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Design and characterization of flexible lithium-ion batteries

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Thesis submitted in fulfilment of
the degree of Doctor in Sciences

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Abbreviations and Symbols

r_{sp}	Set-point amplitude ratio
AB	Acetylene black
ACN	Acetonitrile
C rate	Cycling rate corresponding to a full charge in 1 hour
ccp	cubic close-pack
CE	Coulombic efficiency
CMF	Carbon microfiber
CPE	Composite polymer electrolyte
CuAAC	Copper-catalyzed azide-alkyne cycloaddition reaction
DCM	Dichloromