presence of physisorbed polymer, despite extensive washings, was most probably the root cause of such a dramatic behavior. This approach was then abandoned in favor of the addition of Cu(II).

modification of the nanotubes as suspensions of particles grafted with polymers are known to be stabilized when favorable interactions occur between the grafted material and the solvent.^[4,10] When the MWCNT-*g*-PTMPM suspension is added dropwise into a larger volume of acetonitrile, particles collapse. This behavior is obviously due to the non-solvent character of acetonitrile with respect to PTMPM.



Figure 5.4 – Suspensions ($0.5 \text{ mg} \cdot \text{mL}^{-1}$) in CH_2Cl_2 . On the left side: MWCNT-initiator after 5 min rest; on the right: MWCNT-*g*-PTMPM after 24 h rest.

To further support the efficient grafting of PTMPM onto MWCNTs, transmission electron microscopy (TEM) is used to observe an organic layer on the outer wall of the MWCNTs (Figure 5.5). The TEM micrographs uncover the presence of a soft material shell covering the walls of the nanotubes. Measurements obtained from several TEM micrographs lead to the evaluation of the average diameter of the pristine MWCNT-*g*-PTMPM to be equal to $17.3 \pm 0.4 \text{ nm}$ whereas the average diameter for pristine MWCNTs is found to be $10.9 \pm 0.6 \text{ nm}$ (Figure 5.6 displays the diameter distribution histogram for both samples). Hence these significantly different diameters support the evidence of an outer layer attributed to the grafted PTMPM (Figure 5.6).

To confirm the nature of the MWCNT surface modification, XPS analysis has been realized (Table 5.1). The MWCNT-*g*-PTMPM sample is compared to a PTMPM homopolymer. XPS analysis points out atomic concentrations for the MWCNT-*g*-PTMPM sample close to those obtained for a PTMPM sample.

Seemingly, the MWCNT signature is so efficiently screened by the polymeric shell that it is not contributing to the collected signals. The

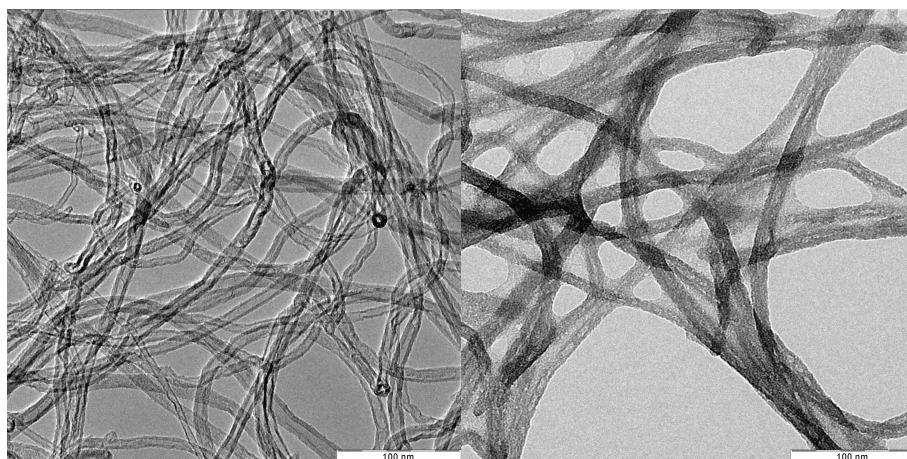


Figure 5.5 – TEM micrographs of pristine (left) and MWCNT-*g*-PTMPM (right). Scale bars: 100 nm.

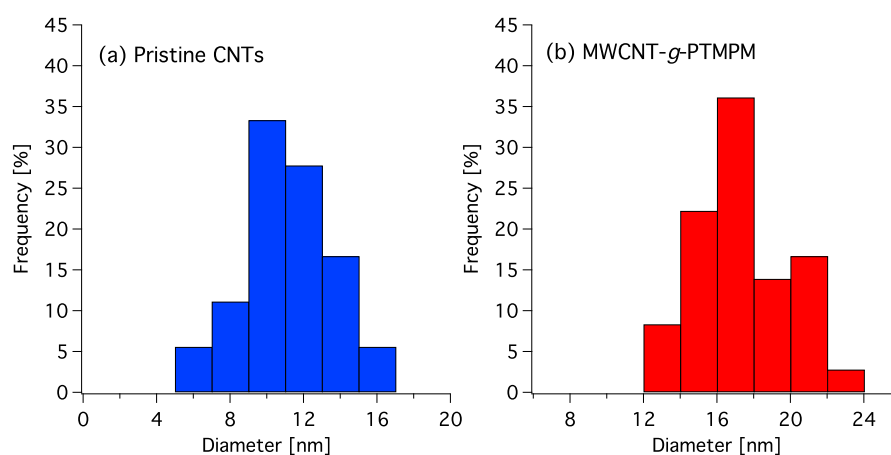


Figure 5.6 – Diameter distribution histograms for (a) pristine nanotubes and (b) MWCNT-*g*-PTMPM. Diameters values are collected by measurements on a collection of TEM micrographs.

C_{1s} line shape signals of MWCNT-initiator exhibits the usual characteristic tail of oxidized CNTs^[11] (MWCNT-initiator, figure 5.7a). In contrast, the line shape for MWCNT-*g*-PTMPM presents a main peak with a shoulder (Figure 5.7c) and the general aspect is more typical of the pure PTMPM sample. These observations tend to demonstrate that a uniform polymer shell efficiently masks the MWCNT core. Moreover the O/C and N/C ratios are fairly matching the ratios that could be

Table 5.1 – Experimental surface atomic concentrations of MWCNT-*g*-PTMPM compared to experimental and predicted values of pure PTMPM.

Spectral Line	Surface atomic concentrations (%)		
	MWCNT- <i>g</i> -PTMPM		PTMPM
	Found	Found	Expected
C _{1s}	83.0	82.4	81.3
O _{1s}	11.7	11.8	12.5
N _{1s}	5.2	5.8	6.3

predicted based on the PTMPM chemical composition (Table 5.1).

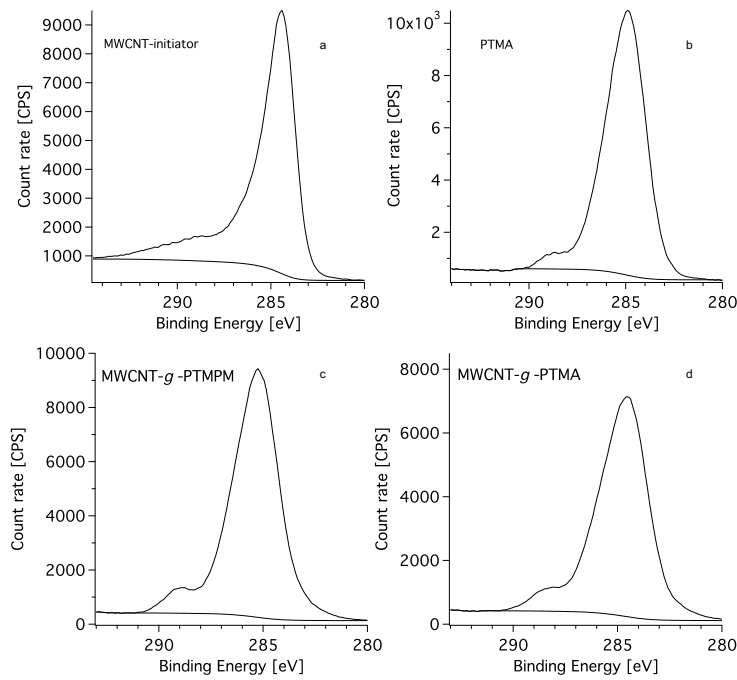


Figure 5.7 – C_{1s} narrow scans of MWCNT-initiator (a), PTMA (b), MWCNT-*g*-PTMPM (c) and MWCNT-*g*-PTMA (d) powder samples.

TGA is again implemented to determine the polymeric fraction of the MWCNT-*g*-PTMPM (Figure 5.8). A considerable mass loss can be seen on the curves of the composite sample around 300 °C. This drop can be

ascribed to the grafted polymer degradation occurring in the same range of temperature as the pure PTMPM sample. The analyses lead to a polymeric content as high as 60% (Figure 5.8). Considering the number of initiating groups per gram of CNTs and an initiator efficiency of 70% close to the value obtained for similar initiator moieties untethered to CNTs,^[9] this leads to an average degree of polymerization of 29 TMPM units per grafted chain. Thus, high density grafting with decently long polymer chains is achieved here (with respect to the usual grafting on MWCNTs), benefiting the specific capacity of the resulting composite.

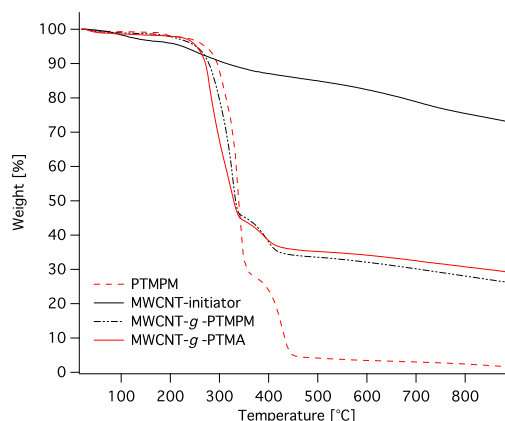


Figure 5.8 – TGA thermograms of pure PTMPM, MWCNT-initiator, MWCNT-*g*-PTMPM and MWCNT-*g*-PTMA. The weight losses between 200 °C and 450 °C are 95%, 10%, 64% and 65%, respectively.

5.4 From MWCNT-*g*-PTMPM to MWCNT-*g*-PTMA

MWCNT-*g*-PTMPM has been oxidized with a procedure similar to the one applied to PTMPM found in the literature.^[4] The absence of polymer desorption during oxidation is verified at the end of the process by means of TGA measurements. The thermogram for MWCNT-*g*-PTMA (Figure 5.8) is affected by a weight loss at a temperature close to the one for the pure PTMA samples.^[12] The hybrid material presents a weight loss (about 65%) similar to MWCNT-*g*-PTMPM confirming that the polymer is firmly attached to the carbon nanotubes.

Table 5.2 – Experimental surface atomic concentrations of MWCNT-*g*-PTMA compared to experimental and predicted values for pure PTMA.

	Surface atomic concentrations (%)		
	MWCNT- <i>g</i> -PTMA	PTMA	
Spectral Line	Found	Found	Expected
C _{1s}	80.1	79.3	76.5
O _{1s}	16.1	15.5	17.6
N _{1s}	3.9	5.1	5.9

More convincingly, XPS analyses deliver similar atomic concentrations for MWCNT-*g*-PTMA and pure PTMA, both close to the expected theoretical values (Table 5.2). Again the C_{1s} signal (figure 5.7d) is consistent with a shell of the polymer around the MWCNTs as the curve does not present the typical tail of oxidized CNTs and the shape is more close to the one displayed for pure PTMA (Figure 5.7b).

All these results tend to demonstrate that no significant degradation or elution of the polymer is taking place during the oxidation. Thermal data, chemical compositions and solubility observations are consistent with PTMA covalently anchored at the MWCNT surface.

5.5 Electrochemical characterization

The cathode fabrication process relies on the realization of functionalized MWCNT mats (buckypaper, figure 5.9).^[13] Practically, pristine MWCNTs dispersed in butanol are first deposited by vacuum filtration to generate a thin film current collector.^[13,14] This layer was also found to allow easy peeling of the electrode at the end of the process. The layer of the active material is then obtained by filtration of a MWCNT-*g*-PTMA suspension in *N*-methylpyrrolidone/CH₂Cl₂ 6:4 (v/v). The thickness of the fabric after processing was measured to be 86 μm.

Cyclic voltammetry analysis is conducted to assess the redox activity of the so-prepared PTMA buckypaper (Figure 5.10). The first cycle reveals a peak centered around 3.6 V *vs.* Li/Li⁺, which corresponds to the oxidation of the nitroxide radical into an oxoammonium cation.^[15]

After the first cycle, the successive anodic and cathodic waves display

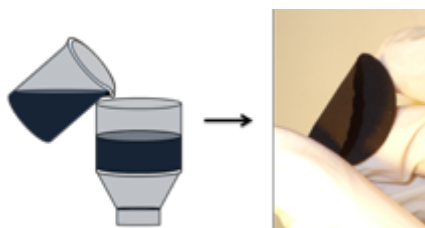


Figure 5.9 – Electrode fabrication process (buckypaper).

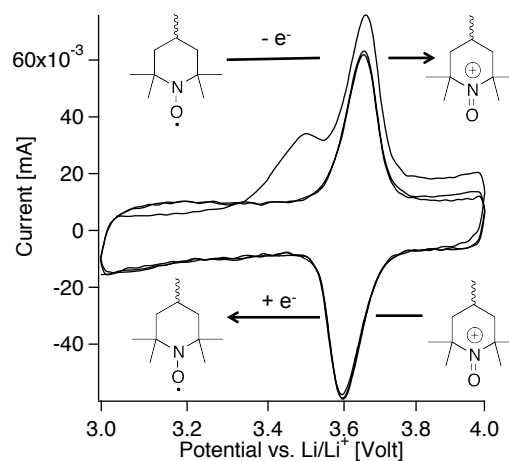


Figure 5.10 – Cyclic voltammogram of MWCNT-*g*-PTMA at $0.1 \text{ mV} \cdot \text{s}^{-1}$ (EC/ DEC/DMC 1:1:1 in v/v/v; 1 M LiPF_6). The first 3 cycles are depicted. Redox reactions associated with positive and negative processes are depicted.

no differences in the redox activity of the electrode, the redox processes being fully reversible with a peak-to-peak separation of 0.06 V.

The electrode capacity retention is evaluated by means of galvanostatic cycling. Figure 5.11 presents the capacity retention plot versus the number of constant current ($220 \text{ mA} \cdot \text{g}^{-1}$) charge/ discharge cycles. At the first cycle, a drop in capacity is observed, ascribed to irreversible redox processes. However, the capacity is then stabilized around $80 \text{ mAh} \cdot \text{g}^{-1}$, which corresponds to 72% of the theoretical capacity. The electrodes display excellent capacity retention with less than 13% capacity loss after 200 cycles.

TGA measurements after cycling experiments demonstrate that no polymer migrates through the electrolyte solution upon cycling. Practically, the cathode after cycling is soaked several times in fresh ace-

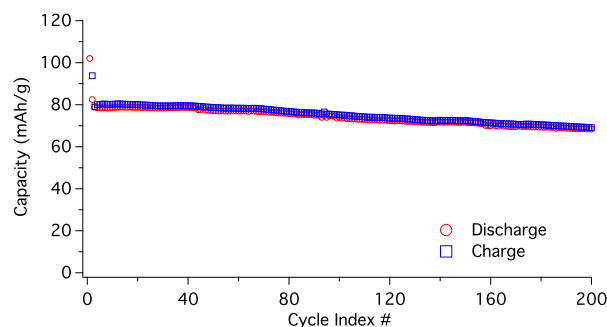


Figure 5.11 – Cycle stability of MWCNT-*g*-PTMA (60 wt% PTMA) at 2C rate over 200 cycles.

tonitrile to remove any Li salt and dried under vacuum. TGA of this cathodic material displays the same composition and degradation profile as the one observed for MWCNT-*g*-PTMA prior cycling (Figure 5.12). The weight loss for the cathode is lower than the one for MWCNT-*g*-PTMA due to the presence of pristine MWCNT, introduced as the first layer during the fabrication process of the electrode. The weight loss between 200°C and 450°C after cycling is 21.0%. Taking into account the mass of the materials in the cathode and the weight loss for the starting material MWCNT-*g*-PTMA (30.5 wt%), the weight loss between 200°C and 450°C can be calculated. This weight loss should be 2/3 of the MWCNT-*g*-PTMA weight loss, i.e. 20.3 wt% (Degradation of pristine MWCNT is considered as negligible). This value is close to the one experimentally found after cycling. Further details are presented in subsection 5.7.2.8. This is therefore evidencing that the polymer has not diffused into the electrolyte solution. The degradation mechanism seems then to occur via a different pathway.

The rate capabilities of the cathodes are measured by cycling the electrodes at different current densities (Figure 5.13). Cycling at C/2 delivers a high reversible capacity of $94 \text{ mAh} \cdot \text{g}^{-1}$ (85% of the theoretical capacity). At higher rates, the capacity decreases only slightly. The capacity at 5C is still half of the nominal value obtained at C/2. Furthermore the charge and discharge profiles at 5C maintain the characteristic plateau of PTMA centered at 3.6 V (*vs.* Li/Li⁺ with a slight polarization of about 100 mV (Figure 5.14) emphasizing the good current collection efficiency of the constructed electrodes. The cathode integrity after the rate capabilities test was measured by cycling the system back to lower

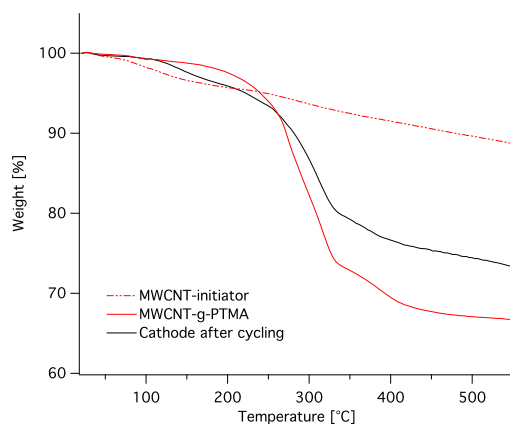


Figure 5.12 – Thermograms of the MWCNT-initiator, MWCNT-*g*-PTMA and the cathode after cycling.

current density ($C/2$). This experiment revealed that the capacity is nearly the same as the one previously observed for the same C-rate.

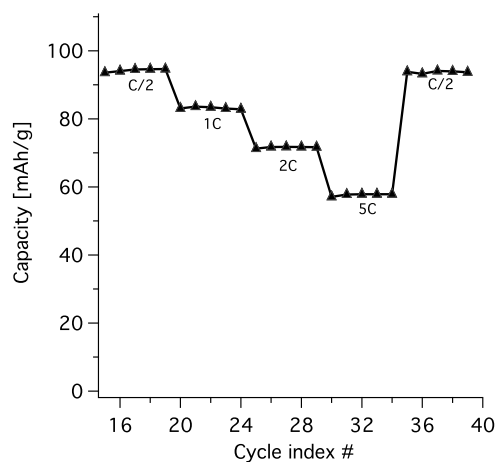


Figure 5.13 – Electrochemical performances of the MWCNT-*g*-PTMA (60 wt% PTMA) cathode at various C rates (EC/DEC/DMC 1:1:1 in volume; 1 M LiPF₆).

In order to evidence the benefits of our grafting strategy, control composite electrodes were prepared via the more conventional physical blending of the active (PTMA) and conductive materials (MWCNTs).

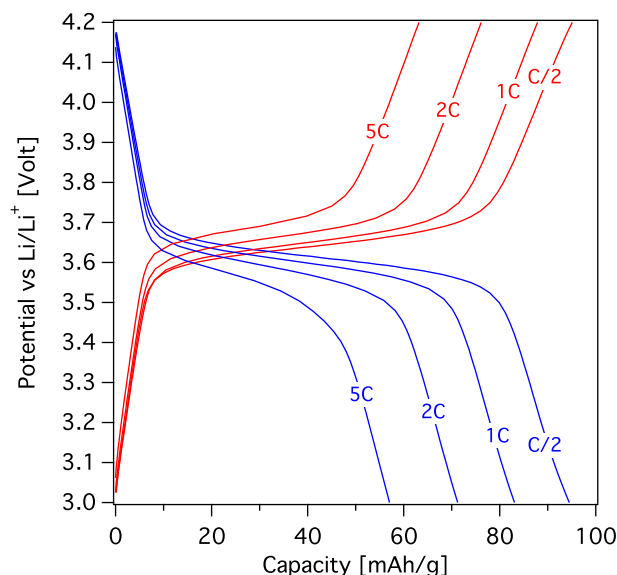


Figure 5.14 – Charge–discharge curves of the MWCNT-*g*-PTMA (60 wt% PTMA) cathode at various C rates (EC/DEC/DMC 1:1:1 in volume; 1 M LiPF_6).

Details on the preparation of the control composite are described in subsection 5.7.2.7. Compared to the MWCNT-*g*-PTMA cyclic voltammogram (Figure 5.10), the cyclic voltammogram of the control composite electrode (Figure 5.15) displays a broader peak-to-peak separation (0.08 V), suggesting poorer charge collection efficiency.

Galvanostatic cycling stability tests on the control composite were also conducted (Figure 5.16). During the initial conditioning cycling steps, the control electrode displayed a satisfying capacity ($71 \text{ mAh}\cdot\text{g}^{-1}$). The subsequent cycles were realized with the same current density as with the MWCNT-*g*-PTMA electrodes. The increased current density resulted in a dramatic decrease in the capacity retention of the control composite, as low as $35 \text{ mAh}\cdot\text{g}^{-1}$ attained at $220 \text{ mA}\cdot\text{g}^{-1}$ (that is 2 times lower than the capacity retention of the grafted material at the same C rate). Moreover, the capacity decay of the control electrode is more pronounced than in the case of the MWCNT-*g*-PTMA electrode. In the latter case, the electrode displayed a capacity retention as high as 87% whereas the control electrode retained only 78% of its capacity.

Concerning the rate capabilities of the tested electrodes, the perfor-

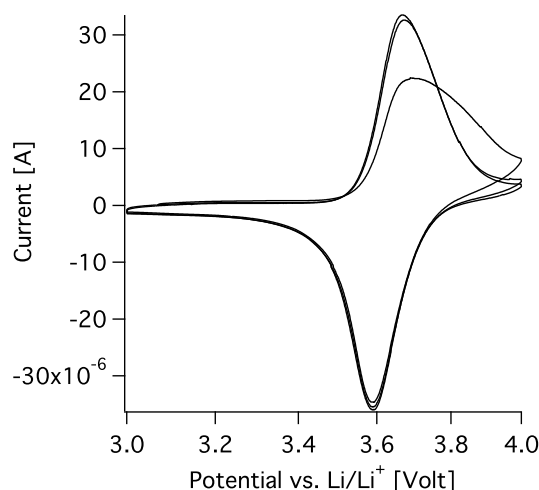


Figure 5.15 – Cyclic voltammogram of the PTMA-based control electrode at $0.1 \text{ mV}\cdot\text{s}^{-1}$ (EC/DEC/DMC 1:1:1 in v:v:v ; 1 M LiPF_6). The 3 first cycles are depicted.

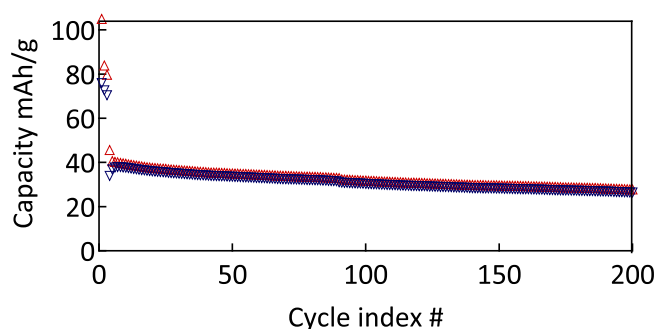


Figure 5.16 – Cycle stability of the PTMA-based control electrode over 200 cycles. The current density was set at $220 \text{ mA}\cdot\text{g}^{-1}$ except the 3 first cycles (conditioning step; $18 \text{ mA}\cdot\text{g}^{-1}$). Charge capacity is displayed as red symbols, discharge capacity as blue symbols.

mances of the control electrode were again inferior to those obtained with the grafted system (charge–discharge curves are depicted in figure 5.17). Indeed, the polymer-grafted material displayed superior power performances than the control composite. With respect to common PTMA/conductive carbon blends, the control electrode displayed limited rate capabilities that can be related to its relatively high thickness and high PTMA content. These two parameters are acting here together

and result in hampered performances since the redox reactions are not fully supported by the conducting matrix (poor charge transfer due to low carbon content)^[16] and because the electrode interfacial resistance increases with the thickness.^[17]

Eventually, for each of the analyzed electrochemical aspect, the comparison plays in favor of the MWCNT-*g*-PTMA electrode. Interestingly, 4 points probe measurements delivered quite close conductivities for the control composite ($11.6 \text{ S}\cdot\text{cm}^{-1}$) and our designed system ($8.1 \text{ S}\cdot\text{cm}^{-1}$). Thus the enhancement of the rate performances is not arising from a general improvement of the conductivity. A more conceivable explanation must be rather an improvement of the electron transfer between the PTMA and the MWCNTs. Compared to the control composite, the boosted electron transfer in the MWCNT-*g*-PTMA system would then originate from a higher degree of homogeneity at the nanoscale along with a more intimate contact between the active and the conductive components.

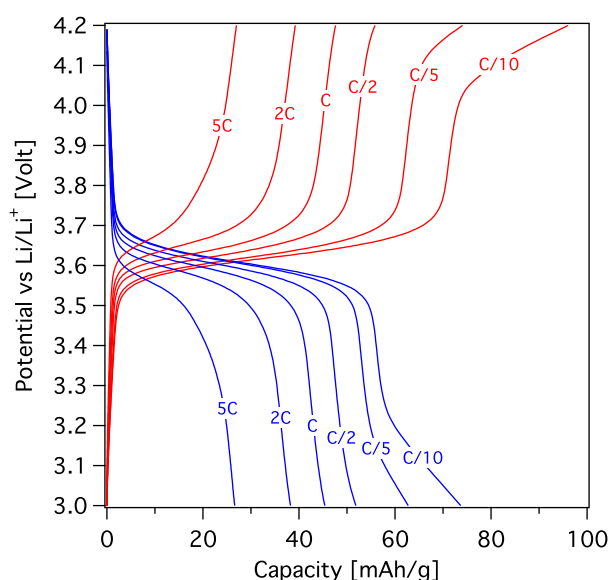


Figure 5.17 – Charge-discharge curves of PTMA-based control cathode (60 wt% PTMA) at various C rates (EC/DEC/DMC 1:1:1 in volume ; 1 M LiPF_6).

5.6 Conclusions

The present chapter exposed the synthesis of an electrochemically active polymer, the PTMA, covalently anchored onto the surface of MWCNTs. The synthetic strategy successfully involved a controlled grafting from technique, i.e. SI-ATRP, to yield MWCNT-*g*-PTMA with a high loading of the active material (up to 60 wt%). TGA, XPS and TEM contributed to characterize the MWCNTs at each step. Particularly these techniques evidenced the nature, the composition and the distribution of grafted materials in the MWCNT-*g*-PTMPM and MWCNT-*g*-PTMA composites.

The MWCNT-*g*-PTMA composite was further processed as a buckypaper electrode via a filtration method. The buckypaper electrode was electrochemically characterized using half-cell configuration with lithium as the reference and working electrode. The cycling stability of the designed cathode was evaluated after 200 cycles, demonstrating an excellent capacity retention (87% of the initial capacity is retained). Moreover, during electrochemical measurements, the composite material reached 85% of its theoretical capacity. This high capacity is ascribed to the high conversion of pendant amino groups into nitroxide redox centers during the oxidation step. Variable rate measurements of the electrode additionally attested the ability of the designed electrode to sustain high charge/discharge rates. Altogether the electrochemical characterization owed to prove the viability of the accordingly synthesized MWCNT-*g*-PTMA composite as cathodic material for lithium batteries.

5.7 Experimental section

5.7.1 Synthesis procedures

5.7.1.1 Materials

CH_2Cl_2 (DCM, HPLC grade, Fisher Scientific) is passed through a SPS solvent dispenser fitted with an alumina column. Triethylamine (Analytical reagent grade, Fischer Scientific) is distilled over CaH_2 under an argon atmosphere. 3-Chloroperoxybenzoic acid (mCPBA, Aldrich, 77% max) was washed with a phosphate pH 7 buffer solution. Thin multiwall carbon nanotubes NC7000 (MWCNT) were kindly provided by Nanocyl. SOCl_2 (99.5+%, Fisher Scientific), 1-methyl-2-pyrrolidone (ACS reagent, Acros Organics), 2-hydroxyethyl bromoisobutyrate (95%, Sigma-Aldrich) (HEBB), HNO_3 (65%, AnalaR NORMAPUR), CuCl (Aldrich, 99.999%), CuBr_2 (Aldrich, 99.999%), TPM (98%, TCI), N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA, 98%, Aldrich), anhydrous toluene (extra dry, 99.85%, over molecular sieves, AcroSeal, Acros Organics), anisole (Acros Organics, 99%) and all other chemicals are used as received.

5.7.1.2 MWCNT oxidation

In a 250 mL round-bottom flask, MWCNTs (1 g) and HNO_3 65% (100 mL) are charged. The mixture is stirred for 2 h at reflux (110°C). The mixture is then filtered over a PTFE 0.45 μm filter. The residue is washed with ultra pure water until the filtrate reaches neutral pH. The remaining solid (MWCNT-COOH) is dried under reduced pressure for 24 h at 35°C.

5.7.1.3 Preparation of MWCNT-COCl

A 100 mL round-bottom Schlenk flask is charged with 100 mg of previously-oxidized MWCNT-COOH. The content of the flask is degassed under reduced pressure at 120°C for 4 hours. 40 mL of anhydrous toluene and 15 mL of SOCl_2 are then charged in the flask under argon. The MWCNTs are dispersed by immersing the Schlenk flask into an ultrasonic bath for 15 min. The reaction is carried out by heating at 80°C

for 24 h to yield MWCNT-COCl. The recovery is done by distillation under reduced pressure until dryness.

5.7.1.4 Preparation of MWCNT-initiator

A 100 mL round-bottom Schlenk flask is charged under argon with 100 mg of MWCNT-COCl, 40 mL of anhydrous toluene, 5 drops of triethylamine and 1.8 g of HEBB. The flask is sealed and ultrasonicated for 30 min. The functionalization is carried out at 100 °C for 24 h. MWCNT-initiator samples are recovered by filtration on a 0.22 µm poly(vinylidene fluoride) (PVDF) filter and washed three times with 50 mL of toluene. The remaining solid is dried overnight under reduced pressure at 35 °C.

5.7.1.5 TPM polymerization via grafting from MWCNT-initiator

First, in a Schlenk flask, 28.6 mg of MWCNT-initiator (8×10^{-3} mmol of initiator groups) are charged and degassed under reduced pressure at room temperature for 3 h. Degassed anisole (10 mL) is introduced via a cannula into the vessel. The resulting mixture is then immersed in an ultrasonic bath for 30 min. TPM (4.4 g, 19.8 mmol, 120 eq), CuBr₂ (254 µL of a solution 7.2 mg·mL⁻¹ in acetonitrile, 0.016 mmol, 0.1 eq, PMDETA (83.2 µL, 0.40 mmol, 2.42 eq) and anisole are charged in the Schlenk flask. This mixture is degassed by 3 freeze-pump-thaw cycles and is transferred via a cannula into a 100 mL round-bottom Schlenk flask containing CuCl (16.3 mg, 0.16 mmol, 1 eq). The MWCNT-initiator suspension is finally added by means of a gas-tight syringe. The reaction mixture is ultrasonicated for 30 min. Polymerization takes place under an argon atmosphere at 60 °C for 16 h.

The solution is quenched by quickly cooling down the medium with liquid nitrogen and exposition of the polymerization medium to air. The medium is concentrated under reduced pressure. The MWCNT-*g*-PTPM suspension is then added dropwise to 200 mL of acetonitrile under vigorous stirring. The solid is recovered by centrifugation and resuspended in 5 mL of DCM. The dropwise addition followed by centrifugation is repeated 2 times in acetonitrile and 1 time in hexane. The remaining solid is dried overnight under reduced pressure at 35 °C. This yields 55 mg of MWCNT-*g*-PTPM.

5.7.1.6 Synthesis of MWCNT-*g*-PTMA

In a 100 mL round-bottom flask, MWCNT-*g*-PTMPM (45 mg, 0.120 mmol of N–H moieties) and 45 mL of dry DCM are charged under argon. The flask is put in an ultrasonic bath for 15 min and subsequently thermostated at 0°C. A solution of mCPBA (25.8 mg, 0.150 mmol, 1.25 eq) in dry DCM (7.5 mL) is added dropwise under stirring at 0°C for 1 h. The suspension is then stirred for the next 2 hours, while its temperature is allowed to go back to room temperature on its own accord. Afterwards the reaction medium is extracted successively twice with an aqueous solution of NaHCO₃ 2% and twice with deionized H₂O. The resulting organic phase is filtered on a 0.22 µm PVDF filter and dried overnight *in vacuo* at 35°C, affording 25 mg of MWCNT-*g*-PTMA.

5.7.2 Characterization

5.7.2.1 Thermogravimetric analysis

Thermogravimetric analyses (TGA) are recorded on a TGA/SDTA 851e instrument from METTLER TOLEDO. These analyses are carried out with a heating ramp of 10°C·min^{−1} and under a N₂ flow (0.1 L·min^{−1}) with the samples (3 – 5 mg) placed into 70 µL alumina containers.

5.7.2.2 Transmission electron microscopy

Transmission electron microscopy (TEM) images are obtained with a LEO 922 OMEGA energy filter transmission electron microscope. The powder samples are suspended in dichloromethane under ultrasonic treatment, then a drop of the supernatant is deposited on a holey carbon film supported on a copper grid, which is dried overnight at room temperature before analysis.

5.7.2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analyses are realized at room temperature by means of a SSI X-Probe (SSX 100/206) photoelectron spectrometer from FISOONS equipped with a monochromatized micro-focus Al X-ray source. Samples are stuck onto sample holders with

a double-face adhesive tape and then placed on an insulating home-made ceramic carousel (Macor[®], Switzerland). The spot size for irradiation is set at 800 μm x 1200 μm . Charge effects are suppressed by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale is calibrated with reference to the Au_{4f7/2} peak at 84 eV. The binding energies were calculated with respect to the C_{1s} peak fixed at 284.8 eV for hybrid and polymer materials, and at 284 eV for MWCNT-initiator. Data treatment is performed with the CasaXPS program (Casa Software Ltd., UK). The peaks are decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

5.7.2.4 Electrode design

Self-standing electrodes are produced using a vacuum filtration process over a PVDF 0.22 μm filter. The filtration device is a Millipore set-up. Pristine MWCNTs (8.0 mg) are dispersed in butanol (250 mL) using bath sonication for 30 min. This first suspension is filtered on the PVDF filter. A suspension of MWCNT-*g*-PTMA (8.0 mg in 100 mL DCM/*N*-methylpyrrolidone, 40:60, bath sonicated for 30 min) is then filtered over the first layer formed on PVDF (3.40 cm diameter). Electrodes are first dried in ambient air at room temperature for 2 hours, then at 60 °C under vacuum for 24 hours. The resulting material is then cut into discs (1.2 cm, total weight of 2.0 mg each) for electrochemical measurements.

5.7.2.5 Cell assembly

Electrodes are tested in half-cell configuration using lithium metal foil (99.9% Alfa Aesar) as a reference and counter electrode. A porous polyethylene membrane was purchased from Celgard and used as a separator. A mix of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) 1:1:1 v/v/v with 1 M of lithium hexafluorophosphate (LiPF₆) was purchased from Novolyte and used as an electrolyte. Cells are assembled in Swagelok cells purchased from X2Labware. All cells are assembled under an argon atmosphere <0.1 ppm H₂O, <0.1 ppm O₂) in a MBraun glovebox.

5.7.2.6 Electrochemical tests

Cyclic voltammetry (CV) and charge/ discharge tests are conducted with an Arbin Instruments Battery Tester BT-2043. Unless specified otherwise, all values of capacity are reported with respect to the redox polymer mass in the electrode, and assuming that the polymer is composed solely of TMA repeating units. The electrical conductivities of the electrodes were measured by a 4-point probe station (Lucas Lab L320) coupled with a Keithley 2410 monitor. The current was adjusted to keep a constant voltage of 10 mV. The film thickness was measured using a Draper Expert digital micrometer.

5.7.2.7 Untethered PTMA control electrodes

A physical blend of untethered PTMA and pristine MWCNTs is prepared in order to conduct electrochemical measurements as control data. For this purpose, a linear PTMA homopolymer (degree of polymerization = 69) is synthesized through ATRP. The control composite measurements are compared to the results obtained for the MWCNT-*g*-PTMA electrodes.

The cathodes are prepared by blending the active material PTMA, MWCNTs (Nanocyl NC7000) and PVDF binder. The blend has the following composition, 60 wt% of PTMA, 30 wt% of MWCNTs and 10 wt% of PVDF binder. 5 mL of *N*-methylpyrrolidone are added per 1 g of solid materials. The ingredients are mixed uniformly at room temperature for 12 hours to yield the slurry. The slurry is cast on an aluminum foil using the doctor blade method (the thickness of the wet film is controlled to be 45 μm) and dried at 60 °C for 12 h. Circular discs of diameter 1 cm are cut and used as cathodes for evaluating the electrochemical properties. The electrodes are assembled following the same protocol as for the MWCNT-*g*-PTMA cathodes. The cyclic voltammogram of the control composite is recorded with a CHI1660B instrument. All others electrochemical measurements on the control composite are conducted with the same devices, apparatus and parameters as for the MWCNT-*g*-PTMA cathodes. 4 points conductivity measurements are obtained with the control composite coated on an insulate substrate. This coating is prepared with the same doctor blade protocol as for the control electrode but cast on a glass slide. The thickness of the coated

material is found to be 30 μm (measured with a Draper Expert digital micrometer).

5.7.2.8 TGA Measurements after cycling

A cathode made of MWCNT-*g*-PTMA and pristine MWCNT (2:1; m/m) was cycled until the capacity is the half of the one at the third cycle (500 cycles). At the end of the test, the battery is fully discharged. The cathode, soaked 3 times in AcCN during 1 week, is dried under reduced pressure. A TGA analysis is conducted.

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CHAPTER 6

MWCNT-G-PTMA, GRAFTING ONTO APPROACH FOR RADICAL CATHODES WITH HIGHER POWER DENSITY

Abstract

This chapter describes the synthesis and characterization of a new hybrid material based on poly(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl methacrylate) (PTMA) for lithium battery applications. Our strategy relies on the anchoring of nitroxide-embedding polymer chains onto multi-walled carbon nanotubes (MWCNTs). The resulting hybrid material (MWCNT-g-PTMA) not only prevents the solubilization of the PTMA active material but also benefits from its structural design aspects. The MWCNT-g-PTMA structure confers high performances thanks to the precise distribution of the PTMA redox material with respect to the MWCNT conductive network, as confirmed by molecular modeling simulations of the polymer/MWCNT interface. Physicochemical characterizations are evidence of the success of MWCNT-g-PTMA synthesis with a polymer loading up to 30 wt%. Electrochemical analysis shows the potential of MWCNT-g-PTMA as a battery material, with a capacity reaching 85% of the theoretical value, a good cyclability (retention > 80% after 150 cycles) and excellent power performances (capacity at 60C exceeding 65% of the nominal value).

6.1 Introduction

In the present chapter we are proposing an original grafting strategy that provides chemical anchoring between polymer chains and multi-walled carbon nanotubes (MWCNTs), with the extra advantage of favoring charge transfer and collection due the intimate contact between the two materials. The content of this chapter is based on our report in RSC Advances.^[1] Compared to our previous report on the “grafting from” approach,^[2] we disclose here a “grafting onto” strategy that offers a more convergent and efficient pathway to achieve covalent bonding between PTMA and MWCNTs. Previous reports about grafting have demonstrated that strong interactions between carbon nanotubes (CNTs) and the polymer are essential to take full advantage of the nitroxide ultra-fast redox process.^[2,3] In other words, electroactive grafted materials provide higher power performances while maintaining the same conductive material content, thanks to robust charge storage and efficient charge transfer. Practically, our strategy relies on the synthesis of a functional polymer that is able to react at the MWCNT surface. As highlighted in the literature, covalent CNT surface modification often requires some pre-functionalization steps.^[4–6] Efficiency-wise, the first step is usually an attack on the sp^2 carbon side-walls by means of a very reactive species, thus generating sites for the next steps of surface modification. These sites can be exploited to introduce moieties of interest so as to perform covalent anchoring of the functional polymer.

The strategy chosen here takes the benefits of a controlled polymerization technique that we reported earlier in order to obtain a functional block copolymer.^[7] This copolymer incorporates a PTMA sequence along with a sequence bearing azide functional groups. Introducing alkyne groups at the MWCNT surface then enables the anchoring of the block copolymer via the well-known copper-catalyzed azide–alkyne cycloaddition (CuAAC; figure 6.1). This strategy yields the grafted material MWCNT-*g*-PTMA with a PTMA content up to 30 wt% while offering superior electrochemical performance with respect to a more traditional blend of PTMA/MWCNTs.

In order to gain a better understanding of the nature and strength of the PTMA/MWCNT interactions and the morphology of the interface, model systems for the interface by means of quantum chemical and molecular modeling simulations have been studied.

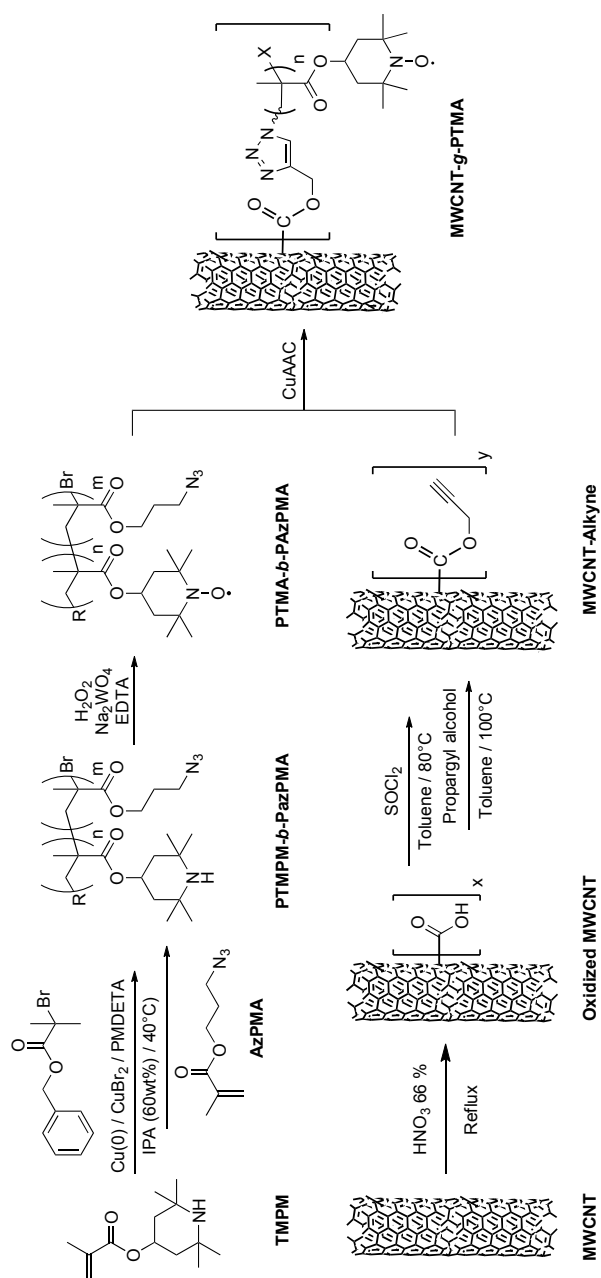


Figure 6.1 – Strategy for the “grafting onto” synthesis of PTMA covalently anchored on MWCNTs (MWCNT-g-PTMA).

6.2 Implementation of SET-LRP for the synthesis of functional PTMA copolymers

This section discloses the synthesis of electro-active polymer precursors by SET-LRP (Figure 6.2). The polymerization of TPM is investigated with Cu(0)/CuBr₂/PMDETA catalyst in isopropanol. The synthesis of oligomers and polymers is demonstrated here. The controlled behavior of the polymerization is verified by kinetic experiments. The living character of the PTMPM produced by SET-LRP is investigated by block copolymerization experiments with 3-azidopropyl methacrylate (AzPMA) via a successive addition process. Finally the resulting block copolymer is oxidized to produce the electro-active PTMA.

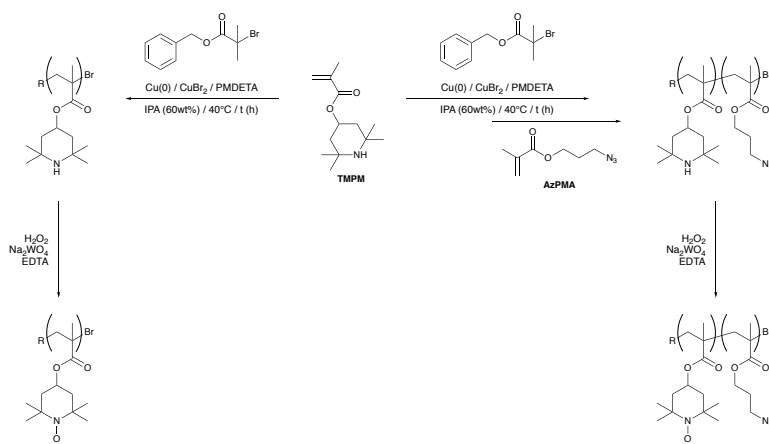


Figure 6.2 – Synthetic strategy towards PTMA and PTMA-*b*-PAzPMA.

6.2.1 Synthesis of PTMPM *via* SET-LRP

The polymerization of TPM was carried out in 2-propanol (IPA). This solvent is reported to induce the disproportionation of Cu(I)Br in the presence of N-containing donor ligand, which is the main requirement

for the SET-LRP.^[8] The polymerization was realized with 5 cm of Cu(0) wire, [benzyl 2-bromoisobutyrate (BnBiB)] / [CuBr₂] / [PMDETA] / [TMPM] = 1/0.05/0.12/51 molar ratios in IPA (60 wt%) at 40°C for 24 h. Under these conditions, quantitative conversion of the monomer was observed leading to a polymer with $M_n = 13,270 \text{ g}\cdot\text{mol}^{-1}$ and $\bar{D} = 1.19$ at full conversion. In the SEC chromatogram (Figure 6.21), a high molar mass population can be observed. The presence of this high molar mass population, even in limited amount, indicates the occurrence of termination at full conversion due to too long polymerization time.

Kinetic experiments of the polymerization of TMPM by SET-LRP were carried out under positive argon atmosphere and with [BnBiB] / [CuBr₂] / [PMDETA] / [TMPM] = 1/0.05/0.12/51 molar ratios in isopropanol (IPA) (60 wt%) at 40°C. The sampling of the polymerization was realized via a cannula in order to minimize the quenching of the polymerization by oxygen. Figure 6.3a presents the kinetic plot of the SET-LRP. The linear first order behavior is observed indicating a constant concentration of active species throughout the polymerization ($k_p = 1.55 \times 10^{-4} \text{ s}^{-1}$) and thus the controlled behavior of the polymerization up to 98% conversion.

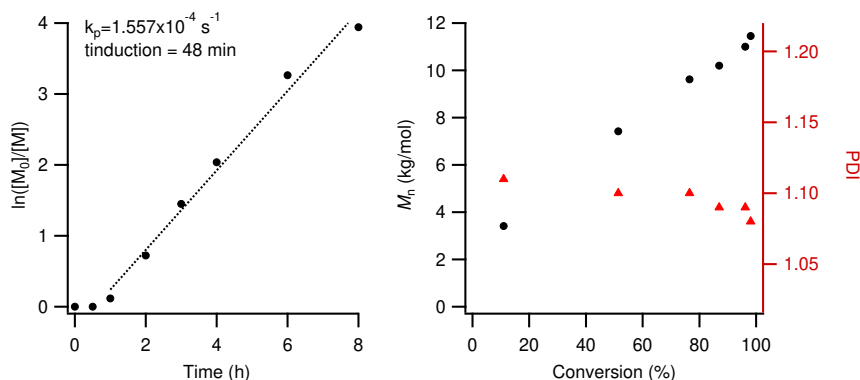


Figure 6.3 – Kinetic study of the SET-LRP of TMPM: (a) $\ln([M_0]/[M])$ vs. time plot, and (b) experimental M_n and $\bar{D}$ vs. conversion.

In the kinetic plot, an induction period of 48 min is observed. In SET-LRP, induction periods may be due to the presence of polymerization inhibitor in the polymerization medium^[9,10] or the presence of a copper oxide coating on the copper wire.^[11,12] Since commercial TMPM

is not stabilized by polymerization inhibitor, the induction period may be attributed to the presence of a copper oxide coating on the copper wire, even after the acidic pre-treatment.

Figure 6.3b presents the evolution of the molar masses and of the dispersity indices ($\bar{D}$) with conversion. The molar masses of the PTMPM increase linearly with the conversion and the molecular weight distribution becomes narrower with an increase of the conversion to reach $\bar{D} = 1.08$ at 98% of conversion. Moreover, no high molar mass population is observed in the steric exclusion chromatography (SEC) plot chromatograms of the PTMPM produced during the kinetic experiments (Figure 6.22).

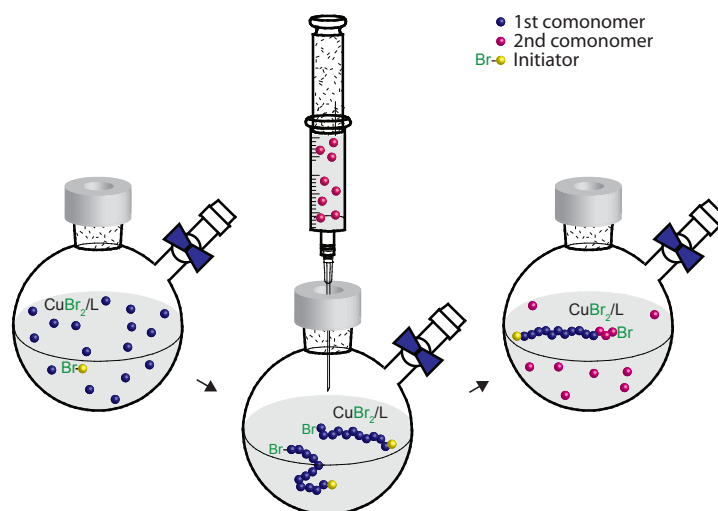
6.2.2 Investigation of the ω chain-end

Since TMPM is a methacrylate derivative, the investigation of the living character of the polymerization, i.e. the presence of the bromide at the ω chain-end of the polymer, is not possible via $^1\text{H-NMR}$. For the purpose of our grafting strategy, we then wish to obtain a block copolymer displaying a first PTMPM block, and a second block bearing the functional azide moieties. The access to a block copolymer architecture requires a living behavior of the polymerization of the first block in order to carry the polymerization of the second one. To confirm that the SET-LRP polymerization produces a living polymer even at high conversion, the block copolymerization was investigated (Figure 6.2).

The copolymerization was realized with 3-azidopropyl methacrylate (AzPMA) via a sequential monomer addition process (Figure 6.4).^[13,14] Table 6.1 presents the results of the block copolymerization. The first PTMPM block was produced with $[\text{BnBiB}] / [\text{CuBr}_2] / [\text{PMDETA}] / [\text{TMPM}] = 1/0.05/0.12/15$ molar ratios and 5 cm of activated Cu(0) wire in IPA (60 wt%) at 40 °C. The TMPM polymerization was conducted for 4 h. The polymerization was sampled via a cannula, the monomer conversion was determined by $^1\text{H-NMR}$ and the PTMPM was characterized by SEC. The absence of vinyl peaks in the crude sample of the polymerization medium (Figure 6.25) indicates that the polymerization is completed, i.e. a block copolymer is expected after the AzPMA addition. A degassed solution of AzPMA in IPA (conditions: $[\text{PTMPM}]/[\text{AzPMA}] = 15/15$ molar ratio) was then injected in the polymerization medium via a cannula and the copolymerization was conducted at 40 °C for 24 h.

Table 6.1 – Study of the synthesis of PTMPM-*b*-PAzPMA.

Entry	t [h]	conv [%]	DP^a [%]	M_n^b [g.mol ⁻¹] [g.mol ⁻¹]	$\bar{D}^b$
PTMPM ^c	4	>99.9	18	3800	1.16
PTMPM- <i>b</i> -PAzPMA ^c	24	>99.9	18/14	7280	1.13
PTMPM ^d	8	>99.9	37	5790	1.14
PTMPM- <i>b</i> -PAzPMA ^d	2	76	37/2.5	6500	1.12

^a Determined by ¹H-NMR on the block copolymer in CDCl₃.^b Determined by SEC in CHCl₃/IPA/Et₃N calibrated with PS standards.^c Reaction conditions: BnBiB/CuBr₂/PMDETA/TMPM/AzPMA = 1/0.05/0.12/15/15; IPA = 60 wt%; Cu(0) wire = 5 cm; T = 40 °C; (m_{TMPM} = 0.5 g).^d Reaction conditions: BnBiB/CuBr₂/PMDETA/TMPM/AzPMA = 1/0.05/0.12/30/1.5; IPA = 60 wt%; Cu(0) wire = 5 cm; T = 40 °C; (m_{TMPM} = 10 g).**Figure 6.4** – PTMPM-*b*-PAzPMA block copolymer synthesis via SET-LRP and sequential monomer addition.

The PTMPM-*b*-PN₃MA block copolymer was characterised by ¹H-NMR and SEC. Figure 6.5 presents the evolution of SEC molecular weight distributions of the *in situ* chain extension. A shift toward higher molar masses clearly demonstrates here the chain extension dur-

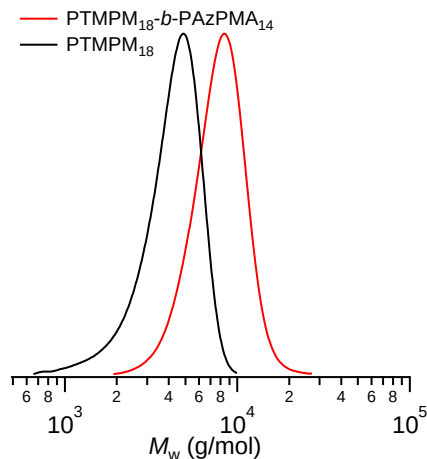


Figure 6.5 – Evolution of the molecular weight distributions of PTMPM₁₈ and PTMPM₁₈-*b*-PAzPMA₁₄.

ing the copolymerization process. Moreover, the decrease observed for the dispersity between PTMPM₁₈ and PTMPM₁₈-*b*-PAzPMA₁₄ is obviously related to the controlled behavior of the polymerization process and is also related to the conservation of the living chain-end during the homopolymerization. The sequential monomer addition was also realized with a small amount of AzPMA for the “functionalization” of the PTMPM chain-end. The polymerization was realized with $[\text{BnBiB}]/[\text{CuBr}_2]/[\text{PMDETA}]/[\text{TMPM}]/[\text{AzPMA}] = 1/0.05/0.12/30/1.5$ on a 10 g monomer scale. The TPM polymerization was carried out for 8 h and the AzPMA was added via a cannula in order to run the second block polymerization for 2 h. Under these conditions a well-defined “functionalized” PTMPM₃₇-*b*-PAzPMA_{2.5} was produced ($M_n = 6500 \text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.12$). The copolymerization by sequential monomer addition clearly demonstrates the living character of the PTMPM produced by SET-LRP.

6.3 Synthesis of PTMA-based polymers for grafting onto experiments

In the context of the present research work, we are aiming to obtain polymers that were able to react efficiently with MWCNT-alkyne

while maximizing the amount of electroactive material (PTMA) both in the polymer and the resulting MWCNT-*g*-PTMA composites. Considering this prerequisite, we designed the polymers to incorporate a minimum amount of the azide-containing units (AzPMA). Although controlled techniques such as SET-LRP or SARA-ATRP have been acknowledged to afford well-defined polymers, feeding the reaction with a single AzPMA unit per propagating group does not ensure that every chain will actually incorporate one azide unit (even if this is statistically true). For this reason, we fed the medium with 2 to 3 AzPMA monomer molecules per polymer chain, depending on the targeted degree of polymerization (*DP*).

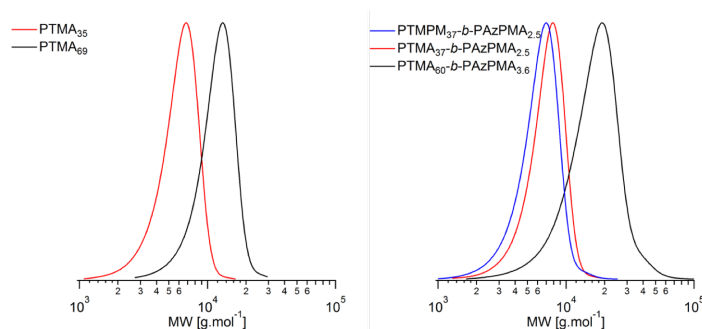


Figure 6.6 – SEC chromatograms of PTMA₃₅ and PTMA₆₉ homopolymers (left) and PTMA₃₇-*b*-PAzPMA_{2.5} and PTMA₆₀-*b*-PAzPMA_{3.6} functional copolymers (right).

For the grafting experiments, we synthesized two copolymers, PTMA₃₇-*b*-PAzPMA_{2.5} and PTMA₆₀-*b*-PAzPMA_{3.6}. PTMA₃₅ and PTMA₆₉ homopolymers were also synthesized using the same SET-LRP technique, as reference ‘dummy’ materials to highlight the interest of the grafting procedure. These homopolymers display overall degree of polymerization comparable to PTMA₃₇-*b*-PAzPMA_{2.5} and PTMA₆₀-*b*-PAzPMA_{3.6}.

All the PTMA-based polymers were obtained after oxidation of the corresponding PTMPM derivatives with Na₂WO₄/H₂O₂. This chemical oxidation converts the amine functions of the TPM units into nitroxides. Table 6.2 lists some of the characteristics of the PTMA polymers. The degrees of oxidation are almost quantitative, as evidenced by means of UV-Vis spectroscopy using TEMPO-*tert*-butyrate

in CH₂Cl₂ for calibration (details about the procedure are provided in the experimental part 6.9.1.13 and figure 6.28). TEMPO-*tert*-butyrate was selected since it is the isomorphous version of the PTMA unit. The degrees of polymerization were determined for the PTMPM derivatives based on ¹H-NMR measurements (Figures 6.26 and 6.27) and the controlled character of the polymerization was confirmed through recording the SEC chromatograms (low dispersity, $\bar{D} < 1.2$, figure 6.6).

Table 6.2 – Synthesis of the polymers for grafting onto experiments.

Entry ^a	M_n [g.mol ⁻¹]	$\bar{D}$ ^b	Oxidation yield ^c [%]
PTMPM ₃₇ - <i>b</i> -PAzPMA _{2.5}	6500	1.12	-
PTMA ₃₇ - <i>b</i> -PAzPMA _{2.5}	6640	1.12	95.2
PTMA ₆₀ - <i>b</i> -PAzPMA _{3.6}	13,200	1.20	94.0
PTMA ₃₅	5800	1.14	95.5
PTMA ₆₉	10,900	1.11	96.7

^a Determined by ¹H-NMR on the block copolymer in CDCl₃.

^b Determined by SEC in CHCl₃/IPA/Et₃N calibrated with PS standards.

^c Determined by UV-Vis using TEMPO-*tert*-butyrate calibration.

Retention of the azide functionality was confirmed using Fourier transform infrared (FTIR) measurements (Figure 6.7 ; $\nu_{azide} = 2100 \text{ cm}^{-1}$). Altogether these characterizations prove the viability of these copolymers as functional materials for grafting experiments.

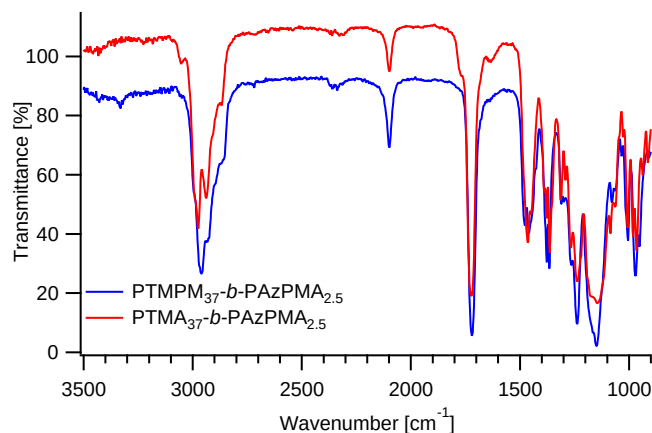


Figure 6.7 – Overlay of FT-IR spectra of PTMPM₃₇-*b*-PAzPMA_{2.5} (blue curve) and of PTMA₃₇-*b*-PAzPMA_{2.5} (red curve).

6.4 MWCNT pre-functionalization with alkyne moieties

As mentioned in section 6.1, our grafting onto strategy benefits from the development of the controlled synthesis of the PTMA-*b*-PAzPMA functional polymer.^[7] Indeed, section 6.2 demonstrated that SET-LRP is a powerful technique to yield PTMA-*b*-PAzPMA, a polymer bearing nitroxides as well as azides as pendant groups (Figure 6.1). Then, in section 6.3 the design of functional PTMA-*b*-PAzPMA block copolymers for grafting experiments has been detailed.

In the present section, the azide groups of these latter block copolymers are exploited to generate covalent bonding to the CNT conductive support. When it comes to azides as coupling moieties, their reacting counterparts tend to be alkynes in order to create covalent links under CuAAC conditions.^[15–17] Therefore, we built our CNT pre-functionalization strategy around the formation of these alkyne functions. This strategy shares similarities with our pre-functionalization procedure reported for SI-CRP from CNTs.^[2] A significant difference here lies in the introduction of the alkyne functions instead of initiating groups leading to alkyne functionalized MWCNTs (MWCNT-alkyne).

MWCNT-alkyne is prepared via esterification of carboxylic functions with propargyl alcohol. These carboxylic groups are generated, among

other functions, through oxidation with nitric acid^[18] and are activated using SOCl₂ prior to their esterification. Consideration of the reactivity and density of the anchoring groups led us to use this method as these parameters can drastically influence the loading of active PTMA on the MWCNT-*g*-PTMA composite.

Monitoring of the pre-functionalization procedure was carried out at each step using thermogravimetric analyses (TGA). MWCNT-COOH displays a 3.5 wt% weight loss between 200 °C and 500 °C while pristine MWCNTs show only a little degradation (1.5 wt%) in the same temperature range. The higher weight loss for MWCNT-COOH is indicative of the presence of oxidized functions being generated on the walls of the MWCNTs.^[19]

Concerning MWCNT-alkyne, the weight loss in the same temperature region (200 °C to 500 °C) amounts to 4.5 wt%. The difference in weight loss between MWCNT-COOH and MWCNT-alkyne is attributed to the newly bound propargyl groups. Based on this weight loss difference (1.0 wt%) and on the molar mass of the propargyl group (39 g·mol⁻¹), the number of alkyne functions can be evaluated. The calculation leads to a value of 3 functions per 1000 carbon atoms, which is in agreement with values reported previously for esterifications performed using comparable procedures.^[20]

6.5 Synthesis of MWCNT-*g*-PTMA via grafting onto

The PTMA active material loading is one of the key parameters for the performance of our target material, i.e. MWCNT-*g*-PTMA. The target is to achieve a loading similar to the common value in the literature for PTMA composites (i.e. 30 wt%).^[21] However, concerning grafting onto CNTs, reaching such loadings is often difficult. Surface functionalization by polymers via a grafting onto approach can be challenging since the free polymer chains may have poor access to the surface, with the already anchored chains masking some of the reacting sites.^[22] Additionally in the case of CNTs, their propensity to self-aggregation is another delicate parameter to handle.

Given these considerations, we optimized the grafting conditions *via*

screening of some relevant parameters, such as the nature of the polymer (PTMA or PTMPM derivative), the nature of the ligand for the CuAAC, the reaction solvent, the polymer to MWCNT-alkyne weight ratio and the *DP* of the polymer to graft. TGA measurements were systematically performed to evaluate the influence of these parameters on the polymer material loading. As a starting point, some parameters were set for the grafting syntheses, such as the catalyst (CuCl), the ligand (PMDETA) and the relative amount of polymer (200 mg) to MWCNT-alkyne (20 mg) (weight ratio = 10).

The first parameter is the nature of the polymer to be grafted. For efficiency reasons, a synthetic pathway is more advantageous when it is convergent. In this regard, the grafting would be more expedient if it was involving PTMA-*b*-PAzPMA rather than PTMPM-*b*-PAzPMA. Incidentally the grafting of the former allows more comprehensive characterization of the polymer chains.

Nevertheless, one can expect differences between PTMPM and PTMA in terms of polymer loading in the resulting hybrid materials. Other things being equal, PTMA₃₇-*b*-PAzPMA_{2.5} and PTMPM₃₇-*b*-PAzPMA_{2.5} originating from the same polymerization batch were engaged in comparative grafting experiments. The TGAs obtained from both experiments are typical for those systems and very similar to those obtained previously with our “grafting from” approach (Figure 6.8).^[2] The TGA experiments have been conducted under a nitrogen flow to avoid degradation of the MWCNTs and to obtain more reliable results. From the TGA recordings, the resulting MWCNT-*g*-PTMA displays a slightly higher polymeric content (24.0 wt%) compared to MWCNT-*g*-PTMPM (23.7 wt%).¹ Since no benefits in terms of loading were observed when grafting PTMPM derivatives, PTMA-*b*-PAzPMA was chosen as the polymer to graft.

The catalytic system is often considered as a critical parameter for the efficiency of CuAAC. Notably, the catalytic activity can be modulated by the ligand surrounding the metal center. Although PMDETA (Figure 6.9) is often chosen, this ligand is not the most activating for CuAAC by far.^[17] As an alternative, a grafting synthesis with the more active tris(benzyltriazolylmethyl)amine ligand (TBTA ; figure 6.9) was also

¹The weight loss values presented in the “Synthesis of MWCNT-*g*-PTMA via grafting onto” section were obtained for the 200 °C to 500 °C temperature range after subtraction of the MWCNT-alkyne contribution.

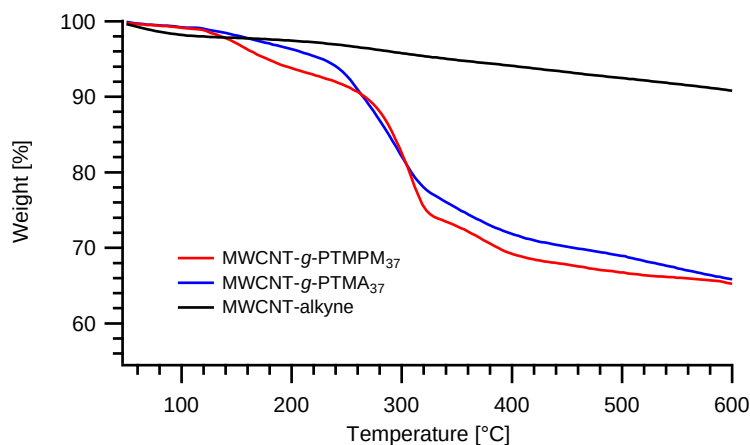


Figure 6.8 – TGA thermograms of MWCNT-*g*-PTMPM₃₇ and MWCNT-*g*-PTMA₃₇ grafted materials. The curve obtained for alkyne-functionalized MWCNTs (MWCNT-alkyne) is also shown.

conducted but it afforded no polymer loading improvement (23.2 wt% loss).

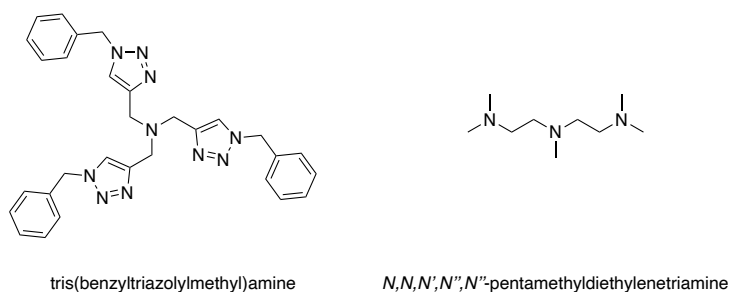


Figure 6.9 – Structures of ligands tested for grafting onto via CuAAC.

The surface chemistry of particles is also dependent on the availability of the surface to the dissolved coupling molecules. Related to that, the quality of particle dispersion can influence the yield of the reaction. *N*-Methyl-2-pyrrolidone (NMP) is typically a solvent recognized as an excellent dispersant for MWCNTs.^[23] However, the grafting experiments using NMP instead of anisole afforded MWCNT-*g*-PTMA with no increase in polymer loading (23.4 wt%). Seemingly the availability of the surface and the activity of the catalyst are not parameters that can be changed to permit us to reach towards the 30 wt% target.

The next parameter tested was the polymer to MWCNT-alkyne weight ratio. The ratios are defined as the mass of PTMA_{37-*b*}-PAzPMA_{2.5} relative to the mass of MWCNT-alkyne (ranging from 1 to 20). Practically, we varied the mass of polymer, while all the other parameters remained identical. From the TGAs, the loading of PTMA in the synthesized material increased with the ratio, as expected (Figure 6.10). However, considering that the highest two ratios tested (10 and 20) presented very close loading values (24.0 wt% and 24.6 wt%), the polymer content in the MWCNT-*g*-PTMA seems to level off at this point.

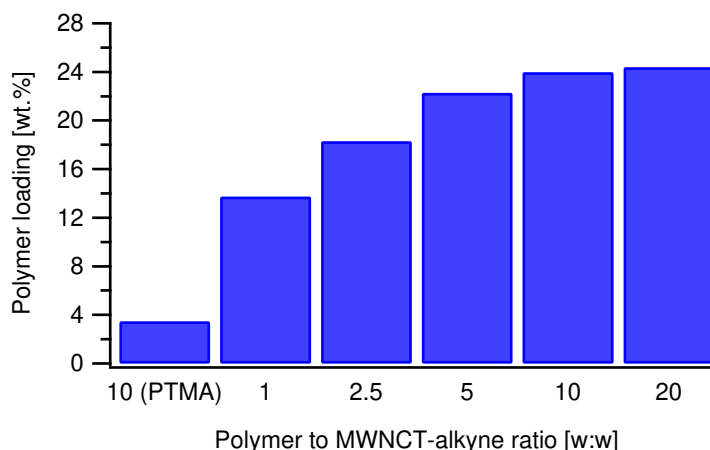


Figure 6.10 – Dependence of the polymer to MWCNT-alkyne ratio (w:w) on the polymer loading in the resulting material. The variation of the ratio was performed using PTMA_{37-*b*}-PAzPMA_{2.5}. The polymer loadings were obtained from the weight losses measured via TGA. The result obtained with PTMA₃₅ as a dummy polymer is also shown as a reference.

From these results, we infer that by increasing the amount of polymer with respect to the substrate, at some stage, accessibility to the surface becomes an issue. In other words, the reacting groups of the polymer may be unable to interact with the anchoring points on the substrate due to steric hindrance by the already attached polymer chains. This kind of phenomenon is well-known when dealing with grafting onto approaches applied to flat substrates^[24] and seems to also occur with the present system.

And yet, high surface area materials like MWCNTs are inherently prone to physisorption phenomena that can sometimes be difficult to dis-

tinguish from chemisorption. To settle this matter, a blank experiment involving a dummy polymer was conducted. The dummy compound was a linear PTMA₃₅ homopolymer exhibiting a *DP* close to that of the functional PTMA₃₇-*b*-PAzPMA_{2.5}. This PTMA₃₅ was submitted to exactly the same treatments in the presence of MWCNT-alkyne (ratio w/w = 10). As for the grafting experiments, extensive washing of the recovered material was performed until no polymer residue could be found in the filtrate after evaporation to dryness. The TGA measurements on the recovered material displayed only a 3.5 wt% weight loss attributed to physisorbed species (Figure 6.10). The considerably higher weight loss of MWCNT-*g*-PTMA (24.0 wt%) was then quantitatively accounting for chemically-bound PTMA.

In another attempt to reach a higher value of active material, a longer functional polymer was synthesized for the grafting experiments. This PTMA₆₀-*b*-PAzPMA_{3.6} polymer was designed to have the same TMA to AzPMA ratio as PTMA₃₇-*b*-PAzPMA_{2.5}. The grafting experiment with this longer polymer reached our expectations, with a polymeric content comparable to the literature standards (29.5 wt%).

XPS was implemented to assess the nature of the MWCNT-alkyne and MWCNT-*g*-PTMA₆₀ materials. The XPS measurements indicated quite distinct surface elemental and chemical compositions for MWCNT-*g*-PTMA₆₀ compared to MWCNT-alkyne. For MWCNT-*g*-PTMA₆₀, the N_{1s}, O_{1s} and C_{1s} surface atomic concentrations correspond to a composition close to the composition of PTMA₆₀-*b*-PAzPMA_{3.6} and distinctly different from the composition of MWCNT-alkyne (Table 6.3).

Regarding the line shape, the MWCNT-alkyne C_{1s} signal presents a pronounced tail typical of oxidized MWCNTs.^[18] In contrast, MWCNT-*g*-PTMA₆₀ exhibits a shoulder more characteristic of pure PTMA (Figure 6.11).^[2] Consistent with this, C_{1s} peak deconvolution of the hybrid material can be performed considering the three components corresponding to the O-C=O, C-(N,O) and C-(C,H) chemical states. Interestingly, the quantification of these chemical states leads to values very similar to those expected for PTMA₆₀-*b*-PAzPMA_{3.6} (Table 6.4). Regarding the N_{1s} signal of our hybrid material, the peak position (400.5 eV) is consistent with nitrogen bound to other heteroatoms. Moreover the N_{1s} peak presents a shoulder on the high-energy side (Figure 6.12). The shape and position of the peak is consistent with the contribution of triazole rings^[25] overlapping the TMA units signal. The XPS analyses therefore

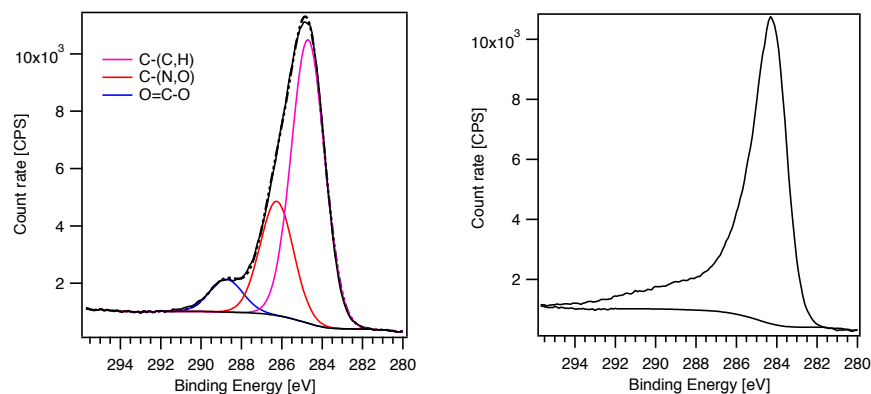


Figure 6.11 – XPS C_{1s} peaks of MWCNT-*g*-PTMA₆₀ (left) and MWCNT-alkyne (right). The components obtained after fitting are displayed for MWCNT-*g*-PTMA₆₀.

clearly highlight the presence of the grafted polymer in the hybrid material and are in agreement with a core-shell structure where the MWCNT XPS signal is hidden by the surrounding grafted polymer.

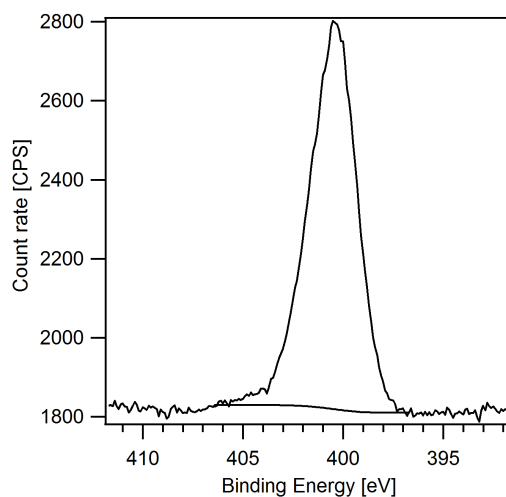


Figure 6.12 – XPS N_{1s} peaks of MWCNT-*g*-PTMA₆₀.

Table 6.3 – Experimental surface atomic concentrations of MWCNT-*g*-PTMA₆₀ compared to experimental values for MWCNT-alkyne and predicted values for PTMA₆₀-*b*-PAzPMA_{3.6}. Peak positions are displayed within brackets.

Spectral lines	MWCNT-alkyne	MWCNT- <i>g</i> -PTMA ₆₀	PTMA ₆₀ - <i>b</i> -PAzPMA _{3.6}
	Found	Found	Expected
C _{1s}	84.6% (284.8 eV)	80.4% (284.8 eV)	75.7%
O _{1s}	14.7% (532.3 eV)	15.4% (532.5 eV)	17.6%
N _{1s}	0.68% (402.1 eV)	4.2% (400.5 eV)	6.7%

Table 6.4 – C_{1s} peak fitting results for MWCNT-*g*-PTMA₆₀ compared to the expected values for the PTMA₆₀-*b*-PAzPMA_{3.6} copolymer. Component positions are displayed within brackets.

Components	MWCNT- <i>g</i> -PTMA ₆₀	PTMA ₆₀ - <i>b</i> -PAzPMA _{3.6}
	Found	Expected
C-(C,H)	65.9% (284.6 eV)	68.9%
C-(N,O)	26.5% (286.2 eV)	23.2%
O=C-O	7.6% (288.7 eV)	7.9%

6.6 Structure of the polymer/nanotube interface

These modeling studies have been carried out in the research group of Prof. Roberto Lazzaroni (UMONS). To understand in detail how the polymer chains organize at the interface with the nanotubes, the first step in the modeling studies was to investigate how the PTMA functional groups interact when adsorbed on the nanotube wall. In particular, it is essential to determine whether, upon interacting with the nanotube, (i) the radical remains localized on the nitroxide group of the PTMA unit, (ii) it becomes delocalized on the π -system of the surface, or (iii) a chemical bond forms between the NO group and the unsaturated carbon surface. The DFT results for the model system, i.e., the TEMPO fragment interacting with a graphene flake, showed that even when the nitroxide group is pointing directly towards the carbon surface (Figure 6.13), there is no formation of a chemical bond nor is there delocalization of the radical, which remains fully localized on the nitroxide group. Those groups therefore remain available for redox processes.

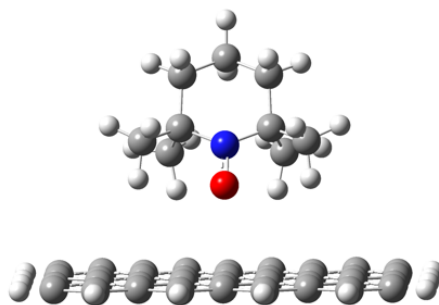


Figure 6.13 – Adsorption geometry for a TEMPO fragment on a graphene flake, as a model system for the PTMA chain on the nanotube surface.

This is due to the fact that the nitroxide moiety is “protected” by the four methyl groups, which keep the oxygen atom in the NO group about 0.3 nm above the carbon surface, hence suppressing any direct, strong interaction between the two species. Consistent with this, the interaction between the molecule and the carbon surface is mainly due to CH- π interactions. As the second step, the intrinsic behavior of the PTMA₃₇

polymer chain was modeled via molecular dynamic (MD) simulations, highlighting the capability of the polymer chain to coil on itself. The time evolution of the radius of gyration calculated for the polymer chain using the MDs simulation (Figure 6.14) shows that PTMA₃₇ has no strong tendency to fold on itself, meaning that the chain is rather rigid and linear.

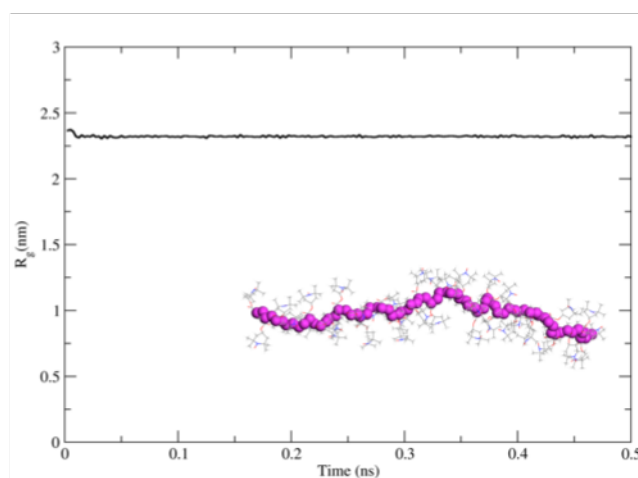


Figure 6.14 – Evolution of the gyration radius for a single PTMA₃₇ polymer chain in a vacuum (NPT MD run). A typical conformation for the PTMA chain is shown on the graph, with the polymer backbone highlighted in purple.

This is probably due to steric hindrance between the TEMPO lateral groups in the monomer units and the atactic nature of the polymer chain, which does not favor the formation of organized, compact conformations (under the same conditions a polyethylene chain with the same backbone length folds readily).

As the final step, the CNT-*g*-PTMA₃₇ grafted system was modeled. Based on the experimental composition of the composite (24 wt% in polymer), 15 PTMA₃₇ polymer chains were grafted to a 5 nm-long periodic unit cell of the model nanotube surface. Figure 6.15 shows the final morphology of the system after combination of energy minimization and MD runs: all the PTMA₃₇ chains are mostly in an extended conformation, stretching roughly perpendicular from the nanotube surface into the surrounding medium. This organization appears to be particu-

larly favorable in real systems because it allows for efficient interactions between each chain and both the carbon nanotube surface and the surrounding electrolyte phase. Moreover, this organization is also in perfect agreement with the experimental results that show that non-grafted PTMA (the dummy sample previously described in this contribution) is not physisorbed or wrapped around the CNT. This further justifies the need to chemically graft PTMA onto CNTs in order to obtain useful electrode materials.

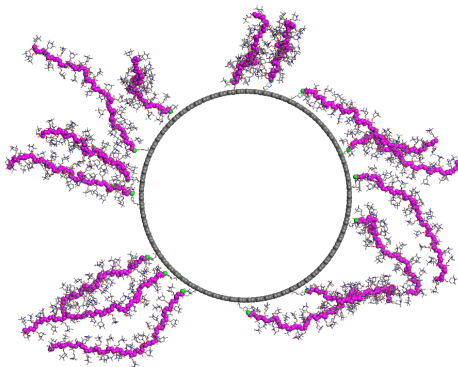


Figure 6.15 – Final morphology of CNT-*g*-PTMA₃₇ system after MD runs. The polymer chain backbones are color coded in purple.

6.7 MWCNT-*g*-PTMA electrochemical characterizations

To proceed with the electrochemical measurements, the MWCNT-*g*-PTMA₆₀ material required processing. The processing relied on a vacuum filtration method^[26,27] that we applied successfully in our previous work.^[2] More specifically, this filtration method allows the formation of MWCNT mats (buckypaper), which are obtained by successive filtration of a first dispersion of pristine MWCNTs, followed by a second dispersion of the MWCNT-*g*-PTMA material. The first layer of pristine MWCNTs acts as a current collector and also permits the easy peeling of the fabric from the filter at the end of the process. Compared to our previous work on the grafting from approach, the MWCNTs for the current collector layer has been adjusted to a lower amount (20 wt% of the whole fabric,

50 wt% previously). The mixture of NMP and CH₂Cl₂ that was used previously as the dispersion medium for the active material here was replaced by the more benign solvent methanol.

For comparison purposes, control electrodes were also prepared via a more traditional coating method (details about the preparation of which are provided in the experimental section). The coating on aluminum foils was carried out by spreading a slurry composed of the PTMA₆₉ homopolymer, pristine MWCNTs and PVDF (30/60/10, w:w:w).

The electrodes made of one type of active material, MWCNT-*g*-PTMA or PTMA₆₉, were then assembled in a half-cell configuration *vs.* Li/Li⁺ in order to carry out the electrochemical characterization.

Cyclic voltammetry measurements were first performed to confirm the redox response of the MWCNT-*g*-PTMA electrodes (Figure 6.16). As expected, cycling revealed a pair of clean and sharp redox peaks centered around 3.6 V, with the peak during the forward scan corresponding to the oxidation of the nitroxide into the oxoammonium cation.^[28] The reverse scan displays the cathodic peak corresponding to the reduction of the system. After the first cycle, the redox response was fully stable with a narrow peak-to-peak separation ($\Delta E_p < 100$ mV).

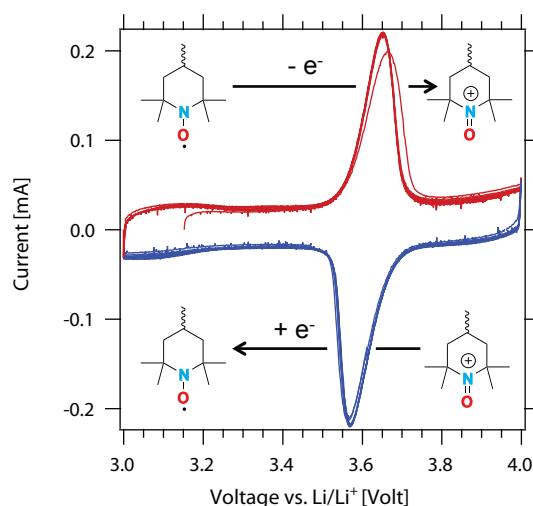


Figure 6.16 – Cyclic voltammograms of the MWCNT-*g*-PTMA₆₀ electrode at 0.2 mV·s⁻¹ (EC/DEC 1:1 v/v; 1 M LiPF₆).

The cyclability of the MWCNT-*g*-PTMA electrode was evaluated by means of galvanostatic charge/discharge measurements at a constant rate of C/2 ($55.5 \text{ mA}\cdot\text{g}^{-1}$; 1C rate = $111 \text{ mA}\cdot\text{g}^{-1}$). During the first three conditioning cycles, a slight drop of the capacity was observed, which was attributed to irreversible processes (Figure 6.17). Afterwards the capacity tends to stabilize at $94 \text{ mAh}\cdot\text{g}^{-1}$, i.e. 85% of the theoretical $111 \text{ mAh}\cdot\text{g}^{-1}$. This value is consistent with the expected $104 \text{ mAh}\cdot\text{g}^{-1}$ taking into account the oxidation yield (94%) of PTMPM₆₀-*b*-PAzPMA_{3.6} into PTMPM₆₀-*b*-PAzPMA_{3.6}.

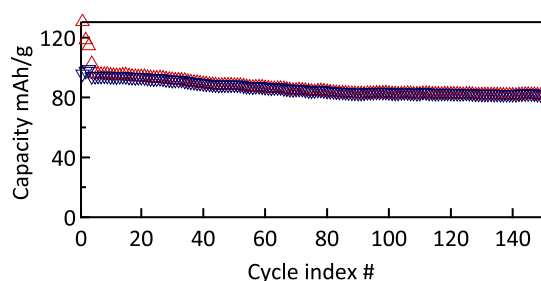


Figure 6.17 – Cycle stability of MWCNT-*g*-PTMA₆₀ at a rate of C/2 over 150 cycles (EC/DEC 1:1 v/v; 1 M LiPF₆). Charge capacity is displayed as red symbols, discharge capacity as blue symbols.

Furthermore a good capacity retention was also observed after 150 cycles, with $80 \text{ mAh}\cdot\text{g}^{-1}$ still being available (>80% of the nominal value). In contrast, the control electrode behaves much less efficiently under the same conditions (Figure 6.18). After the irreversible drop of the first conditioning cycles, the control electrode still displayed a pronounced fade in capacity over a few tens of cycles. After cycle 40, the capacity tends to stabilize at a value of $42 \text{ mAh}\cdot\text{g}^{-1}$. This lack of performance compared to the grafted material is most probably related to the fact that the active material is not immobilized.^[29] The control electrodes made of PTMA₆₉ untethered chains are likely subject to the loss of active material through solubilization while in contact with the electrolyte solution, i.e., two processes that can be detrimental to the cycling performance.

The power capability of the electrodes was evaluated via galvanostatic measurements at variable rates (figure 6.19). The MWCNT-*g*-PTMA electrode displayed relatively good performances, the capacity being only slightly affected when increasing the rate from C to 10C.

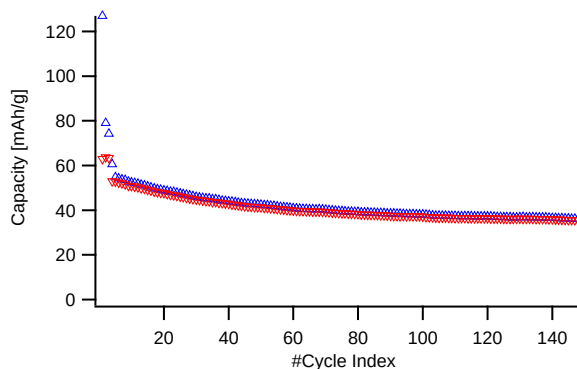


Figure 6.18 – Cycle stability of the PTMA₆₉-based control electrode at C/2 rate over 150 cycles (The 3 first cycles were recorded at C/10 rate ; EC/DEC 1:1 v/v; 1 M LiPF₆). Charge capacity is displayed as red symbols, discharge capacity as blue symbols.

With regards to the charge-discharge profiles, the typical plateau of PTMA centered at 3.6 V (*vs.* Li/Li⁺)^[30] was only affected by polarization (< 100 mV) for all rates up to 10C. Even at the highest rate of 60C (charge or discharge < 1 min), more than 65% of the nominal capacity was still available (61 mAh·g⁻¹) while the above mentioned plateau was still maintained. These rate performances underline the good electron transfer properties of the electrode made of the hybrid material. The electrode integrity after the rate capability measurements was confirmed by cycling back the electrode to lower current densities. Under these conditions the electrode displayed an appreciable recovery, obtaining nearly the same capacity as previously at the same current density.

From a power performance standpoint, the control and MWCNT-*g*-PTMA composite electrodes were also compared on the basis of their capacity retention at various C rates, as depicted in figure 6.20 (the capacities are normalized with respect to the capacity obtained at C/2). Again the comparison clearly points to MWCNT-*g*-PTMA offering more superior rate capabilities. The power performances of PTMA-based systems rely strongly on the electron transfer between the conductive charge and the active material^[2,31,32] but they can also depend on the conductivity of the overall system.^[33] The electrical conductivity was evaluated for both systems via 4-point probe measurements. The conductivity is 53 S·cm⁻¹ and 28 S·cm⁻¹ for the MWCNT-*g*-PTMA electrode and the control electrode, respectively. These values are within the same order

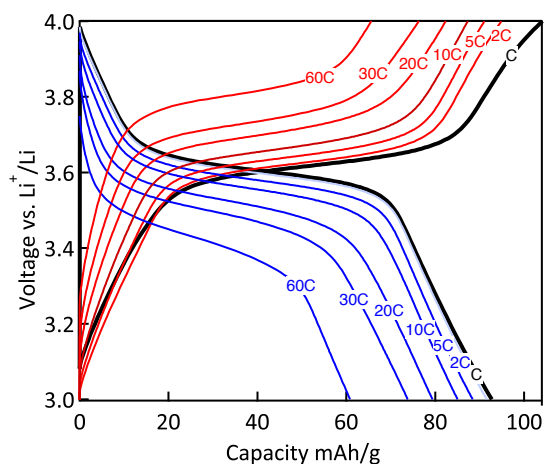


Figure 6.19 – Charge–discharge curves of the MWCNT-*g*-PTMA₆₀ electrode at various C rates (EC/DEC 1:1 v/v; 1 M LiPF₆).

of magnitude and cannot be solely accounting for the difference in power performances. Seemingly the higher level of homogeneity of the grafted material results in an improved support for the redox reactions by the conductive charge, as already pointed out in previous studies.^[31]

In every electrochemical aspect, the grafted material MWCNT-*g*-PTMA thus offers advantageous performances thanks to the precise distribution and anchoring of the active polymer around the conductive support.

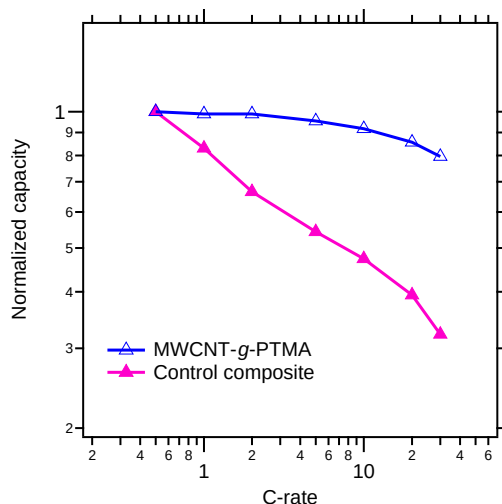


Figure 6.20 – Comparison of the MWCNT-*g*-PTMA₆₀ and control composite electrodes on the basis of their capacity retention at various C rates (EC/DEC 1:1 v/v; 1 M LiPF₆).

6.8 Conclusion

This chapter presented an original strategy towards the successful synthesis of a MWCNT-*g*-PTMA hybrid material via a grafting onto approach. The strategy takes the benefits of the synthesis of the PTMA-*b*-PAzPMA functional polymer via SET-LRP. This polymer contains nitroxide as well as azide functionalities, the latter being involved in the tethering of the chains to the MWCNT surface. Notably, this approach allows the full characterization of the polymer prior to grafting, in particular the oxidation yield. The physicochemical characterization of the hybrid materials is consistent with their core-shell structures and demonstrates an incorporation of the electroactive polymer up to 30 wt%. Molecular modeling shows that in the core-shell structure, the grafted PTMA chains are not wrapped around the nanotubes but strongly extend from the nanotube surface into the surrounding medium, which is expected to favor interactions with the electrolyte.

Electrochemical characterizations of MWCNT-*g*-PTMA processed as a buckypaper electrode were carried out to assess their performance in a half-cell configuration *vs.* Li/Li⁺. Galvanostatic measurements indicated excellent extraction of the theoretical capacity (85%) along

with a good cycling stability ($> 80\%$ retention of the initial capacity after 150 cycles). Variable-rate measurements demonstrate the ability of the material to sustain high charge/discharge current densities with the capacity exceeding $60 \text{ mAh}\cdot\text{g}^{-1}$ at 60°C . This approach not only affords a means to suppress the solubilization of the active material but also permits high power performances thanks to the intimate contact between PTMA and the MWCNT conductive network.

6.9 Experimental section

6.9.1 Synthesis procedures

6.9.1.1 Materials

Copper wire (diameter = 0.25 mm) is pretreated by washing in hydrochloric acid for 15 min and rinsed thoroughly with Milli-Q water, dried under nitrogen and used immediately. Triethylamine (analytical reagent grade, Fischer Scientific) is distilled over CaH_2 under an argon atmosphere. Multi-walled carbon nanotubes (MWCNTs) NC7000 are kindly provided by Nanocyl. SOCl_2 (99.5+%, Fisher Scientific), HNO_3 (65%, AnalaR NORMAPUR, VWR Chemicals), anhydrous toluene (extra dry, 99.85%, over molecular sieves, AcroSeal, Acros Organics), propargyl alcohol (99%, Acros), isopropanol (IPA, 99%, Acros), sodium azide (99.9%, Acros), methacryloyl chloride (97%, containing 200 ppm MEHQ, Sigma-Aldrich), CuCl (99.999%, Aldrich), CuBr_2 (99.999%, Aldrich), 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPPM, >98%, TCI), PMDETA (98%, Aldrich), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (purum, 99%, Sigma-Aldrich), anisole (99%, Acros), ethyl- α -bromoisobutyrate (EBiB, Acros, 98%), 3-chloropropanol (Acros, 98%), benzyl alcohol (Aldrich, 99%), α -bromoisobutyryl bromide (Aldrich, 98%), 4-hydroxy-2,2,6,6-tetramethyl-piperidineoxy (Acros, 98%), trimethylacetyl chloride (Acros, 99%), tris(benzyltriazolylmethyl)amine (TBTA), 1-methyl-2-pyrrolidone (NMP, >99.0%, TCI) and all other chemicals are used as received.

6.9.1.2 MWCNT oxidation

In a 250 mL round-bottom flask, MWCNTs (1 g) and HNO_3 65% (100 mL) are charged. The mixture is stirred for 2 h at reflux (110 °C). The mixture is then filtered over a PTFE 0.45 μm filter. The residue is washed with ultra pure water until the filtrate reaches neutral pH. The remaining solid (MWCNT-COOH) is dried under reduced pressure for 24 h at 35 °C.

6.9.1.3 Preparation of MWCNT-COCl

A 100 mL round-bottom Schlenk flask is charged with 100 mg of previously-oxidized MWCNT-COOH. The content of the flask is degassed under reduced pressure at 120 °C for 4 hours. 40 mL of anhydrous toluene and 15 mL of SOCl₂ are then charged in the flask under argon. The MWCNTs are dispersed by immersing the Schlenk flask into an ultrasonic bath for 15 min. The reaction is carried out by heating at 80 °C for 24 h to yield MWCNT-COCl. The recovery is done by distillation under reduced pressure until dryness.

6.9.1.4 Preparation of MWCNT-alkyne

A 100 mL round-bottom Schlenk flask is loaded under argon with 100 mg of MWCNT-COCl, 40 mL of anhydrous toluene, 5 drops of triethylamine and 2.0 g of propargyl alcohol. The flask is sealed and ultrasonicated for 30 min. The functionalization is carried out at 100 °C for 24 h. The MWCNT-alkyne samples are recovered by filtration on a poly(vinylidene fluoride) (PVDF) filter (0.22 µm pore size) and washed three times with 50 mL of toluene. The remaining solid is dried for 24 h under reduced pressure at 40 °C.

6.9.1.5 Synthesis of benzyl-2-bromoisobutyrate (BnBiB)

BnBiB is synthesized as previously described in the literature.^[7]
¹H-NMR (300 MHz, CDCl₃): 6.11 (m, 1H, =CH), 5.58 (m, 1H, =CH), 4.24 (t, 2H, CH₂-O), 3.52 (t, 2H, CH₂-N₃) and 1.91–2.02 (m, 5H, overlapping CH₃-C and C-CH₂-C).

6.9.1.6 Synthesis of 3-azidopropanol

In a round bottomed flask (100 mL), 3-chloropropanol (22.1 mL, 25.0 g, 0.264 mol, 1 eq) is added to a mixture of water (40 mL), sodium azide (34.4 g, 0.529 mol, 2 eq), and NBu₄Br (1 g, 0.003 mol, 0.012 eq). The mixture is stirred at 80 °C for 24 h and then at room temperature for 16 h. The product is extracted with ether three times, the organic phase is dried over MgSO₄. The solution is then concentrated and 3-azido

propanol is distilled under vacuum (Yield: 23.5 g, 88%).

^1H -NMR (300 MHz, CDCl_3): 3.76 (t, 2H, $\text{CH}_2\text{-O}$), 3.46 (t, 2H, CH_2N_3), and 1.84 (t, 2H, $\text{C-CH}_2\text{-C}$).

6.9.1.7 Synthesis of 3-azidopropyl methacrylate

AzPMA is synthesized as previously described in the literature.^[7,15] A solution of 3-azidopropanol (16.4 g, 0.162 mol, 1 eq), triethylamine (26.0 mL, 0.187 mol, 1.15 eq) and CH_2Cl_2 (140 mL) is cooled in an ice-water bath. A solution of methacryloyl chloride (17.5 mL, 0.179 mol, 1.1 eq) in CH_2Cl_2 (20 mL) is added dropwise over a period of 30 min. The mixture is slowly brought to 20 °C and stirred overnight. The mixture is extracted successively with an aqueous solution of hydrochloric acid (0.1 M), a saturated solution of NaHCO_3 , and water. The organic phase is dried over MgSO_4 . The solution is concentrated and 3-azidopropyl methacrylate is purified by column chromatography on SiO_2 (eluent: petroleum ether/ethyl acetate 95:5).

^1H -NMR (300 MHz, CDCl_3): 6.11 (m, 1H, =CH), 5.58 (m, 1H, =CH), 4.24 (t, 2H, $\text{CH}_2\text{-O}$), 3.52 (t, 2H, $\text{CH}_2\text{-N}_3$) and 1.91-2.02 (m, 5H, overlapping $\text{CH}_3\text{-C}$ and $\text{C-CH}_2\text{-C}$).

6.9.1.8 Typical synthesis of PTMPM

A Schlenk tube is filled with benzyl-2-bromoisobutyrate (BnBiB, 20.5 μL , 0.112 mmol, 1 eq), 2-propanol (IPA, 2.40 mL), TMPM (1.28 g, 5.69 mmol, 51 eq) and 62.3 μL of a solution of CuBr_2 /PMDETA in IPA ($C_{\text{CuBr}_2} = 20 \text{ g}\cdot\text{L}^{-1}$; CuBr_2 : 1.25 mg, 5.58 μmol , 0.05 eq; PMDETA: 2.88 mg, 1.13×10^{-2} mmol, 0.12 eq)). This solution is degassed by freeze-pump-thaw cycling. A magnetic stirring bar rubbed with 5 cm of activated Cu(0) wire is then introduced under Argon flux. The solution is immersed in an oil bath at 40 °C and stirred for 8 h (conv > 99%). The polymerization is quenched by quickly cooling the tube in a water-ice bath and exposing the reaction mixture to air. The reaction mixture is filtered over basic Al_2O_3 (eluent: CH_2Cl_2). The solvent is removed under reduced pressure. The residue is precipitated in hexane, filtered and dried *in vacuo* at 30 °C over night, affording a white solid.

M_n (SEC) = 10,870 $\text{g}\cdot\text{mol}^{-1}$; D (SEC) = 1.12 (Figure 6.21); ^1H -NMR (300 MHz, CDCl_3) PTMPM₆₉: 7.45–7.30 (b, 5H, H_{Ar} chain-end),

5.25–4.90 (b, 69H; CH–O), 4.07 (m, 138H; CH₂–O chain end), 2.05–1.51 (b, 1035H; CH₃ + CH₃ backbone), 1.51–0.80 (b, 414H; CH₂ + CH₂ backbone).

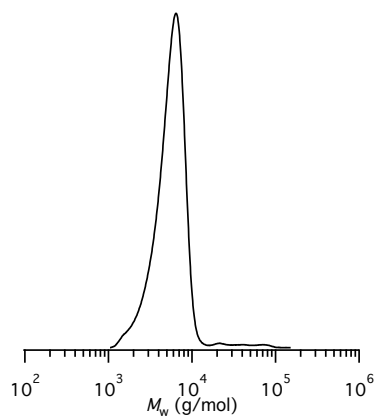


Figure 6.21 – SEC chromatogram of PTMPM synthesized by SET-LRP (24 h reaction time).

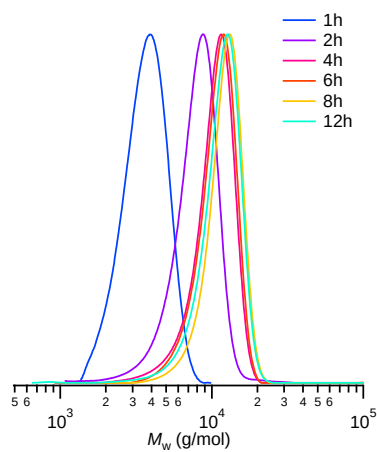


Figure 6.22 – Evolution of the SEC chromatograms with the polymerization time for the kinetic experiment.

6.9.1.9 Synthesis of the electro-active PTMA

A round-bottomed flask equipped with a condenser is filled with PTMPM₆₉ (232 mg, 1.03 mmol of amine functions, 1 eq), Na₂WO₄·2H₂O (84.9 mg, 0.26 mmol, 0.25 eq) and EDTA (34.7 mg, 0.15 mmol, 0.15 eq) and methanol (12 mL). The solution is stirred at 60 °C for 5 min and H₂O₂ (1.17 mL, 10.3 mmol, 10 eq) is added dropwise over 60 min. The solution is stirred at 60 °C for 24 h. The polymer was extracted with CH₂Cl₂. The organic phase is dried with MgSO₄. The solvent is removed under reduced pressure. The residue is precipitated in hexane, filtered and dried *in vacuo* at 30 °C over night, affording an orange solid.

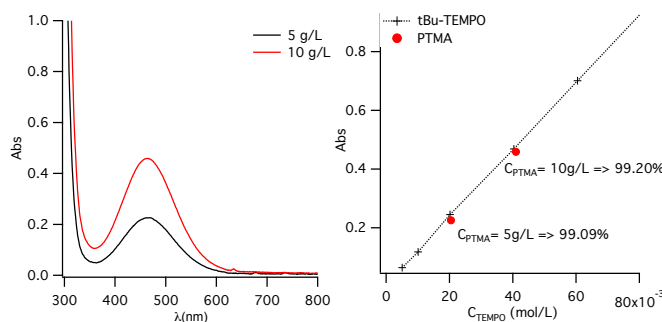


Figure 6.23 – Determination of the oxidation degree by UV-Vis analyses thanks to a TEMPO-*tert*-butyrate calibration in CH₂Cl₂. The UV-Vis spectra of solutions of PTMA₆₉ in CH₂Cl₂ are depicted on the left inset (red and blue curves, 5 g·L⁻¹ and 10 g·L⁻¹, respectively). The maximum of absorbance ($\lambda_{max} = 464$ nm) was measured for the two different concentrations and compared to a TEMPO-*tert*-butyrate calibration (dashed line in the right inset).

UV-Vis spectroscopy is used to determine the degree of oxidation of the PTMA. The UV-Vis spectra of solutions of PTMA ($C = 5$ g·L⁻¹ and 10 g·L⁻¹ in polymer) in CH₂Cl₂ are shown in figure 6.23 left. The maximum of absorbance ($\lambda_{max} = 464$ nm) is measured and compared to a TEMPO *tert*-butyrate calibration (dashed black line in Figure 6.23 right). M_n (SEC) = 10,840 g·mol⁻¹; D (SEC) = 1.12, $D_{OX} = 99\%$.

6.9.1.10 Synthesis of 2,2,6,6-tetramethyl-piperidineoxy *tert*-butyrate (TEMPO-*t*Bu)

A solution of 4-hydroxy-2,2,6,6-tetramethyl-piperidineoxy *tert*-butyrate (1.02 g, 5.89 mmol, 1 eq), triethylamine (0.9 mL, 6.49 mmol, 1.11 eq) and CH₂Cl₂ (20 mL) is cooled in an ice-water bath. A solution of trimethylacetyl chloride (0.8 mL, 6.49 mmol, 1.1 eq) in CH₂Cl₂ (4 mL) is added dropwise over a period of 30 min. The mixture is slowly brought to 20 °C and stirred overnight. The mixture is extracted with water three times. The organic phase is dried over MgSO₄. The solution is concentrated and the TEMPO-*t*Bu is purified by column chromatography on SiO₂ (eluent: petroleum ether/ethyl acetate 95:5 ; yield: 535 mg, 35%). FT-IR (cm⁻¹): 1720 (C=O), 1481 (C–O) 1350 (N–O); MS (ESI): *m/z* = 258.2 ([M+2H]²⁺, 20), 257.1 ([M], 27), 256.1 ([M], 100), 154 ([C₉H₁₆NO], 21), 85 ([C₅H₉O], 6). Figure 6.24: UV-Vis Spectra.

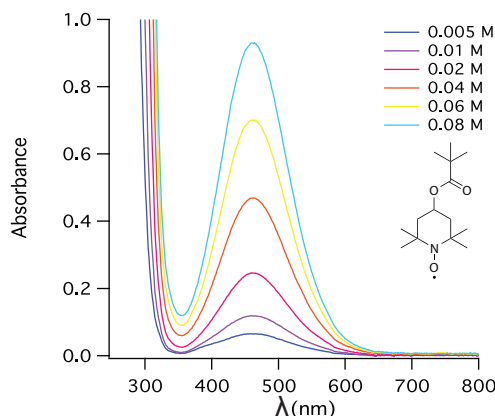


Figure 6.24 – UV-Vis spectra of TEMPO-*t*Bu in CH₂Cl₂.

6.9.1.11 Synthesis of PTMPM

A Schlenk tube is filled with BnBiB (35.9 μL, 0.2 mmol, 1 eq), IPA (4.06 mL), TMPM (2253 mg, 10 mmol, 50 eq) and 110 μL of a solution of CuBr₂/PMDETA in IPA (*C*_{CuBr₂} 20 g·L⁻¹; CuBr₂: 2.2 mg, 1 μmol, 0.05 eq; PMDETA: 4.16 mg, 2.4 × 10⁻² mmol, 0.12 eq). This solution is degassed by freeze–pump–thaw cycling. A magnetic stirring bar,

around which an activated Cu(0) wire (0.25 mm, 5 cm length) is wound, is then introduced under argon flux. The solution is emerged in an oil bath at 40 °C and stirred for 4 h (conv > 99%).

6.9.1.12 Synthesis of PTMPM-*b*-PAzPMA

A degassed solution of AzPMA (169 mg, 0.6 mmol, 3 eq) in IPA (0.50 mL) is introduced into the Schlenk tube via a cannula. The solution is stirred in an oil bath at 40 °C for 24 h (conv > 99%). The polymerization is quenched by quickly cooling the tube in a water/ice bath and exposing the reaction mixture to air. The reaction mixture is filtered over basic Al₂O₃ (eluent: CH₂Cl₂). The solvent is removed under reduced pressure. The residue is precipitated in hexane, filtered and dried under reduced pressure at 40 °C for 24 h, affording a white solid.

M_n (SEC) 13,200 g·mol⁻¹; $\bar{D}$ (SEC) 1.20; ¹H-NMR (300 MHz, CDCl₃) PTMPM₆₀-*b*-PAzPMA_{3.6}: 7.45–7.30 (b, 5H, H_{Ar} chain-end), 5.25–4.90 (b, 60H, CH–O PTMPM), 4.20–3.90 (b, 7.2H, CH₂–O PAzPMA), 3.55–3.30 (b, 7.2H, CH₂–N₃ PAzPMA), 2.20–0.60 (b, 1292H, –CH₃ + –CH₂ backbone and side groups).

6.9.1.13 Synthesis of PTMA-*b*-PAzPMA

A round-bottom flask equipped with a condenser is filled with PTMPM₆₀-*b*-PAzPMA_{3.6} (1000 mg, 4.24 mmol of amine functions, 1 eq), Na₂WO₄·2H₂O (350 mg, 10.6 mmol, 0.25 eq), EDTA (143 mg, 0.64 mmol, 0.15 eq) and methanol (50 mL). The solution is stirred at 60 °C for 5 min and H₂O₂ (4.81 mL, 42.4 mmol, 10 eq) is added dropwise over 60 min. The solution is then stirred at 60 °C for 24 h. The polymer is extracted using CH₂Cl₂. The organic phase is dried using MgSO₄. The solvent is removed under reduced pressure. The residue is precipitated in hexane, filtered and dried *in vacuo* at 40 °C for 24 h, affording an orange solid (0.75 g).

M_n (SEC) 10,400 g·mol⁻¹; $\bar{D}$ (SEC) 1.20 ; oxidation yield 94% (Figure 6.28).

6.9.1.14 Synthesis of MWCNT-*g*-PTMA

First, a Schlenk flask is loaded with MWCNT-alkyne (20 mg, 7.7 mmol of alkyne functions²), PTMA₆₀-*b*-PAzPMA_{3.6} (200 mg, 50 mmol of azide functions) and 40 mL of anisole. The resulting mixture is degassed using argon bubbling while immersed in an ultrasonic bath for 30 min. CuCl (10 mg, 0.1 mmol) and a degassed solution of PMDETA (200 µL, 0.95 mmol) in anisole (10 mL) are loaded into a second Schlenk flask. This mixture is degassed by 3 freeze-pump-thaw cycles and is added into the 100 mL round-bottom Schlenk flask containing the MWCNT-alkyne suspension using a gas-tight syringe. The reaction mixture is then ultrasonicated for 30 min. The grafting onto reaction is taking place under an argon atmosphere at 80 °C for 24 h under ultrasonication. The solid material is recovered by filtration on a PTFE membrane (0.45 µm pore size) and successive washings with CH₂Cl₂, methanol and diethyl ether. The remaining solid is dried for 24 h under reduced pressure at 40 °C affording 25 mg of MWCNT-*g*-PTMA.

²As determined based on calculations made on TGA results

6.9.2 Characterization

6.9.2.1 Thermogravimetric analysis

Thermogravimetric analyses (TGA) are carried out on a TGA/SDTA 851e instrument from METTLER TOLEDO. These analyses are carried out with a heating ramp of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and under a N_2 flow ($0.1\text{ L}\cdot\text{min}^{-1}$) with the samples ($3 - 5\text{ mg}$) placed into $70\text{ }\mu\text{L}$ alumina containers.

6.9.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analyses are realized at room temperature by means of a SSI X-Probe (SSX 100/206) photoelectron spectrometer from FISONs equipped with a monochromatized micro-focus Al X-ray source. Samples are stuck onto sample holders with a double-face adhesive tape and then placed on an insulating home-made ceramic carousel (Macor[®], Switzerland). The spot size for irradiation is set at $800\text{ }\mu\text{m} \times 1200\text{ }\mu\text{m}$. Charge effects are suppressed by placing a nickel grid above the samples and using a flood gun set at 8 eV . The energy scale is calibrated with reference to the $\text{Au}_{4f7/2}$ peak at 84 eV , and the binding energies were calculated with respect to the C_{1s} peak fixed at 285 eV . Data treatment is performed with the CasaXPS program (Casa Software Ltd., UK). The peaks are decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

6.9.2.3 Electrode design

Self-standing electrodes are produced using a vacuum filtration process over a PVDF filter ($0.45\text{ }\mu\text{m}$ pore size). The filtration device is a Millipore set-up. Pristine MWCNTs (5.0 mg) are dispersed in butanol (250 mL) using bath sonication for 30 min . This first suspension is filtered on the PVDF filter. A suspension of MWCNT-*g*-PTMA (20 mg in 600 mL of methanol, bath sonicated for 30 min) is then filtered over the first layer formed on the PVDF filter (3.40 cm diameter). Electrodes are first dried in ambient air at room temperature for 2 h , then at 70°C under vacuum for 24 h . The resulting material is then cut into discs (0.5 inch

diameter, total weight of 3.50 mg each, overall thickness of 84 μm) for electrochemical measurements.

6.9.2.4 Cell assembly

Electrodes are tested in a half-cell configuration using lithium metal foil (99.9%, purchased from Gelon) as a reference and counter electrode. A porous polyethylene membrane is purchased from Celgard and used as the separator. A mix of ethylene carbonate (EC), diethyl carbonate (DEC) 1:1 v/v with 1 M of lithium hexafluorophosphate (LiPF_6) is purchased from Solvionic and used as the electrolyte. Cells are assembled in CR2032 coin cells. All cells are assembled under an argon atmosphere (<0.1 ppm H_2O , <0.1 ppm O_2) in an INERT LAB glovebox. Spare parts for the CR2032 coin cell assembly are purchased from MTI Corp.

6.9.2.5 Electrochemical tests

Cyclic voltammetry (CV) and charge/ discharge tests are conducted using an Arbin Instruments Battery Tester BT-2043. Unless specified otherwise, all values of capacity are reported with respect to the redox polymer mass in the electrode, and assuming that the polymer is composed solely of TMA repeating units. The electrical conductivity of the electrodes is measured using a 4-point probe station (Lucas Lab L320) coupled with a Keithley 2410 monitor. The current is adjusted to keep a constant voltage of 10 mV. The film thickness is measured using a Draper Expert digital micrometer.

6.9.2.6 Proton nuclear magnetic resonance

Proton nuclear magnetic resonance (^1H -NMR) spectra are acquired in CDCl_3 on a 300 MHz Bruker Avance II.

6.9.2.7 Fourier-transform infrared spectroscopy

Fourier-transform infrared (FT-IR) spectra are recorded with a Shimadzu FTIR-8400S spectrometer from thin films deposited onto a ZnS crystal plate.

6.9.2.8 UV-visible

The samples were prepared in quartz cuvettes. The studies are carried out with a Varian Cary 50 UV-Vis Spectrophotometer with absorption spectra recorded from 250 nm to 1000 nm.

6.9.2.9 Size exclusion chromatography

Average molar masses (M_n and M_w) and dispersity ($\bar{D}$) are measured on an Agilent size exclusion chromatography (SEC) system equipped with an Agilent 1100/1200 pump (25 °C; eluent: CHCl₃ / Et₃N / IPA, 94:4:2 v/v/v; flow rate: 1 ml·min⁻¹), an Agilent differential refractometer and two PSS SDV columns (Beads 10 μm; porosity of column 1, 10,000 Å; porosity of column 2, 1000 Å). The calibration is performed using polystyrene standards.

6.9.2.10 Untethered PTMA control electrodes

A physical blend of untethered PTMA and pristine MWCNTs is prepared in order to conduct electrochemical measurements as control data. For this purpose, a linear PTMA homopolymer (degree of polymerization = 69) is synthesized through ATRP. The control composite measurements are compared to the results obtained for the MWCNT-*g*-PTMA₆₀ electrodes.

The cathodes are prepared by blending the active material PTMA₆₉, MWCNTs (Nanocyl NC7000) and PVDF binder. The blend has the following composition, 30 wt% of PTMA₆₉, 60 wt% of MWCNTs and 10 wt% of PVDF binder. 12 mL of *N*-methylpyrrolidone are added per 1 g of solid materials. The ingredients are mixed uniformly in a ball-mill apparatus at room temperature for 30 min to yield the slurry. The slurry is cast on an aluminum foil using the doctor blade method (the thickness of the wet film is controlled to be 200 μm) and dried at 60 °C for 24 h. Circular discs of diameter 1.25 cm are cut and used as cathodes for evaluating the electrochemical properties. The electrodes are assembled following the same protocol as for the MWCNT-*g*-PTMA₆₀ cathodes. All electrochemical measurements on the control composite are conducted with the same devices, apparatus and parameters as for the MWCNT-*g*-PTMA₆₀ cathodes. 4 points conductivity measurements

are obtained with the control composite coated on an insulate substrate. This coating is prepared with the same doctor blade protocol as for the control electrode but cast on a glass slide. The thickness of the coated material is found to be 30 μm (measured with a Draper Expert digital micrometer).

6.9.3 Modeling methodology

To investigate the interaction between the radical species and the nanotube wall, the binding energy of a PTMA monomer interacting with a graphene flake is evaluated by means of DFT calculations, using the Gaussian 09 package, and the uwB97xd functional and 6-31g(d) basis set. The correction for basis set superposition error is included in the calculations.

To investigate the morphology of the CNT-*g*-PTMA interface, molecular dynamics simulations are performed using the Materials Studio 7 (MS7) molecular modeling package. In order to properly describe the TEMPO fragments in the PTMA polymer chains, improvements are provided to the standard Amber forcefield, as included in the MS7 package by introducing new force field atom types and parameters taken from the work of Stendardo *et al.*^[34] The partial atomic charges for the PTMA monomer units are calculated by applying the restrained electrostatic potential (RESP)^[35] procedure to the potential grid computed for the PTMA monomer at the HF/6-31g(d) level of theory. Molecular dynamics (MD) simulations are performed in the NVT or NPT ensemble, where temperature and pressure are kept constant by using the Nosé–Hoover thermostat and Parrinello barostat. For all MD simulations, the time step was set to 1 fs. All polymer chains modeled are atactic, i.e., statistical PTMA polymer chains having 37 monomers, for a molecular mass of 8880 $\text{g}\cdot\text{mol}^{-1}$. These polymer chains are referred as PTMA₃₇. As for the PTMA intrinsic behavior was modeled by performing 500 ps-long molecular dynamics (MDs) simulation at 300 K to determine the capability of the polymer chain to coil on itself.

As for the nanotube, a periodic MWCNT is built of seven concentric tubes, the smallest one being a (44,44) SWCNT with a diameter of about 6 nm, with a tube separation of 0.33 nm. The resulting MWCNT has 35 carbon atoms, a periodic length of 5.165 nm and its external wall is an armchair nanotube with a diameter of about 10 nm and it contains

6216 carbon atoms. Knowing the total number of atoms in the whole MWCNT allows the calculation of a polymer grafting density in the model that matches the experimental value. To keep the computational effort on a tractable level, only the external tube is included in the actual simulations of the polymer/nanotube interface; it is considered as a rigid body, to account for the MWCNT rigidity. Because of the high grafting density and the rigidity of the polymer chains, a series of MD simulation runs were performed to explore better the potential energy landscape of the system: first, a 1 ns-long MD simulation was run at 600 K, followed by a geometry minimization and a 500 ps MD run at 300 K.

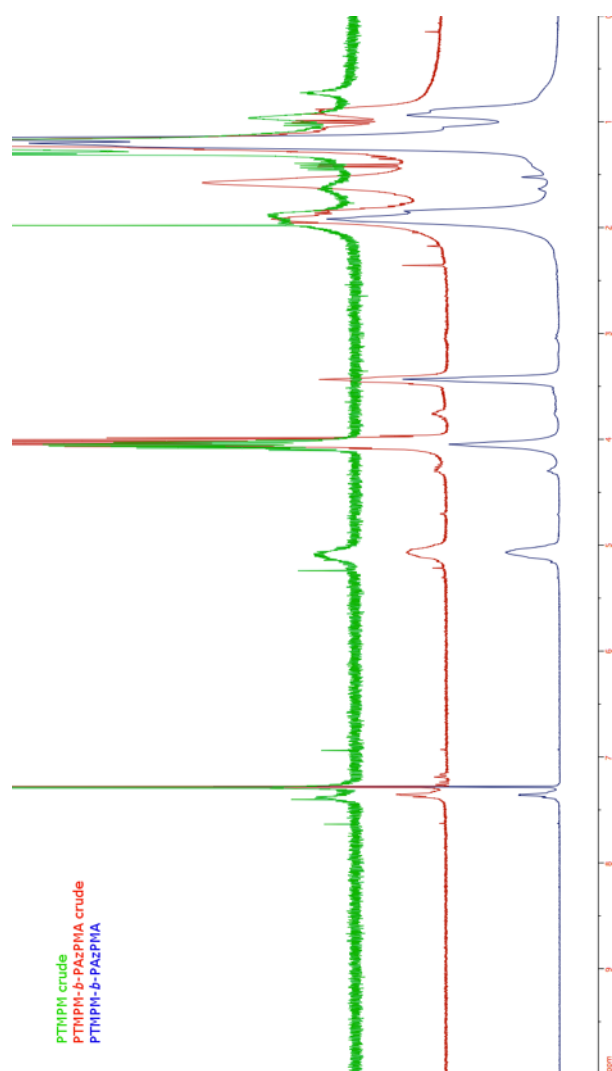


Figure 6.25 – ^1H -NMR spectra of the crude PTMPM₁₈, crude PTMPM₁₈-*b*-PAzPMA₁₄ and pure PTMPM₁₈-*b*-PAzPMA₁₄.

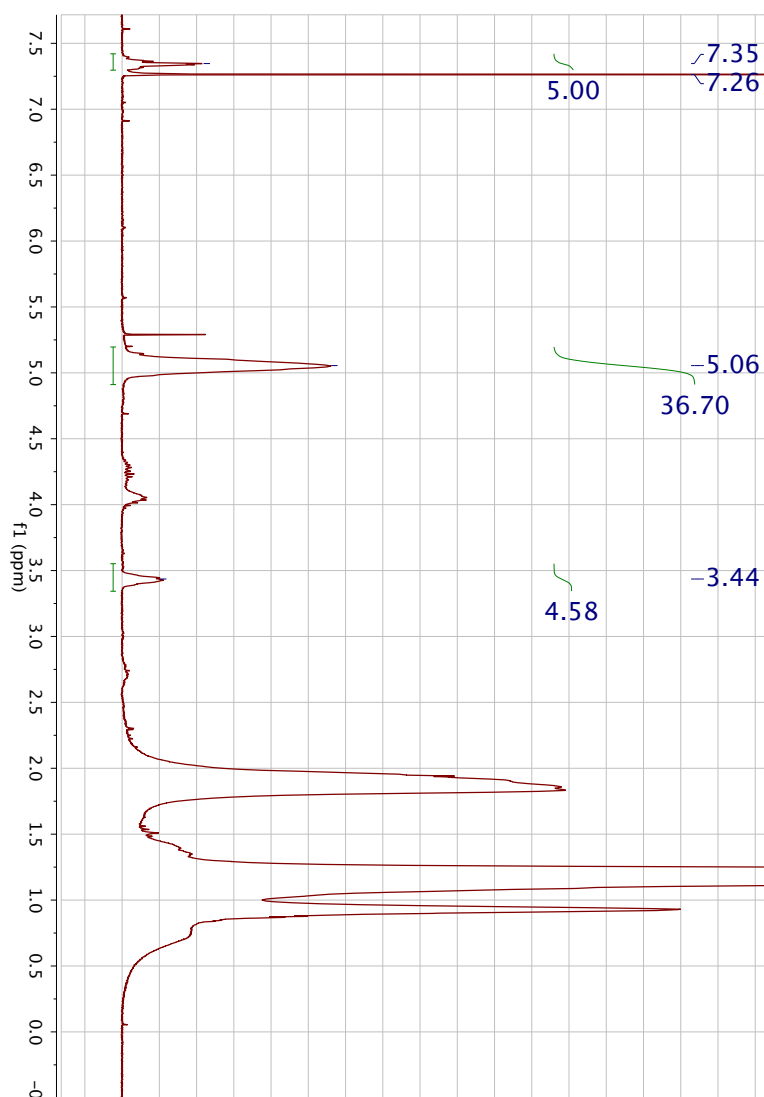


Figure 6.26 – ^1H -NMR spectrum of the pure PTMPL₃₇-b-PAAzPMA_{2.5}.

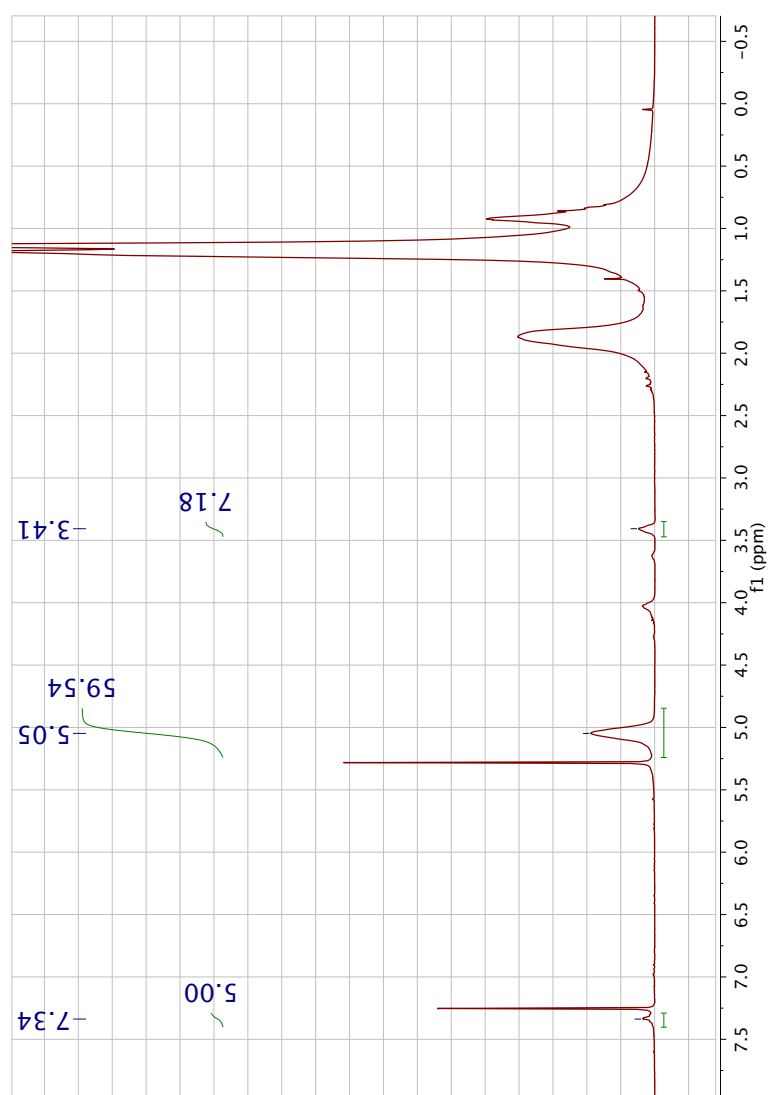


Figure 6.27 – ^1H -NMR spectrum of the pure PTMPPM₆₀-*b*-PAzPMA_{3.6}.

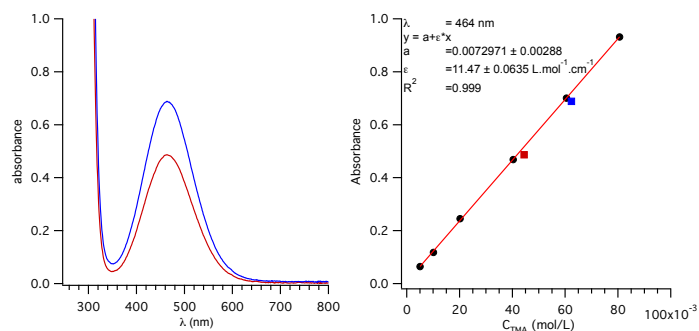


Figure 6.28 – Determination of the oxidation degree by UV-Vis analyses thanks to a TEMPO-*tert*-butyrate calibration in CH_2Cl_2 . The UV-Vis spectra of solutions of PTMA₃₇-*b*-PAzPMA_{2.5} in CH_2Cl_2 are depicted on the left inset (red and blue curves, $11.25 \text{ g} \cdot \text{L}^{-1}$ and $16.25 \text{ g} \cdot \text{L}^{-1}$, respectively). The maximum of absorbance ($\lambda_{\text{max}} = 464 \text{ nm}$) was measured for the two different concentrations and compared to a TEMPO-*tert*-butyrate calibration (red line in the right inset).

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CHAPTER 7

PDHA, AN HYBRID CONDUCTING-REDOX POLYMER FOR HIGH ENERGY DENSITY ELECTRODES

Abstract

The electrochemistry of poly(2,5-dihydroxyaniline) (PDHA), a novel hybrid molecular configuration with redox active sites and electrical charge conduction along the polymer chain is presented here. The theoretical capacity of this material is estimated at $443 \text{ mAh}\cdot\text{g}^{-1}$, with high power performances being proposed given the intrinsic electrical conductivity. In this chapter we detail the optimization of the chemical synthesis and electrode formulation for poly(2,5-dihydroxyaniline) resulting in improved cycling stability, power performances and defined electrochemical response. We also detail the alternative electrochemical synthesis and activation route for PDHA and compare the results with the chemical approach.

7.1 Introduction

Regardless of the organic material, the requirements for a battery electrode are: (i) reversible redox process; (ii) low molar mass accompanied by a multi-electron exchange process, preferentially; (iii) limited or no solubility to avoid elution of the active material from the electrode (yet, adequate swelling is preferred to enable efficient ion transport) in battery electrolytes; (iv) finite electrical conductivity for efficient charge collection; and (v) simple materials and synthesis approaches. Merging all these characteristics within a single material seems rather difficult and many of the studied organic materials so far fail to comply with all these requirements at the same time.^[1]

Among organic redox active materials, quinone derivatives constitute a very promising class of Li-ion battery electrode materials, with electrochemical characteristics challenging those of conventional inorganic cathode materials.^[2–5] Various quinone-based formulations have been used so far with intrinsic advantages and drawbacks. The first and simplest quinone compound to be considered as electrode material is the 1,4-benzoquinone (BQ), with a theoretical capacity of about $500 \text{ mAh}\cdot\text{g}^{-1}$ given the two-electron reversible redox and low molar mass.^[6]

Unfortunately, most organic compounds, such as pure quinones, hardly satisfy some of the above listed requirements. Many approaches have been thus developed over the past years to render this class of materials battery relevant including solid-state cells,^[7–9] use of high surface area host materials for efficient physisorption^[10–12] or other strategies limiting the solubility of the material. As part of the second option, surface grafting methods have been explored for BQ units,^[3,13–16] while others used BQ derivatives (for instance, dicarboxylates) with intrinsic limited solubility.^[17–19] The drawback of the latter is the increased molar mass leading to lower theoretical capacities. The third, and probably the most promising route to reduce the solubility is the use of polymeric quinones.^[20–24]

Simple polyquinone molecular formulations are of particular interest because they maintain the high specific capacity and can limit to a certain extent the solubility.^[25–27] For example, halogenated polyquinone oligomers were originally proposed by Foos^[28], and later developments detailed on the use of poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) as a promising active material for lithium batteries.^[21] However,

probably due to the limited electrical conductivity, finite solubility as well as partial material utilization, under-estimated performances were attained (about 20 to 35% of the theoretical capacity was accessed at the first cycle). Recently, poly(quinone-sulfide) was synthesized and successfully applied as a positive electrode battery material and shown to have excellent performances. Nonetheless, the specific capacity was penalized by the large molar mass and no details were provided regarding the electrical conduction properties of poly(quinone-sulfides).^[29] Although excellent advances have been provided to date, there is large room for further improvements.^[2]

The present chapter is based on two successive publications in Journal of Materials Chemistry Part A, and Scientific Reports.^[5,30] The latter publication was featuring research carried out by Louis Sieuw for his master thesis, which has been led under the author's supervision. Globally this research topic was relying on a common strategy. The strategy exposed herein is relying on certain polyquinone derivatives. Notably, we will detail the synthesis and battery use of poly(2,5-dihydroxyaniline) (PDHA). The molecular design of this BQ-based polymeric material (Figure 7.1) presents appealing properties for battery applications. The hybrid redox node-electron conducting chain structure was expected to enable simultaneous charge conduction and *n*-type redox while maintaining a low molar mass per repeating unit. Aside from its electrical conductivity, the polyaniline (PANI) backbone was also selected given the limited solubility of high molar mass polyanilines. The theoretical charge storage capacity for a two-electron redox process in BQ units of PDHA was estimated at 443 mAh·g⁻¹.

Given its conductive conjugated backbone, PDHA should be qualified for high power performances. Yet, even though polyaniline is the oldest known synthetic conjugated polymer, its molecular structure is still matter of debate. The fact that polyaniline and its derivatives are displaying structures markedly influenced by the synthetic conditions is not helping to overcome this situation. Furthermore, as for the capacity extraction, Poizot *et al.*^[31] postulated that structural aspects can induce the redox process to be limited to one-electron redox per BQ instead of the theoretical two.

In this respect, we also aimed at getting a better understanding of the limitations at play with PDHA in order to optimize its performances, particularly regarding the specific capacity and the capacity retention

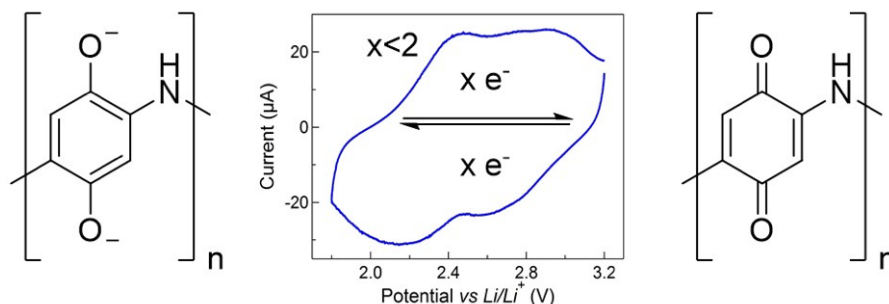


Figure 7.1 – Molecular design and target electrochemistry of the hybrid redox node-electron-conducting PDHA.

upon cycling. Therefore, the focus was set on several aspects regarding the electrode formulation but also the material synthesis and processing. More specifically, our optimization included optimization of the parameters of the chemical demethylation step of poly-2,5-dimethoxyaniline (PDMA_{CHEM}) in the chemical synthesis approach of PDHA_{CHEM}. Additionally, we also explored and discuss the all-electrochemical synthesis route for PDHA_{E-CHEM}^[32–35]: electro-polymerization of the poly-2,5-dimethoxyaniline (PDMA_{E-CHEM}), followed by electro-oxidative demethylation. Eventually, our attention has been focused on improving the active material-additives slurry formulation and electrode processing.

7.2 Electrochemical route toward poly(2,5-dihydroxyaniline)

First, the results of the electrochemical synthesis of PDHA_{E-CHEM} are detailed. The motivation for this approach was that it can directly afford PDMA (and potentially PDHA) as an electrode, i.e. the pure deposited material without any additives (carbon, binder). Not only would this grant electrochemical cells with higher energy densities, but it also makes for a very simple and straightforward procedure. The electrodeposition conditions on stainless steel substrate (potential window, voltage sweep rate, number of scans) were first screened to obtain homogeneous, compact and adherent PDMA films.

A series of typical samples and associated cyclic voltammograms for the electro-polymerization and the demethylation steps are shown in

figure 7.2. The voltammogram in figure 7.2b shows progressive current increase with each cycle, significant of an increased amount of polymer being electrodeposited for each subsequent cycle. The porosity and thus the surface area increase allows for more monomer to be electro-oxidized, leading to a signal increase at every cycle. However, excessive deposition resulted in delamination of the PDMA film upon washing and drying, this step thus requiring further optimization. Films obtained after 10 scan cycles were found to be optimal (photographs A, B in figure 7.2a). A scan rate of $5\text{ mV}\cdot\text{s}^{-1}$ was also found optimal; for faster scan rates, non-uniform deposits were obtained (photographs B, C, D in figure 7.2a). Finally, the optimal scan potential window was determined to be -0.2 V to 0.85 V *vs.* Ag/AgCl. The cyclic voltammogram of the electro-polymerization (figure 7.2b) displays a broad anodic peak around 0.8 V *vs.* Ag/AgCl, corresponding to the oxidation of the monomer and the electro-polymerization. The second anodic peak (0.3 V *vs.* Ag/AgCl) and the associated cathodic peak (0.2 V *vs.* Ag/AgCl), which are less visible at the beginning but become more pronounced with each cycle, are ascribed to the redox of the formed polymer. The most conclusive result (photograph A in figure 7.2a) in terms of homogeneity and structural integrity of the film was thus achieved with the following parameters: -0.2 V to 0.85 V *vs.* Ag/AgCl, $5\text{ mV}\cdot\text{s}^{-1}$, 10 cycles. Subsequent analysis was carried out on PDMA_{E-CHEM} samples synthesized using these parameters.

After electro-polymerization, the samples were washed to remove any trace of monomer and electrochemical demethylation was tested. The mechanism for electrochemical demethylation reaction (Figure 7.3) proceeds through the oxidation of PDMA_{E-CHEM} (schematized here for the 2 electrons reaction per monomer unit), followed by the elimination of two methyl cations.¹ The conditions were similar to those of the polymerization except for the absence of monomer: voltammetry scans in 0.5 M H_2SO_4 aqueous electrolyte. The potential scan window was limited to -0.2 V to 0.7 V *vs.* Ag/AgCl at a scan rate of $1\text{ mV}\cdot\text{s}^{-1}$ (Figure 7.2c). Two sets of redox peaks can be distinguished on the voltammogram. The reversible waves at 0.2 V and 0.3 V *vs.* Ag/AgCl are characteristic of the polymer backbone redox (leucoemeraldine - emeraldine couple).

¹Chemical demethylation of PDMA_{E-CHEM} was also tested but unsatisfactory results are obtained. During the reaction in conditions similar to above, the stainless-steel disk displays signs of corrosion (progressive appearance of a dark-brown film/deposit) accompanied by delamination of the PDMA film.

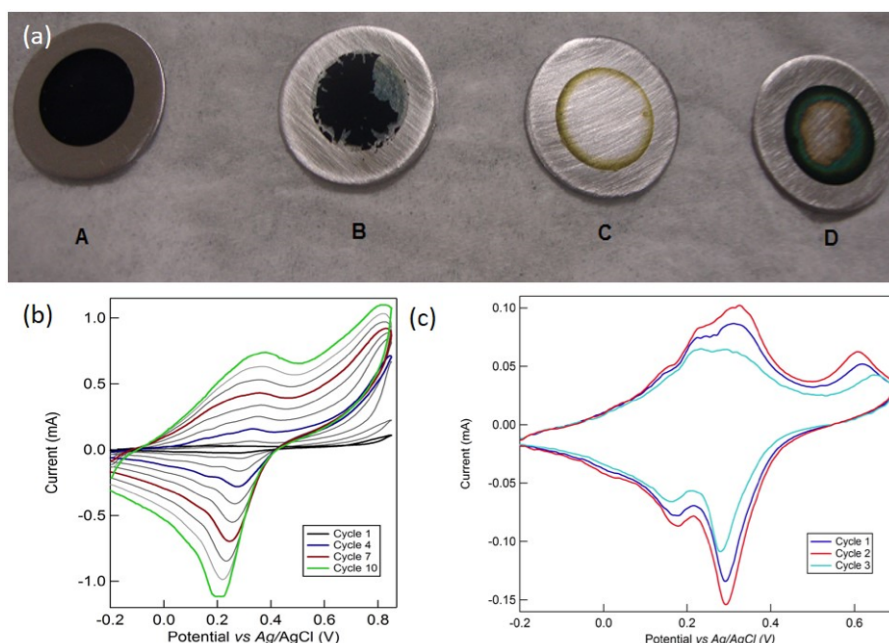


Figure 7.2 – (a) Photographs of PDMA_{E-CHEM} films electrodeposited on stainless steel disks under various conditions (A) -0.2 V to 0.85 V, $5 \text{ mV}\cdot\text{s}^{-1}$, 10 scans; (B) -0.2 V to 0.8 V, $5 \text{ mV}\cdot\text{s}^{-1}$, 15 scans; (C) -0.2 V to 0.8 V, $15 \text{ mV}\cdot\text{s}^{-1}$, 5 scans; (D) -0.2 V to 0.8 V, $10 \text{ mV}\cdot\text{s}^{-1}$, 10 scans. Cyclic voltammogram for (b) typical PDMA_{E-CHEM} synthesis (scan rate $5 \text{ mV}\cdot\text{s}^{-1}$) and (c) associated voltammogram for the electrochemical demethylation process (scan rate $1 \text{ mV}\cdot\text{s}^{-1}$).

The peak at 0.65 V *vs.* Ag/AgCl is indicative only of an irreversible process that we assign to the oxidative demethylation of the PDMA. It should be noted that the emeraldine - (per)nigraniline redox potential in acidic solution was reported to be in the range of 0.65 V to 0.85 V *vs.* Ag/AgCl with this process being partially reversible and leading to chain degradation when in presence of oxygen.^[36–38] It is thus possible that the oxidative demethylation and the redox of the backbone are concurrent processes, leading to difficulties in precisely quantifying the specific contribution of each. Moreover, both processes can account for the irreversible chain degradation. It should also be noted that the peak at 0.65 V did not entirely vanish, even after extended scanning, which would have been expected in the case of complete demethylation of PDMA without interference of the emeraldine - (per)nigraniline redox process. Besides, the possibility of the chain degradation is supported

by the global decrease of the whole signal after each voltammetry cycle. The physico-chemical and electrochemical characterizations that are following are providing some insight about the nature and the extent of the processes occurring during this synthetic approach.

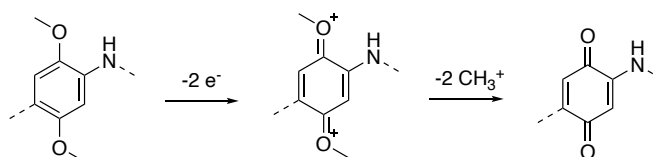


Figure 7.3 – Electrochemical approach for the demethylation of PDMA into PDHA_{E-CHEM}.

7.3 Chemical route toward poly(2,5-dihydroxyaniline)

Regarding our second approach, consisting in the chemical demethylation of PDMA_{CHEM}, the method consists in (i) oxidative polymerization of 2,5-dimethoxyaniline using ammonium persulfate as oxidizing agent to obtain PDMA, followed by (ii) chemical demethylation of PDMA with boron tribromide to give PDHA^[5] (Figure 7.4).

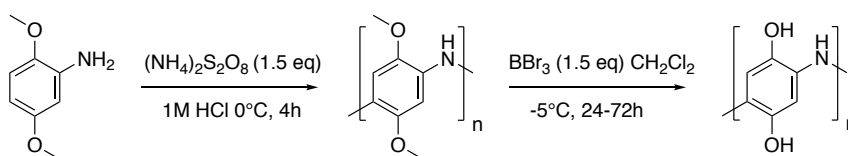


Figure 7.4 – Chemical approach for the synthesis of PDHA_{E-CHEM}.

The PDHA_{CHEM} is obtained following literature reports.^[36,39,40] The demethylation yield of its PDMA precursor was comprehensively tuned by the amount of BBr₃ equivalents as well as the reaction time. The demethylation yield was evaluated through elemental analysis (see the characterization section) and the capacity extracted from electrochemical measurements in coin cells (see the electrochemical characterization

section). For one equivalent of methoxy groups, the yield increased significantly from 1.5 equivalents up to 3 equivalents of demethylating agent; going up from 3 equivalents, the yield gain was much less pronounced. Regardless of the excess of BBr_3 , the reaction is relatively slow, and a total time of 72 hours was finally retained to ensure a maximum demethylation yield. The obtained product has a solid consistency with a dark-green color. The dissolution tests showed that PDHA has a much lower solubility than starting PDMA, with reduced solubility in typical battery electrolyte constituents (Figure 7.5 and figure 7.6).

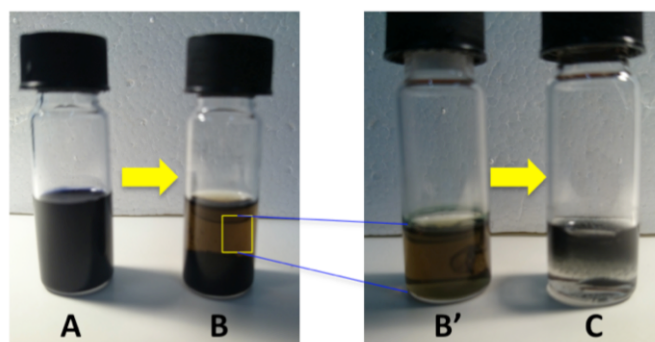


Figure 7.5 – Solubility of the reactants and products during the demethylation reaction. A - PDMA dispersed in dichloromethane; B - after the demethylation reaction. Most of the product has precipitated. B' - Part of the supernatant in B was extracted and filtered through PTFE 0.22 μm , then quenched in C by the addition of water. No soluble species were detected. CH_3Br was found with ^1H -NMR analysis, an observation proving selective demethylation and that prior quenching, adducts of BBr_3 and PDMA were present that have reacted with water subsequently.

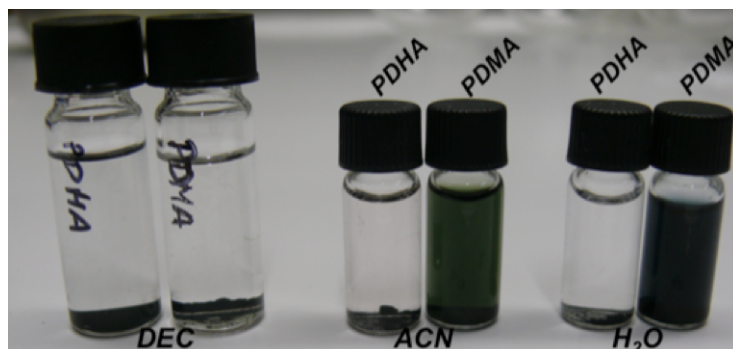


Figure 7.6 – Solubility tests with PDMA_{CHEM} and PDHA_{CHEM} in diethyl carbonate, acetonitrile and deionized water.

7.4 Poly(2,5-dihydroxyaniline), physico-chemical characterizations

Albeit highly desirable and beneficial for battery electrodes manufacturing and operation, the insolubility of highly demethylated PDHA precluded their extensive chemical characterization. The solubility was found to decrease with the extent of demethylation with PDMA being soluble enough to be characterized by $^1\text{H-NMR}$ whilst PDHA being at best at the limit of solubility for accurate $^1\text{H-NMR}$ characterization. For example, the room temperature solubility of PDHA in dimethyl sulfoxide (DMSO), found to be one of the best solubilizing solvents, was found to be significantly lower than $0.01\text{ g}\cdot\text{L}^{-1}$. Related to that, $^1\text{H-NMR}$ analysis was impossible since the amount of material was too low for an accurate signal-to-noise ratio. Other solvents found to slightly solubilize PDHA, as indicated by the blue coloration of the supernatant phase, are the following: dimethylformamide, trifluoroacetic acid, methanol, *N*-methyl-2-pyrrolidone, and butanol. It is however important to note that possibly low molecular weight oligomers are being solubilized here. During another series of solubility tests, where extensive washing with ether and water after the synthesis was applied (up to the point when washing liquids were found colorless) the apparent solubility was even lower (with very light or even no coloration of the supernatant phase for the respective solvents). The following non-solvents have been found (no coloration of the liquid phase independently of the processing route): H_2O , acetonitrile, 1,2-dichlorobenzene, CH_2Cl_2 , CHCl_3 , diethylcarbon-

ate.

The electroactive polymers synthesized using both chemical and electrochemical methods were characterized to determine the chemical composition and molecular structure. In both cases, the precursor polymer and the product of demethylation exhibited IR peaks around 1520 cm^{-1} (marked with * in figures 7.7 and 7.8) – stretching mode of the benzenoid ring – and 1590 cm^{-1} (marked with ** in figures 7.7 and 7.8) – stretching mode of the quinoid ring. The presence of the respective vibration modes supports the polymeric formula with polyaniline backbone in emeraldine oxidation state.^[41] The N-H stretching peak (3300 cm^{-1}) (marked with *** in figures 7.7 and 7.8) of the secondary amines of the polymer backbone is distinguishable for both PDMA_{CHEM/E-CHEM} and PDHA_{CHEM/E-CHEM}. It is however more intense for PDMA_{E-CHEM} and PDHA_{E-CHEM}, which hinders the observation of the O-H peak (marked with **** in figure 7.7) in the spectrum of PDHA_{E-CHEM} (Figure 7.8b). This is not the case for the chemical synthesis route, and the O-H for PDHA_{CHEM} is clearly distinguishable (figure 7.7b), confirming the success of the demethylation reaction. This analysis suggests a higher demethylation yield for the chemical approach (PDHA_{CHEM}).

To quantify the demethylation extent in PDMA_{CHEM}/PDHA_{CHEM}, elemental analysis was employed (Table 7.1) in addition to the capacities extracted from galvanostatic discharge (see the electrochemical characterization section). Outside the four main elements contained (C, H, N, O), the remaining percentage (17.51%) is attributed to Cl from the emeraldine salt. The obtained C/H, C/N and C/O ratios are compared to the theoretically estimated ratios based on molecular formulas for emeraldine form of PDMA ($\text{C}_{32}\text{H}_{34}\text{O}_8\text{N}_4\text{Cl}_2$) and PDHA ($\text{C}_{24}\text{H}_{18}\text{O}_8\text{N}_4\text{Cl}_2$). A clear trend after demethylation is the decrease of C/N and C/O ratios, accompanied by C/H ratio increase. The C/N, C/O and C/H ratios closest to the expected values were measured for PDHA_{CHEM} samples with the following demethylation conditions: 72 h at -5°C with 3 or more equivalents of BBr₃. However, the demethylation yield derived from this analysis shows rather important variations (55% to 130%) depending on the ratio on which we base our calculations (C/N, C/O or C/H). This lack of precision is most certainly due to the contamination from the substrate during the mechanical film peeling, as well as the limited amount of material available per single batch. The yields derived from the galvanostatic discharge capacities were in

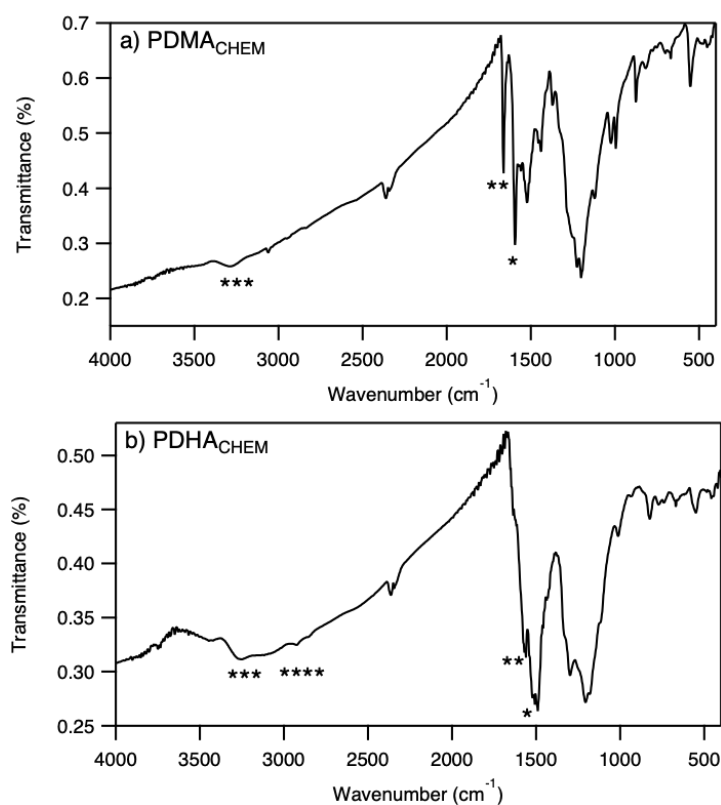


Figure 7.7 – IR spectra of PDMA and PDHA synthesized by chemical approach: (a) PDMA_{CHEM} and (b) PDHA_{CHEM}.

that regard more conclusive, as will be illustrated in the electrochemical characterization section.

Table 7.1 – Elemental analysis. Atomic (C, H, N, O) percentages for PDMA_{CHEM} and PDHA_{CHEM}.

	%C	%H	%N	%O	%rest	C/H	C/N	C/O
PDMA _{Theor}						0.9	8.0	4.0
PDMA _{CHEM}	47.3	5.2	5.8	24.4	17.5	0.8	9.6	2.6
PDHA _{Theor}						1.3	6.0	3.0
PDHA _{CHEM}	51.2	4.1	8.4	25.0	11.3	1.0	7.0	2.0

The XPS survey scans for both PDMA_{CHEM} and PDHA_{CHEM} present

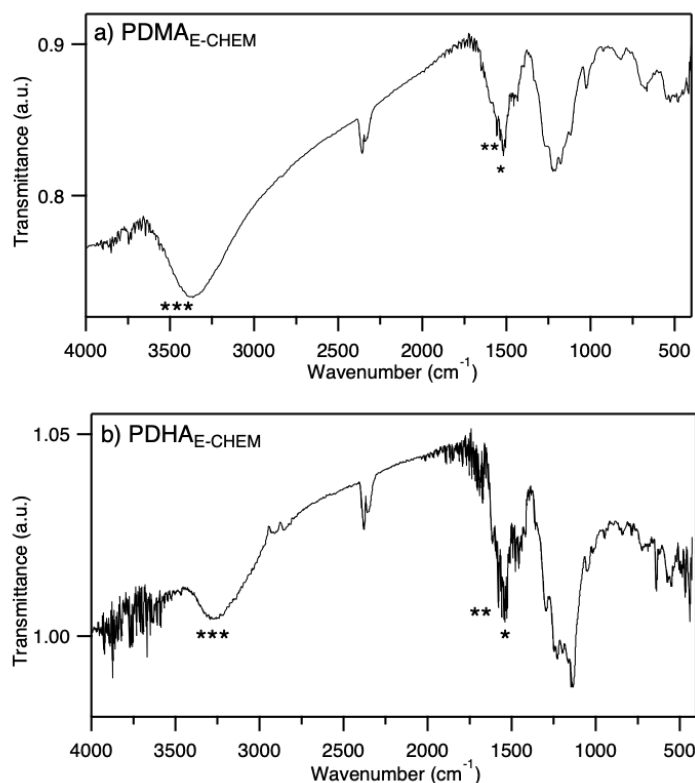


Figure 7.8 – IR spectra of PDMA and PDHA synthesized by electrochemical approach: (a) PDMA_{E-CHEM} and (b) PDHA_{E-CHEM}.

signal characteristics of carbon, oxygen, nitrogen and chlorine (Figure 7.9a) No signs of boron or bromide could be detected. Chlorine presence is consistent with the doped nature of PDMA_{CHEM} and PDHA_{CHEM} as the workup after polymerization or demethylation are systematically ended with HCl washings. Considering the narrow scans for C_{1s}, N_{1s} and O_{1s} the peaks positions for PDMA_{CHEM} are in good agreement with values presented in the literature (Figure 7.9b).^[42] The chemical structures being close for PDHA and PDMA, peaks for both polymers are located at nearly the same positions and the signals are observed in the same range of binding energies. Particularly the C_{1s} narrow scans exhibit broadened signals (10 eV)^[43] and similar shapes for both PDMA_{CHEM} and PDHA_{CHEM}.

The shape of the C_{1s} signals for both polymers present asymmetries

typical of polyaniline systems. Within the class of conjugated aromatic systems, the line shape of the C_{1s} shows a low kinetic energy tail typical of the conducting form of these polymers. The tail arises from the aromatic satellite signal that is observed closer to the main C_{1s} peak.^[42] Quantification results yield to C/O atomic ratios being close to the predicted values based on the chemical structures (Table 7.2). C/N ratios are sensibly higher than the theoretical values, meaning a nitrogen atomic concentration lower than expected. This observation may be due to contamination increasing the carbon signals. Nevertheless C/N and C/O ratios are lower for the PDHA_{CHEM} compared to the PDMA_{CHEM}. The trend is following the expectations since carbon contribution should be decreasing after demethylation.

Table 7.2 – XPS. Atomic (C, N, O) percentages as well as C/N and C/O atomic ratios for PDMA_{CHEM} and PDHA_{CHEM}.

Sample	Surface atomic concentrations (%)			Atomic ratio	
	C	N	O	C/N	C/O
PDMA _{CHEM}	73.8	6.1	20.1	12	3.7
PDMA _{THEOR}	72.7	9.1	18.2	8	4
PDHA _{CHEM}	68.0	9.4	22.6	7.2	3
PDHA _{THEOR}	66.7	11.1	22.2	6	3

Conductivity measurements carried out on PDMA_{CHEM} and PDHA_{CHEM} confirmed that PDHA partially preserves the electrical conductivity of the emeraldine, with characteristic acid-base doping/undoping behavior (Figure 7.10). Consistent with the literature,^[44] conductivity of 1 M HCl doped PDMA was of 1 S·cm⁻¹ with one order of magnitude loss in conductivity accompanying the demethylation. This could be ascribed to a partial Π -conjugation degradation.

Finally, SEM analysis was carried out on PDHA_{E-CHEM} electrodes given that particle delamination was noticed during the electropolymerization (Figure 7.11a,b). The polymer film is composed of nano- and micro-particles (1 μ m to 10 μ m) with indeed loosely bound particles present on the surface. The bulk film remains compact with no significant porosity being detected by SEM. The polymer film can however be easily swelled by a solvent, implying a mesoporous morphology. By allowing an easy access of the electrolyte to the active material, this should have a favorable impact on the electrochemical performances/properties that have to be studied next.

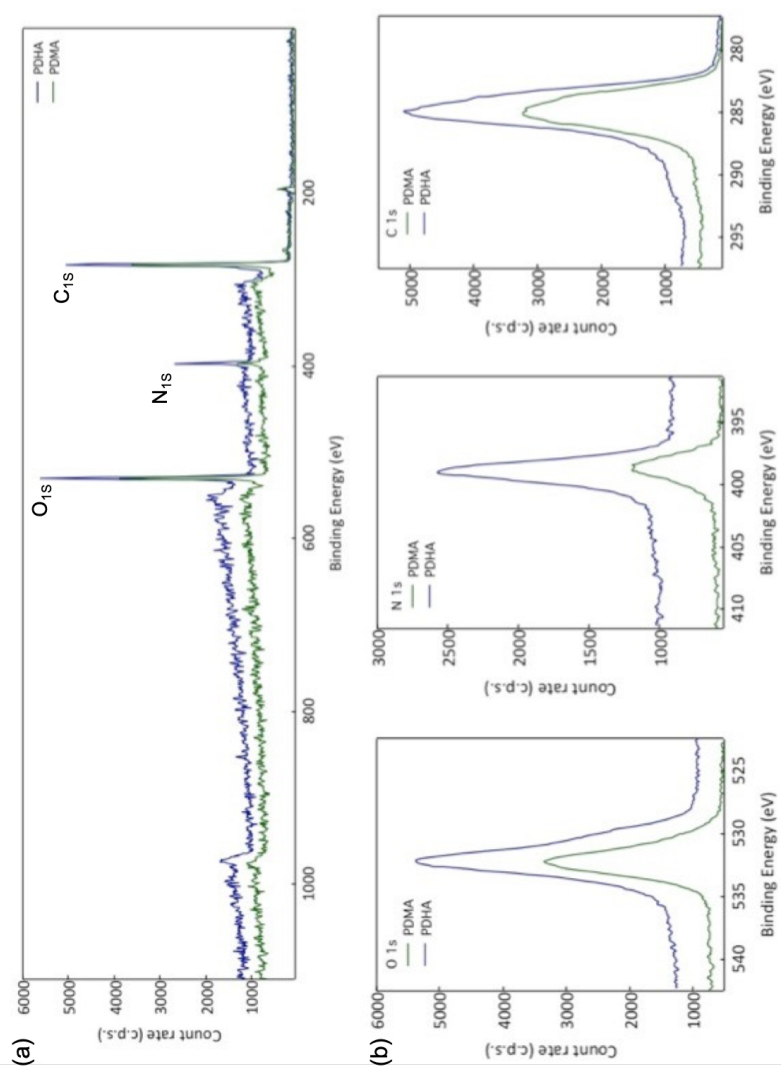


Figure 7.9 – (a) XPS survey scans and (b) C_{1s}, N_{1s} and O_{1s} narrow scans of PDMA_{CHEM} and PDHA_{CHEM}.

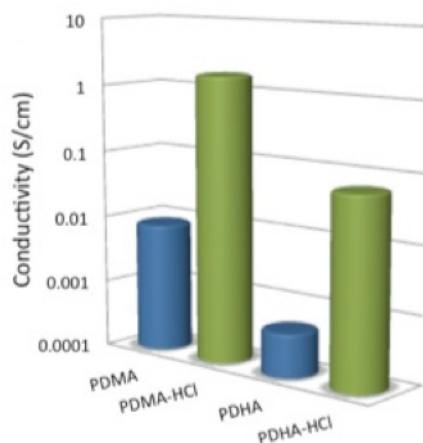


Figure 7.10 – Electrical conductivity of PDMA_{CHEM} and PDHA_{CHEM} in the acidified and basified forms.

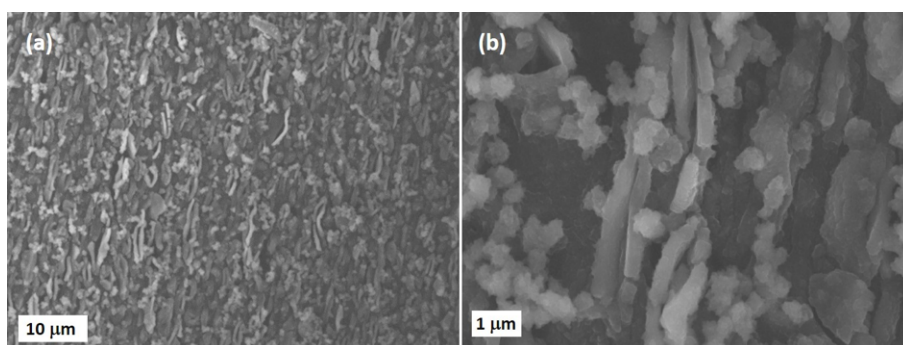


Figure 7.11 – SEM images of PDHA_{E-CHEM} electrodes surfaces: 15 keV, SEI mode, WD = 8.4 mm (a) x1,000 (b) x6,000.

7.5 Poly(2,5-dihydroxyaniline), electrochemical characterizations

With both materials (PDHA_{CHEM} and PDHA_{E-CHEM}) synthesized and characterized, we entailed electrochemical characterization in non-aqueous Li-half-cell configuration (Figure 7.12a). The half-cells typically had an open circuit potential of 2.8 V – 3.2 V *vs.* Li/Li⁺ and required an initial cathodic polarization scan. The electrodes made of PDHA_{CHEM} display reversible behavior with two pairs of peaks centered at 2.3 V and 2.7 V *vs.* Li/Li⁺, which are ascribed to the 2 electrons of the redox process, typical for quinone redox in aprotic electrolytes.^[2] The absence of such peaks in pristine PDMA_{CHEM} electrodes^[5] constitutes an indication of successful demethylation. For comparison, the CV of the previously reported PDHA_{CHEM} material^[5] is shown in figure 7.12b. A visible improvement concerning the definition of the redox response is observable, implying a higher demethylation yield obtained using the current method than with the previous reaction parameters. This also corroborates the higher capacities obtained on galvanostatic cycling of PDHA_{CHEM} synthesized in this work, involving higher activation of quinone redox moieties.

In contrast, the electrochemical analysis of PDHA_{E-CHEM} shows a different behavior from PDHA_{CHEM}. Two redox waves centered at 2.8 V and 3.2 V *vs.* Li/Li⁺ can be distinguished (Figure 7.12c). The processes are reversible, with a slight decrease in intensity of the peak at 2.8 V observed with increasing cycle number. It should be noted that others have also attempted the electrochemical synthesis of PDHA for charge storage applications.^[32–35] However, we find a lower redox activity window for PDHA_{E-CHEM}: 2.5 V to 3.6 V *vs.* Li/Li⁺ compared to the 3.0 V - 4.0 V *vs.* Li/Li⁺ window previously reported. The assigned redox peak values are also not consistent with the electrochemistry of benzoquinone in non-aqueous electrolytes. The redox process centered at 3.2 V *vs.* Li/Li⁺ is characteristic of the redox reaction of the electroactive polyaniline chain (refer also to figure 7.2b,c).^[45,46] While the peak centered at 2.8 V *vs.* Li/Li⁺ could be assigned to PDHA redox, the absence of the second associated redox peak (typically located between 2.0 V and 2.6 V *vs.* Li/Li⁺ as seen in figure 7.12a,b) could be an indication that we are confronted with a different redox process than the classical quinone redox couple.

The explanation for this could be the high anodic polarization required for PDMA demethylation that also increases the redox state within the polyaniline chain. When in presence of oxygen, the (per)nigraniline has been reported unstable with irreversible degradation of the polymer matrix. The additional presence of methoxy/hydroxyl groups here could lead to complex electrochemical stability - response interplay requiring further investigation. Overall, this analysis suggests that the electrochemical synthesis route of PDHA requires further optimization to reach results similar to the chemical demethylation approach.

Table 7.3 – Demethylation conditions for the PDMA_{CHEM} and corresponding specific capacities for PDHA_{CHEM}.

PDHA _{CHEM} batch	BBr ₃ [eq]	t [h]	Specific Capacity [mAh·g ⁻¹]
1	1.5	24	120
2	1.5	72	165
3	3.5	72	290

Next, galvanostatic cycling tests were run on PDHA_{CHEM} assembled

electrodes to determine the attainable reversible capacities and cycling stability. PDHA_{CHEM} half-cells were cycled within a potential range from 1.8 V to 3.0 V *vs.* Li/Li⁺. The voltage window was preliminarily determined by cyclic voltammetry (CV) (Figure 7.12a) and the upper limit was set to 3 V to avoid any overlap with the polyaniline backbone redox. The specific capacities, directly linked to the demethylation yields, varied with the demethylation conditions, as illustrated in table 7.3. Higher excesses of BBr₃ demethylating agent and longer reaction times allow for an improved conversion of methoxy groups, and thus a higher amount of hydroxy chemical functions accessible for the electrochemical process. Accordingly, we observe an uptake of the specific capacity when these two reaction parameters are increased.

The best demethylation conditions led to an initial discharge capacity of 290 mAh·g⁻¹ (Figure 7.13a). This constitutes the highest to date capacity for this class of materials, and is attributed to improved synthesis, limited exposure to air of the demethylated material and storage in controlled atmosphere prior utilization.

Another major improvement is the enhancement of the capacity retention (Figure 7.13a,b). For instance, 90% of the initial capacity (270 mAh·g⁻¹) was lost in the first three cycles for the highest capacity PDHA previously reported^[5]. As illustrated in figure 7.13b, the PDHA_{CHEM} electrodes analyzed here retain more than 50% of the initial capacity after more than 30 cycles. These gains are the result of an improved synthesis method, an adequate current collector implementation (carbon-coated aluminum foil here *vs.* nickel foam used in our earlier work,^[5]) and an improved adhesion of the coated electrodes.

The coulombic efficiency for the PDHA_{CHEM} electrodes is also illustrated in figure 7.13b, with initial values above 100%. High reversibilities of carbonyl groups have been reported before for other organic electrode materials, with associated good coulombic efficiencies.^[17,21,22,47,48] In this case, the excessive values obtained for a current density of 16 mA·g⁻¹ (C/20) are ascribed to irreversible redox processes in the polymer backbone. With cycling, the coulombic efficiency values stabilizes at 100%, which implies limited irreversible redox of the backbone.

Lastly, the power performances of PDHA_{CHEM} have also been measured. Figure 7.14 displays the stable reversible capacity obtained - the electrodes delivered specific capacities of 160 mAh·g⁻¹, 130 mAh·g⁻¹,

110 mA $\cdot$ g $^{-1}$ and 100 mA $\cdot$ g $^{-1}$ at 16 mA $\cdot$ g $^{-1}$ (C/10), 32 mA $\cdot$ g $^{-1}$ (C/5), 80 mA $\cdot$ g $^{-1}$ (C/2) and 160 mA $\cdot$ g $^{-1}$ (1C), respectively. Moreover, after the power-rate evaluation, the PDHA_{CHEM} retained most of the initial capacity of 125 mA $\cdot$ g $^{-1}$, thus 80% of the initial value. For comparison, the best rate performances achieved in our previous report are also shown. Despite a lower initial value at C/10 (160 mA $\cdot$ g $^{-1}$ vs. 190 mA $\cdot$ g $^{-1}$), the capacities delivered at C/2 (110 mA $\cdot$ g $^{-1}$ vs. 85 mA $\cdot$ g $^{-1}$) and 1C (100 mA $\cdot$ g $^{-1}$ vs. 60 mA $\cdot$ g $^{-1}$) are significantly higher in current work. These improved power properties are ascribed to optimized synthesis and formulation parameters, and notably to the change of current collector with carbon-coated aluminum foil used this time instead of Ni foam.

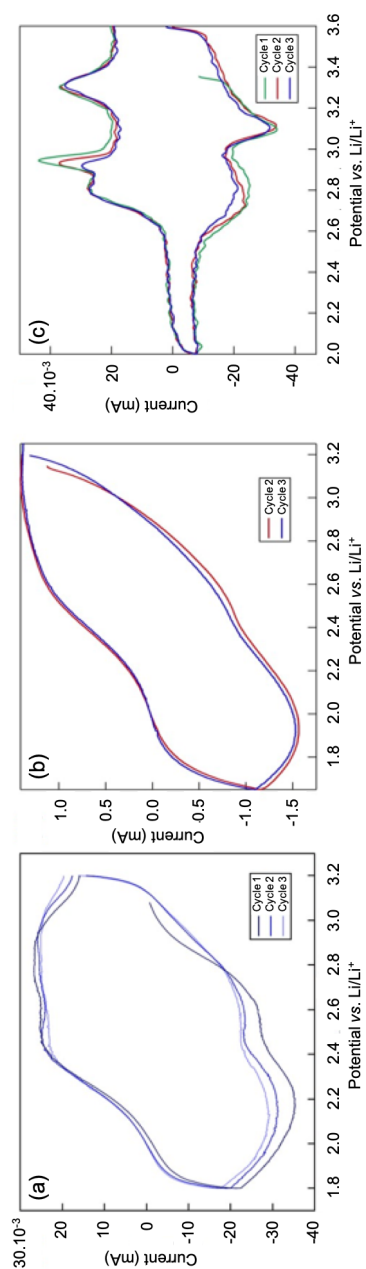


Figure 7.12 – Cyclic voltammetry. (a) PDHA_{CHEM} - potential range: 1.8 V to 3.2 V *vs.* Li/Li⁺, rate: 0.1 mV·s⁻¹. (b) PDHA_{CHEM} as reported earlier by Vlad *et al.* [5] - potential range: 1.8 V to 3.2 V *vs.* Li/Li⁺, rate: 1 mV·s⁻¹. (c) PDHA_{E-CHEM} - potential range: 2.0 V to 3.6 V *vs.* Li/Li⁺, rate: 1 mV·s⁻¹.

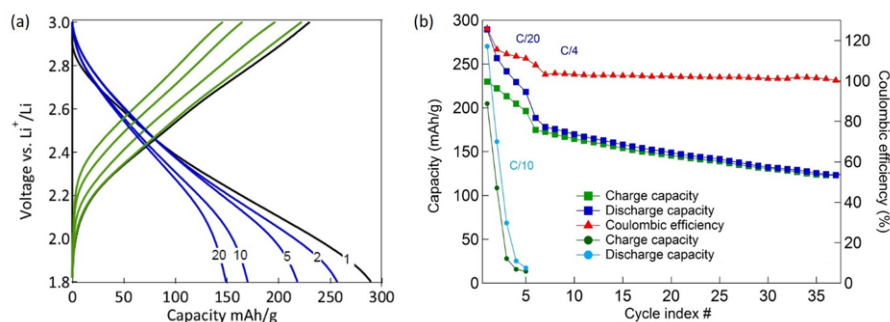


Figure 7.13 – Galvanostatic charge-discharge tests of PDHA_{CHEM} electrodes. (a) Voltage *vs.* capacity profiles for PDHA_{CHEM} electrodes. (b) Capacity retention plot for PDHA_{CHEM} electrodes; Data from galvanostatic cycling of the material as obtained thanks to the present optimization study is represented with square symbols; Round symbols are used for data obtained prior optimization as reported earlier by Vlad *et al.* [5]

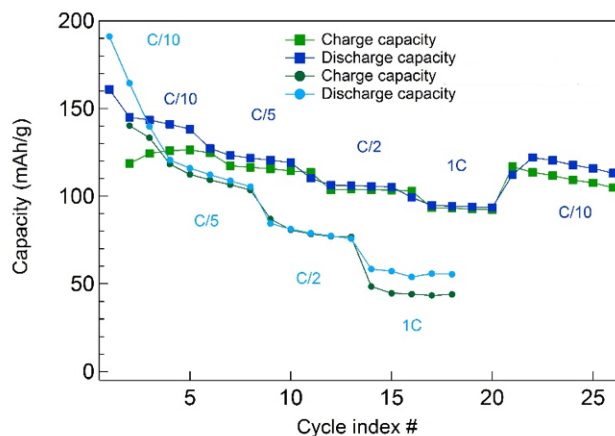


Figure 7.14 – Variable rate capacity retention plots. Data for the material as obtained thanks to the present optimization study is represented with square symbols; Round symbols are used for data obtained prior optimization as reported earlier by Vlad *et al.* [5]

7.6 Conclusion

To summarize, this chapter detailed the chemical and electrochemical synthesis of poly(2,5-dihydroxyaniline) coupled to electrochemical analysis of the synthesized materials. Full and reversible capacity utilization in this hybrid redox-conductive polymer still remains elusive with however some important insights being presented in this work. The electrochemical method was tested as it can provide pure PDMA (and potentially PDHA) electrodes to truly benefit from intrinsic electrical conductivity, electrolyte insolubility and high capacity of this material. Nevertheless, the electroanalytical analysis of PDHA_{E-CHEM} points towards a mechanism differing from the demethylation, with possible enhanced degradation given the high anodic polarization required. Further improvement of the electrochemical demethylation method is thus required for it to deliver more satisfactory results. The optimization of the chemical synthesis, electrode processing and assembly protocol in turn has led to clear improvements in terms of first cycle capacity, cycle capacity retention and power performance. This work is expected to lead to further progress in this direction by enabling full capacity utilization in PDHA and gives guidelines for new alike hybrid redox-conductive polymers materials for energy storage.

7.7 Experimental section

7.7.1 Synthesis procedures

7.7.1.1 Materials

The 2,5-dimethoxyaniline monomer ($\text{C}_8\text{H}_{11}\text{O}_2\text{N}$, DMA, Acros Organics, 99+%) is sublimed twice at 80°C under reduced pressure prior to polymerization. Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, Acros Organics, 98%), hydrochloric acid (HCl , Fisher chemical, 37%), diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$, VWR, GPR), ammonium hydroxide (NH_4OH , ChemLab, 28–30%), boron tribromide (BBr_3 , Sigma Aldrich, 99.9%) and sulfuric acid (H_2SO_4 , Sigma Aldrich, 98%) are used as purchased. Dichloromethane (CH_2Cl_2 , VWR, HPLC grade) is deoxygenated by argon purging before utilization.

7.7.1.2 Electrochemical synthesis of PDMA and PDHA

The electrochemical synthesis is carried out in a one-compartment three-electrode cell. A polished stainless steel disk (SS-304) is used as the working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as reference electrode. All the experiments are performed using an Arbin instruments BT-2043 multichannel potentiostat. $\text{PDMA}_{\text{E-CHEM}}$ films are deposited by means of cyclic voltammetry from an aqueous solution containing $0.05 \text{ mol}\cdot\text{L}^{-1}$ DMA and $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 . The potential range, the scan rate and the number of scans are optimized in order to obtain adherent and homogeneous deposits. After the electro-polymerization, the films are rinsed with water and dried. For the oxidative demethylation (yielding $\text{PDHA}_{\text{E-CHEM}}$), the obtained $\text{PDMA}_{\text{E-CHEM}}$ films on stainless steel substrates are used as the working electrode and exposed to cyclic voltammetry polarization scans in a $0.5 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 aqueous solution. After several optimization tests, the following parameters are found as optimal: the potential is cycled between -0.2 V and 0.7 V *vs.* Ag/AgCl with a scanning rate of $1 \text{ mV}\cdot\text{s}^{-1}$.

7.7.1.3 Chemical synthesis of PDMA and PDHA

The PDMA_{CHEM} is obtained following the literature reports.^[36,39,40] In a 500 mL round bottomed flask, DMA (1 g, 6.53 mmol) is dissolved in 150 mL of 1 M HCl aqueous solution followed by slow addition of ammonium persulfate ((NH₄)₂S₂O₈, 2.2 g, 9.80 mmol, 1.5 eq, dissolved in 10 mL of 1 M HCl) as oxidizing agent at 0°C. Quickly after the beginning of addition, the reaction mixture turns deep dark. The reaction is further stirred for 4 h at 0°C. The obtained PDMA_{CHEM} is retrieved by centrifugation and washed with 0.1 M HCl, and diethyl ether. The polymer (75% yield) is further stored under argon atmosphere. ¹H-NMR ((ppm): 2H, H_{Ar}, 6.8–7.7 (br.) ; 1H, –NH–, 5.75–6.1 (br.) ; 6H, O–CH₃, 3.5–4.25 (br.)

For the chemical hydrolysis of the methoxy groups, the reaction time, temperature and the amount of demethylating agent are screened to find the optimal conditions. First, PDMA_{CHEM} is basified with an ammonium hydroxide solution (NH₄OH 0.1 M) then dried overnight under reduced pressure at 35°C. This yields the emeraldine base of PDMA as a deep blue powder. The PDMA_{CHEM} emeraldine salt is then dispersed in dichloromethane (with also partial dissolution) and the solution was cooled to –5°C. Afterwards, boron tribromide (BBr₃) (1.5 eq to 5 eq) is added dropwise over 1 hour. The reaction time varied from 24 h to 72 h while maintaining the temperature at –5°C. The reaction is quenched with deionized water, recovered by vacuum filtration and washed with 0.1 M HCl, and diethyl ether. The obtained product (PDHA_{CHEM}) displayed the expected green color (acidified form of polyanilines) and solid consistency, whereas the solubility in water and acetonitrile considerably decreased compared to the PDMA_{CHEM} precursor.

7.7.2 Characterization

7.7.2.1 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectra of PDMA/PDHA_{CHEM}/E-CHEM products are acquired in transmission mode with a Bruker Equinox 55 spectrometer by mixing the powders with KBr.

7.7.2.2 Elemental analysis

Elemental analysis is performed by soliciting Medac Ltd services, with a stated absolute precision of 0.3%.

7.7.2.3 Scanning electron microscopy

Scanning Electron Microscopy (SEM) images are acquired using a LEO 982 FEG-SEM.

7.7.2.4 Electrode design

To prepare the electrodes, PDHA_{CHEM} is first ball-milled with carbon black (SC45, Timcall, MTI).² The best results in terms of coating integrity during manipulation as well as post-cycling analysis are obtained using the formulation containing PDHA_{CHEM}:SC45:PVDF - 30:60:10 (mass ratio) coated on carbon-coated aluminum foil (EQ-CC-Al-18u-260, MTI) as current collector.³ Pure PDHA electrodes are prepared by means of electrochemical synthesis as detailed in the synthesis section. The PDHA_{E-CHEM} on SS disks are used as such without any further processing or additive incorporation.

7.7.2.5 Cell assembly

PDHA_{CHEM}/E-CHEM electrodes are tested in half-cell configuration using lithium metal (Gelon) as reference and counter electrode. A porous polyethylene membrane (Celgard) is used as separator. A mixture of

²It should be mentioned that similarly to our previous work,^[5] carbon black was primarily used as reinforcement filler material to enhance the structural integrity of the coatings. Without added carbon black, coatings are found to crack and delaminate from current collectors even in presence of excess amount of binder. Two binder formulations are tested: PVDF-NMP (poly(vinylidene fluoride) dissolved in *N*-methylpyrrolidone) and CMC/SBR-water (aqueous solution of carboxymethyl cellulose and styrene-butadiene rubber).

³Attempts are made to reduce the proportion of carbon, but results in an important loss of integrity of the electrode during handling, cycling, and first cycle irreversible capacity loss.

ethylene carbonate (EC), diethyl carbonate (DEC) and dimethylcarbonate (DMC) with a 1:1:1 volume ratio with 1 M of lithium hexafluorophosphate (LiPF_6) was used as electrolyte (Solvionic). Electrochemical cells were assembled in nutlock-type cells (X2 Labwares). The assembly was made under protective argon atmosphere (<0.1 ppm H_2O , <0.1 ppm O_2) in a MBraun glovebox.

7.7.2.6 Electrochemical tests

All the galvanostatic cycling experiments are performed using an Arbin BT-2043 multichannel potentiostat. Unless specified otherwise, all values of capacity are reported with respect to the redox polymer mass in the electrode, and assuming that the polymer is composed solely of redox active repeating units.

7.7.2.7 Conductivity measurements

PDMA and PDHA powders are first treated with HCl 1 M followed by filtering and vacuum drying or washed abundantly with DI water. Pellets of thus acidified and neutralized PDMA and PDHA composites are fabricated by pressing 10 mg to 50 mg of powder (sandwiched between two aluminum foils) using a hydraulic press at $8 \text{ tons}\cdot\text{cm}^{-2}$. The conductivity is measured by acquiring current-voltage curves in a two-point configuration using Arbin BT-2043 battery tester.

7.7.2.8 X-ray photoelectron spectroscopy

XPS analyses are carried out at room temperature on a SSI-X-probe (SSX 100/206) photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocus Al X-ray source. Polymer Powder samples are stuck on small sample holders with double-face adhesive tape and placed on an insulating ceramic carousel (Macor, Switzerland). Charge effects are avoided by fixing a nickel grid over the samples and using a flood gun set at 8 eV. Data are treated with the program Casa XPS (Casa Software Ltd., UK) after subtraction of a Shirley type baseline. The peak ratios for various elements are corrected by sensitivity factors. The energy scale was calibrated with

reference to the $\text{Au}_{4f7/2}$ peak at 84 eV and the binding energies were calculated with respect to the C_{1s} peak fixed at 285 eV. Analysis chamber pressure during the scans is below 10^{-8} torr.

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CHAPTER 8

HIGH ENERGY HYBRID BATTERIES AND THE USE OF SPECIAL ELECTROLYTE FORMULATIONS

Abstract

Fire-retardant electrolyte chemistries have attracted great attention given their potential to solve the grand challenges of alkali-ion batteries: safety, use of metallic anodes and anodic stability. Whereas extensive analysis and correlations are drawn to explain their unusual electrochemical behavior, one essential property, their effect on redox potentials of battery components (redox potential shift) pervasively lacks a strict description and quantification. Here evidences are provided that the strong solvation of Li^+ by organic phosphates, the widely used flame-retardant constituents, induces a negative redox potential shift by as much as 500 mV. These evidences then lead to the demonstration that the redox potential shift is characteristic of Li-cation (de)-solvation processes whereas negligible for other processes. This has important consequences for high energy hybrid batteries. These findings also shine a different light on the enhanced anodic stability of these unconventional battery electrolyte formulations, but also serve as a proof of concept that the output voltage, and consequently the energy density, of a dual-ion graphite or organic battery can be increased by the proper choice of an electrolyte that induces a shift in the redox potential of lithium-based electrodes.

8.1 Generalities

From the early stages of battery developments, carbonate solvents have been used to dissolve LiPF_6 salt providing electrolytes with optimal ionic conductivities, viscosity and surface passivation properties.^[1] Due to necessity of further development of LIBs, other electrolyte properties such as high voltage stability, anode and lithium metal passivation, as well as safety regulations have been brought to the fore over the recent years. These have however required non-incremental changes of the electrolyte chemistry. Yet changing the electrolyte composition implies systematic differences in the Li-cation (Li^+) (de)solvation energies, bulk transports and interfacial transfer kinetics. In a battery, processes occurring at the interfaces will be affected if the solvation structure of Li-cation changes. The energy barrier for the transport of Li^+ at the liquid-solid interface might be closely related to the solvation ability of the solvents, and stripping off the last solvent molecule might be not only the rate-determining step but might also be affecting the electrochemical potential.

Recent developments draw particular attention to the redox potential when changing the electrolyte solvent,^[2,3] with interestingly, the redox potential changes being measurable mainly for non (Li^+)-(de)solvation processes. The works of Nakanishi *et al.* and Leverick *et al.* detailing on the impact of solvent and salt concentration on the redox potential of the I^-/I^0 redox mediator couple being noticeable recent examples.^[4,5] Further considerations on this could also benefit from the reported redox potentials in various solvent environments measured with special electrochemical cell setups.^[2,6,7] However, little is reported so far on the impact of these in Li-ion or Li-metal practical format cells.

While finalizing this work, Marinaro *et al.* published a complementary study on the influence of Li-salt concentration on the redox potential of lithium metal.^[8] Whereas this report is based on measurements performed in a concentration cell design, and the only solvent analyzed is DMSO, it provides a series of important findings that further corroborates with our results. First, it also shows that ferrocene (Fc) can be used as a reliable and unambiguous internal reference. Furthermore, authors find a non-linear redox potential dependence with salt concentration that cannot be estimated from simple consideration of Nernst equation. These points are also discussed in this work yet from a dif-

ferent perspective. Importantly, Marinaro’s work further highlights the impact of the minor changes of the electrolyte chemistry on the redox potential.

With these considerations in mind, we started the research work that we later reported in ACS Applied Energy Materials and that served as a basis for this chapter.^[9] The research disclosed herein focuses on the impact of organic phosphate solvents on the redox potential values, what could be the consequences and how these can be further exploited. In particular, low molecular weight organic phosphates have been proposed as promising non-flammable solvents or electrolyte additives, because they possess similar physical and chemical properties to carbonates such as a wide range of operating temperatures, good solubility of Li salts, low viscosity and in particular, a wide electrochemical stability window.^[10–14] High voltage stability was also observed, assigned either to improved cathode electrolyte interphase (CEI) or highest occupied molecular orbital / lowest unoccupied molecular orbital (HOMO/LUMO) bands offset for various applied phosphate chemistries.

However, the organic phosphates are also known for their strong coordination (solvation) ability toward alkali metal cations, in particular Li^+ . This has been exploited for Li-cation extraction from brines.^[15,16] Phosphate-lithium complexes can be also synthesized and isolated, further significative of strong binding of lithium cations.^[17,18] The results and discussion presented here are showing that this strong solvation (or coordination) ability of organic phosphate solvents induces a significant redox potential shift in the negative direction if the process is based on a Li^+ (de)-solvation process. On the contrary, non-lithium redox processes are not affected. When set *vs.* a Li-based reference, higher voltages are then measured for non-lithium (de)-solvation processes. Such situations can notably be met in organic radical or dual-ion batteries, but also when dealing with the observation of enhanced anodic stability of electrolytes.

8.2 Observing and quantifying the redox potential shift in presence of organic phosphates

This work was started due to intriguing experimental inconsistencies on organic radical batteries in lithium based organic phosphate electrolytes,^[19,20] which were further motivated by findings obtained

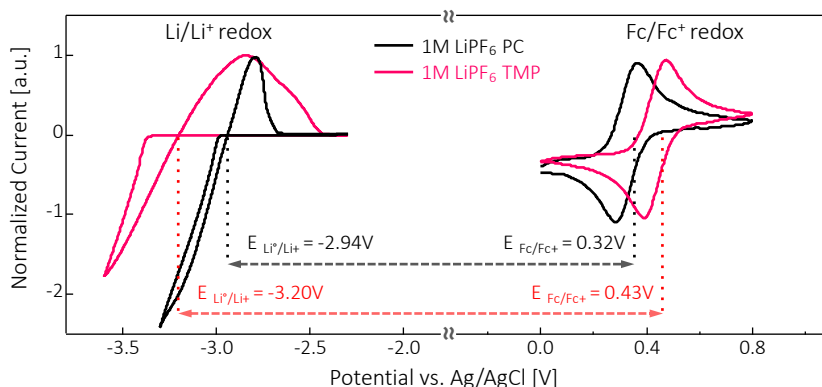


Figure 8.1 – Cyclic voltammetry of the Li/Li⁺ redox process measured in two different electrolyte solvents at 1 mV·s⁻¹ (cathodic scan) with a Ni disc as working electrode (WE), Li metal as counter-electrode (CE) and Ag/AgCl as pseudo-RE (propylene carbonate - PC and trimethyl phosphate - TMP).

For the anodic scan (Fc/Fc⁺ redox) the following conditions were applied: Ag/AgCl pseudo-RE, Pt disc as WE and Pt wire as CE; Fc concentration = 10 mM; scan rate = 25 mV·s⁻¹.

through literature survey.^[21] It has been then decided to initiate a project aiming at an in-depth analysis of the electrochemistry and determination of redox potentials in phosphate-based electrolytes, given their high affinity toward lithium cations.

To avoid any interference of the studied organic phosphate systems on the reference electrode (RE) potential, a non-Li pseudo-RE (Ag/AgCl) was implemented in the system. To further avoid any effect of the phosphate on the pseudo-RE, a internal reference redox system (RRS) was used to calibrate the redox potential. A typical example obtained by using this pseudo-RE (Ag/AgCl) together with Fc/Fc⁺ (as RRS) is shown in figure 8.1.

The first noticeable fact is the negative shift of the Li/Li⁺ redox potential (*vs.* Ag/AgCl) when replacing the propylene carbonate (PC) by trimethyl phosphate (TMP). Herein the intersection of the reduction and oxidation curves for the Li/Li⁺ process was used to determine the redox potential of the Li/Li⁺ couple.^[22] This yielded results that have been also confirmed by OCP measurements of non-polarized electrodes. A potential shift by as much as -260 mV *vs.* Ag/AgCl can be observed between the two electrolytes chemistries.

Table 8.1 – Redox response of Fc/Fc^+ evidencing the redox shift of a sodium electrode and its corresponding Na/Na^+ redox couple when changing the solvent from EC/DEC to TMP.

	$E_{1/2}$ <i>vs.</i> Na/Na^+ (V)	$E_{1/2}$ <i>vs.</i> Ag/AgCl (V)
EC/DEC	3.13	0.22
TMP	3.34	0.43

Since redox potential was measured *vs.* Ag/AgCl pseudo-RE (refer to the experimental section for details), and that this reference is known to be sensitive to the electrolyte solvent composition,^[23] the measured potential was calibrated *vs.* Fc/Fc^+ as RRS, as it was also the case in Marinaro’s work.^[8] The data shown in figure 8.1 indeed display different pseudo-RE values for Ag/AgCl electrode as the value for Fc/Fc^+ *vs.* Ag/AgCl is found +110 mV higher when TMP is added. However, the shift is opposite to the Li/Li^+ redox and the combination of the two effects results in an overall shift of -370 mV for the Li/Li^+ redox when changing the solvent from PC to TMP.

Other pseudo-RE electrodes have been also used (Ag and Pt wire) with also other RRS, such as $\text{TEMPO}/\text{TEMPO}^+$ redox. Whereas the relative values (*vs.* the pseudo-RE) were different as expected, the difference between the Li/Li^+ and internal reference redox was found consistently within the range of $-400 \text{ mV} \pm 50 \text{ mV}$ when changing the solvent from carbonates (EC, DMC, PC or mix of these) to TMP (refer also to figures 8.5 and 8.6). This confirms that the applied methods are suitable for redox potential determination. To be further mentioned that Na/Na^+ redox potential has been found to shift when changing the solvents from carbonates to phosphates (Figure 8.2). In this set of experiments, the effect of phosphates is found to significantly affect the redox potential of the Na/Na^+ couple in a similar manner as for the Li/Li^+ redox couple. The redox shift measured in these conditions was found to be of ca. 210 mV (Table 8.1). The lower magnitude of this shift being than for Li/Li^+ is explained by the lower solvation ability of Na^+ by phosphates.

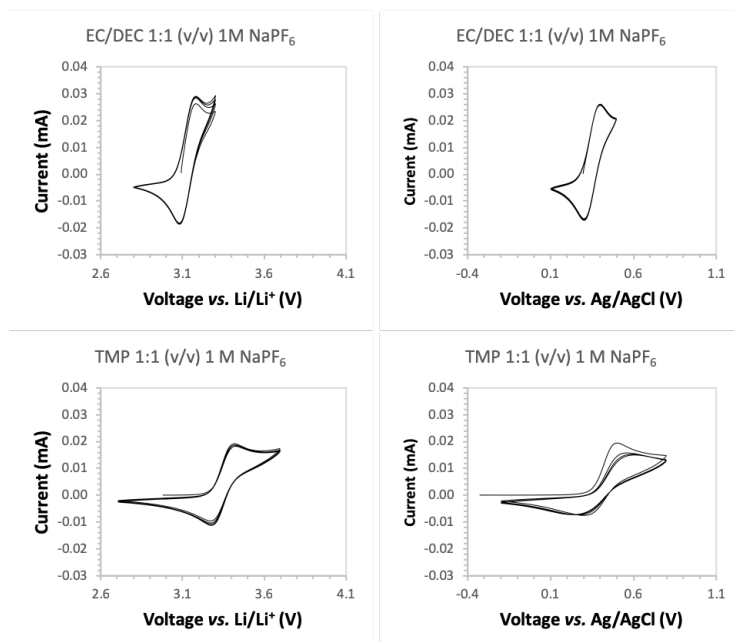


Figure 8.2 – Cyclic voltammetry experiments on a Ni disc to record ferrocene redox response (anodic polarization) at $50 \text{ mV} \cdot \text{s}^{-1}$ both versus the Na/Na⁺ CE and the Ag/AgCl in presence of NBu₄Cl (0.004 M) pseudo-RE.

8.3 Phosphate concentration impact and solvation shell structure

This intriguing significant redox potential shift was further motivating an extensive analysis of the impact of other phosphates (TMP and TEP) and their concentrations by measuring the redox potential shift (Figure 8.3a) as well as the NMR chemical shifts of selected elements - ^7Li , ^{31}P and ^{13}C (Figure 8.3b). A 1 M LiPF_6 solution in EC-DEC was used as baseline for all measurements.

The electrochemical shift analysis shows several interesting processes. First, the nature of the phosphate differently impacts the redox shift with higher values attained for TEP than TMP for the same phosphate-to-lithium molar ratio (Figure 8.3a). This can be explained by the bulkiness of the alkyl moieties. As the steric hindrance of these moieties increases, the Li^+ center is more efficiently shielded, yielding to higher stability of the solvated cation, which in turn further lowers the redox potential. This corroborates with the redox potential shift measured for other phosphorus-based chemistries (Figure 8.4).

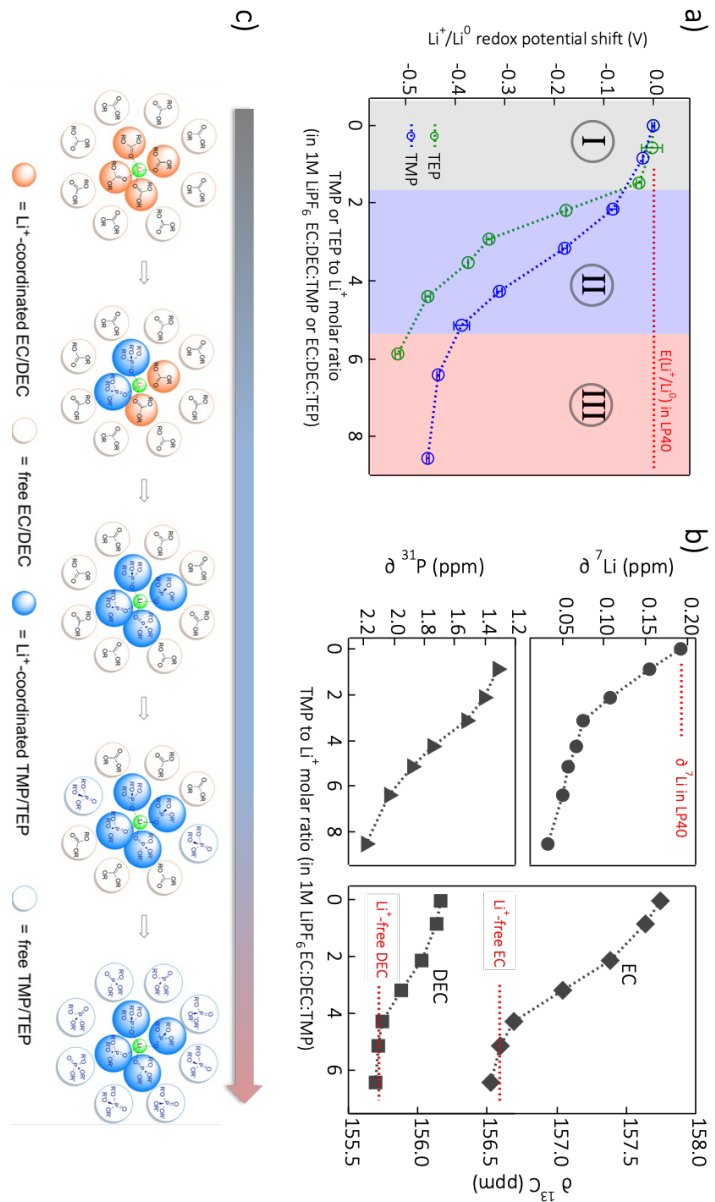
Trimethyl thiophosphate did not yield any significant shift (the shift being in fact positive, of about 30 mV, figure 8.4) in comparison to phosphates, whereas trimethyl phosphine oxide induced an important shift. This also corroborates the knowledge that the Li-cation solvation proceeds primarily via the lone pair of oxygen atoms (in this case, of the phosphate group), but also that sulphur is poorly coordinating^[17] the Li-cation. For instance, the trimethyl phosphine oxide does not contain other oxygen than the double bonded one to interact with the metal center.

An interesting aspect is the “S”-shaped dependence of the redox potential shift with the increased phosphate ratio. Three distinct regimes can be identified, that can be explained through a modified Nernst equation potential change. The equation represented hereafter considers the Li^+ activity (a_{Li}) rather than Li-salt concentration (all being maintained at 1 M in figure 8.3):

$$E = E^\circ - \frac{RT}{nF} \ln a_{\text{Li}}$$

Lithium activity in turn is the result of a complex interplay between the dissociation of the cation solvation or ion-pair complexes present

Figure 8.3 – (a) Li/Li^+ redox potential shift as function of phosphate concentration while maintaining a concentration of 1 M LiPF_6 in a ternary EC:DEC:TMP/TEP solvent. The zero shift baseline corresponds to Li/Li^+ redox potential as measured in 1 M LiPF_6 in EC-DEC. (b) Corresponding ^7Li , ^{31}P and ^{13}C shifts for various TMP concentrations in the baseline 1 M LiPF_6 in EC-DEC. (c) Schematics of the Li^+ -solvation shell upon increasing the phosphate content as suggested by NMR experiments.



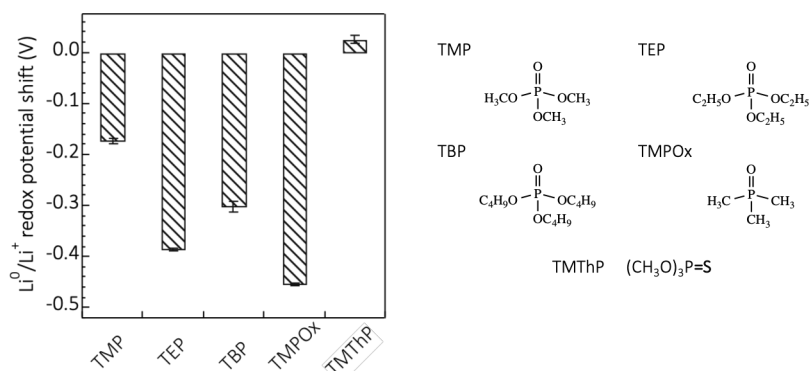
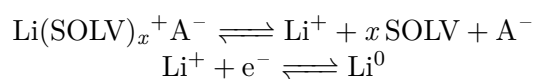


Figure 8.4 – Redox potential shift with other organophosphorous solvents derivatives. All data are obtained at a concentration of 3.68 M phosphate in the ternary EC/DEC/Organophosphorous system, all at 1 M lithium salt.

in solution (Figure 8.3c) that can be broadly resumed to the following equations:



Marinaro's work^[8] effectively predicts the redox potential variation for different salt concentrations, with a rationale based on the concentration (activity) of free solvent molecules (DMSO in their respective case). Whereas their experimental and calculated values are in good agreement, the present work relies on another rationale. The solvent (SOLV) concentration will indeed affect the desolvation equilibrium of the above-presented equation, so that at high SOLV concentrations (i.e. diluted salt regime) the equilibrium will be displaced to the left resulting in low a_{Li} .

In the ternary solvent system (EC-DEC-TMP) presented in figure 8.3, the concentration of Li^+ salt is kept at 1 M, with total solvent-to-lithium molar ratios (Table 8.5, experimental section) being well above the coordination number of lithium, broadly accepted of being around $x \approx < 4.4$ ^[12] so that the transition from excess to limited free-solvent as presented by Marinaro *et al.*^[8] cannot explain the large redox potential shift observed here.

The solvate complex dissociation constant in turn will effectively regulate the activity and thus the redox potential E . In the dilute phos-

phate region I, the solvation complexes are of $\text{Li}(\text{DEC}/\text{EC})_x(\text{TMP}/\text{TEP})_y$ general structure, where $x + y \approx 4.4$ and $x \gg y$ (Figure 8.3c, and table 8.5 in experimental section). The lithium solvation environment is largely controlled by the carbonate species so that the redox potential is marginally affected. At the other extreme, region III, saturation is observed, and the strong solvation of phosphates displaces the equilibrium toward lower a_{Li} and thus large negative redox potential shift ($E - E^\circ \ll 0V$). The intermediate region II is certainly the most sensitive to the concentration of phosphate species with a redox potential shift of 300 mV to 400 mV in a narrow phosphate concentration window.

Additional hints on the solvation strength are provided by NMR analysis of the ternary EC-DEC-TMP electrolytes (Figure 8.3b). From the carbonate group ^{13}C NMR shift (refer also to experimental section, figure 8.14, table 8.5) it can be noticed that at concentrations corresponding to a molar ratio of phosphate to lithium above 4.4, the EC and DEC are in the free, non-solvating forms, despite still being present in excess (TMP to total EC+DEC molar ratio of 0.7, refer to table 8.5, experimental section). Also, increasing the phosphate concentration results in a ^7Li NMR signal upfield shift due to replacement of carbonates by phosphates in the Li^+ solvation sphere (Figure 8.15, experimental section). ^{31}P NMR chemical shift also follows a similar trend with the free phosphate being downfielded compared to the Li-coordinated species (Figure 8.16, experimental section). Whereas electronegativity would suggest a reverse trend, our data indicate that the Li-coordination by phosphates leads to an upfield shift of the ^{31}P signal because of a major degree of d -orbital occupancy in the P-O bonds once Li cation is coordinated to $\text{O}=\text{P}$.^[24]

In addition, diffusion-ordered spectroscopy (DOSY) NMR experiments have been also performed and reported in our publication on this topic. This allowed us to determine the solvent coordination ratio of the different electrolytes as well as the lithium coordination numbers. The extensive details of this analysis are provided in the work that we reported in the literature.^[9] The analysis showed that even at low TMP content, the amount of phosphate coordinated to Li^+ reaches values as high as 95% and for slightly higher concentrations of TMP, the carbonate molecules are mostly non-coordinated, further corroborating the ^7Li , ^{31}P and ^{13}C NMR data. Coordination number of Li^+ is found between 4 and 4.8 depending on the composition of the electrolyte, consistent with

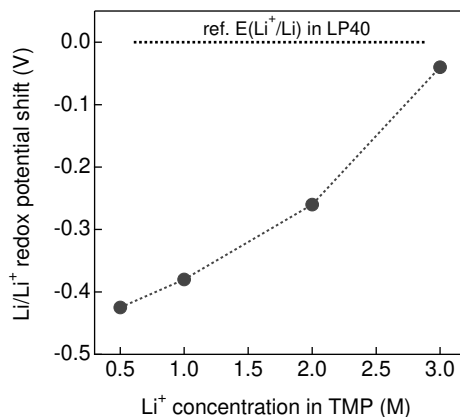


Figure 8.5 – Redox potential shift as function of Li^+ salt concentration in TMP solvent.

the reported values.^[12] Thus, both NMR and electrochemical data interpretation support the strong solvation of Li^+ by organic phosphates, so that the weak dissociation of $\text{Li}(\text{SOLV})_x + \text{complexes}$ leads to low a_{Li} resulting in a negative redox potential shift when referenced to a weaker solvating electrolyte (LP40 here; 1 M LiPF_6 in EC-DEC).

According to the analysis above, increasing the a_{Li} , should result in a positive increase of E . This is expected to be achieved by also changing the concentration of the salt and the results of various Li-salt concentrations in TMP are shown in figures 8.5 and 8.6. The set of CV experiments evidences the influence of Li salt concentration on Li/Li^+ redox potential in TMP based electrolytes. According to Nernst equation, the effect on the measured voltage difference between the TEMPO redox couple and the Li/Li^+ should affect both electrodes symmetrically: (i) Due to the increase of the counter-anion concentration (TFSI^-), TEMPO should be shifted towards lower values by a factor of 59 mV per concentration decade;^[25] (ii) the Li electrode should be affected the same way, 59 mV per decade, due to the increase of the Li^+ concentration of the system;^[8] (iii) these two effects should be canceling out each other on the resulting voltage. Yet a much important difference (about 410 mV) is observed between the lowest and highest electrolyte concentration (respectively 0.5 M and 3 M).

Corroborating Marinaro's work, dealing also with strongly solvating DMSO electrolyte solvent, the redox potential shift does not scale at

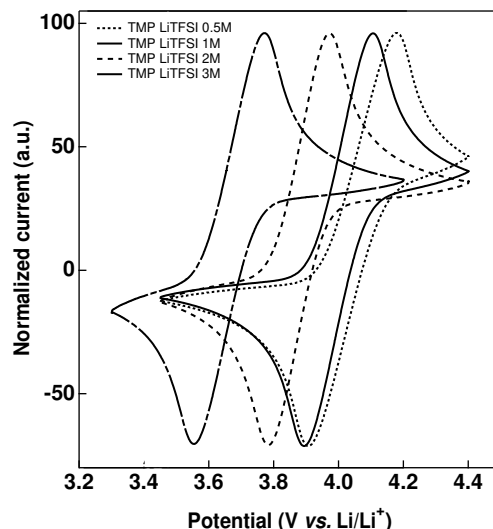


Figure 8.6 – CV of TEMPO redox responses recorded in TMP based electrolytes against a Li/Li⁺ electrode while varying the salt concentration.

59 mV/decade in the high concentration regime, as it could be expected from simple considerations of Nernst equation. This is because the increase of salt concentration affects the lithium solvation complex structure and a_{Li} does not follow a linear trend with Li-salt concentration, in particular in strongly solvating solvents. At a salt concentration below 2 M, the phosphate to lithium molar ratio is above 4.3 (8.6 for 1 M, 4.3 for 2 M) and a_{Li} is low given the strong solvation by TMP. At higher salt concentrations, there is no sufficient solvent to saturate the solvation shell and ion pairing needs to be considered to properly estimate a_{Li} . Certainly, when considering especially strongly solvating systems, salt concentration effect should not be considered as a simple extension of dilute systems.

8.4 Differentiating Li⁺ vs. non-Li⁺ (de)solvating processes

Whereas it is clear that phosphates can induce a large redox potential shift, it is worth recalling that all values reported above are based on non-Li RRS (ferrocene, TEMPO). In other words, all RRS used in this work

rely on a redox mechanism that uses anions instead of cations for charge compensation. This led us to the hypothesis that all redox processes that operate through anion rather than Li-cation charge compensation will appear shifted if measured *vs.* a Li-based pseudo-RE.

To examine this, a series of hybrid active material electrodes was prepared and tested with different electrolytes. The active material electrodes were intentionally designed so that they operate through different redox charge compensation: a Li-ion active material requiring Li^+ -(de)solvation at the electrolyte-electrode interface (e.g. LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiMn_2O_4); and a nitroxide radical (TEMPO) containing polymer (PTMA) that relies on anion and not Li-cation charge compensation during redox.

A typical set of results is shown in figure 8.7a. The cell configuration was a two-electrodes, with PTMA/LFP^[26] working electrode (WE), and Li metal counter-electrode (CE) and pseudo-RE. With such configuration, the measured cell voltage (or as typically reported potentials *vs.* Li/Li^+) is the difference between the electrode potentials of the WE and of the pseudo-RE.

The PTMA and LFP constituent responses in the two sets of electrolytes are strikingly different. There is no apparent effect on the redox potential for the $\text{LiFePO}_4/\text{FePO}_4$ couple, with a half wave redox potential at 3.42 V, that is widely acknowledged as the equilibrium redox potential of LiFePO_4 (when measured in a lithium cell). Markedly however, the half wave redox potential of PTMA increases by as much as 360 mV when in presence of 50 vol% TMP: from 3.61 V (*vs.* Li/Li^+ in 1 M LiPF_6 EC/DEC) up to 3.96 V (*vs.* Li/Li^+ in 1 M LiPF_6 EC/DEC+TMP). While the former is widely acknowledged as the redox potential of the nitroxide couple measured in aprotic electrolytes (and referenced *vs.* Li/Li^+), the latter is unusually high.

The nitroxide surrounding molecular environment has been shown to affect the reactivity (and thus, presumably, the redox potential) of the nitroxide group, but this is more related to modifications of the chemical structure of the TEMPO moiety via the introduction of functional groups.^[27] Yet there are no reported interactions mechanisms with the organic phosphates, or other solvents, as to enable such a strong redox shift. This is also supported by measurements carried out with Fc/Fc^+ and $\text{TEMPO}/\text{TEMPO}^+$ in a representative set of solvents: TMP, ace-

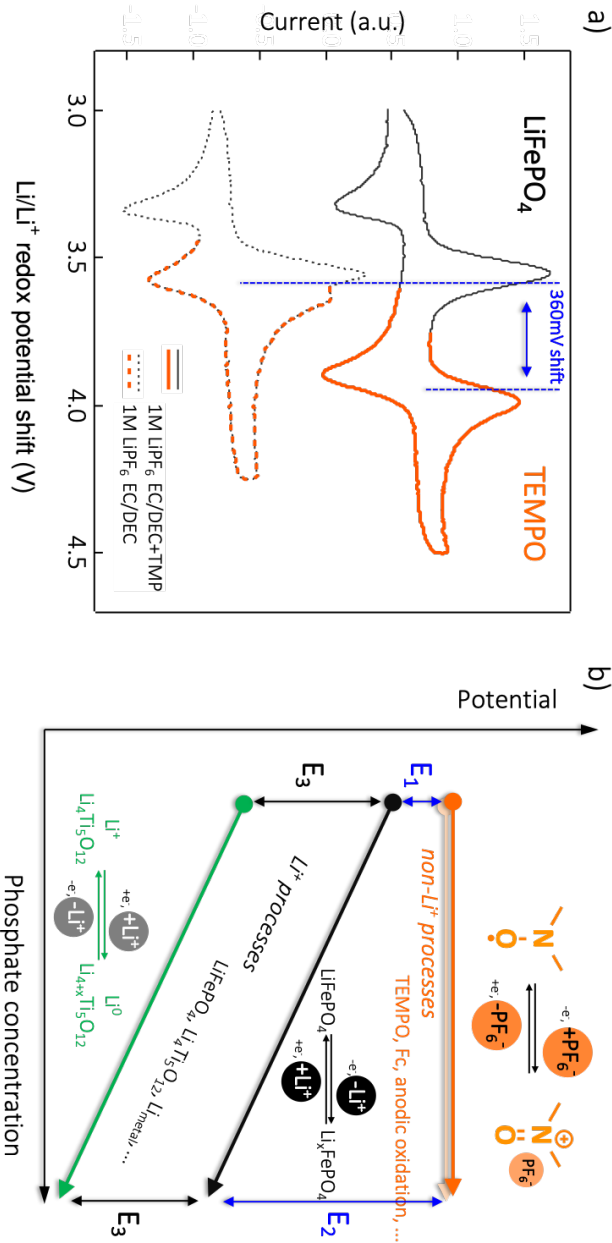


Figure 8.7 – (a) Cyclic voltammetry of a hybrid PTMA/ LiFePO_4 electrode measured in a two-electrode cell configuration, *vs.* lithium metal pseudo-reference with two different electrolytes: 1 M LiPF_6 in EC/DEC and 1 M LiPF_6 in EC/DEC/TMP. (b) Schematics of Li^+ *vs.* non- Li^+ (de)solvation redox differentiation. In the case of Li-ion cells, the influence of the solvent on the Li^+ chemical potential (or the redox potential E_3) can be considered as symmetrically affected at the positive and negative electrode interfaces.

tone, *N*-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and acetonitrile (AcCN). The results and conditions are presented in the experimental section, tables 8.3 and 8.4, respectively. During these measurements the relative positions of the redox processes of these two couples are marginally affected (± 15 mV) and on the same level as what is reported elsewhere as deviations for the values of Fc/Fc^+ in different solvents (± 12 mV).^[23] Based on these observations, TEMPO is fulfilling all criteria of RRSs as defined by Gritzner *et al.*^[23] Accordingly, another mechanism is responsible for such a high shift.

Based on the observations detailed so far, the following rationale is advanced (Figure 8.7b):

- All redox processes involving lithium (de)solvation are affected by the solvation strength with the redox potential shift affected proportionally (as schematically depicted in figure 8.7b, where E_3 will remain constant). In the case of organic phosphates, as shown by the experiments detailed above, the shift is negative, lowering thus the redox potential (Figures 8.1 and 8.7). Increasing the salt concentration reverses the trend (Figure 8.5).
- All redox processes that do not involve lithium (de)solvation are not affected by the solvation strength and their redox (or chemical) potential is barely affected or not influenced at all by the lithium-cation solvation strength or the salt concentration.

The analysis of data in figures 8.1 and 8.3 further supports this hypothesis and the results presented in figure 8.7 take a different signification in the light of these. The redox potential of PTMA is not up-shifted, and remains close to its nominal value, of 3.63 V (as for instance reported *vs.* Li pseudo-RE in carbonate electrolytes with 1 M salt). In turn, the redox potential of LiFePO_4 , but essentially, also of Li/Li^+ redox (used here as pseudo-RE) processes, are shifted to lower values. This results in no apparent redox shift of LiFePO_4 , since the working and the pseudo-RE operate through symmetrical lithium (de)solvation; yet this results in an apparent increase of the redox potential of PTMA.

The redox potential shift function of solvation strength can be generalized also to other processes that either rely, or not, on lithium (de)solvation steps, or via a combination of both (Figures 8.1 and 8.7b).

The magnitude of the shift will be dependent on the nature of the solvent (Figure 8.3) but also on the relative concentrations of both lithium salt and solvent (Figure 8.5).

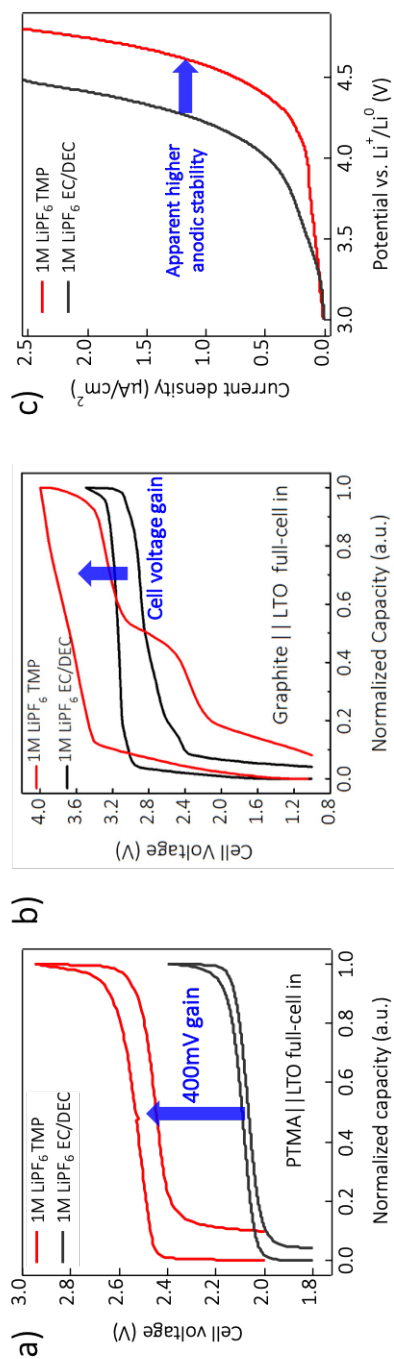


Figure 8.8 – Voltage gain in dual-ion (a) PTMA-LTO and (b) graphite-LTO cells, as well as (c) increased apparent anodic stability by tuning the lithium cation solvation strength.

8.5 Impact on potential applications

Considering the potential general impact of these findings, the next step was the design and study of electrochemical cells where the redox potential differentiation between lithium and non-lithium (de)solvation processes can lead to significative improvements.

The first set of experiments concerns the dual-ion battery chemistries (Figure 8.8a, b) since these have asymmetric redox charge compensation mechanisms: Li^+ redox or (de)solvation at the anode and anion insertion at the cathode. The latter implies no Li^+ (de)solvation at the cathode electrode interface so any redox potential shift induced by Li^+ solvation will not be measured here. In other words, the redox potential will not be affected for the nitroxide radical in the PTMA electrode (Figure 8.8a), or for PF_6^- anion intercalation into graphite electrode (Figure 8.8b). In turn, at the anode electrode side, since Li^+ (de)solvation is required, either for Li^+ intercalation in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 8.8a, b), or for Li/Li^+ redox (Figure 8.9) the solvation strength will shift the redox potential to lower values.

And as designed, the cell voltage of the cells is increased as expected when replacing the carbonate solvents by TMP. A PTMA-LTO cell has a nominal voltage of 2.07 V when operated in carbonate electrolytes. This is consistent with known and measured values for PTMA and LTO redox potential, when measured in 1 M salt carbonate electrolytes: 3.63 V and 1.6 V, respectively. When assembled with 1 M LiPF_6 in TMP electrolyte, an average cell voltage of 2.45 V is measured, that could be frenziedly assigned to some exotic interactions between the phosphate molecules and the nitroxide redox centre. Yet according to the analysis presented in this chapter, this is the result of shifting the chemical potential at LTO interface to lower values. A similar rationale applies for the graphite anion cell (Figures 8.8b and 8.9) where the operational voltage window while changing the electrolyte chemistry and composition can lead to different performances as also observed in some recent reports.^[28–31]

Another important consequence is the apparent enhanced anodic stability of the electrolytes, if the measurement is done *vs.* a Li-based pseudo-RE (Figure 8.8c). In the absence of active Li-ion cathode materials, the reactions taking place at the working electrode under high anodic polarization is a complex interplay between the oxidation of anion salts, oxidation of solvent molecules as well as corrosion of current col-

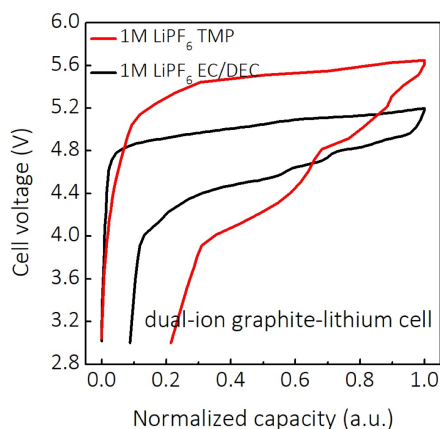
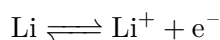


Figure 8.9 – Dual-ion graphite-Li cells cycled with 1 M LiPF₆ in EC-DEC and TMP electrolytes. The higher polarization in the phosphate electrolyte is also the result of high solvation strength by phosphates resulting in poorer de-solvation kinetics of the lithium cations.

lector. These can be all treated as having the following general reaction equation:



Important, in the light of the analysis presented in this chapter, the lithium solvation strength can be expected to affect insignificantly the chemical potential of these oxidation processes since these are not based on Li (de)-solvation processes. Indeed, when performing a linear voltammetry scan on stainless steel electrode surface of the most significative electrolyte formulation examples in this work, an enhanced anodic stability is noticed while increasing the amount of organic phosphate constituents. As shown in figure 8.8c, the onset^[32] as well as the electro-oxidation amplitude are shifted to higher redox potential when comparing 1 M LiPF₆ in TMP to EC/DEC electrolyte systems. To note, the magnitude of the shift is comparable to the redox potential shift when in the presence of TMP (Figure 8.3). Although surface passivation from TMP molecules could be also taken into account, the apparent increased anodic stability is rather the result of lowering the pseudo-RE lithium metal electrode potential in the strongly solvating environment. Such considerations on redox potentials and stability of components should be carefully reviewed when dealing with custom electrolyte formulations,

whatever the type of cell considered. In the context of dual-ion battery applications, a systematic study of these effects on all processes involved could certainly help such approaches to go beyond the proof of concept.

8.6 First attempts toward a LTO-PTMA full cell

To demonstrate the practical use of organophosphate-based electrolytes in an actual application, we decided to assemble a few half and full cells. The full cell demonstration is relying on LTO as negative electrode material.

Electrodes based on LTO were produced following a typical procedure, i.e. the doctor blade method. All electrodes produced for this study are displaying the same composition: LTO / SC45 / PVDF 80:10:10 (w:w:w) and have been casted on aluminum foil. This coated material was punched into discs (1.25 cm, coated with typically 3.5 mg of composite) for coin cell assembly. Further details about the electrode preparation are provided in experimental section.

For the positive electrode material, we decided to rely on crosslinked PTMA. This PTMA has been synthesized as reported earlier by us.^[33] This material was processed using a non-conventional method, similar to the one we implemented for our MWCNT-*g*-PTMA materials.^[19,34] The advantage of this method is that it allows more easily a precise control over the active material loading. This is useful to realize a good capacity match with respect to the LTO negative electrode to be used in the resulting full cell.

Practically, MWCNTs were dispersed in butanol under sonication and filtered over a PVDF membrane. Next, PTMA-10%C was suspended together with MWCNTs (4/1 ratio, w:w) in butanol and filtered over the first MWCNT layer. MWCNTs were added to the second layer to enhance the electrical conductivity but more importantly to provide a good integrity of the final fabric. On the other hand, the first layer mat is acting as a current collector and was found to allow an easy peel-off from the membrane. The resulting buckypaper was finally punched into discs (1.25 cm diameter, typically with mass targets between 4 mg and 8 mg) with overall composition of 33 wt% MWCNTs and 66 wt%

PTMA-10%C.

The electrochemical of these accordingly prepared electrodes was first evaluated in half-cell two-electrode configuration with lithium metal acting as both counter and pseudo-reference electrode. The evaluation was carried out to compare the TMP-based electrolyte with the standard carbonate-based formulation.

The electrolyte composition selected for half-cell evaluation and the full-cell implementation had the following composition: EC-DEC-TMP 1/1/2 (v:v:v), 1 M LiPF₆. In the results presented next, the cell behaviors are evaluated against the corresponding standard formulation: EC-DEC 1/1 (v:v), 1 M LiPF₆. The TMP-based formulation was chosen thanks to its ability to afford a significant redox shift as demonstrated in the previous sections.

Based on these experimental requirements, LTO-based electrodes were first assembled in coin cells using a half-cell configuration. The results of galvanostatic cycling at C/10 are depicted in figure 8.10. Using the standard EC-DEC formulation, the LTO electrode displays its characteristic plateau centered at 1.54 V *vs.* Li/Li⁺ with moderate polarization (90 mV). The capacity displayed by the electrode (ca. 140 mAh·g⁻¹) remains stable over the cycles and is reasonably close to the practical capacity frequently reported in the literature (about 150 mAh·g⁻¹).^[35] As for the cell cycled with TMP-based electrolyte, the charge-discharge plateaus are centered at 1.55 V *vs.* Li/Li⁺ in agreement with our expectations. Regarding the cycling capacity, the initial charge-discharge value (120 mAh·g⁻¹) is observed to be lower than expected, yielding 80% of the value achieved with the standard formulation. Interestingly, a capacity decay is observed during the first ten cycles but is less pronounced during the following cycles, concomitant with the decrease of the polarization gap decreasing from 190 mV to 100 mV around the same cycle index value. This could be tentatively ascribed to irreversible phenomena happening at the surface of the LTO electrode material.

As for PTMA-based electrodes, some peculiar electrochemical phenomena led us to change the cycling procedure to provide a better insight. Indeed it was decided to cycle the half-cells in cyclic voltammetry mode. This is justified by the excellent rate capabilities of PTMA but more importantly by the fact that cyclic voltammetry offers a better reading of overlapping and complex electrochemical behavior in the

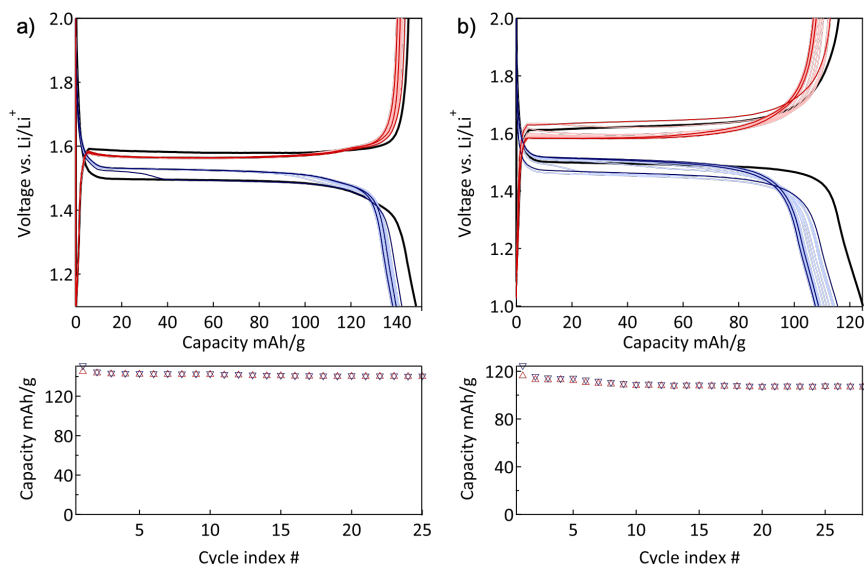


Figure 8.10 – LTO-Li half-cell galvanostatic cycling with (a) standard carbonate-based *vs.* (b) TMP-based electrolyte. The electrolytes had the following compositions, 1 M LiPF_6 in EC-DEC 1:1 (v:v), and 1 M LiPF_6 in EC-DEC-TMP 1:1:1 (v:v:v), respectively. The cells were cycled at C/10.

present case. The results for both electrolyte compositions are presented in figure 8.11a. As for the PTMA half-cell using standard formulation, the electrochemical response is centered around 3.6 V *vs.* Li/Li^+ with a relatively narrow peak-to-peak separation 170 mV, as expected. Over the cycles, the peaks are well superimposed and the capacity remained almost constant.

As for the TMP-based electrolyte, the electrochemical response is observed at 4 V, consistent with the shift results presented in the previous sections (Figure 8.11b). In contrast to the half-cell using the standard electrolyte, the redox response is not fully reversible and is affected by a second peak at 4.3 V during the oxidation. While this second peak disappears during the subsequent oxidation scan, the main peak remains relatively broad. This should be ascribed to a remaining irreversible process overlapping with the expected oxidation of the nitroxide function into the oxoammonium cation. Over the following cycles, the oxidation peak becomes narrower, the reversibility is improving and the peak-to-peak separation decreases (120 mV). After ten cycles the capacity decay levels off and the overall capacity retention is about 65%

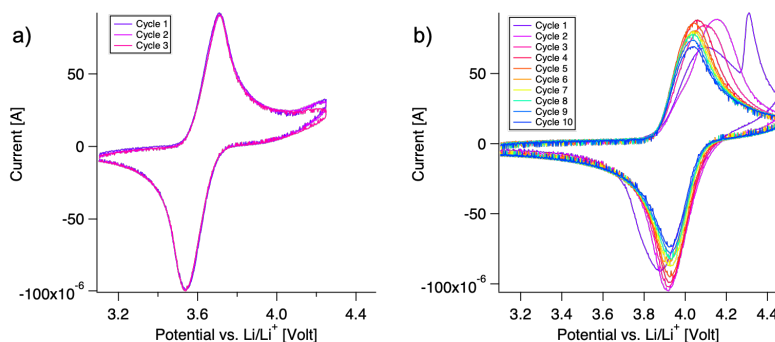


Figure 8.11 – PTMA-Li half-cell CV cycling with (a) standard carbonate-based *vs.* (b) TMP-based electrolyte. The electrolytes had the following compositions, 1 M LiPF₆ in EC-DEC 1:1 (v:v), and 1 M LiPF₆ in EC-DEC-TMP 1:1:1 (v:v:v), respectively. CV scans were recorded at $0.2 \text{ mV} \cdot \text{s}^{-1}$.

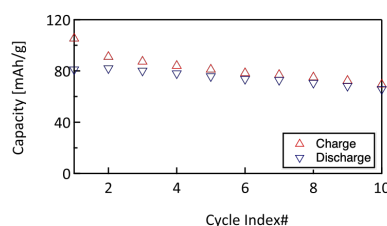


Figure 8.12 – PTMA-Li half-cell CV cycling with TMP-based electrolyte. The electrolyte had the following composition, 1 M LiPF₆ in EC-DEC-TMP 1:1:1 (v:v:v). CV scans were recorded at $0.2 \text{ mV} \cdot \text{s}^{-1}$.

(Figure 8.12). Although no evidence can be provided at this point, the irreversible process observed here could be related to impurities present in the commercial TMP used for the electrolyte formulation which could be originating from its synthesis. Nevertheless, these PTMA-based electrodes, as well as the LTO ones, are considered as valuable materials for a full-cell demonstration.

As first step for our LTO-PTMA full-cell evaluation, we carried the assembly of a cell using the standard carbonate formulation. This cell is designed to embed a moderate excess of PTMA capacity (10%) with respect to the negative LTO electrode (theoretical values). The charge discharge curves and the capacity retention plot are presented in figure 8.13a. The capacity displayed in the chart is relative to the LTO active material and the cell was cycled at C/10 with respect to the neg-

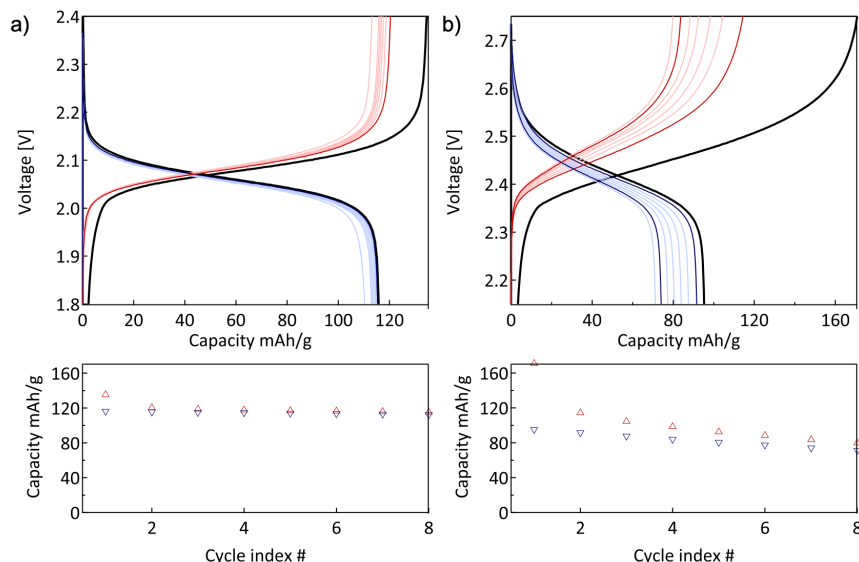


Figure 8.13 – PTMA-LTO full-cell galvanostatic cycling with (a) standard carbonate-based *vs.* (b) TMP-based electrolyte. The electrolytes had the following compositions, 1 M LiPF₆ in EC-DEC 1:1 (v:v), and 1 M LiPF₆ in EC-DEC-TMP 1:1:1 (v:v:v), respectively. The cells were cycled at C/10. Both cells have their electrodes designed to display slight excess (10%) of positive electrode *vs.* negative electrode capacity on the basis of their theoretical values. The capacity is plotted with respect to LTO active material loading.

ative electrode. In this experiment, the cell delivered a stable capacity (about 116 mAh·g⁻¹ with respect to LTO active material loading) relatively close to the expected values based on half-cell testing (which allowed LTO to deliver 140 mAh·g⁻¹). In addition, the overall redox response was occurring within a voltage window lower than 150 mV, and the charge-discharge plateaus was found centered around 2.07 V, as expected based on $E_{1/2}$ of PTMA and LTO. Based on these results, the components and design of the cell were considered as valuable for further testing with the TMP-based formulation.

The same full cell design was then implemented with LiPF₆ in EC-DEC-TMP 1:1:1 (v:v:v) and testing was carried out relying on the same conditions (galvanostatic cycling at C/10). Due to a pronounced irreversible behavior in the first cycle, the capacity extracted from the cell (95 mAh·g⁻¹) is significantly lower than with the standard carbonate for-

Table 8.2 – Comparison of characteristic redox responses values of PTMA-Li, LTO-Li, and PTMA-LTO cells. The electrolytes are either a standard carbonate-based formulation or a TMP-based formulation, both using 1 M LiPF₆.

Cell	Solvent	Ratio	E_{ox} [V]	E_{red} [V]	$E_{1/2}$ [V]
PTMA-Li	EC/DEC	1/1	3.71	3.54	3.62
PTMA-Li	EC/DEC/TMP	1/1/2	4.04	3.92	3.98
LTO-Li	EC/DEC	1/1	1.58	1.49	1.53
LTO-Li	EC/DEC/TMP	1/1/2	1.65	1.46	1.55
PTMA-LTO	EC/DEC	1/1	2.08	2.07	2.07
PTMA-LTO	EC/DEC/TMP	1/1/2	2.48	2.42	2.45

mulation (Figure 8.13). The initial capacity loss is certainly related to the irreversible redox response observed earlier with PTMA-Li half-cell measurements. Nonetheless, over the next cycles the loss of capacity leveled off and the redox response was found centered at a value of 2.45 V. This value is consistent with our earlier experiments presented in previous sections and corresponds to a redox shift of about 0.43 V compared to the similar PTMA-LTO cell using standard formulation (Table 8.2). The redox response was occurring over a relatively wider voltage window (200 mV) than with the standard formulation.

A first element of answer to this polarization effect could be a difference in conductivity. Yet the conductivity of TMP-based electrolytes (a few $\text{mS}\cdot\text{cm}^{-1}$) is only slightly lower than the conductivity of usual carbonate-based electrolytes (about $8\text{ mS}\cdot\text{cm}^{-1}$).^[36] On the other hand, different studies have evidenced large differences in the solvent de-solvation energies of lithium between carbonates and trimethyl phosphates (about $50\text{ kJ}\cdot\text{mol}^{-1}$),^[7,37] and it has been suggested that there is a correlation between these energies and the activation energies of the lithium de-solvation process. Since TMP is displaying a higher de-solvation energy, it is therefore expected that its activation energy is also higher, which in turns induce lower (de)-solvation kinetics.^[37]

Despite lower capacity metrics, the voltage output gain allowed our PTMA-LTO full cell with TMP to match its carbonate-based electrolyte equivalent in terms of specific energy output since the values of about

240 mWh·g⁻¹ were attained in both cases. With further enhancements of capacity that could be expected by mastering the irreversible capacity loss - using higher purity TMP-based formulations for instance - the voltage gain could enable a 20% energy density improvement to the combination of chemistries involved in this demonstration. In a broader perspective, this approach could be generalized to other dual-ion systems, opening up new possibilities for other electrode material combinations to supersede their analogous standard electrolyte implementation but also raising their competitiveness with respect to other chemistries.

8.7 Conclusion

In this work the strong solvation of lithium cation by the flame-retardant organic phosphates was demonstrated to have an important effect on the relevance of the measured electrochemical potentials if a non-adequate electrochemical configuration is employed. When both, working and pseudo-electrodes rely on lithium (de)solvation, the effect is not detectable since the redox potential shifts proportionally. The redox potential shift will thus remain elusive for any measurement set against the potential of a lithium-based reference process, independent whether a two or three-electrode set-up is used. The readings of the non-lithium processes however will be strongly affected, resulting in apparently higher redox potentials, with the amplitude of the shift being proportional to the solvation strength. The amplitude of the redox potential shift with the studied organic phosphates can be as high as -500 mV when compared to conventional carbonate-based electrolytes.

It was also demonstrated that the use of custom-formulations based on alkyl-phosphates is enabling hybrid and dual-ion batteries with higher voltage output than those based on same electrode formulations in presence of commercial carbonate-based electrolytes for lithium-ion batteries. With further optimization on the cathodic stability as well as (de)solvation kinetics, these electrolyte systems could be further exploited to build high voltage dual-ion batteries with enhanced energy density. This could be also an interesting strategy to enable high voltage cathode chemistries and batteries. Although it may be a long way to realize such electrolytes in practical application after resolving the problems above, this peculiar electrochemical feature and the mechanism presented here could be of great value not only in the development

of next-generation advanced batteries but also in the fundamental research in electrochemistry and solution chemistry.

8.8 experimental section

8.8.1 Materials

Lithium metal foils purchased from Gelon. Trimethyl phosphate (TMP, 99%, Acros), triethyl phosphate (TEP, ReagentPlus, $\geq 99.8\%$), triphenyl phosphate (TPhP, 99+%, Acros), tributyl phosphate (TBP, $\geq 99\%$, Sigma-Aldrich), trimethylphosphine oxide (TMPOx, Alfa Aesar) and trimethyl thiophosphate (TMThP, Alfa-Aesar) were dried in vacuum before use. 2,2,6,6-Tetramethylpiperidine 1-oxyl free radical (TEMPO, $>98.0\%$, TCI), ferrocene (Fc, Sigma-Aldrich), LiPF_6 (battery grade $\geq 99.99\%$ trace metals basis, Sigma-Aldrich), LiTFSI (battery grade, Sigma-Aldrich), NaPF_6 (battery grade, Sigma-Aldrich) and all phosphorous-based chemicals are degassed under vacuum prior use in an argon filled glovebox. All electrolyte solutions were purchased from Solvionic and were used as received: EC/DEC 1:1 (v:v) 1 M LiPF_6 ; PC 1 M LiPF_6 ; EC/DEC 1 M LiPF_6 ; EC/DEC 1 M NaPF_6 . 1-Butanol (99%, extra pure, Acros), MWCNT NC7000 (Nanocyl, Ltd.), copper wire (0.64 mm diameter, Puratronic, 99.999% metal basis, oxygen free, $\approx 2.87 \text{ g}\cdot\text{m}^{-1}$, Alfa Aesar), NMP (ACS Reagent, Acros), were used as received. Ag, Ni and Pt pseudo-RE disc electrodes (diameter 2 mm), and Pt wire counter-electrodes, styrene-butadiene rubber (SBR) and carboxymethyl cellulose (CMC) are purchased from MTI Corp.

8.8.2 Methods

8.8.2.1 Cyclic voltammetry of the Li/Li^+ redox process

This experiment was carried in a glovebox under argon. A beaker cell was loaded with the electrolyte solution, TMP 1 M LiPF_6 . The first electrochemical test involved the following set of electrodes: a Ni disc as WE, a lithium chip stuck on a copper support as CE, Ag/AgCl in presence of NBu_4Cl (0.004 M) as pseudo-RE electrode. Using this setup, a linear scan voltammetry was performed at $1 \text{ mV}\cdot\text{s}^{-1}$ (cathodic polarization) between -2.30 V and -3.60 V *vs.* Ag/AgCl.

Next the calibration (anodic polarization) was carried out using Fc ($2 \text{ mg}\cdot\text{mL}^{-1}$) added to the same electrolyte medium as reference redox system, in combination with and a Pt disc WE, a Pt wire CE and same

Ag/AgCl RE. The voltage window was scanned between 0.00 V and 0.80 V *vs.* Ag/AgCl at 50 mV·s⁻¹.

The same two experiments were then carried out with PC 1 M LiPF₆ commercial electrolyte, only the voltage window for the cathodic polarization was adjusted to be -2.3 V to -3.3 V *vs.* Ag/AgCl.

8.8.2.2 Cyclic voltammetry to study the Li-salt concentration effect

The same setup presented beforehand to study the Li/Li⁺ redox process was used to evidence the voltage upshift effect via the variation of the Li⁺ salt concentration in TMP. The electrolytes used here are based on LiTFSI, varying the concentrations thereof (0.5 M; 1 M; 2 M; 3 M) dissolved in TMP.

8.8.2.3 Synthesis of PTMA-10%C

The synthesis was carried out as reported elsewhere.^[33] This material has been used for all PTMA-based electrodes.

8.8.2.4 PTMA electrodes used for studies of phosphate concentration effect

600 mg of PTMA-10%C composite were mixed with 250 mg of SC45 and thoroughly grinded. To this mixture, 50 mg of SBR (dissolved in water, 5 wt%) and 100 mg of CMC (dissolved in water at a concentration of 2 wt% - 4 wt%) were added and thoroughly stirred. The obtained slurry was coated on carbon coated aluminum foil followed by drying in air at 50 °C. Disks of 0.5 in diameter (loading around 5 mg·cm⁻²) were subsequently punched and pressed at 6 tons·cm⁻². Prior the cell assembly, the electrodes were dried at 55 °C in vacuum for 12 h.

The electrodes were tested in half-cell configuration using Li-metal foil as reference and counter electrode. CR2032 coin-cells were used. One sheet of Celgard separator was placed in between the working electrode and lithium disk. The cells were activated by soaking the electrodes and the separator with the electrolyte solution. The electrolyte solution

was prepared by mixing EC/DEC 1 M LiPF₆ commercial electrolyte, adding either TEP or TMP, and LiPF₆ to adjust the final lithium salt concentration to be equal to 1 M. The cells were assembled in an argon-filled glove box.

8.8.2.5 PTMA-based hybrid electrodes preparation

Same procedure as described beforehand for all-PTMA slurry preparation and coin-cell assembly was applied for hybrid electrodes with the following compositions (weight ratios): PTMA-10%C / LiFePO₄ / SC45 / CMC / SBR 40:20:25:10:5. These cells were tested in cyclic voltammetry experiments using either EC/DEC/TMP 25:25:50 (v:v:v) 1 M LiPF₆ or EC/DEC 50:50 (v/v) 1 M LiPF₆ (scan rate = 0.2 mV·s⁻¹).

8.8.2.6 Cell design of Li₄Ti₅O₁₂-PTMA dual-ions batteries

Li₄Ti₅O₁₂ (LTO) anode. Slurry preparation from LTO, SC45 and PVDF (80:10:10 w/w/w) through ball-milling of the constituents (400 rpm, 45 min). The slurry was spread on carbon coated Al foil by means of the doctor blade method. The wet film thicknesses were adjusted to 500 μm (loadings around 3.0 mg·cm⁻²). The coated foil was then cut into discs (diameter, 0.5 in, coating mass around 8.0 mg each).

PTMA cathode. Self-standing electrodes were produced using a vacuum filtration process over a PVDF 0.2 μm filter. The filtration device is a Millipore set-up. Pristine MWCNTs (6.25 mg) were dispersed in butanol (200 mL) using bath sonication for 30 min. This first suspension was filtered on the PVDF filter. A suspension of PTMA/10%C (25 mg) and pristine MWCNTs (6.25 mg) was then prepared in BuOH (400 mL, bath sonicated for 30 min) and filtered over the first layer formed on PVDF (3.40 cm diameter). Electrodes were first dried in ambient air at room temperature for 2 h, then at 60 °C under vacuum for 24 h. The resulting buckypaper was then cut into discs (diameter, 0.5 in, mass around 7.5 mg each).

Cell assembly. The electrodes were assembled in a CR2025 case, using Celgard separator, in a glovebox under argon, using either EC/DEC 1 M LiPF₆, or TMP 1 M LiPF₆ as electrolyte.

Electrochemical testing. Galvanostatic cycling was carried out at C-rate equal to C/5 with respect to the LTO electrode capacity.

8.8.2.7 Electrolyte stability window

The electrolyte anodic stability was obtained in a CR2032 coin cell assembled in an Ar filled glovebox, using Li as WE and pseudo-RE, carbon-coated Al foil as CE and Celgard as separator. The electrolyte was either TMP 1 M LiPF₆ or either EC/DEC 1 M LiPF₆ and cyclic voltammetry experiments were carried out at 1 mV·s⁻¹.

8.8.2.8 Voltage shifts with other phosphorus-based derivatives

These experiments are relying on the same procedure designed to study the phosphate concentration effect. The electrolytes used here have the following composition: EC / DEC / Pi 25:25:50 (v/v/v) 1 M LiPF₆, where Pi is one of the following compounds, TBP, TMPOx, TMThP.

8.8.2.9 Na based systems

This experiment was carried in a glovebox under argon. A beaker cell was loaded with the electrolyte solution, TMP 1 M NaPF₆. The first test involved the following set of electrodes: a Ni disc as WE, a sodium chip stuck on a copper support as CE, Ag/AgCl in presence of NBu₄Cl (0.004 M) as pseudo-RE electrode. Fc (2 mg·mL⁻¹) was added to the electrolyte medium as reference redox system (RRS). An anodic polarization was carried out and ferrocene redox response was recorded at 50 mV·s⁻¹ both versus the Na/Na⁺ CE and the Ag/AgCl pseudo-RE.

8.8.2.10 Redox potential of TEMPO/TEMPO⁺ vs. Fc/Fc⁺

First TEMPO is dissolved (0.02 M) and cyclic voltammetry measurements are performed. Afterwards Fc is dissolved in the same medium as

TEMPO. TEMPO and ferrocene are dissolved in the solvent for measurements at approximately the same molar concentrations. Then another set of cyclic voltammetry scans is performed, allowing to observe the redox activities of both TEMPO and Fc redox species.

8.8.2.11 Electrochemical testing instrumentation

All cyclic voltammetry experiments have been carried out under an argon atmosphere (<0.1 ppm H_2O , <0.1 ppm O_2) in a glovebox from Innovative Technology, Inc., using a PARTSTAT 3000 potentiostat from Princeton Applied Research. All galvanostatic cycling experiments are performed using an Arbin BT-2043 multichannel potentiostat. Unless specified otherwise, all values of capacity are reported with respect to the redox active material mass in the electrode.

8.8.3 NMR experiments

A series of electrolyte solutions were prepared in an argon atmosphere glovebox by dissolving 1 M LiPF_6 or LiTFSI in a mixture of EC/DEC/TMP or EC/DMC/TMP (1:1:x, v:v:v %), respectively. Percentage of TMP ranges from 0 (EC/DEC/TMP or EC/DMC/TMP 1:1:0 v:v:v) to 100 (EC/DEC/TMP or EC/DMC/TPM 0:0:1 v:v:v), passing by 10%, 25%, 37.5%, 50%, 60% and 75% (as reported in the table 8.5). Toluene (Sigma-Aldrich, anhydrous, aliquots of 25 μL to each NMR tube) was added as internal standard for DOSY NMR analyses. Moreover, in DOSY NMR analyses some of these solutions have been compared with the corresponding unsalted electrolyte mixtures.

Neat samples of these solutions were analyzed by NMR spectroscopy using standard 5 mm thin-walled tubes with coaxial NMR inserts (0.15 mL of C_6D_6 (Eurisotop) therein) placed inside the NMR tubes. All ^1H , ^7Li , ^{13}C , and ^{31}P NMR spectra were recorded at room temperature (296 K) on a Bruker Avance 500 spectrometer operating at 500.13 MHz, 194.37 MHz, 125.76 MHz and 202.46 MHz, respectively. Experiments were run using a BBO{1H,X} probehead equipped with a z -gradient coil, allowing a maximum gradient strength of $0.5 \text{ T}\cdot\text{m}^{-1}$. The ^1H and ^{13}C resonances were referenced to C_6D_6 (7.16 ppm for ^1H and 128.06 ppm for ^{13}C NMR spectra). ^{31}P and ^7Li NMR spectra were calibrated using external references: a 85% H_3PO_3 solution in H_2O ($\delta = 0.00$ ppm)

for ^{31}P NMR spectra and 1.0 M $^7\text{LiCl}$ solution in D_2O for ^7Li NMR experiments. Standard zg programs were employed for 1D NMR experiments. A Waltz-16 decoupling scheme with a pulse of 80 μsec was used for $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR analyses. ^1H DOSY measurements were performed using the standard Bruker ledbpgp2s pulse program with 16 t_1 increments on 32 K data points. Acquisition times were fixed to 4.2 s, 2.0 s and 0.65 s for ^1H , ^7Li and ^{31}P , respectively, and relaxation delays (D_1) ranged from 2 s (^7Li and ^{31}P) to 30 s (^1H). Diffusion times (D_{20}) of 0.5 s (^1H) and 1.0 s (^7Li and ^{31}P) and rectangular gradient pulse durations (P_{30}) of 0.8 ms, 2 ms and 3.0 ms were applied for ^1H , ^7Li and ^{31}P , respectively. Gradient recovery delays between 0.15 ms (^1H) and 0.5 ms (^7Li and ^{31}P) followed the application of each gradient pulse. Data were accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% for 16 gradient increment values. Individual rows of the quasi-2D diffusion databases were phased and baseline corrected. Processing of NMR data were performed using Topspin software (by Bruker supplier), and the actual diffusion coefficients used for diffusion analysis were measured by T_1/T_2 relaxation module.

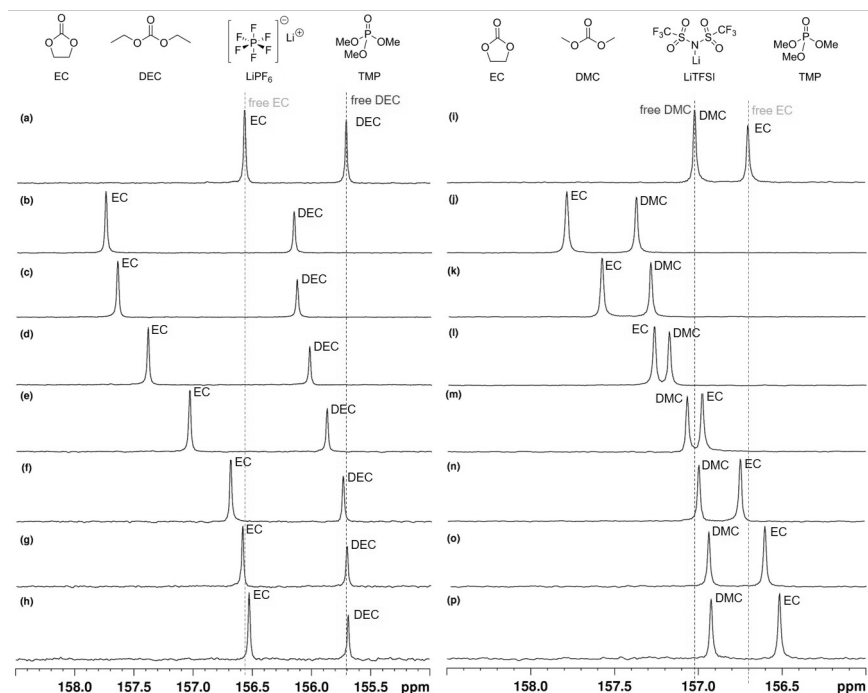


Figure 8.14 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Left: (a) EC + DEC, (b) EC + DEC + LiPF_6 , (c) EC + DMC + LiPF_6 + (10%) TMP, (d) EC + DEC + LiPF_6 + (25%) TMP, (e) EC + DEC + LiPF_6 + (37.5%) TMP, (f) EC + DEC + LiPF_6 + (50%) TMP, (g) EC + DEC + LiPF_6 + (60%) TMP, (h) EC + DEC + LiPF_6 + (75%) TMP. Right: (i) EC + DMC, (j) EC + DMC + LiTFSI , (k) EC + DMC + LiTFSI + (10%) TMP, (l) EC + DMC + LiTFSI + (25%) TMP, (m) EC + DMC + LiTFSI + (37.5%) TMP, (n) EC + DMC + LiTFSI + (50%) TMP, (o) EC + DMC + LiTFSI + (60%) TMP, (p) EC + DMC + LiTFSI + (75%) TMP. The spectra are restricted to the 160.0 ppm $\div$ 155.0 ppm zone. Note that, on the spectra on the right, NMR chemical shifts of "free" DMC/EC in (i) and the "supposed" to be "free DMC/EC species" in (n-p) don't line up well probably because of a different viscosity of the solutions.

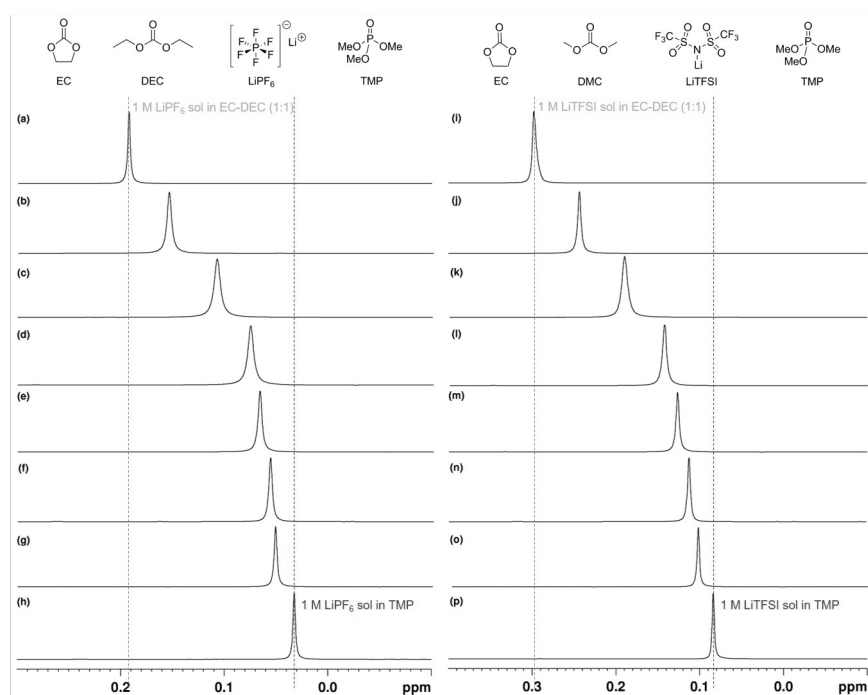


Figure 8.15 – ^7Li NMR spectra. Left: (a) EC + DEC + LiPF₆, (b) EC + DMC + LiPF₆ + (10%) TMP, (c) EC + DEC + LiPF₆ + (25%) TMP, (d) EC + DEC + LiPF₆ + (37.5%) TMP, (e) EC + DEC + LiPF₆ + (50%) TMP, (f) EC + DEC + LiPF₆ + (60%) TMP, (g) EC + DEC + LiPF₆ + (75%) TMP, (h) LiPF₆ + TMP. Right: (i) EC + DMC + LiTFSI, (j) EC + DMC + LiTFSI + (10%) TMP, (k) EC + DMC + LiTFSI + (25%) TMP, (l) EC + DMC + LiTFSI + (37.5%) TMP, (m) EC + DMC + LiTFSI + (50%) TMP, (n) EC + DMC + LiTFSI + (60%) TMP, (o) EC + DMC + LiTFSI + (75%) TMP (p) LiTFSI + TMP.

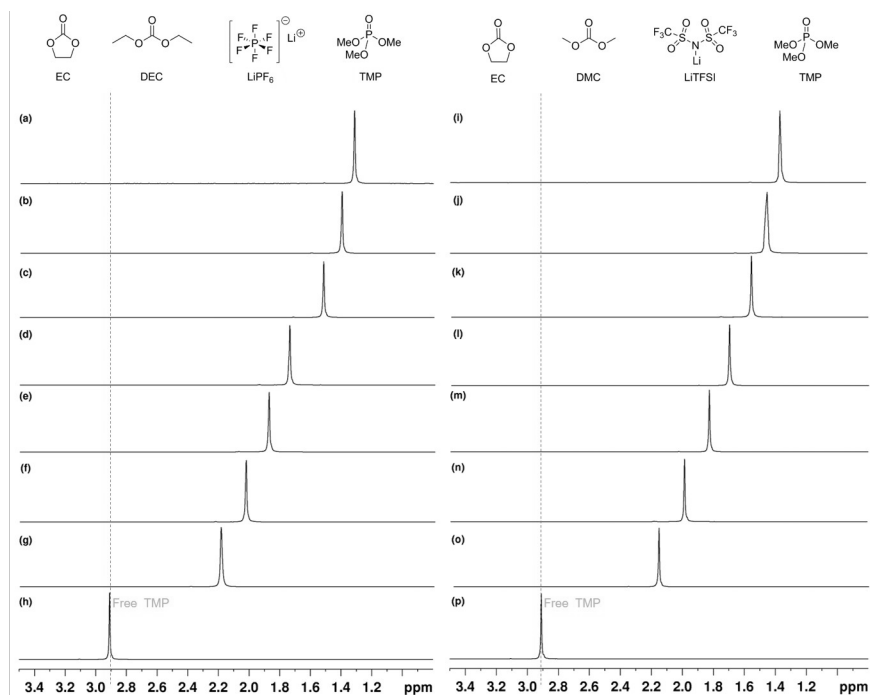


Figure 8.16 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Left (a) EC + DMC + LiPF_6 + (10%) TMP, (b) EC + DEC + LiPF_6 + (25%) TMP, (c) EC + DEC + LiPF_6 + (37.5%) TMP, (d) EC + DEC + LiPF_6 + (50%) TMP, (e) EC + DEC + LiPF_6 + (60%) TMP, (f) EC + DEC + LiPF_6 + (75%) TMP, (g) LiPF_6 + TMP, (h) TMP. Right: (i) EC + DMC + LiTFSI + (10%) TMP, (j) EC + DMC + LiTFSI + (25%) TMP, (k) EC + DMC + LiTFSI + (37.5%) TMP, (l) EC + DMC + LiTFSI + (50%) TMP, (m) EC + DMC + LiTFSI + (60%) TMP, (n) EC + DMC + LiTFSI + (75%) TMP, (o) LiTFSI + TMP, (p) TMP.

Table 8.3 – Conditions for CV of TEMPO/TEMPO⁺ vs. Fc/Fc⁺ with different electrolyte compositions.

Solvent	Fc (mM)	TEMPO (mM)	WE	CE	Pseudo-RE	Salt	Salt Conc. [M]	Scan rate (V.s ⁻¹)
TMP	5	5	Pt disc	Pt wire	Pt wire	LiClO ₄	0.1	100
Acetone	5	5	Glassy C disc	Pt wire	Pt wire	LiClO ₄	0.1	100
NMP	5	10	Glassy C disc	Pt wire	Pt wire	TBAClO ₄	0.1	100
DMF	5	5	Pt disc	Pt wire	Pt wire	TBAClO ₄	0.1	100
AcCN	5	5	Glassy C disc	Pt wire	Pt wire	TBAClO ₄	0.1	100

Table 8.4 – CV results of TEMPO/TEMPO⁺ vs. Fc/Fc⁺ with different electrolyte compositions.

Solvent	Fc/Fc ⁺		TEMPO/TEMPO ⁺				$\Delta E_{1/2}$ (mV vs. Fc/Fc ⁺)
	E_{ox} (mV)	E_{red} (mV)	$E_{1/2}$ (mV)	E_{ox} (mV)	E_{red} (mV)	$E_{1/2}$ (mV)	
TMP	259	59	159	474	308	391	232
Acetone	315	168	241	556	406	481	240
NMP	577	410	494	818	593	706	212
DMF	542	405	473	776	628	702	229
AcCN	340	230	285	595	449	522	236

Table 8.5 – Composition and molar ratio of the ternary systems used for characterization of Li/Li^+ redox potential shifts and their correlations with NMR experiments.

TMP/Li (mol/mol)	TMP (vol%)	EC (vol%)	DEC (vol%)	Li^+ (M)	EC/Li (mol/mol)	DEC/Li (mol/mol)	TMP/(EC+DEC) (mol/mol)	Solvent/Li (mol/mol)
0	0	50	50	1	7.5	4.1	0	11.6
0.9	10	45	45	1	6.7	3.7	0.08	11.3
2.1	25	37.5	37.5	1	5.6	3.1	0.25	10.9
3.2	37.5	31.25	31.25	1	4.7	2.6	0.44	10.4
4.3	50	25	25	1	3.7	2.1	0.73	10.1
5.1	60	20	20	1	3.0	1.7	1.10	9.8
6.4	75	12.5	12.5	1	1.9	1.0	2.21	9.3
8.6	100	0	0	1	0	0	/	8.6

TEP/Li (mol/mol)	TEP (vol%)	EC (vol%)	DEC (vol%)	Li^+ (M)	EC/Li (mol/mol)	DEC/Li (mol/mol)	TEP/(EC+DEC) (mol/mol)	Solvent/Li (mol/mol)
0	0	50	50	1	7.5	4.1	0	11.6
0.6	10	45	45	1	6.7	3.7	0.06	11.0
1.5	25	37.5	37.5	1	5.6	3.1	0.17	10.2
2.2	37.5	31.25	31.25	1	4.7	2.6	0.30	9.4
2.9	50	25	25	1	3.7	2.1	0.51	8.8
3.5	60	20	20	1	3.0	1.7	0.76	8.2
4.4	75	12.5	12.5	1	1.9	1.0	1.52	7.3
5.9	100	0	0	1	0	0	/	5.9

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Part IV

Concluding remarks

CHAPTER 9

CONCLUSIONS AND PERSPECTIVES

9.1 Conclusions

The road journey of this thesis until its conclusion was paved of extensive bibliographic survey, synthetic efforts, assembly technique developments and characterization data. This results in a work that should attract attention of the community or researchers working on redox organics, and more specifically those dedicated to energy storage applications. In this research work, we explored strategies based on macromolecular engineering and rational design to enable performance improvements. These improvements are targeting critical parameters relevant toward applications: energy density, power density and cyclability.

Additionally, the new chemical structures and pathways as well as the interesting findings and observations related to the systems that we have developed should be found appealing by the broader community of researchers working on batteries and capacitors but also by those working on diverse topics such as conductive and/or electroactive materials, surface modification, catalysis or smart polymer materials etc.

Since this thesis is intrinsically multidisciplinary, the introductory part is presenting an overview of the current knowledge on key topics underlying the research work. The first chapter is dedicated to battery technology with an emphasis on Li-ion cells and covers aspects such as their working principle, components, materials, chemistry thereof as well

as production process and performance parameters.

In the second chapter, a short survey on organic redox materials for energy storage applications is presented. This survey introduces the main classes along with representative examples of these materials while highlighting their benefits and current limitations but also their possible implementation configuration. The main classes of materials depicted in this chapter are conjugated polymers, organosulfur compounds, radical-bearing polymers and carbonyl-based compounds. For each of these, the chapter also features noticeable contributions that have been reported to overcome their current shortcomings.

The third chapter from this introduction part is focusing on controlled radical polymerization techniques, surface modification strategies with polymers and carbon nanotube chemical functionalization. This chapter is highly relevant with respect to our research part devoted to poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) and its composites.

This research work was motivated in the context of a challenging era where mankind has to face up the pressing need for more sustainable, cleaner, and yet cost-efficient energy supply chains. In this respect the next part is presenting the goal, motivations and strategies providing the lead through our research developments (Chapter 4). While the common thread is dealing with polymeric redox architectures, several axes of developments are presented to push forward their performance metrics. To this end, we proposed new designs for (i) radical polymer composites with high power capabilities while improving their specific capacity and cyclability, (ii) high specific capacity polymeric quinones with enhanced specific power capability and cyclability, and (iii) a general strategy relying on electrolyte formulation to improve the energy density of Li-organic cell (or any dual-ion battery) by modification of the output voltage.

The third part is unveiling the results and discussion carried around the experimental work. In the first chapter of this part, we demonstrated the successful synthesis of a PTMA-based composite via grafting from a MWCNT conductive substrate (Chapter 5). Our original strategy allowed us to reach high active material loading (up to 60 wt% by TGA) with high functionalization degree (>85%). Via its processing as a buckypaper electrode and structural characterization techniques (XPS and

SEM), we confirmed a robust tethering of the polymer chains and a near ideal dispersion of the electroactive material around the conductive charge in the resulting material. These properties allowed excellent cycling performances. Upon cycling, our MWCNT-*g*-PTMA material displayed a capacity retention higher than 87% over 200 cycles along with the ability to deliver more than half of its nominal capacity at the rate of 5C. Furthermore, the power performances of this chemically anchored electrode material were proved superior to an electrode made of the same components that has been prepared by a traditional physical blend method.

In the next chapter, we explored another strategy toward MWCNT-*g*-PTMA, this time relying on grafting to (Chapter 6). This strategy enabled a more convergent and efficient chemical pathway. The implementation of a new polymerization technique, namely SET-LRP, greatly contributed to the success of this second strategy. This technique allowed us to prepare functional polymers with great control and high yields that were subsequently grafted to the CNT surface via copper-catalyzed azide-alkyne cycloaddition. The resulting material displayed a high functionalization degree (>85%), and an active material content (30 wt% by TGA) comparable to the usual reported values for such composites prepared by a traditional physical blend method. Thanks to the robust tethering and high degree of homogeneity, our MWCNT-*g*-PTMA buckypaper material also displayed good cycling stability (>80% capacity retention over 150 cycles and excellent power performances (more than half the theoretical capacity at 60C) , outperforming its traditional blend counterpart.

Subsequently, we presented the chemical and electrochemical syntheses of poly(2,5-dihydroxyaniline), a cross-hybrid molecular architecture of redox quinone and electron conductive polyaniline with a theoretical capacity as high as $443 \text{ mAh}\cdot\text{g}^{-1}$ (Chapter 7). For both approaches we carried chemical and electrochemical characterizations in parallel. Overall we demonstrated that the oxidative polymerization of 2,5-dimethoxyaniline followed by chemical demethylation is more efficient and affords better electrochemical properties than the all-electrochemical route. The success of the chemical pathway allowed the electrical conductivity of PDHA to reach values as high as $0.1 \text{ S}\cdot\text{cm}^{-1}$, ranking this material among the most conductive positive electrodes for Li-ion batteries. The active material was processed into a slurry with conduc-

tive carbon and PVDF binder, which is subsequently spread on carbon-coated aluminum foil. We also discussed the chemical synthesis parameters as well as electrode processing optimization routes. The CV response points in the direction of a two electron reversible redox process attributed to the quinone groups. A specific capacity of $290 \text{ mAh}\cdot\text{g}^{-1}$ was achieved via galvanostatic charge-discharge measurements with a potential window of 1.8 V - 3.2 V (*vs.* Li/Li⁺) at a C/10 rate in a half-cell configuration. PDHA holds thus great potential as an active component for Li-ion batteries, with room for further improvements in terms of energy density and capacity retention.

The last developments that we brought in this thesis were involving organophosphate-based electrolyte formulation (Chapter 8). Via this research work, we demonstrated that such molecular liquids, well-known as flame-retardants additives for LIBs, are able to strongly coordinate alkali-metals ions. In turn, this behavior has an important impact on the electrochemical potential of electrodes involving the related ions in their process. In the case of lithium-based electrode processes, our measurements evidenced a redox shift as high as -500 mV when compared to conventional carbonate-based electrolytes used for LIBs. Through a series of complementary 2- and 3-electrode measurements, with different pseudo-reference electrodes and reference redox systems, the redox potential shift was found to be ruled mainly by Li-cation (de)solvation processes whereas the redox potential shift of other, non Li-cation (de)solvation processes is negligible. Solvent coordination ratio, cation valence number as well as self-diffusion coefficients were also characterized via NMR/DOSY methods and correlated with the electrochemical measurements. We then further highlighted how these processes can impact developments on high-energy hybrid battery concepts such as higher voltage dual-carbon (dual-ion) or organic batteries as well as the apparent enhancement of the anodic stability. Lastly, we carried the implementation of trimethyl phosphate as electrolyte constituent in a LTO-PTMA full-cell. This implementation demonstrated the benefits that can be expected by the chemical shift in a dual-ion configuration. This full-cell design effectively delivered an output voltage gain of about 0.4 V compared to the same cell configuration with standard carbonate-based electrolyte. Despite significant initial capacity losses with PTMA-based cells using TMP, our results showed that improvements of the energy delivered can be expected by as much as 20% for a given capacity. Surely, this achievement is a major step on our jour-

ney toward organic redox systems with improved energy density. These systems should reveal their full benefits by mastering the reversibility and redox kinetics associated with these organophosphorous-based systems.

To summarize, the original contribution and significance of this thesis work is three-fold. From an applied sciences standpoint, this research work provides guidelines and genuine strategies for the elaboration of organic-based redox systems with improved characteristics at several levels: power density, energy density, and cyclability. From a fundamental standpoint, this thesis demonstrated the relationship between the structures of the original systems that have been developed and their electrochemical properties. Lastly, this research work opens up a stimulating perspective for future developments and applications in the exciting field of electrochemical energy storage.

9.2 Perspective

From the perspective of enhancing electrode performances of redox organics, this class of materials again demonstrated here that it allows versatile functional and structural manipulations to tailor their resulting electrochemical properties. This demonstration combined with their contextual advantage of being more environment-friendly than currently used inorganic materials should motivate further developments into more elaborated devices. Nevertheless, this thesis is carrying messages and perspectives for future developments that should extend beyond the work continuation on materials and systems developed during this research. Although this work was mainly focused on developments of batteries based on redox organics, projections can be anticipated to other area of material sciences and electrochemistry where similar concepts and strategies are applicable.

As for our MWCNT-*g*-PTMA grafted materials, they intrinsically display performances that could fill the gap between electrochemical capacitors and LIBs in terms of energy density *vs.* power density, and this is where they could meet application demands. Yet, in terms of implementation, they could find their way by combining them with other electroactive components within a single electrode. For instance, they could advantageously be hybridized with an inorganic component such

as LFP (or LMO) to mitigate their relatively low energy density but also to take advantage of synergistic effects regarding the charge (or discharge) performances of the resulting electrode material.^[1,2]

Another possibility would be to take advantage of the enhanced dispersion properties of our grafted material. Over the course of our developments, we demonstrated the benefits of an intimate contact between the electroactive component and the conductive charge. We also evidenced that the best electrochemical properties do not always pair with the highest macroscale electrical conductivity; this is an observation that has also been reported with another PTMA-based system.^[3] As a matter of fact, the best dispersion of these systems implies the formation of a continuous layer of the electroactive material around the conductive charge. In so doing, the percolation of electrons is hindered but the conductive charge may better support the redox processes. Therefore, efforts in the development of related hybrid materials should focus on the dispersability of the conductive charge. Since it is often challenging to reach an efficient distribution without dispersing additives, our grafted material could be acting as compatibilizing agent to help in the formation of the desired polymer - conductive charge hybrid structure.

Regarding other potential applications, catalysis is a field where nitroxide are well-known as mediating species for the oxidation of alcohols but also other functions such as amines or terminal alkenes.^[4] In this respect, nitroxide reagents have also been extensively used as catalysts under electrochemical conditions in the absence of chemical oxidants and are envisioned as such to carry industrial-scale reactions. Notably, a reported strategy consists in the use of an aminoxyl-modified mesoporous silica film at the surface of a conductive carbon electrode.^[5] Compared to homogeneous catalysis, such strategies are alleviating kinetic losses associated with mass transfer of the nitroxide mediating species to and from the electrode. Additionally, a porous structure allows electron transfer between the electrode and nitroxide groups while making the latter accessible to dissolved substrate species. Using MWCNT-*g*-PTMA instead would allow to circumvent the issue of significant overpotentials required by the use of an insulating nitroxide containing silica matrix. Moreover, the higher specific density of nitroxide groups in our grafted materials could lead to higher turnover rates and conversions.

As for the developments of alkyne-bearing copolymers, they already proved their usefulness in the field of energy storage by the preparation

of MWCNT-*g*-PTMA hybrid materials for the purpose of this thesis work. Yet, they are already a couple of other contributions from our group on polymer architectures prepared by a derived strategy. In these contributions, azide moieties have been exploited to provide cross-links nodes, hence giving rise to an insoluble gel network preventing the dissolution of active species in the electrolyte.^[6,7] In the later contribution, the azide groups have been further exploited to generate 1,2,3-triazolium cross-links that eventually enhance the ionic conductivity of the network.^[7] Given the acknowledged versatility of the chemistry associated with azide moieties, which is a representative example of click reagents, further developments can be envisioned: other complex macromolecular architectures, hybrid materials, bio-conjugates etc.

Regarding poly(2,5-dihydroxyaniline), since cathode materials for commercial LIBs are lagging behind their anode counterparts in term of energy density, this material holds great potential as an active component thanks to its high theoretical specific capacity, electrical conductivity, and insolubility in common electrolytes. We envisage that further studies of such materials will afford a clearer understanding of the effect of the chemical structure on the electrochemical performances as well as full material utilization based on a two-electron process and stable cycling. Owing to its pioneer position, we hope that our cross-hybrid molecular architecture of redox quinone and electron conductive polyaniline will also trigger the elaboration of other designs that aim at fusing the benefits of conductive polymers and non-conjugated organic compounds.

Our work on the impact of electrolyte formulations on electrode redox potentials is setting several bases for further developments. In that respect, we provided a full-cell implementation as a proof-of-concept on the use of trimethyl phosphate to raise the voltage output when a dual-ion charge balancing mechanism is involved. The continuation of this work should take the direction toward a device that fully translates the voltage gain in terms of energy. To this end, attention should be dedicated to achieve better cycling performances. This could be obtained by defining the proper balancing between positive and negative electrode capacity but also by understanding and limiting the irreversible capacity losses observed for the positive electrode material (PTMA). Since this capacity loss might be due to impurities or side-reactions related to TMP itself, efforts on defining more appropriate formulations might

be required: further purification, use of additives, evaluation of other organophosphorous-based compounds etc.

Since the concept that we developed is broadly applicable to any dual-ion battery, this work should encourage to explore applications with other electrode materials or chemistries. As we have experimentally explored, graphite-graphite dual-ion batteries could be one of these, but generally any other positive electrode materials able to undergo p-doping could be considered (polyaniline, polypyrrole, conjugated amines, ferrocene-based compounds etc.). As also suggested by our measurements, the redox shift induced by organophosphates in comparison to standard carbonates is not limited to lithium-based systems. Hence, other systems based on alkali-ions, such as sodium batteries, could benefit from a similar strategy. Furthermore, other aprotic solvents with strong donor properties (DMSO, NMP etc.) might be evaluated in the light of our findings to modulate electrode redox potentials. Lastly, these findings may also trigger the re-evaluation of the electrochemical stability mechanisms of organophosphates flame-retardant electrolytes but also other non-conventional battery electrolyte formulations toward a more realistic picture.

At this point of the journey, we wish that this work will constitute a milestone on the way to bring redox organics to the fore, and serve as a seminal work for research developments contributing to shape up a brighter future.

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Part V

Appendix A

CHAPTER 10

NON-COVALENT MWCNT FUNCTIONALIZATIONS

Abstract

In the quest of electroactive materials with enhanced performances, composites can be considered as almost ubiquitous. In that respect, electrodes based on nitroxide bearing polymers could be regarded as an illustrative example since they are requiring a precise incorporation of conductive charges to meet performance expectations. In the main text of this thesis work, we unveiled the syntheses and properties of MWCNT-based composites via covalent grafting. In parallel to covalent approaches, we also contributed to the development of composites based on non-covalent approaches relying on supramolecular chemistry. The purpose of this chapter is then to introduce the context, objectives and strategies relative to such composites.

10.1 Context of this research

Non-covalent approaches are affording a straightforward route toward the surface modification of MWCNTs since synthetic efforts are limited to the preparation of functional polymers. As further advantage, non-covalent approaches are not altering the sp^2 structure of MWCNTs, thus allowing to preserve their intrinsic conductivity.

In this research work, two distinct architectures are explored to promote π - π supramolecular interactions: block copolymers, and pyrene-tagged (co)polymers. The synthesis of the polymers displaying these architectures is part of a collaboration with the Laboratory of Polymeric and Composite Materials (LPCM, UMons). This collaboration was set in the frame of the HYB2HYB project funded by the Walloon Region where the LPCM group is focusing their efforts on the electroactive polymer syntheses. Our research group at the Institute of Condensed Matter and Nanosciences (IMCN, UCLouvain) is contributing to the synthetic efforts by providing a knowledge transfer thanks to our previous work on PTMA synthesis.^[1,2]

After synthesis, the part relative to the electroactive polymers processing into MWCNT composite films and their subsequent electrochemical characterizations is carried out in the environment of our research group at the IMCN. The author's contribution was then to collaborate with Dr. Noémie Hergué in her research work by providing expertise on the active material processing, electrochemical measurement implementation and result interpretation. The success of our research work lead us to two distinct reports in Batteries & Supercaps,^[3] and Polymer Chemistry,^[4] where the author contributed to the writing of electrochemical parts. These two publications served as a basis for the two next chapters of this appendix.

10.2 Objectives and strategies

In the **pyrene-tag** approach, the synthetic strategy aims at statistical P(TMA-*co*-pyrene methacrylate) copolymers and pyrene end-functionalized PTMA homopolymers. The design of pyrene-tagged structures has already proven its usefulness to provide polymer-MWCNT conjugates with enhanced stability.^[5] The polymerizations are strictly

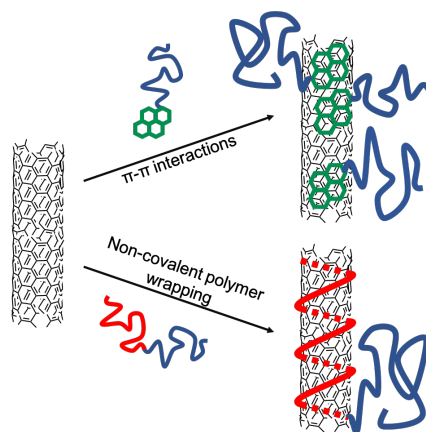


Figure 10.1 – Illustration of two non-covalent modification strategies to chemically anchor polymers on a CNT surface. The depicted strategies are relying on π - π interactions using either a pyrene-tagged (green end) polymer chains, or a block copolymer bearing a segment (red) favorably interacting with the CNT walls. When the red block is long enough, this latter strategy can lead to polymer wrapping around CNTs. In the context of this project, the blue segments are representing the radical polymer part.

relying on CRP methods. The choice of a CRP method, namely atom transfer radical polymerization (ATRP), is motivated by its precise control over composition, ensuring that all polymer chains are possessing the required functionality to interact with MWCNT surface. This control should permit to vary the amount of pyrene tags and then seek for the minimal amount required to prevent migration of the redox polymer upon cycling, that is limiting the trade-off of an improved charge transfer and cyclability in exchange of a decreased specific capacity. To our knowledge, no prior examples were reported regarding designs of PTMA-based architectures optimized for π - π interactions using pyrene or similar tags.

As for the **block copolymer** approach, the concept is based on the combination of an electroactive block (PTMA) and a second block designed to interact favorably with MWCNTs. Poly(3-hexylthiophene) (P3HT) has been selected as second block since it has been recognized to display strong interactions forces with CNTs as demonstrated by its wrapping behavior when appropriate conditions are met.^[5,6] Consequently, the P3HT-*b*-PTMA block copolymer chain should self-organize at the MWCNT interface, with interactions toward the CNT wall hap-

Table 10.1 – Non-covalent modifications of MWCNTs with PTMA: comparisons of the potential relative benefits with grafting approaches.

benefits	π - π interactions		grafting	
	pyrene tag	P3HT- <i>b</i> -PTMA	from	onto
ease of synthesis	++	+	--	-
robustness	-	-	+	+
capacity	+	-	++	+
CNT conductivity	+	+	-	-
charge transfer	+	+	-	-

pening through the P3HT block, and with the electrolyte-swollen PTMA block extending away from the surface. This organization is expected to both suppress the solubilization of PTMA chains in the electrolyte and to favor the charge transfer between the redox polymer and the nanotube via the conjugated system of the P3HT block.

Overall, the relative benefits of these non-covalent strategies with respect to covalent ones is summarized in Table 10.1. Both non-covalent approaches should provide enhanced cycling stability in comparison to traditional blends of linear polymers and conductive charge. These two strategies should also be expected to deliver the enhanced power performances thanks to the close contact of PTMA and MWCNTs, and in particular the unaltered conductivity of MWCNTs in comparison to covalent strategies.

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CHAPTER 11

MULTI-PYRENE PTMA STRUCTURES, $\pi - \pi$ SUPRAMOLECULAR INTERACTIONS FOR IMPROVED CYCLABILITY

Abstract

Well-defined pyrene-based poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) (co)polymers have been synthesized and combined with multi-wall carbon nanotubes (CNTs) as electrode material for organic radical batteries. The influence of the number of pyrene pendent groups on the electrochemical response of the nanocomposite materials has been assessed, focusing on the capacity retention upon charge/discharge cycling and on the cycling rate. In parallel, the interactions between the polymethacrylate chains and the CNT surface have been investigated with molecular modeling techniques, to shed light on the nature and stability of the functionalized PTMA/ CNT interface.

11.1 Introduction

While designing PTMA-based electrodes, the main challenges to overcome are its poor electrical conductivity and its propensity to solubilize in common carbonate-based LIB electrolytes. These two factors are otherwise limiting the high power capability of this redox polymer and are hindering the full redox material utilization. The traditional way to circumvent these issues relies on the use of conductive charges with high specific surface area in order to provide a framework for the charge collection and electronic transport as well as to adsorb soluble species, yet at the expense of the specific capacity of the electrodes.

Therefore many groups have reported strategies aiming to improve the design of PTMA-based electrodes: Zhang *et al.* showed that the PTMA molecular weight has a major effect on the polymer solubility and thus, on its electrochemical properties.^[1] In addition, both, capacity and rate performance are much better with PTMA of high molar masses. Another way to decrease the solubility of the active material is to use cross-linked PTMA, creating a polymer network^[2-4] or to graft PTMA on the conductive material.^[2,5-7] Non-covalent interactions between PTMA and the conductive material have also been considered with imidazolium^[8] (cation- π interaction) and pyrene^[1] ($\pi - \pi$ stacking) as anchoring points to immobilize PTMA onto nanostructured carbon derivatives. Zhang *et al.* recently reported a non-covalent interaction between a pyrene-functionalized PTMA and reduced graphene oxide (rGO).^[1] In that study, a two-electron redox process promoted by the rGO led to high capacities. To the best of our knowledge our contribution disclosed in the current chapter represented the first example of a pyrene-based PTMA used in batteries so far.^[9]

Since the PTMA/rGO composites developed by Zhang present a decrease in capacity (from 1 to 10–20C) when submitted to variable rates, here we have decided to investigate the importance of the number of pyrene units anchored along the PTMA chain to improve the performance of the corresponding PTMA/CNT nanocomposites. In this chapter, two pyrene-based PTMA structures have been studied and used with multi-wall CNTs (MWCNTs): the first one is a PTMA polymer bearing a single pyrene end-group; it was intentionally designed to confer a low steric hindrance and less conformational constraints to the homopolymer, when the pyrene interacts with the carbon surface.

For the second system, pyrene units have been incorporated along the PTMA chain, by copolymerization of a pyrene-substituted methacrylate with the TEMPO-substituted methacrylate. The influence of the macromolecular architecture on the electrochemical response has been assessed, focusing on the capacity retention upon cycling and on the cycling rate. To shed light on the nature and stability of the functionalized PTMA/CNT interface, the interactions between the (co)polymer chains and the carbon surface have been investigated with molecular modeling techniques in parallel.

The main drawback encountered when organic electrodes are prepared from a simple physical mixing of PTMA and CNTs remains on the partial migration of PTMA out of the electrode during the battery operation, due to its solubility in the battery electrolyte. Cross-linking of PTMA has been proposed as a solution to that issue, but the process raises other challenges, such as: (i) problems of processing due to the insolubility of cross-linked PTMA in the solvents used during electrode fabrication, (ii) impossibility to obtain close contact between conductive carbon-based materials, e.g., CNTs, and cross-linked PTMA particles, (iii) non-homogeneous cross-linking of PTMA, leading to the release of non-crosslinked chains. One way to circumvent these drawbacks would be to directly attach PTMA chains on conductive carbon-based materials, either *via* "grafting from" or "grafting onto" as presented in chapter 5 and chapter 6. The PTMA could thus be immobilized on the electrode, leading to electrochemical cells with higher capacity and stability. The *grafting onto* approach allows a better control of the material characterization than the *grafting from* technique. However, both grafting methods involve covalent chemical modifications of the CNTs disrupting the conductive network of sp^2 carbon atoms along the nanotube and reducing their inherent conductivity.^[10,11]

Taking advantage of non-covalent/supramolecular interactions would allow a close contact between CNTs and PTMA chains without modifying the CNT network and therefore their conductivity. In this chapter, two kinds of (co)polymer structures were considered to reach such a goal: a PTMA end-functionalized at one end by a single pyrene molecule, i.e., able to interact with the CNT surface via $\pi - \pi$ bonding, and a PTMA bearing multiple pyrene molecules as side groups and one pyrene as chain-end. A single terminal pyrene unit is expected to promote the immobilization of PTMA chains on the CNT by their extremity while

a multi-pyrene structure would favor interaction of the whole PTMA chain with the CNT.

11.2 Synthesis of multi-pyrene PTMA (co)polymers

The controlled synthesis of PTMA-based (co)polymers was achieved via atom transfer radical (co)polymerization (ATRP). Since the dangling nitroxide groups of the PTMA can be readily obtained by oxidation of the corresponding secondary amine, 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM) has been used as comonomer in the process.

The typical synthesis via ATRP of PTMA-based (co)polymers is depicted on figure 11.1. The synthesis of pyrene-terminated polymers was performed by homopolymerization of the TMPM starting from a pyrene methyl- α -bromoisobutyrate (Pyr-Ini) initiator (Figure 11.6). The use of Pyr-Ini allows an efficient functionalization of the polymer as well as an easy determination of the polymerization degree (DP) by $^1\text{H-NMR}$, due to the distinct peaks of the pyrene unit in the aromatic region.

Table 11.1 – Molecular characterizations of the PTMPM homopolymers.

Entry	Code	R-Ini	n^a	$M_{n,NMR}^a$ [g·mol $^{-1}$]	$M_{n,SEC}^b$ [g·mol $^{-1}$]	$\bar{D}^b$
1	P1	Ethyl	110	26,600	17,300	1.16
2	P2	Pyrene	84	20,600	12,200	1.16
3	P3	Pyrene	350	84,400	48,200	1.28

^a Polymerization degree as determined by $^1\text{H-NMR}$.

^b Determined by SEC in $\text{CHCl}_3/\text{IPA}/\text{Et}_3\text{N}$ calibrated with PMMA standards.

Prior to any copolymerization, the homopolymerization of TMPM was first performed to assess the possibility to control the ATRP process of such a monomer. To that end, TMPM was polymerized by using a $\text{CuBr}/\text{HMTETA}$ catalytic complex ($[\text{CuBr}]_0/[\text{HMTETA}]_0 = 0.5$) in toluene ($[\text{TMPM}]_0 = 3.2 \text{ mol/L}$) at 60°C from a freshly prepared pyrene methyl- α -bromoisobutyrate initiator.^[12] The reaction times were adapted according to the targeted DP. As presented in table 11.1,

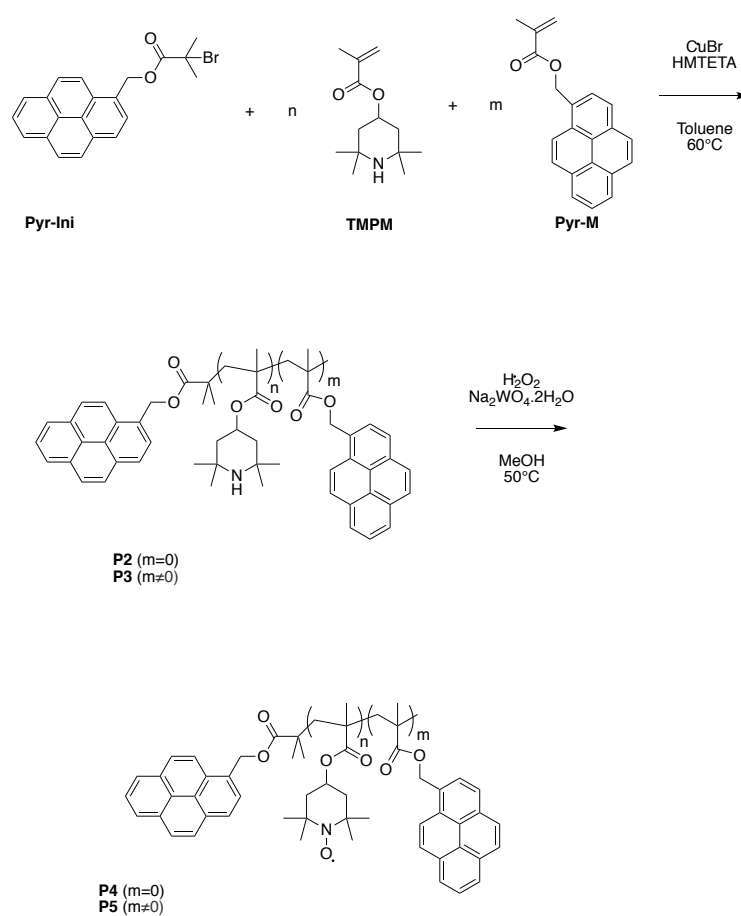


Figure 11.1 – Synthetic routes toward the formation of PTMA-based (co)polymers via (co)polymerization of the TPM precursor monomer by ATRP followed by oxidation of the amine groups into nitroxides.

PTMPM homopolymers (entries 2-3) of variable molar masses have been obtained presenting narrow dispersity indices ($M_w/M_n = \bar{D} < 1.3$). In order to highlight the importance of the pyrene moiety on the final material properties, a non-functionalized PTMPM homopolymer has been prepared by using ethyl bromoisobutryl bromide as initiator (Entry 1, Table 11.1).

Associated to those three samples, a multi-pyrene PTMPM (**P4**) has been prepared by copolymerizing a mixture of TMPM and pyrene methyl methacrylate (PyrM). A random copolymer structure was targeted to favor the $\pi - \pi$ interactions with the CNTs. The PyrM comonomer was prepared from 1-pyrenemethanol using methacryloyl chloride and triethylamine in THF (see Experimental Part). The copolymerization was performed in the same experimental conditions that the ones applied to the homopolymerization while starting with a $[\text{TMPM}]_0/[\text{PyrM}]_0$ ratio of 5.3 (corresponding to an expected molar ratio of 85/15). Such a ratio has been chosen to favor the $\pi - \pi$ interactions between the MWCNTs and the pyrene units along the chains while keeping a high content in redox-active species. After reaction, $^1\text{H-NMR}$ analysis of the statistical copolymer reveals a $[\text{TMPM}]/[\text{PyrM}]$ ratio of 82/18 (Entry 1, sample **P4**, table 11.2).

Table 11.2 – Molecular characterizations of the PTMPM homopolymers.

Entry	Code	R-Ini	M_1^a [%] ^b	PyrM [%] ^b	$M_{n,SEC}^c$ [g·mol ⁻¹]	$\bar{D}^c$
1	P4	Pyrene	82	18	9300	1.18
2	P5	Pyrene	84	16	20500	1.15

^a M_1 corresponds to TMPM in the case of **P4** and to BMA for **P5**.

^b Ratio of comonomers as determined by $^1\text{H-NMR}$.

^c Determined by SEC in $\text{CHCl}_3/\text{IPA}/\text{Et}_3\text{N}$ calibrated with PMMA standards.

Finally, all PTMPM-based (co)polymers were oxidized using an excess of H_2O_2 in the presence of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}/\text{EDTA}$. Oxidations were carried out in MeOH at a concentration in (co)polymer of $20 \text{ g} \cdot \text{L}^{-1}$ at 50°C for 24 h.^[13] As expected, the PTMA-based (co)polymers are showing an orange color consistent with the absorption peak attributed to the nitroxide group around 460 nm. The degree of oxidation determined

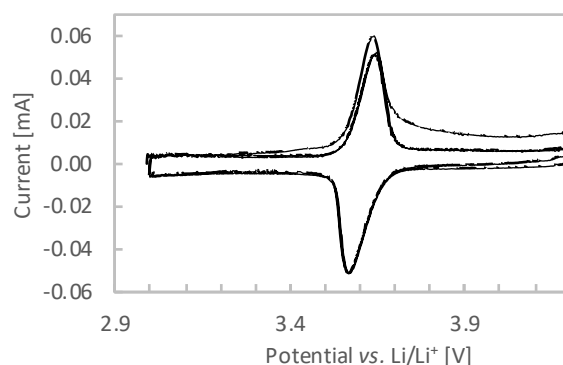
from the intensity of that peak is 98%. For clarity, each oxidized sample has been named Pn -ox with n corresponding to the number of the sample and going from 1 to 4. SEC traces before and after oxidation displayed the same shape with no evidence of adventitious side-reactions.

11.3 Electrochemical characterizations of multi-pyrene PTMA-based (co)polymers

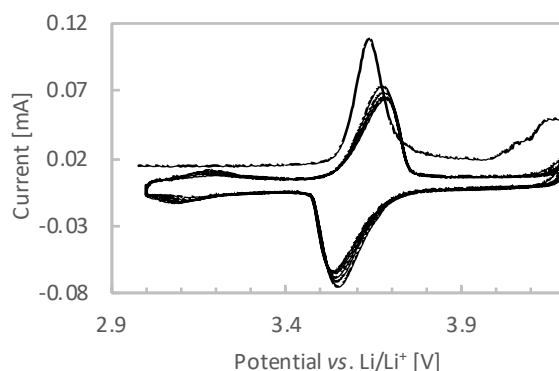
Composites made by blending PTMA-based (co)polymers with MWCNTs were prepared for the generation of electrodes. The composition of the slurry was selected to be 30/60/10 (wt%) in PTMA/CNTs/binder.^[14] The elaboration of a slurry showing a good viscosity and favoring the interactions between CNTs and pyrene-based PTMA needed some adjustments of the previously-described procedures.^[15] To favor supramolecular interactions, the two components have to be intimately mixed and NMP was found to be the best solvent to solubilize/disperse PTMA and CNTs. The films obtained via a classical mixing using ball miller were not homogeneous and the associated performances were not satisfactory (data not shown here). To improve the quality of the slurry, CNTs were gradually dispersed in NMP using a sonoprobe, then the PTMA (solubilized in NMP) was added to the dispersion under sonication. The binder was incorporated before further mixing in a ball miller at medium speed (400 rpm) to get a homogeneous slurry. Thin films of this viscous slurry were obtained using the Doctor Blade method with a clearance adjusted to 400 μm (bar type film applicator). Disks of those composite films were cut, and half-cells were assembled under argon atmosphere in a glove box.

Cyclic voltammetry analyses were performed on these cells to confirm the redox behavior of the PTMA-based (co)polymers (Figure 11.2). All the (co)polymers display a reversible oxidation peak centered at 3.6 V *vs.* Li/Li⁺, characteristic of the nitroxide radical oxidation into the oxoammonium cation. This process is stable with cycling, with a constant oxidation potential as well as a constant intensity of the oxidation peak as demonstrated by the superimposition of the curves of cycles 2 and 3. The voltammograms of **P3ox** and **P4ox**, in respective figures 11.2(A) and 11.2(B), exhibit a sharp peak-to-peak separation of 0.09 V and 0.14 V *vs.* Li/Li⁺, respectively, demonstrating a faster charge transfer for the

homopolymer in the electrochemical processes. In the voltammogram of **P4ox**, a second process is visible at lower potential (around 3.1 V *vs.* Li/Li⁺). The possible origin of this reversible oxidation peak will be discussed later.



(A) Homopolymer **P4b**.



(B) Copolymer **P5**.

Figure 11.2 – Cyclic voltammograms of PTMA based (co)polymers at $0.1 \text{ mV} \cdot \text{s}^{-1}$ in EC/DEC 1:1 (v:v), 1 M LiPF₆.

The performances of the PTMA electrodes were recorded during galvanostatic cycles at a current density of C/5 for the three cycles then at C/2 for the following cycles, with a voltage ranging between 3.0 V and 4.2 V. The capacity retention of the (co)polymers over 170 cycles are shown in figure 11.3. All the (co)polymers show a first drop in the capacity due to irreversible processes. The capacity of **P1ox** shows a

continuous, substantial decrease over the first hundred cycles (33% loss). This capacity loss during the charge/discharge cycling is attributed to a partial solubilization of PTMA in the electrolyte, as already observed by others.^[16] The pyrene-containing PTMA is characterized by a much milder decrease over the cycles. The longer monofunctionalized pyrene-based PTMA (**P3ox**) displays a higher initial charge capacity than its shorter counterpart **P2ox** ($63 \text{ mAh}\cdot\text{g}^{-1}$ *vs.* $37 \text{ mAh}\cdot\text{g}^{-1}$). This behavior is probably due to a more pronounced solubilization of the low molar mass polymer in the electrolyte during the equilibration period before the measurements, despite the presence of the anchoring pyrene unit. The **P2ox** capacity around $37 \text{ mAh}\cdot\text{g}^{-1}$ corresponds to 30% of the theoretical capacity. Excluding the first cycles, the capacity retention of this polymer is quite high, around 93% over 170 cycles. **P3ox** displays a capacity around $63 \text{ mAh}\cdot\text{g}^{-1}$ (50% of the theoretical capacity) with a loss of 10% between the 5th and the 170th cycles. The introduction of a single pyrene group on PTMA thus leads to good capacities as soon as the molar mass of the structure is sufficiently high. Moreover, the capacity retention is highly improved with respect to non-functionalized PTMA, even for relatively short pyrene-PTMA chains.

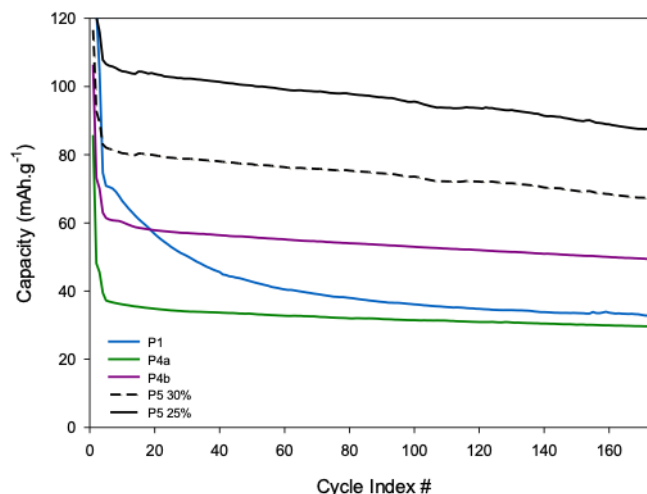


Figure 11.3 – Capacity retention of Pyr-based (co)polymers/CNTs cathodes at $C/2$ rate over 170 cycles.

The DFT calculations show that the pyrene molecule adsorbs flat

on the graphene surface, interacting with it via $\pi - \pi$ interactions. In contrast, the TMA fragment interacts mainly via weaker CH- π interactions; the nitroxide group does not strongly interact with the graphene surface and the radical remains localized on the oxygen atom. Since the adsorption of a single pyrene unit is stronger than that of a TMA by about $3 \text{ kcal} \cdot \text{mol}^{-1}$, the pyrene functionalization indeed appears as a valuable strategy to improve the anchorage of functionalized PTMA polymer chains on carbon nanotubes.

As expected, the multi-pyrene copolymer **P4ox** presents a well higher initial capacity of above $80 \text{ mAh} \cdot \text{g}^{-1}$ (dashed black line, figure 11.3). After 170 cycles, the capacity remains at $70 \text{ mAh} \cdot \text{g}^{-1}$ (67% of the theoretical value). Over this cycling process, the capacity retention is good, with only 13% loss. Those values have been normalized on the basis of a 30 wt% amount of active material in the electrode. On the contrary to both **P2ox** and **P3ox**, the percentage of radical units in the random **P4ox** copolymer is however limited to 77 wt% (82% mol). Considering the real percentage of active redox units (23 wt% instead of 30 wt%), the actual capacity value is then larger by $20 \text{ mAh} \cdot \text{g}^{-1}$ to $25 \text{ mAh} \cdot \text{g}^{-1}$ (solid black curve in Figure 3). Note here that such assumption is correct only if the PyrM repeating units present no redox activity. To clarify it, a complementary experiment has been performed by preparing a new copolymer (**P5**, figure 11.4) composed by butyl methacrylate (BMA) and PyrM comonomer (no redox unit). BMA was chosen for its non-redox activity. Both comonomers were copolymerized in the same conditions than those used for the preparation of **P4** (Entry 1, table 11.2). As expected, no redox activity was observed from an electrode containing **P5**. Galvanostatic cycling led only to very low capacity values of around 10 mAh per gram of PBMA with no trace of redox activity. This low capacity is here attributed to the carbonated material. The lack of redox activity for PyrM was thus confirmed with this complementary study and attests the capacity calculated for the **P4ox** copolymer.

This last multi-pyrene sample demonstrates high and stable capacities during cycling at C/2, with values well above those of mono-functionalized PTMA (**P2ox** and **P3ox**) or physical blended PTMA (**P1ox**). Performances of this copolymer are also slightly better than the results reported previously for PTMA grafted onto CNTs, which showed a capacity of $80 \text{ mAh} \cdot \text{g}^{-1}$.^[17]

It is important to point out the relatively low molar mass of the **P5ox**

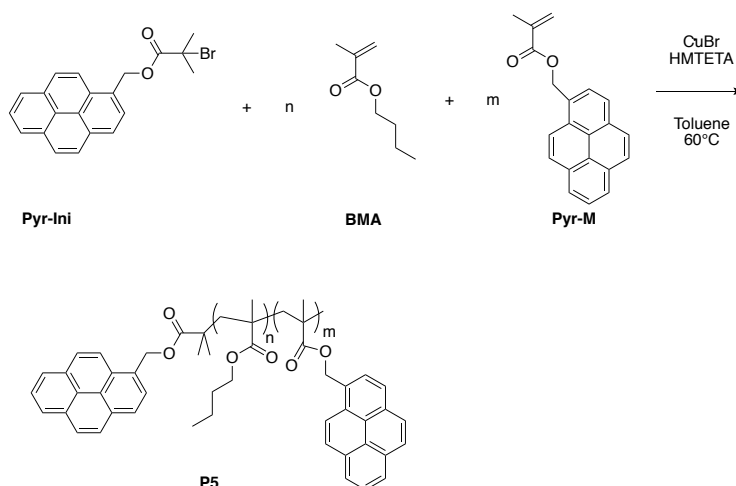


Figure 11.4 – Synthetic routes toward the formation of PBMA-based copolymer, **P5**, by ATRP using a pyrene initiator, butylmethacrylate and PyrM monomers.

copolymer ($M_{n,SEC} = 9100 \text{ g}\cdot\text{mol}^{-1}$ vs. PMMA standards). ^1H -NMR did not allow the determination of the real DP; nevertheless, the SEC value is a good indication of the short length of this copolymer (strict comparison is not possible, since the polymer and the copolymer have different hydrodynamic volumes). A pure PTMA with a similar M_n is extremely soluble in the electrolyte and presents low performances during battery testing.

The improved capacity of the multi-pyrene PTMA can originate from two phenomena: on one hand, the pyrene-containing copolymer could be less soluble than the corresponding pure PTMA compound, which would reduce the leaching in the electrolyte. On the other hand, the presence of the pyrene units is likely to induce stronger intermolecular interactions between the polymer chains and the CNT surface, favoring physical anchoring and improving the resistance towards solubilization. To verify such hypothesis, the adsorption has been modeled and compared the adsorption energy on a (77,77) CNT of a chain of the

Pyr-PTMA copolymer with that of an equivalent PTMA homopolymer chain (More details about the modeling methodology are provided in the experimental part of this chapter). Both polymer chains are found to adsorb on the nanotube and remain partially coiled. Yet, it was found *via* the modeling of the cylindrical distribution functions (CDFs, which are a reflection of the distribution of the molecular fragments near the CNT surface) and *via* calculations of the density of adsorption energy (*DAE*, table 11.3) that Pyr-PTMA does indeed adsorb much stronger than PTMA on the nanotube.

Table 11.3 – Adsorption Energy (AE) and Density of Adsorption Energy (*DAE*) for the Pyr-PTMA and PTMA chains on the CNT.

Polymer on CNT	<i>AE</i> [kJ·mol ⁻¹]	<i>DAE</i> [kJ·mol ⁻¹ ·nm ⁻²]
Pyr-PTMA	-648.8	-61.2
PTMA	-565.2	-47.1

The rate performances of representative **P3ox** and **P4ox** cathodes were studied, increasing the current density from C/ 15 to 40C and C/11 to 105C, respectively (Figure 11.5). The charge/ discharge capacities are decreasing with increasing the current density, as expected. At C/7, the **P3ox** cathode delivers 70 mAh·g⁻¹. This capacity is decreased by 18% at C, by 40% at 20C and keeps half of the initial value at 40C. The typical plateau of PTMA is centered at 3.6 V *vs.* Li/Li⁺. At high current density, a spreading of the charge and discharge plateaus is appearing, due to polarization.

At C/6, the **P4ox** cathode delivers a high capacity of 110 mAh·g⁻¹. This value is decreased by 25% at C, by 50% at 20C. During charge and discharge, the PTMA plateau is centered around 3.6 V *vs.* Li/Li⁺. These curves also exhibit a spreading of the plateaus while increasing the current density. This spreading is more pronounced for the discharge, meaning that the polarization is stronger during this part of the redox process. In this case, a second phenomenon is appearing above 4C, with the coexistence of two plateaus that progressively combine. The whole process is visible on the charge and discharge curves at 4C. However, at 9C, even if the charge process seems to display a single plateau at 3.7 V, the discharge process is displaying two distinct redox responses around

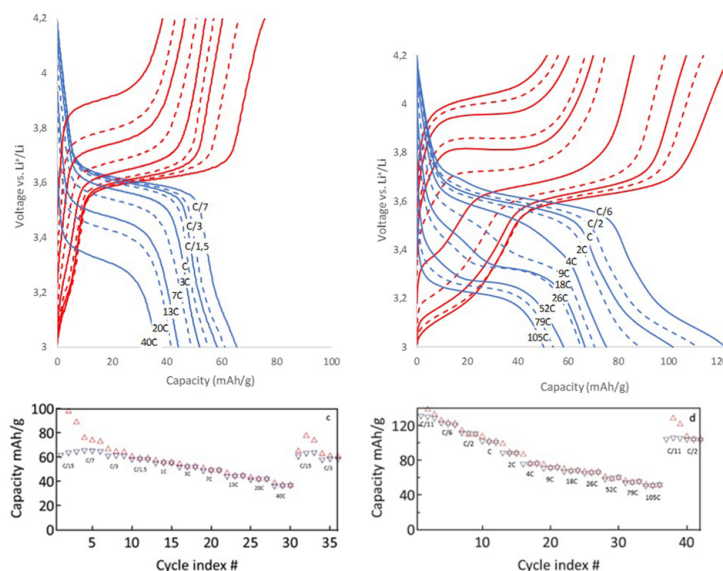


Figure 11.5 – Charge/discharge curves and rate performances of **P3ox/CNTs** (a, c) and **P4ox/CNTs** (b, d) cathodes under variable C rates.

3.5 V and 3.4 V.

Upon increasing the cycling rate up to 52C, this discharge behavior is still present but tends to disappear as the redox responses begin to merge in a single one with $E_{1/2}$ around 3.6 V. Considering the reversibility for each cycling rate, it seems reasonable that for all discharge curves obtained between 4C and 52C, the different faradic responses should still be related to the PTMA redox process only. This discharge behavior can be related to an inhomogeneity of the cathode, with areas showing different performances depending of the current density. This could originate from a partial ion diffusion issue. At low current density, a slope change is clearly visible around 3.2 V *vs.* Li/Li⁺. This process cannot be attributed to PTMA since no mirror effect centered at 3.6 V *vs.* Li/Li⁺ is observed in the charge curve. This inflection that is clearly visible at low current density disappears at higher value, confirming the process dependency on the current density. According to the literature, this value is neither related to traces of the amine precursor of the nitroxide function,^[18] nor to CNTs. This slope change could hardly be related to traces of residual catalyst (from the CNTs synthesis or from the polymer synthesis) since metallic catalysts are oxidized below 3 V *vs.* Li/Li⁺. Another possible origin could be a redox activity of the pyrene

unit. This hypothesis was considered but no proof could be found on the voltammogram of **P5**. Still another possibility explaining this inflection could be traces of oxidation residues (EDTA, Na_2WO_4), which would contaminate the samples despite the purification steps. Finally, the systems were cycled back to low C rates showing values similar to the initial capacities, thus demonstrating a good stability of the cathodes.

11.4 Conclusion

In this chapter, we synthesized pyrene-based PTMA with one pyrene end- group and bearing multiple pyrene units along the polymer backbone, to study the effect of the pyrene number. Copolymerization was achieved using ATRP to access a defined molecular weight and pyrene/TMA ratio. These copolymers were blended with carbon nanotubes to prepare cathodes for batteries. Composite materials of copolymer/CNTs/binder were prepared with a 30/60/10 ratio and incorporated in half-cells. Electrochemical behavior of the cells attested an improvement of the capacity as well as the cycling stability due to the introduction of pyrene in the PTMA. This effect is even enhanced for the copolymer containing 18 mol% of pyrene with capacities reaching $105 \text{ mAh}\cdot\text{g}^{-1}$ at a C/2 rate and a loss of 13% over 180 charge/discharge cycles. Its performance under variable C rates confirm the good stability of the cathodes with still a capacity of $50 \text{ mAh}\cdot\text{g}^{-1}$ at 105C. The interaction of the pyrene units with the CNTs was confirmed through quantum-chemical and molecular modeling simulations, showing a stronger adsorption of the pyrene-based PTMA on CNTs compared to PTMA.

11.5 Experimental section

11.5.1 Synthesis procedures

11.5.1.1 Materials

Toluene (VWR, 99%), tetrahydrofuran (THF, VWR, 99%) and DCM (CH_2Cl_2 , VWR, 99%) were dried using an MBraun solvent purification system under N_2 . Multiwall carbon nanotubes NC7000 (MWCNT) were provided by Nanocyl. 1-Pyrenemethanol (98%, Aldrich), bromoisobutyryl bromide (98%, Aldrich), 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM, $\geq 98\%$, TCI), copper(I) bromide (CuBr , 98%, Sigma Aldrich), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$, Sigma Aldrich), hydrogen peroxide solution (50vol%, VWR), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, $\geq 98\%$, Sigma Aldrich), methacryloyl chloride (97%, Aldrich), triethylamine ($\geq 99\%$ Merck), and all other chemicals were used as received.

11.5.1.2 Pyrene methyl- α -bromoisobutyrate (Pyr-Ini)

Figure 11.6 displays the reaction affording Pyr-Ini. In a two-necked round-bottom flask, 1-pyrene methanol (2 g, 8.6 mmol, 1 eq) is solubilized into 50 mL of a toluene/THF (4/1) mixture. Bromoisobutyryl bromide (1.2 mL, 9.7 mmol, 1.13 eq), previously solubilized in 5 mL of THF, is added dropwise to the alcohol solution at 0°C . The mixture is stirred overnight at r.t.. After filtration, the residue is washed with water (3x) and dried under vacuum (Yield: 3.16 g, 96%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm): 1.94 (6H, s), 5.92 (2H, s), 8.02–8.30 (9H, m)

11.5.1.3 Pyrene methyl methacrylate (Pyr-M)

In a two-necked round-bottom flask, 1-pyrene methanol (1 g, 4.3 mmol, 1 eq) is solubilized into 50 mL of dry THF. Et_3N (1.25 mL, 12.9 mmol, 3 eq) is added and the mixture is cooled down to 0°C . Methacryloyl chloride (1.8 mL, 12.9 mmol, 3 eq) is added dropwise under N_2 and the

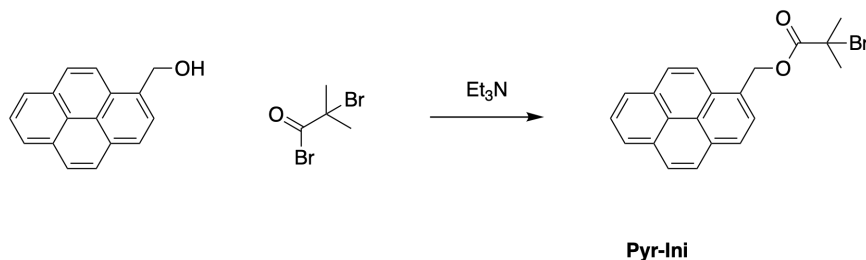


Figure 11.6 – Synthesis of the pyrene initiator.

medium is allowed to warm up to r.t. and kept under stirring for 12 h. After filtration of the $\text{NEt}_3\cdot\text{HCl}$ salt, the solvent is removed. The residue is solubilized in Et_2O and washed twice with water. The organic layer is dried over MgSO_4 , filtered and concentrated. The purification was done by recrystallization in EtOH (50 mL) at 40°C , filtrated while hot and the solid was dried under vacuum. Pyr-M was obtained as a white solid (Yield: 480 mg, 37%).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) $\delta(\text{ppm})$: 1.98 (3H, s), 5.57 (1H, s), 5.92 (2H, s), 6.16 (1H, s), 8.02–8.33 (9H, m)

11.5.1.4 Synthesis of Pyr-PTMPM (P2, P3)

In a round-bottom flask, a solution of Pyr-Ini (20 mg, 53 μmol , 1 eq), TMPM (3 g, 13 mmol, 250 eq) and HMTETA (30 mL, 0.11 mmol, 2 eq) in 4.2 mL of anhydrous THF was degassed by 3 freeze-pump-thaw cycles. In a second round-bottom flask, CuBr (8 mg, 5.3×10^{-2} mmol, 1 eq) was degassed by vacuum-nitrogen cycles. After the transfer of the monomer mixture onto CuBr, the resulting solution was degassed one more time by a freeze-pump-thaw cycle then heated at 90°C for 2 h. The polymerization was quenched by cooling down the reaction and putting it back to air. After filtration on basic alumina with DCM, the solvent was removed. The residue was solubilized in a small amount of DCM and precipitated in cold pentane. The white solid was isolated by filtration and dried at 40°C under vacuum (Yield: 1.962 g, 47%).

11.5.1.5 PTMPM-based (co)polymers oxidation into PTMA (co)polymers (Pox)

In a round-bottom flask Pyr-PTMPM (1.5 g, 6.5 mmol), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (600 mg, 1.8 mmol, 0.28 eq *vs.* N–H functions) and EDTA.2Na (390 mg, 1 mmol, 0.16 eq *vs.* N–H functions) are solubilized in 70 mL of MeOH. The mixture is heated at 60°C for 15 min, then H_2O_2 (7.5 mL, 0.13 mol, 20 eq *vs.* N–H functions) is added slowly and the reaction is carried out at the same temperature for 24 h. At r.t., the mixture is extracted with DCM, the organic layer is washed with water (3 times) and dried over MgSO_4 . After filtration, the solvent is removed and a purification is realized by re-precipitation in pentane to obtain the oxidized polymer as an orange solid (Yield: 1.331 g, 83%).

11.5.2 Modeling Methodology

To gain a better understanding of the quality of the interactions between the pyrene-PTMA polymer chains and the carbon nanotubes, we performed quantum-chemical DFT calculations on isolated pyrene and TMA fragments interacting with a graphene flake. The graphene flake is used as a model for the external wall of the nanotube and the physisorption of the molecular fragment has been assessed with equation 11.1. The uwB97xd DFT functional was used with the 6-31g** basis set; the counterpoise method was used to estimate the basis set superposition error (*BSSE*).

The adsorption energy, AE , was calculated as the difference between the potential energy of the adsorbed system and the sum of the potential energies for the isolated chain and nanotube. The contact surface area between the polymer chain and the nanotube, CSA, was estimated using the ‘solvent accessible surface area’ method and it is used to calculate the density of adsorption energy, DAE . The DAE allows to readily compare the strength of the polymer-nanotube interactions between the two systems.

$$AE = E_{sys} - (E_{mol} + E_{gr}) - BSSE \quad (11.1)$$

Where AE is the adsorption energy, E_{sys} the total energy of the system, E_{mol} and E_{gr} the potential energies of the molecular fragment

and the graphene flake as isolated, non-interacting, species.

To study the physisorption of the polymer chains on carbon nanotubes, we built a 60 monomer-long, random Pyr-PTMA copolymer chain having a molecular mass of 15000 and a 15:85 Pyr:TMA composition, which is representative of the real copolymers. This polymer is made to interact with a (77,77) single-wall nanotube with a diameter of about 10 nm. These calculations have been carried out by means of molecular dynamics (MD) simulations in vacuum at 300 K. The MD simulations were performed with the Gromacs 2016 molecular code and the Amber99sb force field. The Nose-Hoover thermostat was used to control the temperature and the LINCS algorithm was used to constrain the bond length to the force field value. The nanotube was considered as a periodic rigid body representing the outer surface of a typical MWCNT. The first step in the modeling is to allow the isolated polymer chain to coil up. The coiled polymer chain is then moved close to the nanotube and its adsorption and equilibration on the CNT are followed during a 10 ns – long MD simulation. Cylindrical distribution functions (CDF), which are a statistical measure of the positions of the different atoms with respect to the nanotube wall, were collected over the last 5 ns of the MD simulations, once the polymer chains have equilibrated.

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CHAPTER 12

P3HT-*B*-PTMA, THE USE OF A CONJUGATED BLOCK FOR IMPROVED CHARGE TRANSFER

Abstract

End-functionalized poly(3-hexylthiophene) (P3HT) and poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) were synthesized using controlled polymerization techniques and linked together to lead to a diblock copolymer structure via click cycloaddition. These diblock copolymers were further blended with carbon nanotubes (CNTs) to be used as cathodes in organic radical batteries. The performances of these batteries were studied during charge/discharge cycling at constant and variable current densities (C rate). In order to shed light on the importance of the diblock copolymer architecture, the results were compared to the capacities measured on electrodes made of blends of P3HT and PTMA homopolymers.

12.1 Introduction

The use of supramolecular interactions between PTMA and the conductive carbon additives allows for a high control on the polymer structure and the use of pristine conductive materials. In most of the reported studies, TEMPO units are integrated into a polymeric structure playing only the role of a matrix in order to lower the solubility or to enable interactions with the conductive carbon materials. Few examples deal with the combination between TEMPO groups and a conductive polymer backbone structure such as polypyrrole^[1,2] and polythiophene^[3,4] able to improve the overall charge transport.

The present chapter deals with the synthesis and the electrochemical properties of diblock copolymers associating a conjugated polymer (poly(3-hexylthiophene), P3HT) and a stable radical polymer (PTMA). Using a conjugated polymer block, we are aiming to: (i) improve the overall electrode performances by increasing the charge transport properties and (ii) take advantage of the supramolecular interactions between P3HT and CNTs^[5] to immobilize PTMA and minimize capacity losses during cycling. In the previous literature, the compounds associating TEMPO and P3HT are either made by electrodeposition or chemical polymerization of a thiophene ring bearing a TEMPO unit on the 3 position,^[4,6,7] or via the synthesis of copolymer architectures in which TEMPO units are connected through the 3 position via various linkers.^[8] Here, we design an architecture where the two blocks (P3HT and PTMA) are linked together as a diblock structure in order to preserve the individual properties of each constituent block.

12.2 Synthesis of the diblock copolymers

The synthetic pathway consisted in a direct coupling reaction between two pre-synthesized and end-functionalized P3HT and PTMA blocks. This strategy relies on a copper azide-alkyne coupling cycloaddition (CuAAC) of an azide end-functionalized PTMA (N3-PTMA) and an alkyne end-functionalized P3HT (P3HT-Alk) homopolymers.¹

¹The growing of the polymer precursor of the PTMA block, i.e. a poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate) (PTMPM) from a P3HT chain by atom transfer radical polymerization (ATRP) of the 2,2,6,6-tetramethyl-4-piperidyl methacry-

12.2.1 Synthesis of the N₃-PTMA block

The synthesis of the N₃-PTMA block, depicted on figure 12.1, follows a two-step process involving the homopolymerization of TPM from an azide-based initiator, followed by an oxidative treatment of the secondary amine functions into nitroxide groups.

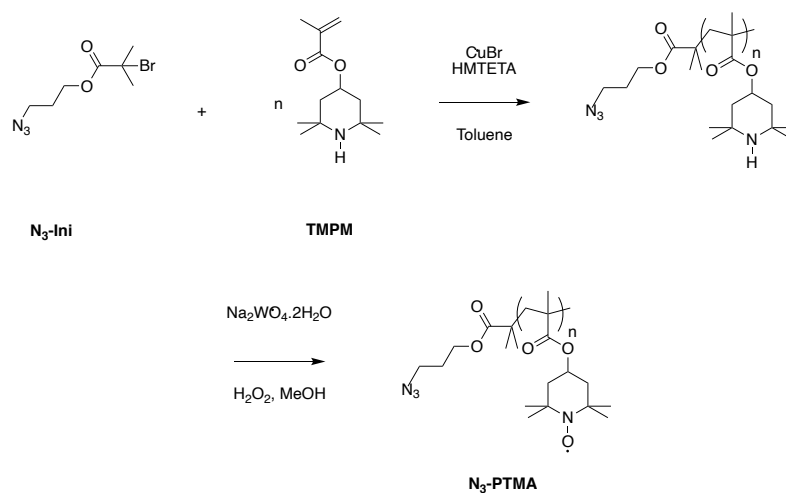


Figure 12.1 – Synthetic pathway to N₃-PTMAs.

Prior to the polymerization, the azide-based initiator (N₃-Ini) was prepared in a two-step process from the commercially available 3-bromo-1-propanol (Figure 12.2). The use of N₃-Ini also allows for an easy determination of the degree of polymerization (*DP*) by ¹H-NMR.

The homopolymerization of TPM ([TPM]₀ = 2.8 mol·L⁻¹) was then performed in toluene at 60 °C using a CuBr/HMTETA catalytic complex and the N₃-based initiator ([N₃-Ini]₀/[CuBr]₀/[HMTETA]₀ = 1/1/2).^[9] The reaction times were adjusted depending on the targeted *DP*. Two different N₃-PTMPM polymers were synthesized and characterized by both ¹H-NMR and SEC analysis. Experimental *DP*s were of 48 and 87 while the dispersity values equaled 1.21 and 1.18, respectively. These two compounds, abbreviated as N₃-PTMPM₄₈ and N₃-PTMPM₈₇, were then oxidized with an excess of H₂O₂ in the pres-

late (TPM) monomer was also considered but was impeded by the degradation of the P3HT block during oxidation of the PTMPM into PTMA.

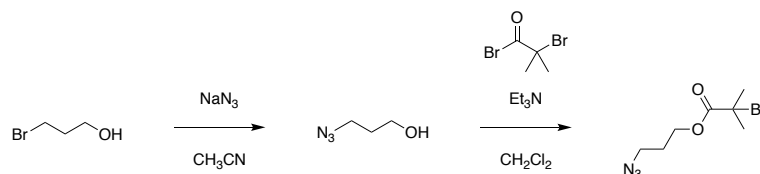


Figure 12.2 – Synthesis of the 3-azidopropyl 2-bromoisobutyrate (N_3 -Ini).

ence of $Na_2WO_4 \cdot 2H_2O$ /EDTA in methanol at 50°C for 24 hours ($[N_3\text{-PTMPM}]_0 = 20 \text{ g} \cdot \text{L}^{-1}$). The oxidation degrees of both $N_3\text{-PTMA}_{48}$ and $N_3\text{-PTMA}_{87}$ were determined by UV-visible absorption spectroscopy to be above 98% in each case.

12.2.2 Synthesis of P3HT-Alk block

The second block is prepared via a Kumada catalyst-transfer polycondensation (KCTP) on a 3-hexylthiophene-based monomer.^[10] This well-known KCTP procedure allows for a controlled polymerization in terms of molar mass and dispersity.^[11]

Regarding the synthetic pathway, a modified catalyst without any “ring-walking effect” along the polymer chain² was selected.^[12] The preparation of pure mono-functionalized P3HTs was then achieved in THF starting from a tolyl-modified catalyst freshly prepared using TMP-MgCl.LiCl (Figure 12.3). Homopolymerization of 3-hexyl-2-bromothiophene ($[3HT]_0 = 0.1 \text{ mol} \cdot \text{L}^{-1}$) was achieved in THF at -4°C using a (*o*-tolyl)Ni(dppp)Br prepared *in situ* by ligand exchange of (*o*-tolyl)Ni(PPh₃)₂Br by dppp (ratio 1 to 2) and 1 equivalent of TMP-MgCl.LiCl. Two homopolymers were prepared targeting *DP*s of 30 and 36, respectively. As determined by $^1\text{H-NMR}$, experimental *DP*s were determined to be 31 and 35, respectively, in very good agreement with the targeted values. Reactions were then quenched by addition of an

²the first attempts were carried out using TMPMgCl.LiCl but lead to the formation of di-functionalized P3HTs (evidenced by MALDI-ToF; 30%, as determined by $^1\text{H-NMR}$) contaminating the mono-functionalized P3HTs. This could lead to the formation of undesired tri-block structures.

excess of ((trimethylsilyl)ethynyl)magnesium chloride. The efficiency of the end-group functionalization was confirmed by recording matrix assisted laser desorption ionization - time of flight (MALDI-ToF) mass spectra (more details are provided in the experimental part).

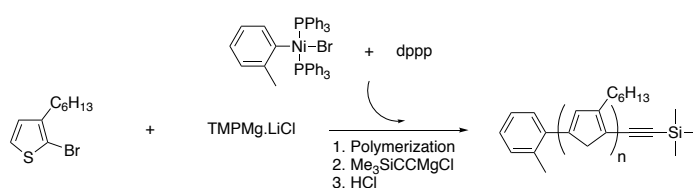


Figure 12.3 – Synthetic pathway to prepare the mono protected P3HT-Alk.

12.2.3 Coupling between P3HT-Alk and N₃-PTMA homopolymers

Both P3HT-PrAlk were deprotected at room temperature just before the coupling reaction using 2 equivalents of tetra-*n*-butylammonium fluoride in THF for 2 hours ($[P3HT-PrAlk]_0 = 0.47 \text{ mmol} \cdot \text{L}^{-1}$). The as-obtained deprotected P3HTs-Alk were then coupled with the N₃-PTMAs by CuAAC in THF ($0.94 \text{ mmol} \cdot \text{L}^{-1}$) using copper bromide and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as catalytic complex ($[CuBr]_0/[PMDETA]_0 = 0.86$) in the presence of sodium ascorbate ($[C_6H_7NaO_6]_0 = 1.9 \text{ mmol} \cdot \text{L}^{-1}$) at room temperature for 1.5 hours (Figure 12.4). Table 12.1 summarizes the experimental parameters of the P3HTs and the PTMAs involved in the coupling processes as well as the experimental parameters of the two obtained P3HT-*b*-PTMA diblock copolymers.

As represented for the P3HT₃₅-*b*-PTMA₄₈ sample, SEC analysis confirms the efficiency of the coupling process by a clear shift of the elution peak as compared to the P3HT₃₅-PrAlk engaged for the reaction. The efficiency of both couplings was also qualitatively attested by the disappearance, after CuAAC, of the alkyne and azide groups in FTIR (Figure 12.5).

Table 12.1 – Molecular characteristic features of the P3HT-*b*-PTMA diblock copolymers.

	$M_{n,P3HT}^a$ $\text{g}\cdot\text{mol}^{-1}$	$M_{n,PTMA}^c$ $\text{g}\cdot\text{mol}^{-1}$	$M_{n,COPO}^d$ $[\text{g}\cdot\text{mol}^{-1}]$	$\bar{D}^d$
P3HT ₃₅ - <i>b</i> -PTMA ₄₈ ^b	8300	6900	17,700	1.33
P3HT ₃₁ - <i>b</i> -PTMA ₈₇ ^b	7200	9900	11,800	1.34

^a As determined by SEC in CHCl₃ before coupling process.

^b Homopolymer experimental *DPs* determined by ¹H-NMR (CDCl₃, 500 MHz).

^c As determined by SEC in CHCl₃/IPA/Et₃N, 94/2/4 (in volume) before coupling process.

^d Diblock copolymer molar mass and associated dispersity value as determined by SEC (CHCl₃/IPA/Et₃N, 94/2/4 in volume).

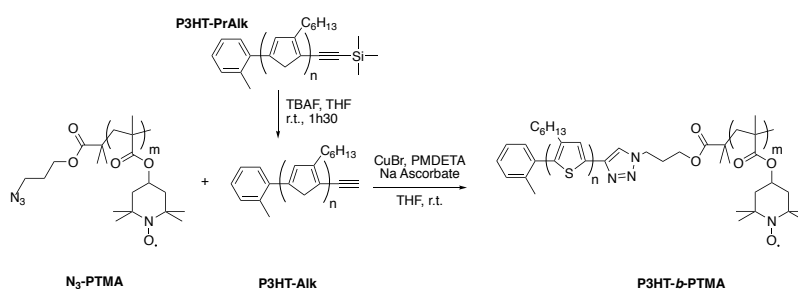


Figure 12.4 – Synthesis of P3HT-*b*-PTMA diblock copolymers by copper azide-alkyne coupling cycloaddition from P3HT-Alk and N₃-PTMA.

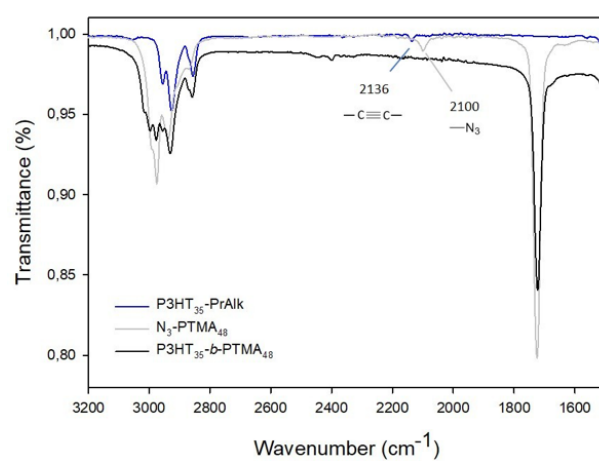


Figure 12.5 – FTIR spectra of the parent homopolymers *vs.* block copolymers P3HT-*b*-PTMA.

12.3 P3HT-*b*-PTMA copolymers, electrochemical characterizations

The diblock copolymers have been blended with multi-walled carbon nanotubes (MWCNTs) to prepare electrodes for electro-chemical measurements. A slurry made of a diblock copolymer/CNTs/binder mixture with a 30/60/10 wt% composition was prepared following a previously reported procedure^[9] to favor interactions between the diblock copolymer and the CNTs and thus enhance the stability of the composite. CNTs were first dispersed in NMP using short pulses of ultrasonication, then a solution of the copolymer was incorporated under sonication and the binder was added to this mixture directly before further stirring using a ball mill. 400 nm – thick films were obtained by deposition with a Doctor Blade and disks were cut to be used as the cathode in a half cell, prepared in the glove box under argon atmosphere. A lithium foil has been used as anode and reference electrode. All electrochemical tests have been performed using the same electrolyte, namely LiPF₆ at 1 M in EC/DEC (1:1; v:v).

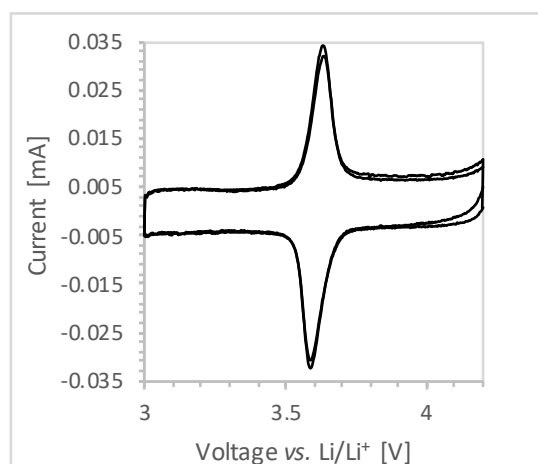


Figure 12.6 – Cyclic voltammogram of P3HT₃₅-*b*-PTMA₄₈ recorded at 0.1 mV·s⁻¹.

The electrochemical properties of the cells were first studied by cyclic voltammetry between 3.0 V and 4.2 V *vs.* Li/Li⁺. The P3HT-*b*-PTMA diblock copolymers exhibit the redox behavior of PTMA with a re-

versible oxidation peak centered at 3.6 V *vs.* Li/Li⁺ (Figure 12.6). This peak is characteristic of the oxidation of the nitroxide radical into oxoammonium cation. This process displays a fast charge transfer characterized by a narrow peak to peak separation (40 mV) and it is fully reversible, with successive curves overlapping each other.

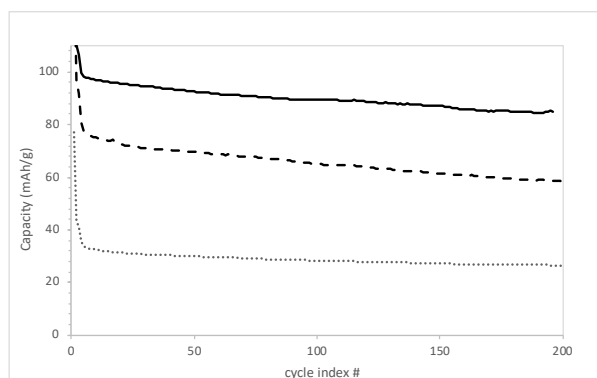


Figure 12.7 – Capacity retention of the P3HT-*b*-PTMA/CNTs cathodes at C/2 rate over 180 cycles; P3HT-*b*-PTMA, P3HT₃₅-*b*-PTMA₄₈ (solid line), P3HT₃₁-*b*-PTMA₈₇ (dash line), PTMA₈₀ (dot line).

The retention capacity behavior of the P3HT-*b*-PTMA-based cathodes was studied over 180 cycles by galvanostatic measurements at a C-rate of C/2 (corresponding to a full charge or discharge in 2 hours) between 3.0 V and 4.0 V *vs.* Li/Li⁺ (Figure 12.7). The performances of the P3HT-*b*-PTMA diblock copolymers are compared to those of a PTMA homopolymer of a similar molar mass ($DP = 84$). An initial capacity drop, due to irreversible processes, is observed for the three studied polymers during the first cycles. Compared to homo-PTMA cells, which are showing a loss of 54% after 180 cycles, the P3HT-*b*-PTMA electrodes are showing more stable capacities with only 13% and 20% loss for the P3HT₃₅-*b*-PTMA₄₈ and P3HT₃₁-*b*-PTMA₈₇ diblock copolymers, respectively. After 180 cycles the capacities of the P3HT-*b*-PTMA based cells remain high. P3HT₃₁-*b*-PTMA₈₇ displays a capacity of 60 mAh·g⁻¹ (54% of the theoretical value) while P3HT₃₅-*b*-PTMA₄₈ demonstrates a higher capacity of 85 mAh·g⁻¹ (77% of the theoretical value). These results are demonstrating good performances for the block copolymers, in particular for P3HT₃₅-*b*-PTMA₄₈.

The rate performances of the block copolymer P3HT₃₅-*b*-PTMA₄₈

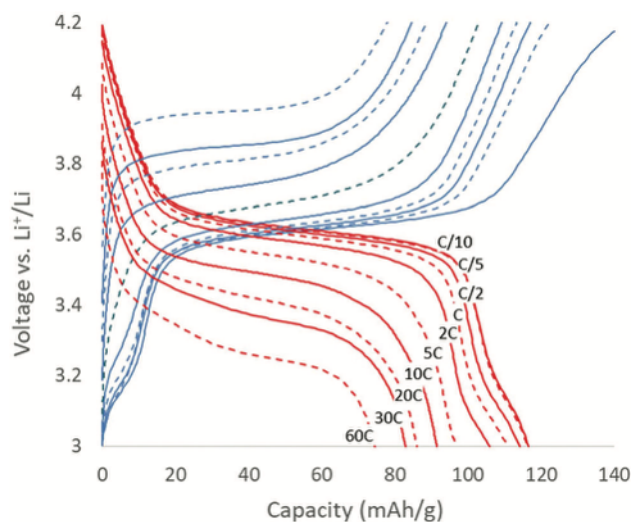


Figure 12.8 – Charge/discharge curves of P3HT₃₅-*b*-PTMA₄₈ from C/10 to 60C.

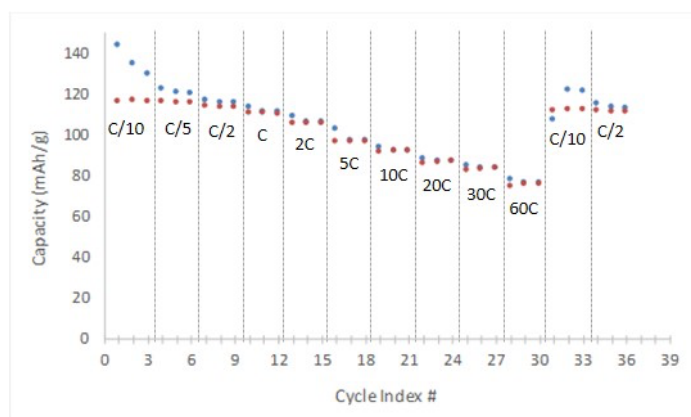


Figure 12.9 – Rate performances of P3HT₃₅-*b*-PTMA₄₈ from C/10 to 60C.

was investigated through charge/discharge cycles at different C-rates (from C/10 to 60 C) between 3.0 V and 4.2 V (Figure 12.8 and 12.9). When increasing the current density, the capacities are decreasing. At C/10 the cathode exhibits a capacity of $116 \text{ mAh}\cdot\text{g}^{-1}$. This value is moderately decreased to reach a capacity of $75 \text{ mAh}\cdot\text{g}^{-1}$ at 60 C, which is still over 67% of the nominal capacity at this high C-rate. At C/5 the curves are showing a plateau centered at 3.6 V *vs.* Li/Li⁺, characteristic of PTMA. Because of the polarization, this plateau is spread when in-

creasing the current density and keeps a symmetrical shape centered on 3.6 V *vs.* Li/Li⁺. At high C-rates, the spread of the charge and discharge curves is limited, with a polarization lower than 200 mV at 60 C. This is indicating a fast charge transfer between the active species and the electrically conductive charges thanks to favorable interactions between the two components. At low C-rate, the discharge curves are showing a change of slope at around 3.2 V *vs.* Li/Li⁺. In agreement with our previous work,^[9] such a behavior cannot be attributed to PTMA block while its origin has not been clearly identified.

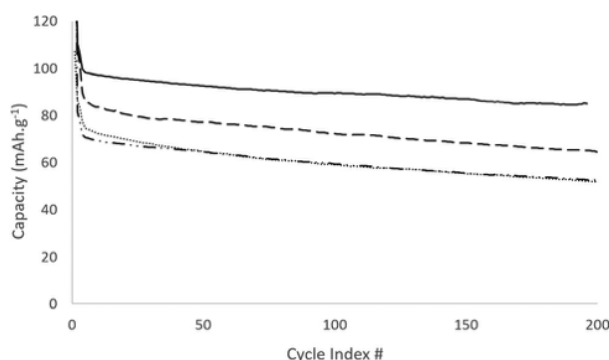


Figure 12.10 – Capacity retention of the block copolymer half-cells compared to PTMA and P3HT/PTMA physical blend in half-cells at C/2 rate over 200 cycles; P3HT-*b*-PTMA, P3HT₃₅-*b*-PTMA₄₈ (solid line), P3HT₃₁-*b*-PTMA₈₇ (dash line), PTMA₃₅₀ (dash/dot line), PTMA₃₅₀/P3HT physical blend (dot line).

In order to understand the effect of the conjugated polymer on the electrochemical behavior, control experiments were carried out with cathodes made from physical blends of P3HT and PTMA homopolymers, with the same P3HT/PTMA/CNTs/binder wt% ratio than previously used (10/20/60/10). The capacity retention of the resulting cells was measured using the same conditions (Figure 12.10). The cathode prepared from the homo-P3HT/homo-PTMA physical blend is displaying lower performances, similar to those of homo-PTMA-based cathodes, demonstrating the interest of the block copolymer design.

12.4 Modeling of P3HT-*b*-PTMA/CNT interfaces

In order to get insight on the interactions between P3HT-*b*-PTMA and CNT, molecular modeling simulations on the polymer/CNT interface were performed. In particular, molecular dynamics simulation (MD) was carried out to investigate whether the two blocks can mix at the interface or whether there is selective physisorption on the nanotube wall (More details are provided in the experimental part).

In order to reduce the computational cost of the simulations, a block copolymer composition intermediate between those of the polymers reported in table 12.1 was chosen. The model block copolymer consists of a P3HT block of 32 monomer units ($M_n = 5300 \text{ g}\cdot\text{mol}^{-1}$) combined with a PTMA block of 60 monomer units ($M_n = 14,600 \text{ g}\cdot\text{mol}^{-1}$) having a total molar mass $M_n = 19,900 \text{ g}\cdot\text{mol}^{-1}$. As model for the CNTs, we used a rigid, periodic single wall nanotube having a diameter of 5.4 nm, representing the outer wall of a multi-wall CNT.

At first, the adsorption energy and morphology on the CNT surface of the two blocks, considered as separate polymers were investigated. The adsorption energy, i.e. the polymer/nanotube interaction energy, E_{ads} , is calculated with equation 12.1.

$$E_{ads} = E_{sys} - (E_{poly} + E_{CNT}) \quad (12.1)$$

Where E_{sys} is the total potential energy of the polymer/CNT interface while E_{poly} and E_{CNT} are the internal potential energies for the polymer chain and the nanotube, respectively. In this model, since the nanotube was treated as a rigid body, its internal energy is considered to be equal to zero.

In order to understand whether one block interacts preferentially with the nanotube, the total adsorption energy calculated for the block copolymer chain has been decomposed in the energetic contributions coming from the adsorption of the P3HT and PTMA blocks. The results of this energetic analysis are reported in table 12.2. For comparison, the adsorption energies on the nanotube for the two blocks considered as homopolymers have also been calculated. Finally, since the blocks have different lengths and weights, the adsorption energy per monomer

unit (E_{mon}) has been calculated for an easier comparison of the affinities between the blocks and the nanotube.

Table 12.2 – Energetic analysis of the (co)polymer/CNT interfaces.

System	E_{sys} [kcal/mol]	E_{poly} [kcal/mol]	E_{ads} [kcal/mol]	E_{mon} [kcal/mol]
homo-P3HT	161.7	743.7	-582.0	-18.2
homo-PTMA	2959.3	3399.3	-440.0	-7.3
P3HT- <i>b</i> -PTMA	3268.7	3916.0	-647.3	-7.0
P3HT block	336.2	768.0	-431.8	-13.5
PTMA block	3173.5	3395.7	-222.2	-3.7

From the energetic analysis, the P3HT block has a much stronger affinity with the nanotube than PTMA. The adsorption energy per 3HT monomer unit is more than twice as large as that of the TMA units in the homopolymers. The difference is even larger in the copolymer, probably because the P3HT block reorganizes more efficiently when adsorbing on the CNT surface. The strength of the interaction between P3HT and CNTs stems from both $\pi-\pi$ stacking (favorable interactions between the heteroaromatic ring and the sp^2 -carbon surface) and CH- π interactions (weak hydrogen-bond interactions between the alkyl side groups and the CNT surface).^[13]

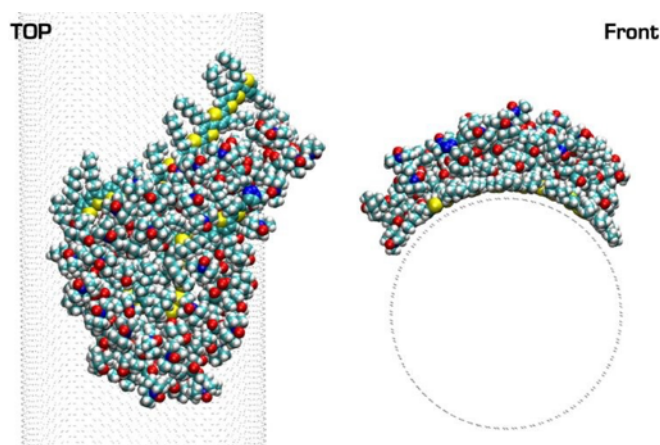


Figure 12.11 – Top (left) and front (right) views of the model P3HT-*b*-PTMA/CNT interface (nitrogen: blue; oxygen: red; sulfur: yellow).

Figure 12.11 shows top and front views of the interface. They illustrate the fact that the block copolymer/CNT contact takes place predominantly with the P3HT block (note the quasi absence of nitrogen and oxygen atoms at the CNT surface in the front view) and that the PTMA block lies away from the surface. Overall, these simulations thus indicate that the P3HT-*b*-PTMA copolymer chains interact with nanotubes mainly via the P3HT blocks, which act as strong anchor groups to keep the PTMA blocks in contact with the nanotubes. This organization is expected to both suppress the solubilization of the PTMA chains in the electrolyte and to favor the charge transfer between the redox polymer and the nanotube via the conjugated system. In contrast, PTMA in a mixture with P3HT does not benefit from these two features.

12.5 Conclusion

In this chapter a block copolymer associating poly(3-hexylthiophene) and poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (P3HT-*b*-PTMA) has been designed and synthesized. While PTMA segments were prepared by ATRP, P3HT blocks were generated by KCTP. Both types of blocks were characterized by defined molar masses, narrow dispersities and controlled end-groups. Very efficiently, P3HT-*b*-PTMA diblock copolymers were obtained by a copper azide-alkyne coupling cycloaddition of these two end-functionalized blocks.

Films of P3HT-*b*-PTMA/CNTs/binder (30/60/10 in weight) were used as cathodes and their performances in half-cells were studied. As compared to homopolymers or physical mixtures of both P3HT and PTMA, the diblock topology allows a real improvement of the capacity cells to be obtained. The electrochemical properties of the half-cells are improved by 25% for P3HT₃₁-*b*-PTMA₈₇ with a capacity of 60 mAh·g⁻¹ after 180 cycles (54% of theoretical capacity) and by 60% for P3HT₃₅-*b*-PTMA₄₈ (85 mAh·g⁻¹ after 180 cycles, 77% of theoretical capacity). The rate performances recorded between C/10 and 60C show a decrease in capacity from 116 mAh·g⁻¹ to 75 mAh·g⁻¹ (67% of the nominal capacity). The initial properties were recovered while using the initial rate at the end of the experiment, confirming the stability of the P3HT-*b*-PTMA electrodes.

Molecular modeling simulations were used to investigate the block

copolymer/CNT interface. These calculations show a stronger interaction between CNTs and P3HT than with PTMA. The block copolymer behaved as PTMA is immobilized close to the CNTs via P3HT anchoring groups, confirming the high stability observed in capacity and the good cell performances probably resulting from a facilitated electron transfer between the CNT and the redox units of the close by PTMA chains.

12.6 Experimental section

12.6.1 Materials

Tetrahydrofuran (THF, VWR, 99%) is dried using an MBraun solvent purification system under N₂. 3-Bromo-1-propanol (97%, Acros), sodium azide (≥99%, Merck), bromoisobutyryl bromide (98%, Aldrich), 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM, >98%, TCI), copper(I) bromide (CuBr, 98%, Sigma aldrich), HMTETA (97%, Aldrich), PMDETA (99%, Aldrich), (+)-sodium *L*-ascorbate (Sigma), sodium tungstate dihydrate (Na₂WO₄·2H₂O, ≥99%, Sigma Aldrich), hydrogen peroxide solution (50 vol%, VWR), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA·2Na, ≥98%, Sigma Aldrich), tetrabutylammonium fluoride solution (TBAF, 1M/THF, Acros), 1,3- bis(diphenylphosphino)-propane (dppp, 97%, Alfa Aesar), 2,5-dibromo-3-hexylthiophene (>97%, TCI), 2-bromo-3-hexylthiophene (>98%, TCI), isopropylmagnesium chloride solution (2 M/THF, Aldrich), ethynyltrimethylsilane (98%, merck), triethylamine, isopropanol and all other chemicals are used as received. Multiwall carbon nanotubes NC7000 (MWCNT) are provided by Nanocyl.

12.6.2 Characterization

12.6.2.1 Proton nuclear magnetic resonance

Proton nuclear magnetic resonance (¹H-NMR) spectra are recorded at room temperature in CDCl₃ at a concentration of 10 mg per 0.6 mL on a Bruker AMX500 (500 MHz) equipment, with a shift reported in ppm downfield from tetramethylsilane used as an internal reference.

12.6.2.2 Size exclusion chromatography

Size exclusion chromatography (SEC) is performed in CHCl₃ / IPA / Et₃N (for PTMA homopolymers) or in THF (for both P3HT homopolymers and corresponding copolymers) at 30°C using an Agilent liquid chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = 1 mL·min⁻¹), an Agilent autosampler (loop volume

= 100 μ L, solution conc. = 1 mg·mL⁻¹), an Agilent-DRI refractive index detector and three columns: a PL gel 10 μ m guard column and two PL gel Mixed-D 10 μ m columns (linear columns for separation of MWPS ranging from 500 to 10×10^7 g·mol⁻¹). PMMA standards are used for calibration for the analyses in CHCl₃/IPA/Et₃N. PS standards are used for calibration in THF.

12.6.2.3 Positive-ion MALDI-mass spectrometry

Positive-ion MALDI-mass spectrometry (MALDI-MS) experiments are recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65 μ J delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses are performed in the reflectron mode at a resolution of about 10,000. All samples are analyzed using trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix,^[14] which is prepared as a 40 mg·mL⁻¹ solution in CHCl₃. This solution (1 μ L) is applied to a stainless-steel target and air-dried. Polymer samples are dissolved in CHCl₃ to obtain 1 mg·mL⁻¹ solutions. Therefore, 1 μ L of this solution is applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) is set to pass all the ions of the distribution, and they are transmitted into the pusher region of the TOF analyzer where they are mass analyzed with 1 s integration time. Data are acquired in continuum mode until acceptable averaged data are obtained.

12.6.2.4 UV-visible spectroscopy

Oxidation degree of the PTMA is determined through UV-visible titration using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO-OH) using the peak at 460 nm.^[15]

12.6.2.5 Electrochemical characterizations

Slurry preparation, electrode design, cell assembly and electrochemical measurements are achieved following the procedures described in a previous work^[9] as disclosed in chapter 11.

12.6.3 Synthesis procedures

12.6.3.1 Synthesis of 3-azido-1-propanol

A solution of 3-bromo-1-propanol (1.54 g, 11 mmol, 1 eq) and NaN₃ (1.44 g, 22 mmol, 2 eq) in 15 mL of acetonitrile (AcCN) is stirred under reflux for 24 h. Water is added, and sodium salts are removed. Aqueous media is extracted with AcCN, then organic layer is dried over MgSO₄ and the solvent is removed. Residue is solubilized in Et₂O, washed twice with water. Organic layer is dried over MgSO₄ and solvent is removed. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm): 3.76 (2H, m, CH₂-OH), 3.46 (2H, t, CH₂-N₃), 1.84 (2H, m, CH₂); FT-IR (ATR, cm⁻¹): 2090 (N₃), 3349 (OH).

12.6.3.2 Synthesis of 3-azidopropyl 2-bromoisobutyrate (N₃-Ini)

3-Azido-1-propanol (750 mg, 7.4 mmol, 1 eq) is solubilized in 20 mL of dry CH₂Cl₂. At 0 °C, Et₃N (1.25 mL, 8.9 mmol, 1.2 eq) is added and mixture is stirred for 1 min. Then, bromoisobutyryl bromide (1 mL, 8.1 mmol, 1.1 eq) is added dropwise into the solution and the mixture is stirred 2 h at 0 °C, warmed up to r.t. and stirred 15 h. After filtration of the insoluble salts, the organic layer is washed 3 times with water, dried over MgSO₄ and the solvent is removed. Residue is solubilized in THF, Pd/C is added, and the mixture is stirred at r.t. for 24 h before being filtrated onto celite. ¹H-NMR (CDCl₃, 500 MHz): δ (ppm): 4.28 (2H, CH₂-O), 3.45 (2H, CH₂-N₃), 2-1.94 (8H, m, CH₃ and CH₂); FT-IR (ATR, cm⁻¹): 2095 (N₃).

12.6.3.3 Synthesis of N₃-PTMPM

In a round-bottom flask, a solution of N₃-Ini (46 mg, 0.18 mmol, 1 eq), TMPM (2.5 g, 11.1 mmol, 60 eq) and HMTETA (100 μ L, 0.37 mmol, 2 eq) in 4 mL of anhydrous THF is degassed by 3 freeze-pump-thaw cyclings. In a second round-bottom flask, CuBr (26 mg, 0.18 mmol, 1 eq) is degassed by vacuum-nitrogen cycles. After the transfer of the TMPM mixture onto CuBr, the resulting solution is degassed one more time by

a freeze-pump-thaw cycle then heated at 50 °C for 2 h. Polymerization is quenched by cooling down the reaction and exposure to the air. After filtration on basic alumina with DCM, solvent is removed. Residue is solubilized in a small amount of DCM and precipitated in cold pentane. The white solid is isolated by filtration and dried at 40 °C under vacuum (Yield: 1.77 g, 69%).

FT-IR (ATR, cm^{-1}): 2124 (N_3), 3390 (NH).

12.6.3.4 Synthesis of N_3 -PTMA

In a two-necked round-bottom flask fitted out with a condenser, N_3 -PTMPM (1 g, 4.4 mmol of NH functions, 1 eq), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (404 mg, 1.3 mmol, 0.28 eq) and EDTA.2Na (260 mg, 0.7 mmol, 0.16 eq) are solubilized in 50 mL of MeOH. The solution is stirred at 60 °C for 10 min before adding H_2O_2 (5 mL, 50 vol%, 73.5 mmol, 16.7 eq) dropwise over 1 h. The solution is then stirred at 60 °C for 24 h. The polymer is extracted using DCM, organic layer is washed 3 times with water, dried over MgSO_4 and the solvent is removed under reduced pressure. The residue is solubilized in DCM, precipitated in cold pentane, filtered and dried at 40 °C under vacuum overnight to afford an orange solid (Yield: 0.87 g, 82%).

FT-IR (ATR, cm^{-1}): 2099 (N_3).

12.6.3.5 Synthesis of protected P3HT-Alk (P3HT-PrAlk)

A two-necked round-bottom flask is fitted with bromo(o-tolyl)bis-(triethylphosphine) nickel(II) (93 mg, 0.12 mmol, 1 eq) and dppp (102 mg, 0.25 mmol, 2 eq) solubilized in 35 mL of dry THF. This solution is stirred at r.t. for 15 min. 2-Bromo-3-hexylthiophene (0.74 mL, 3.7 mmol, 30 eq) and $\text{TMPMgCl} \cdot \text{LiCl}$ (3.7 mL, 3.7 mmol, 30 eq) are added to the previous mixture and the solution is stirred at is for 40 min. A freshly prepared quencher is added (2 mL, 8 eq) and mixture is allowed to stir 1 h. Precipitation in MeOH, filtration and purification by Soxhlet extraction using MeOH and acetone followed by solubilization in CHCl_3 and reprecipitation in MeOH afford the expected polymer as a dark solid (Yield: 339 mg).

FT-IR (ATR, cm^{-1}): 2136 (alkyne).

Experimental *DP* is calculated from the intensities of the methyl peak of the tolyl group at 2.5 ppm and the one of the first CH₂ of the hexyl side chain at 2.81 ppm, and is found to be in good agreement with the targeted value.

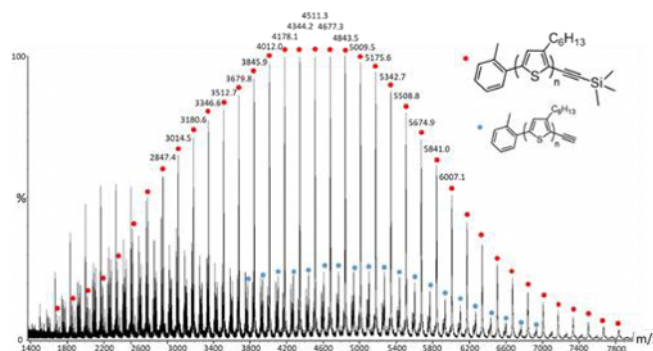


Figure 12.12 – MALDI-ToF spectrum of the P3HT₃₁-PrAlk.

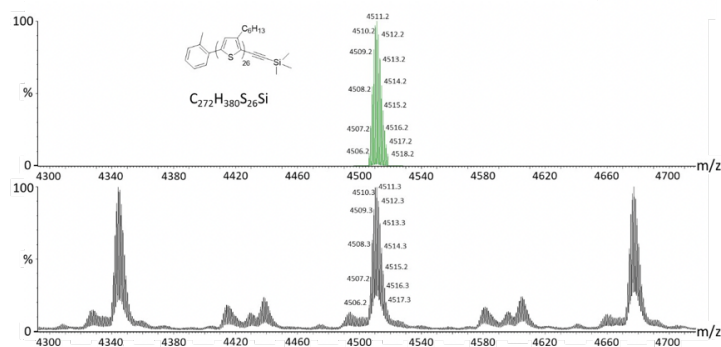


Figure 12.13 – Magnification of the MALDI-ToF spectrum. Comparison between the experimental spectrum (bottom) and the expected polymer (top) with a *DP* of 26. Major peaks are found every 166.1 uma as expected for a 3-hexylthiophene repeating unit (C₁₀H₁₄S).

The MALDI mass spectrum presents one main distribution corresponding to 3-hexylthiophene polymer with the expected end-groups (Figures 12.12 and 12.13). Beside the targeted P3HT end-functionalized with an *o*-tolyl on one side and a protected alkyne on the other side (red dots), deprotected polymer (blue dots) is also formed.

12.6.3.6 Deprotection of trimethylsilylethynyl-P3HT (P3HT-Alk)

In a round-bottom flask trimethylsilylethynyl-P3HT (236 mg, $M_n = 5000 \text{ g}\cdot\text{mol}^{-1}$, $4.72 \times 10^{-5} \text{ mol}$, 1 eq) is solubilized in 100 mL of dry THF. TBAF (95 μL , $9.4 \times 10^{-5} \text{ mol}$, 2 eq) is added and resulting mixture is stirred at r.t. for 2 h. Part of the THF is removed under reduced pressure, then 50 mL of water are added, and the mixture is extracted with 50 mL of CHCl_3 . The as-obtained organic layer is washed 3 times with water (30 mL), dried over MgSO_4 and solvent is removed under reduced pressure, affording ethynyl-P3HT as a dark solid, used directly in the next step.

12.6.3.7 Synthesis of P3HT-*b*-PTMA

A solution of ethynyl-P3HT ($4.72 \times 10^{-5} \text{ mol}$, 1 eq), N_3 -PTMA (557 mg, $4.72 \times 10^{-5} \text{ mol}$, 1 eq), sodium ascorbate (16 mg, $8 \times 10^{-5} \text{ mol}$, 1.7 eq) and PMDETA (16 μL , $7.5 \times 10^{-5} \text{ mol}$, 1.6 eq) solubilized in 50 mL of anhydrous THF is degassed by 3 freeze-pump-thaw cyclings. In a second round-bottom flask, CuBr (10 mg, $6.6 \times 10^{-5} \text{ mol}$, 1.4 eq) is degassed by vacuum-nitrogen cycles. After the transfer of the solution onto CuBr, the resulting solution is degassed one more time by a freeze-pump-thaw cycle and stirred at r.t. for 36 h. Part of the THF is removed under reduced pressure, mixture is precipitated into MeOH, filtered to afford a dark solid dried at 40°C under vacuum overnight (Yield: 690 mg, 87%).

12.6.4 Modeling methodology

Molecular dynamics simulations (MD) are performed with the Biovia Materials Studio 2018 modeling package using a modified version of the Dreiding force field^[16] designed to improve the description of the torsion along the P3HT backbone. This force field has been further optimized to properly describe the flexibility of the PTMA chains. The P3HT-*b*-PTMA polymer chosen for calculations consists of a P3HT block of 32 monomer units combined with a PTMA block of 60 monomer units.

At first, the adsorption energy and morphology on the CNT surface of the two blocks, considered as separate polymers are investigated. A standard procedure is used for all the simulations: first the structure of

the chain is relaxed in vacuum. Next, a MD simulation is performed to allow the chain to change its conformation and possibly coil. Finally, the chain is placed close to the nanotube and a 5 ns long MD simulation is performed at 300 K to allow it to adsorb and diffuse on the nanotube surface.

The adsorption energy E_{ads} is computed considering E_{sys} is the total potential energy of the polymer/CNT interface while E_{poly} and E_{CNT} are the internal potential energies for the polymer chain and the nanotube. The total adsorption energy for the copolymer is decomposed into energetic contributions coming from the adsorption of the P3HT and PTMA blocks to allow the understanding of whether one block interacts preferentially with the nanotube. Since the blocks have different lengths and weights, the adsorption energy per monomer unit, E_{mon} , is calculated for an easier comparison of the affinities between the blocks and the nanotube.

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CHAPTER 13

COMPARISON OF COVALENT AND NON-COVALENT CNT-MODIFICATIONS WITH NITROXIDE POLYMERS

Abstract

This chapter is exposing a comparison of all covalent and non-covalent surface strategies applied for the preparation of electroactive materials based on nitroxide (co)polymers and MWCNTs. The focus is set on their synthetic pathways and their resulting electrochemical properties.

13.1 Introduction

The present thesis work laid down several strategies to achieve higher electrochemical performances from hybrid materials based on carbon nanotubes (CNTs) and derivatives of the redox active poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA). Owing to their inert nature, CNTs in their pristine state do not disperse well in organic matrices. Suitable enhancements of their surface is thus required in order to optimize their dispersion with respect to the organic fraction, which in the frame of our development projects is paramount to enhance the electrochemical properties of the resulting composite. Another aspect of surface chemistry is that it can favor the immobilization of the polymeric structure on the CNTs. This is addressing one of the major issues of PTMA-derived structures, that is their solubilization in common lithium-ion battery (LIB) electrolytes, which is detrimental to the capacity retention during cycling.

Since a relatively broad assortment of strategies have been explored, they deserve a comparison highlighting their relative pros and cons, on which selection criteria can be drawn according to the intended application context.

13.2 Synthetic pathways

Out of the various strategies to achieve surface modifications, two main categories are usually distinguished, i.e. either covalent or non-covalent approaches. During our developments, two strategies have been explored for each of these categories. These strategies are consisting in: (i) the direct polymerization initiated from the CNTs (grafting from, chapter 5),^[1] (ii) the direct anchoring of presynthesized chains onto CNTs (grafting onto, chapter 6),^[2] (iii) the use of polymers structures bearing pyrene-tag moieties susceptible to interact with the CNT walls (Chapter 11),^[3] and (iv) the use of copolymers bearing the electroactive PTMA block in addition to a conjugated poly(3-hexylthiophene) (P3HT) block, the latter being selected for its conducting properties and its susceptibility to adsorb itself on CNTs (Chapter 12).^[4] The two former strategies belong to the covalent category, while the two latter belong to the non-covalent one.

From a synthesis standpoint, grafting onto strategies are usually acknowledged to be more convergent and thus more favorable than grafting from ones. This statement holds true as well for the strategies that we designed in our research projects. Comparing grafting from and grafting onto strategies, for all steps starting from the pristine multi-walled carbon nanotubes (MWCNTs) until the grafting step *per se*, all reactants and synthetic efforts are fairly similar. Yet, taking into account both the polymerization step in the grafting onto case and its subsequent grafting step, significant differences are arising compared to the grafting from. Firstly, in the grafting onto strategy, the polymerization could be done at the gram scale or higher, with full monomer conversion, and the polymer could be directly converted in batch to the electroactive form. Secondly, although the yield of the grafting onto step with respect to the polymer remained relatively low (<10%), this is still much higher than the yield obtained with the grafting from (<1%, set against equivalent of monomers).

Non-covalent strategies advantageously do not require any tedious chemical treatment of the CNT surface, which in contrast represents the major difficulty of covalent strategies, limiting their yield and potential synthesis at larger scales. Comparing the two non-covalent approaches, the synthesis of the pyrene-tagged (co)polymers appears simpler. Notably, the P3HT-*b*-PTMA copolymer involves a significantly higher number of synthetic steps: preparation of the Ni catalyst for the P3HT polymerization, synthesis of the initiator for the polymerization of the PTMA block, polymerization of each block separately, chain-end modification of the mono-protected alkyne-P3HT and coupling of P3HT and PTMA blocks. Comparatively, pyrene-tagged PTMA (co)polymers are only involving the synthesis of pyrene-tagged initiators and comonomer in addition to the typical steps toward the synthesis of PTMA derivatives via radical polymerization methods (polymerization of hindered amine precursor and subsequent oxidation into nitroxide bearing PTMA (co)polymers).

Therefore, all these strategies can be classified as follows, from the least to most simple and efficient: MWCNT-*g*-PTMA, grafting from < MWCNT-*g*-PTMA, grafting onto < P3HT-*b*-PTMA < pyrene-tagged (co)polymers.

13.3 Electrochemical properties

Each of the covalent and non-covalent strategies that we have developed has individually demonstrated their performance superiority over their homopolymer counterpart, bearing solely TMA repeating units. Not only the benefits ascribed to our genuine designs resulted in enhanced capacity retention - thanks to the prevention of PTMA migration — but also resulted in improved power performances thanks to the better contact of PTMA with respect to the CNT conducting charge coming along with an improved dispersion of CNT and redox polymer fractions.

Since these strategies are displaying differences in their designs, their resulting properties should be subject to variations. Yet the properties and relative benefits of each design had still to be compared to each other from an electrochemical standpoint.

Among all tested designs, the MWCNT-*g*-PTMA via grafting from stands out for its superior capacity thanks to its higher PTMA content (60 wt%); all the other designs are displaying similar PTMA contents (between 20 wt% and 30 wt%) and thus similar specific capacities.

Regarding the cyclability, significant differences could be expected between covalent and non-covalent strategies. The former could demonstrate more robust anchoring on the CNT substrate - provided that the covalent bond remains stable - in comparison with non-covalent strategies where the polymer can theoretically desorb at all time. Yet capacity decays were observed with both non-covalent strategies. The related PTMA-based copolymers solved this issue by proper designs embedding a high enough proportion of the block or units dedicated to the interaction with the MWCNT substrate.

The plot presented in figure 13.1 displays galvanostatic performance data obtained with the best design for each strategy as well as the results for 30 wt% and 60 wt% PTMA control electrodes. This plot displays nominal capacities (at the end of the conditioning cycles) and capacities at the cycle 100, on which the capacity retention, also plotted, is expressed as a percentage. The capacities are provided with respect to the whole electrode material, i.e. including CNTs, electroactive PTMA-based (co)polymers, and binder if any. Although the covalent strategies have been proved to afford robust electrode materials, they are dis-

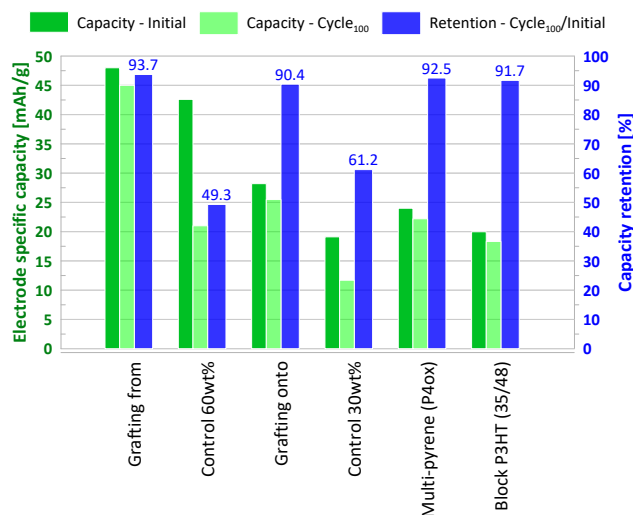


Figure 13.1 – Comparison of specific capacity and capacity retention of all covalent and non-covalent strategies.

playing here no significant advantage over the non-covalent strategies in terms of capacity retention, all of them being able to achieve capacity retention higher than 90%. Nevertheless the covalent strategies are displaying the advantage of higher specific capacities by minimizing the dead weight of the interacting block or groups in the resulting electrode.

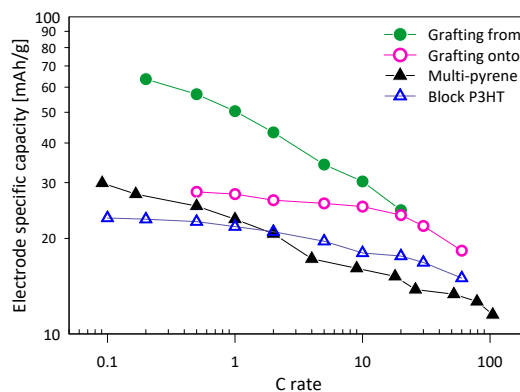


Figure 13.2 – Comparison of power performances of all covalent and non-covalent strategies.

A comparison from the power performance standpoint requires to

have a more detailed picture based on the rate capabilities. To this end, a plot of the capacity at different C-rates allows to compare the power performances (Figure 13.2). Since the plot has to provide a representation of the power performances of the systems, the specific capacity is again set relative to the whole electrode material including MWCNTs, polymeric fraction and binder if any. The C-rate in this chart is still referring to a current density relative to the active material loading, i.e. the PTMA fraction alone. The analysis of this graph suggests that the grafting from strategy offers the best power performances as long as the C-rate is maintained below 20C. At this rate, the material obtained via grafting onto is matching the capacity of the composite obtained via grafting from. Together these two covalent strategies are also exhibiting the best power performances over the common C-rate range explored during our evaluations. The fact that these strategies are exhibiting better rate performances than the non-covalent strategies seems to indicate that dispersion properties had a greater impact on the performances than the preservation of the sp_2 network of the CNT outer walls.

Regarding non-covalent strategies, they allow to reach specific capacities similar to the grafting onto strategy at moderate C-rates. Below 0.5C, the capacity obtained with the pyrene-tagged copolymer can even be slightly higher. Afterwards, the capacity drops, becoming eventually lower than the approach relying on P3HT-*b*-PTMA at C-rates higher than 2C.

13.4 Conclusion

Based on the considerations exposed beforehand, selection criteria can be laid down for each of our designed materials. The selection is mostly based on the balance that has to be put between electrochemical performances and synthesis efforts. Regarding the relative properties of each system, the projections anticipated in chapter 10 can be reformed. The table 13.1 – which is an updated version of table 10.1 – summarizes them.

As evidenced in Figure 13.2, when specific capacity and power performances are critical, grafted materials are the best performing, and the grafted from material is superior to its grafting onto counterpart at

Table 13.1 – Covalent and non-covalent modifications of MWCNTs with PTMA: comparisons of the relative properties.

benefits	π - π interactions		grafting	
	pyrene tag	P3HT- <i>b</i> -PTMA	from	onto
ease of synthesis	++	+	--	–
CNT conductivity	+	+	–	–
robustness	+	+	+	+
capacity	+	–	++	+
high rate performances	–	–	++	++

C-rates up to 20C or below.

Once the requirements are set to the highest specific capacity but only at very high rates (>20C), the grafting onto strategy becomes a more sensible choice thanks to its simpler and more efficient synthetic pathway.

For the sake of efficiency and simplicity of synthesis, the non-covalent approaches become also more relevant if requirements can better tolerate lower specific capacity and power performance metrics than those obtained via covalent approaches. The selection of either of the two non-covalent approaches depends on how valuable are the high rate capabilities with respect to the synthesis efforts. If high power metrics are more desirable, then the P3HT-*b*-PTMA has to be considered.

Lastly, pyrene-tagged copolymers should be favored in a context where the synthesis should be as straightforward as possible, and could also be preferred to the P3HT-*b*-PTMA when better low rate specific capacity is desired.

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Part VI

Appendix B

CHAPTER 14

ELECTROCHEMICAL CHARACTERIZATION TECHNIQUES

Abstract

This chapter presents a review on electrochemical cell configurations, testing methods, and characterization techniques. The concepts described here are frequently encountered during experimental developments and are commonly implemented for evaluations of materials, components and systems in the electrochemical energy storage field.

14.1 Cell setups and configurations

There are various electrochemical techniques and conditions, using multiple and various electrode materials and cell components, that can be implemented in a large set of cell setups. These setups are typically categorized according to the arrangement of electrodes involved in the experiment. The related categories are then distinguished: half-cell, symmetrical cell, and full-cell configuration (Figure 14.1) The former and the latter are often sub-categorized as two-electrode or three-electrode configurations.

The overview of the various electrochemical configurations relevant to battery component testing requires first a definition of the terminology in use regarding the electrodes. In a half-cell setup, the electrodes are usually named as working electrode (WE), counter electrode (CE), and reference electrode (RE).¹ The setup can be either a two-electrode or a three-electrode configuration. In this two-electrode configuration, the WE potential is either measured at very low current density or the WE potential is controlled and monitored *vs.* the CE, acting as a pseudo-RE. In the case of full-cell setups, either in two-electrode or three-electrode configuration, the electrodes undergoing the charge-discharge process are better qualified as negative (N) and positive (P) electrodes.

Regarding the different cell setups, each of them presents some advantages and limitations owed to the nature and arrangement of the electrodes. The proper choice among them is therefore dictated by the aim of the research and its level of development. In more details, the different cell setups and configurations (Figure 14.1) as well as their applications can be described as follows,

- Half-cell: There are two configurations, either with two (a) or either with three electrodes (b). In configuration (a), the materials under study is assigned to the WE, while the other electrode both serves as CE and pseudo-RE. To fill its role as pseudo-reference, this latter electrode should display a limited overpotential and a

¹To be more accurate in this description, in a lot of literature reports, the RE should be better qualified as a pseudo-reference, as all criteria for this electrode cannot be applied or have not been verified in order to consider it as a true reference. This is most often the case when considering a two-electrode configuration and/or when the potential is set against a Li/Li⁺ electrode.

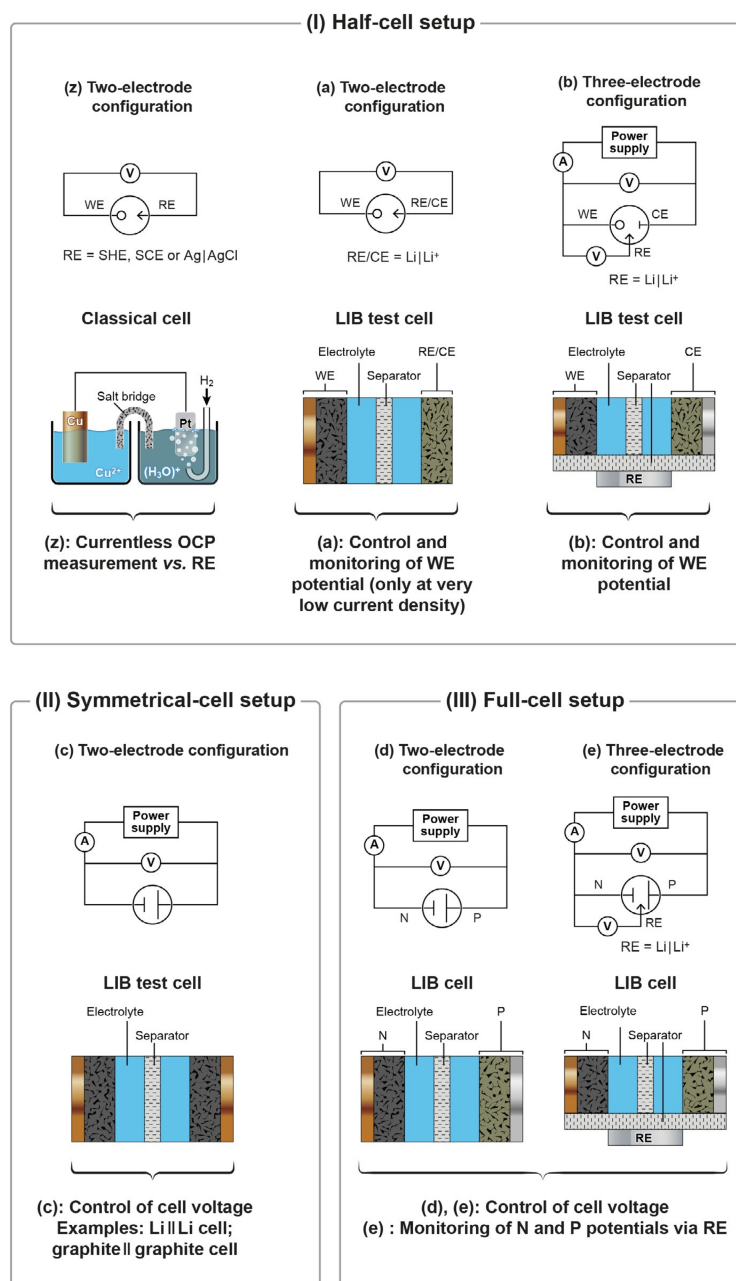


Figure 14.1 – Overview of the different cell setups typically used in battery research. (I) half-cell setup, including (z) setup for OCP measurement *vs.* RE (currentless), (a) two-electrode configuration (gives only accurate electrode potentials at very low current density at RE/CE) and (b) three-electrode configuration; (II, (c)) symmetrical-cell setup; (III) full-cell setup, including (d) two-electrode configuration and (e) three-electrode configuration.^[1]

stable voltage during the whole cycling process. Commonly available two electrode cell designs are typically Swagelok cells and coin cells. In three-electrode configuration (b), the purpose is usually the same as the two-electrode configuration. This configuration is usually implemented when an actual electrode as (pseudo-)reference is suitable. In both cases of electrode configuration, account must be taken that the CE should not limit or affect the cell performances in any way. Critically the CE should display a capacity in large excess compared to the WE. These two half-cell configurations prove to be useful in the initial stages of the research to study the intrinsic electrode properties (reversible capacity, coulombic efficiency, stability, rate capability etc.) Furthermore, the excess of lithium is guaranteed by the CE if Li metal is used.

- Symmetrical cell: The cell is operated via control of the cell voltage during charge-discharge cycles. A representative example is the plating-stripping of lithium using two lithium metal electrodes. In the literature, the cell coupling a material in the lithiated state against the same material in the delithiated state is also described as a symmetrical cell. Examples are found with graphite, NMC etc.^[2-4] However, after assembly the cell should be better referred as being pseudo-symmetrical.^[1] The main use of this setup is the comprehensive investigation of electrolyte components and/or additives. In this setup, the electrolyte behavior can be studied in presence of a single electrode material. This avoids the contribution of phenomenons occurring at the surface of another active material that would be used at the opposite electrode. This setup also allows the study of active materials but with the main advantage of avoiding cross-talk between WE and CE.
- Full-cell setup: During charge-discharge, the cell is operated via monitoring of the voltage. Potentials of N and P are varying simultaneously in dependence of active material compositions and cell operation conditions. Adding a (pseudo-)reference electrode allows the monitoring of the system via the electrode potentials instead of the N-P voltage difference. This latter three-electrode configuration is particularly relevant to study parameters such as balancing N and P capacities, overpotential at the N and P side independently, active lithium losses. This can also lead to a better understanding of failure mechanisms. The full-cell setup is usually

implemented after detailed studies of individual components and electrodes in symmetrical or half-cell setups.

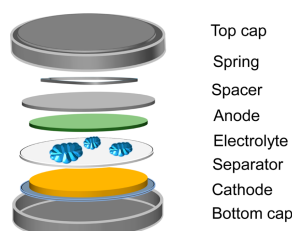


Figure 14.2 – Schematic representation of a coin cell.^[5]

As for the typical cell shapes, readily available designs for two-electrode cell designs are coin cells ((Figure 14.2) and Swagelok cells. Coin cells have been around electrochemical studies for more than a few decades. As they are small, fast and easy to assemble, they allow the testing of limited amount of new materials while maximizing the amount of experimental data output.^[6] Many types of coin cells are available as spare parts, with various diameters and thicknesses, such as the common CR2032 (the numbers are referring to dimensions; here the cell diameter is 20 mm and the thickness is 3.2 mm). Cell caps, spacers and springs are made of stainless steel. It is extremely important to choose a stainless steel with appropriate corrosion resistance with respect to the operating potentials of active materials.

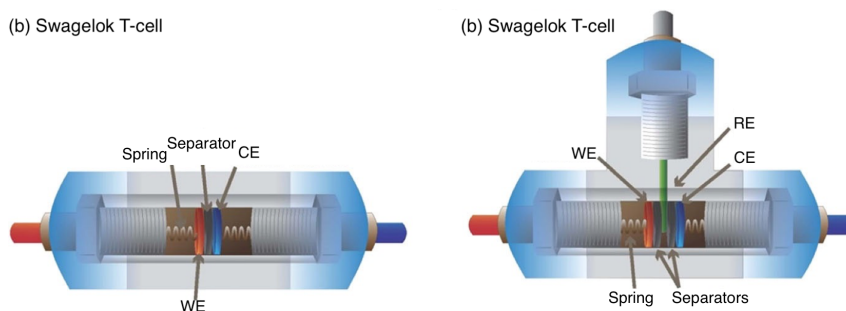


Figure 14.3 – Schemes of (a) a Swagelok cell and (b) Swagelok three-electrode T-cell assembly.^[7]

There are also other available three-electrode cell designs, such as the T-shaped Swagelok cell (Figure 14.3,^[8] Conflat cell (Figure 14.4),^[9]

and modified coin cell.^[10] Once promising formulations and cycling conditions have been defined thanks to these small scale full cell formats, the components under study can be tested in a higher cell format with metrics closer to the industrial standards. For this purpose, pouch cell formats can be implemented at the lab scale,^[11] with the possibility of embedding a RE for three-electrode full cell measurements.^[12]

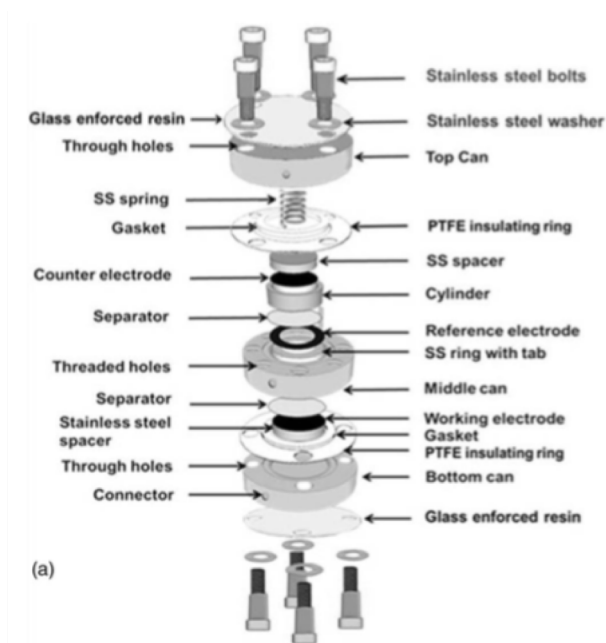


Figure 14.4 – Exploded view of a three-electrode Conflat cell.^[9]

14.2 Reference potentials

An adequate reference potential is one of the key parameters to facilitate a proper quantitative study of an electrochemical system under operation. In aqueous medium, the standard hydrogen electrode is the reference of choice. Yet in the lithium battery community, the electrode potentials are mostly referred to the Li/Li^+ couple since most of the testing and application conditions are using at least one electrode (lithium metal or lithium intercalated in graphite) with a potential close or equal to its value.

However, care must be taken that the reference potential is properly defined in the measurements conditions. Therefore a well established reference in the measurement conditions must be chosen according to previous literature report and/or the calibration of the reference must be carried out via a suitable method. Also, the RE should not disturb the correct operation of the cell.

To provide a good reference potential, a RE must possess the following characteristics,^[13]

- Non-polarizable, i.e. low residual current (< 50 pA) flowing should not affect the potential,
- Reliable and stable potential over time, ideally the reproducibility should be ensured down to the mV,
- Low impedance ($<$ a few k Ω).

Although these criteria are usually satisfactorily met in lithium half-cell, additional considerations related to the lithium CE polarization or the formation of films at the Li surface may require to measure the potential against a third electrode that may even be another reference system.

In addition, due to the strong solvation of the small lithium cation and mainly the different electron donor capacity of most of the solvents used for studies on lithium electrochemistry, the electrode potential of the Li/Li⁺ strongly depends on the solvent used; for instance its potential can vary by as much as 0.5 V between acetonitrile and DMSO.^[14,15] Therefore, the use of custom electrolyte formulation should call for a calibration of any reference electrodes based on Li/Li⁺ in order to draw meaningful conclusion related to potentials of redox processes.

As other reference electrodes that can be used in non-aqueous media, Ag/AgCl, Ag/AgNO₃ or Ag/AgClO₄ can serve this purpose.^[14,16] The drawback of such reference electrodes is that while yielding stable potentials in several solvent,^[14] decomposition limits may occur in others, and their actual potential values may differ from solvent to solvent. Also they are often unpractical to use in modern cells setups used for lithium battery research.

Another possibility to define properly the reference potential lays in the use of reference redox systems (RRS). The use of RRS is the central concept of IUPAC 1983 recommendations on reporting redox

potentials in non-aqueous solvents.^[14] These IUPAC recommendations issued by Gritzner *et al.* are following a study by Strehlow *et al.* on various organometallic complexes,^[17] which led to the formulation of requirements for a suitable reference redox system,

- The ionic species of the redox couple should be spherical with as large a radius as possible,
- The ions should carry a low charge,
- The species should display fast and reversible electrode kinetics,
- The species should be soluble,
- The species should not display any geometrical change under redox conversion,
- The species should display their redox activity in a potential range compatible with as many solvents as possible,
- The species should be stable enough during the time of analysis.

Based on these considerations, Strehlow suggested the systems ferrocene / ferrocenium ion (Fc/Fc^+) and cobaltcene/cobalticenium ion as suitable redox reference. Practically these RRS can have their half-wave redox potential recorded via a CV measurement to calibrate any of the potentials of the system under study, including the pseudo-reference electrodes. The error affecting such calibration can be considered to be similar to the observed deviation from the average value of 1.124 V obtained for 22 solvents, ± 12 mV.^[14]

Alternatively, a reference electrode consisting of a Pt wire in contact with equimolar amounts of the two RRS redox forms can be implemented. The former possibility should be preferred. Indeed, the latter possesses the disadvantage of possible drift of the redox potential of the couple. Also if the system is used with a salt bridge or in a jacketed electrode, there will be a junction potential affecting the measurement, which brings another source of error if not properly evaluated (up to a few tenths of mV). Nevertheless such electrode configurations, while already being difficult to implement, are sometimes the only way to circumvent limitations related to addition of RRS compounds in an actual battery setup for *operando* measurements.

14.3 Cyclic voltammetry

Cyclic voltammetry (CV) is a well-spread tool that can serve a wide variety of uses such as studies regarding reaction pathways,^[18] electrochemically generated radicals,^[19] effects of ligands on redox potentials of ion complexes, approaches for solar energy conversion,^[20] models for enzymatic catalysis,^[21] chemical syntheses^[22] etc. In the context of the research and development on battery technologies, CV is a powerful and popular tool because of the simplicity of the setup in comparison to time-consuming and elaborate tests. CV will be used to assess if a compound is worth of further studies and also provide insight on key properties and crucial processes. More advanced CV modes can be implemented – such as pulse or square wave CV – for higher peak resolution and sensitivity, but the general principles remain the same. CV can also be hyphenated with other techniques such as spectroscopy, microscopy, X-ray diffraction and so on.^[7]

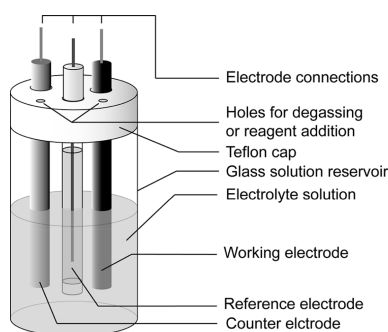


Figure 14.5 – Schematic representation of an electrochemical cell used for classical experiments of analytical CV.^[23]

The classical setup of analytical CV (Figure 14.5) is displaying a three-electrode configuration in a beaker cell, with the analyzed substance being dissolved in a supporting electrolyte. Figure 14.6 shows a typical voltammogram and its applied potential program used to record the CV response of $\text{K}_3\text{Fe}(\text{CN})_6$. In CV experiments, a potential applied to the working electrode is scanned linearly from its initial value (E_i) to a predetermined limit of switching potential ($E_{\lambda 1}$) at a certain scan rate ($\text{mV}\cdot\text{s}^{-1}$). Then the scan direction is reversed toward an other preselected value ($E_{\lambda 2}$). The current response is recorded and plot-

ted against the applied potential calibrated *vs.* the reference potential. In most cases the changes are limited over the scans. However, these changes can bring useful hints about the system under study.

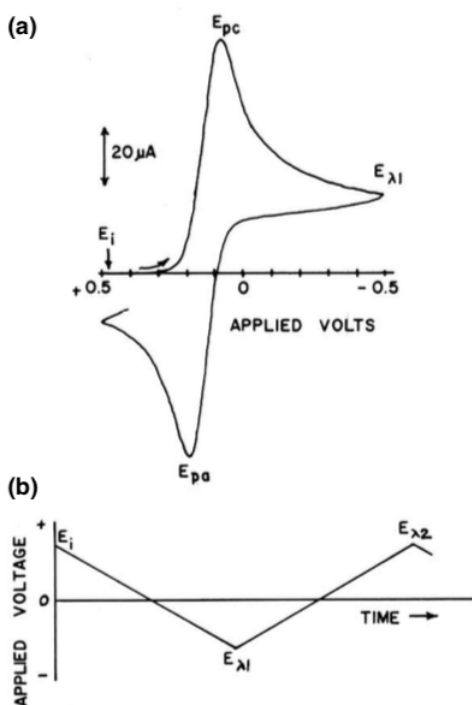


Figure 14.6 – Output data and record parameters during the course of a CV experiment: (a) Typical cyclic voltammogram of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ at a platinum electrode in aqueous 0.1 M KCl solution. The scan rate was $100 \text{ mV}\cdot\text{s}^{-1}$ and the reference electrode was Ag/AgCl in 0.1 M KCl solution; (b) applied potential program. $E_{\lambda 1}$ and $E_{\lambda 2}$ are switching potentials.^[24]

In a liquid medium, the current depends both on the movement and the electron transfer kinetics of the electroactive material at the electrode surface. The electron transfer rate (k_f) can be expressed for a reduction process as follows,

$$k_f = k^\circ \exp \frac{-\alpha n F}{RT} (E - E^\circ)$$

Where k° is the standard heterogeneous electron transfer rate (its value is related to interactions between the electrode surface and the active

species), n is the number of electrons transferred per molecule, F is the Faraday constant, R is the universal gas constant, T is the Kelvin temperature, E° is the standard reduction potential, and α is the transfer coefficient which can display values between zero and unity. This latter coefficient is accounting for the amount of energy put into the system that actually serves to lower the activation energy barrier.^[24]

This exponential relationship of k_f with the applied potential accounts for the steep rise of current at the onset of the electrochemical process because of the stationary electrode and unstirred reaction conditions. Yet, at some point the reaction concentration becomes depleted near the surface. Next, because the process is diffusion limited, the depletion region grows, redox active species must travel an increasing distance to reach the electrode and consequently mass transport decreases. Eventually current reaches a maximum before starting to decrease. Beyond the peak, the current is time dependent and not related to potential anymore. When the scan is reversed, the electrochemically generated species which are still close to the electrode may undergo the reverse redox process. The reverse process is controlled by the applied potential in a similar manner as the process taking place during the forward scan.

Regarding the reversibility, in the electrochemical context of CV, the definition is different than the one used in chemistry. In the present context, reversibility or "reversible electron transfer" is related to the rate of heterogeneous electron transfer at the electrode surface (k^0), and electrochemical reversibility is achieved when the electron transfer between the electrode and the analyte is fast ($k_f > 0.05 \text{ cm}\cdot\text{s}^{-1}$) on the time scale of the mass transfer.^[19] Hence the mass transfer, i.e. diffusion in a liquid medium, is the rate limiting step. In these conditions, ratio of peak currents during forward and reverse scans is close to unity and the separation of the corresponding CV peaks is equal to $57/n \text{ mV}$ at 25°C .^[23] When the electron transfer rate is comprised between $0.05 \text{ cm}\cdot\text{s}^{-1}$ and $10^{-5} \text{ cm}\cdot\text{s}^{-1}$, the system is qualified as quasi-reversible, and the electron transfer rate is comparable to the mass transfer rate.

The disappearance of the return peak due to further chemical reactions of electrochemically generated species is different from an irreversible electron transfer. The disappearance is due to coupled chemical – electrochemical reactions whereas, in the electrochemical context, irreversible means that the electron transfer rate is lower than

$10^{-5} \text{ cm}\cdot\text{s}^{-1}$, the latter resulting in a very broad peak-to-peak separation.^[19]

As one of the main uses of CV is to record electrochemical activity of chemical compounds, it is common practice to characterize this property via the determination of the reduction potential value. To this end, the usual determination method takes the average of the forward and reverse peaks potentials for the redox couple. This method delivers a good approximation, provided that the electron transfer is reversible and that the reduced and oxidized species have similar diffusion coefficients.^[24] In the context of battery research, CV is found frequently applied with two-electrode configurations, on electrodes coated with actual active materials, that are assembled in standard test cells such as coin cells and Swagelok cells. Because the coated materials are in a solid state, a major difference occurs with coated LIB materials in comparison with classical CV in solution and this is affecting the voltammogram shape. The limiting factor is not the diffusion of the analyte in solution to the electrode anymore. Yet other factors can be limiting such as the propagation of the reaction at the interfaces and in the bulk which are linked to the diffusion of electrons and ions in all components of cell media. These factors can broaden the width and separation of the CV peaks. Therefore the CV of coated battery materials can also provide insights on characteristics of coatings which are affecting their rate capabilities.

Another use of CV is to characterize stability of electrolyte components. Oxidative and reductive decompositions can be studied on an electrode that has its potential controlled. However, this task can be a complex process since not only thermodynamic factors are affecting the response, but also kinetic ones such as electrode surface, scan rate, concentration of the species under study etc. There are three different approaches:

- The first approach is deriving from the usual analytical CV (Figure 14.5).^[25] The components are dissolved at dilute concentrations in a supporting electrolyte, and electrodes are made of an inert material (glassy carbon, gold, silver or platinum). This way the actual thermodynamic behavior can be characterized,^[24] and salts and solvents can be studied independently. Yet, LIB electrolyte components have a wide stability window which outperform the operating window of most supporting electrolytes. Additionally

the available working electrodes are displaying a catalytic activity that can be very different than the usual LIB porous electrodes.^[26]

- In the second one, neat electrolytes and actual LIB electrodes can be used in the related application to allow the study to more accurately reflect the actual operating limits.^[25] The drawback is that it may be difficult to separate the individual contributions of the components. Also the stability definition becomes ambiguous because of the passivation films.
- The third approach relying on neat electrolytes with non-active materials as working electrodes is the most common one.^[25] This method alleviates the complexity related to simultaneous active material redox processes and passivation films.

Overall, there is still a certain degree of arbitrariness in the definition of the limits. Whatever is the applied method, disparities are often occurring between authors regarding the onset of decomposition.^[26–29] Therefore the results should always be considered with caution when different sources are compared.

14.4 Electrochemical properties affecting charge / discharge curves

Repeated cycling of a battery is affecting the discharge characteristics, in particular the profile of its voltage, power, and current as a function of time. This profile can display several forms affected by the discharge conditions, electrical properties and other measurements variables.

One of the easiest discharge mode of a battery is obtained at constant current (galvanostatic mode). Typical curves that can be obtained with this discharge mode are displayed in figure 14.7. The plot depicts the change in voltage as a function of the battery capacity, which is proportional to the time of discharge when current is constant.

As for curve I, the battery voltage remains almost flat during a significant fraction of the discharge process. The active material is then merely affected by the progress of the reaction. Curve II displays two distinct discharge plateaus. This characteristic implies a change in the reaction mechanism when transitioning between the two flat domains.

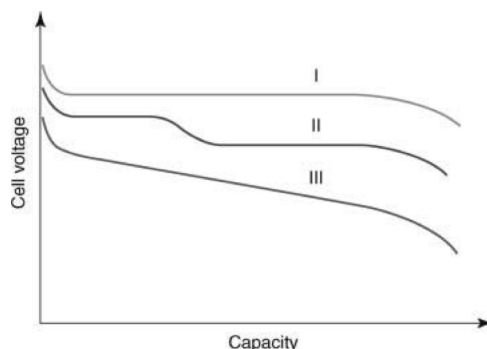


Figure 14.7 – Different discharge patterns due to different electrochemical reaction mechanisms: The active material is not affected by the progress of the reaction in curve I; there is a change of the reaction mechanism during the discharge in curve II; the reactants, products and internal resistance are individually or all together changing throughout the reaction in curve III. ^[30]

Curve III describes the discharge of a battery where some of the reactants, products and internal resistance are individually or all together changing throughout the discharge process.

Formally, an electrode is defined as an interface between an electric and an ionic conductor media. For the electrode material to possess a capacity, there must be a volume expansion as ions intercalate in what is referred as the host lattice. In this system the current lead and the electrolyte serves the only purpose of carrying the charged species and they do not enter the electrochemical process. As for LIBs, the change in battery voltage upon charge / discharge can then be expressed via Armand's equation ^[31]:

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln \frac{\gamma}{(1 - \gamma)} + k\gamma$$

In this equation the electrochemical potential is expressed as a function of the lithium ion occupancy (γ). There is also an additional term ($k\gamma$) accounting for the enthalpy changes due to the interactions between intercalated ions. Overall, the shape of the voltage curves is directly affected. The main factors are lithium ion diffusion rate into the electrode materials, phase transition, change in the lattice structure, and dissolution, as well as additional factors such as the particle size of electrode active materials, temperature, electrolyte characteristics, and porosity of the separator. These factors may change the values of γ and k in

the Armand reaction – thus determining the relative influences of the entropic and enthalpic terms – but also may require to include other factors accounting for more particular phenomena.^[30]

When the active material is based on a transition metal, the reaction can be described as the growth of a sub-lattice in the system, which leads to a plateau in the voltage curves due to an equilibrium between two pseudo-phases.^[31] Each pseudo-phase holds a negligible concentration of the dilute species, and the curve is a type I. There is an overpotential associated to both charge and discharge processes, leading to a charge – discharge hysteresis.

If the active material reaction can be described as occurring in a "solid solution electrode", the voltage curves display a curve III-type shape. The interaction term ($k\gamma$) represents the contribution of interacting charged species to the energy of the system. Since no ordering is taking place in the sublattice, the potential is a smooth decreasing function.

Other terms or phenomena can also affect the shape of the curves. In the case of graphite and other bi-dimensional compounds, the intercalation expands the structure parallel to the planes, and a general model can account for intercalation pressure via a corrective term describing the formation of stages. Also ordered sublattices can appear successively as the concentration of the host increases, yielding curves such as type II.

14.5 Cycling conditions affecting charge / discharge curves

Under low current density conditions, both voltage and discharge capacity come close to the theoretical values as the system evolves close to equilibrium. Yet, as exposed previously in the main text in section 1.2.3.8, iR drop and overvoltage from polarization are affecting the system outside of equilibrium conditions. The larger the current density, the larger the polarization affects the system. Eventually the gradient affecting the discharge curve can reduce the discharge capacity when full material utilization would only be obtained beyond the cut-off voltage (Figure 14.8).

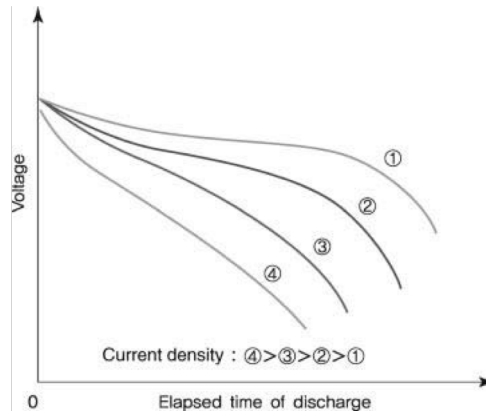


Figure 14.8 – Effect of current density on the battery voltage. ^[30]

As illustrated in figure 14.9, again because of the cut-off limits, discharge capacity can be affected by the effect of temperature. The temperature parameter greatly impacts the gradient of discharge curves. As temperature decreases, the chemical activity is reduced, which leads to a higher internal resistance. However, if temperature is too high, the increase of chemical activity may lead to self-discharge as well as unwanted side reactions.

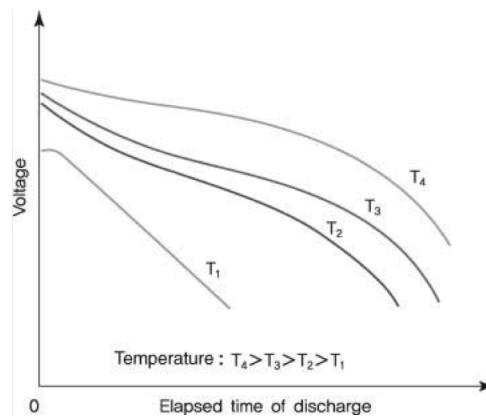


Figure 14.9 – Effect of temperature on the battery capacity. ^[30]

Under testing or operation, there are several normal discharge conditions that can be applied, among which three of them are the most common: constant current (galvanostatic), constant power, and con-

stant external resistance. During discharge, the voltage is monitored, and depending on the discharge mode, current or power can be either set or measured while the following variables can be measured, discharge time, delivered discharge capacity, lithium ion occupancy (fraction of the theoretical capacity) etc. The three discharge modes can be defined as follows:

- (i) Constant resistance: the resistance of the load is constant over the discharge cycle. The current is then decreasing along with the voltage during the discharge,
- (ii) Constant current: the current remains constant while voltage drops until end of cycle conditions are met (for instance cut-off voltage limit),
- (iii) Constant power: the current is increasing during discharge as the voltage is decreasing in order to maintain a constant power as per the following equation, $P = i.E$.

Figure 14.10 depicts the influence of discharge mode on the battery performances. All three above-mentioned discharge modes have their corresponding discharge curves represented in each inset of subfigures 14.10(A), 14.10(B) and 14.10(C). These three insets in each subfigure are plots of discharge current (a), voltage (b), and power (c) over time.

In subfigure 14.10(A), the load is set so that discharge current and thus power are the same for all three discharge modes. The resulting variations of current over time are depicted in inset (a). The discharge time is lower for constant current than constant resistance because in this latter mode the current remains lower – that is according to Ohm's law, $I = E/R$ – than the one in galvanostatic mode. In constant power mode, the discharge time is even lower because the current is higher than in galvanostatic mode according to $I = P/E$.

The insets of subfigure 14.10(B) are depicting the same relationships as in subfigure 14.10(A) but with same discharge time in all three modes. As the resistance of the external circuit is not the same at the start of discharge, initial current, voltage, and power are not the same in all three modes.

From an application standpoint, as battery-powered devices are requiring a minimum power input to operate (cut-off power), one of the most realistic mode assumes same power at end of discharge (Subfigure 14.10(C)). For illustration purpose, the same power at cut-off voltage

has been obtained using an adequate load in each of the three modes. As for constant resistance mode, current and power are supplied in excess of the minimum required. In both cases, as a consequence of the excess of current, the capacity is drained quicker than required, resulting in shorter cycle time. In constant current mode, current and power are above required minima until cut-off, but current is lower than in constant resistance, resulting in higher cycle time. In constant power mode, current is the lowest at the start and the system affords the longest cycle time.

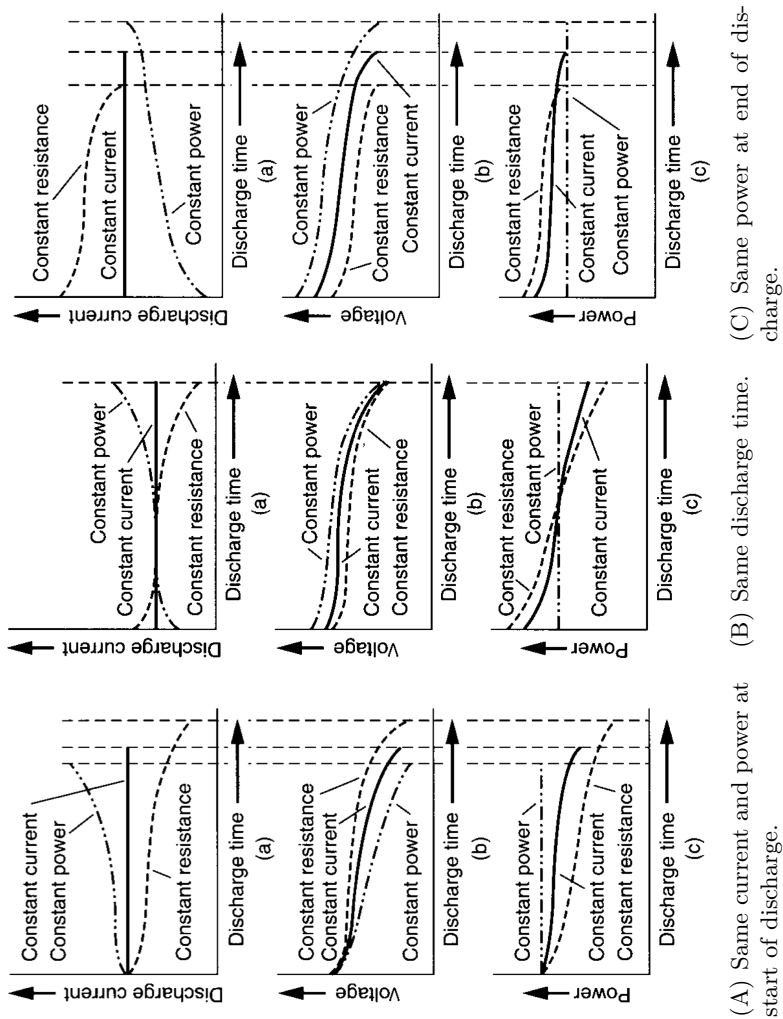


Figure 14.10 – Comparisons of discharge profiles under different discharge modes. In each subfigure, (a) current profile during discharge, (b) voltage profile during discharge, (c) power profile during discharge. [32]

14.6 Performance evaluation based on charge / discharge cycling

When it comes to evaluating the performances of a battery, defining the actual application requirements is particularly relevant so that the choice of the discharge mode can reflect the conditions met by the actual device.

For instance, in actual applications, current and power often vary during the discharge, thus the battery is operated until its cut-off voltage and it should be assessed whether the system is properly designed to deliver the required power until this limit. A proper evaluation may then rely on a constant power or a custom discharge power profile and discharge cut-off conditions would also include a minimum voltage as well as a minimum power limit.

In the case of the evaluation of new active materials or new electrode formulations, galvanostatic charge-discharge cycling is often preferred. This mode allows to cycle at constant current density, hence yielding less influence of internal ohmic contributions on the evaluated parameters. The evaluation is then frequently carried out at relatively moderate currents, with reasonable voltage limits to allow good material utilization. The comparison of subsequent charge and discharge cycles affords coulombic efficiency. During the early cycles of the system under study, this allows to observe the irreversible capacity loss due to passivation events, such as SEI formation, occurring at the surface of materials. Furthermore the cycle life, i.e. the number of cycles achieved until the capacity drops to defined value of the rated capacity, is another key parameter that is often evaluated early in the development of new components. The cycle life is intrinsically related to the coulombic efficiency, that is related to irreversible degradation processes of the components.

A particular mode of galvanostatic cycling is variable rate cycling. This mode is implemented by application of different charge-discharge currents over subsequent cycles. The currents, and consequently C-rates, are usually increased progressively with the cycle index. This allows to evaluate the amount of charge that can be extracted at a given C-rate, highlighting the rate capabilities of the system. Through the successive charge-discharge curves, this also allows to appreciate the hysteresis phenomenon and the extent of polarization which are related

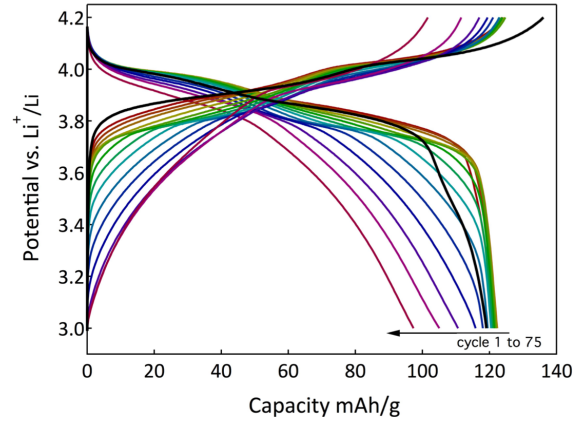


Figure 14.11 – Cycle life evaluation of a LMO-graphite LIB through galvanostatic cycling. The plot presents the evolution of charge-discharge profiles and the associated capacity over the cycles. ^[33]

to the loss of energy at higher rates.

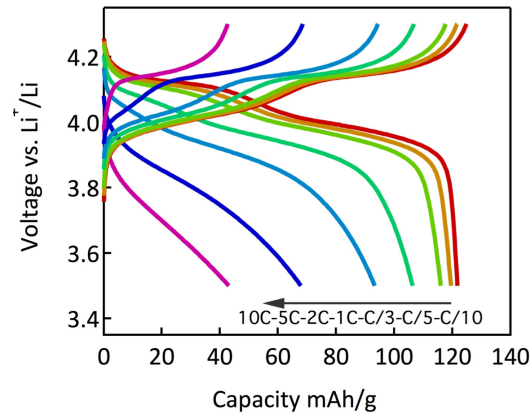


Figure 14.12 – Power performances evaluation via galvanostatic cycling at different C-rates. The plot presents charge-discharge curves of a LMO positive electrode tested against a Li metal acting both as pseudo-reference and counter electrode. ^[33]

In actual applications, the rest time between charge and discharge can vary, and the discharge conditions are less reproducible. Also the charging protocols can rely on more complex parameters as there is usually a trade off between electrical performances and the efficiency of the

charge. To reach a proper balance of these two, an optimized charging methodology needs to be applied as this will influence properties such as the cycle life and the power over the subsequent discharge. Therefore, regarding the charge of a battery, in addition to the application of the three methods presented beforehand, variants and combinations of these modes but also several other modes can be used. The following ones are the most commonly found,

- Trickle charging: A very low rate to maintain battery in fully charged state;
- Constant current, then constant voltage: This is the most popular charge strategy thanks to its easy and inexpensive implementation. It allows to limit charge power in the early stage, and then to maximize the energy efficiency;
- Pulse charging: Complex sequences are designed to minimize polarization and unwanted chemical reactions.

The use of sensors and a battery management system (BMS) can be required in the most advanced procedures to maintain the health of the battery and prevent safety issues. The cycling conditions of commercial batteries differ significantly from the laboratory testing conditions which are made keeping parameters constant. Consequently during the development of new battery technologies, as the materials are further progressing closer to the application stage, the cycling conditions are becoming more complex to better match the real world conditions and better predict the true performances.

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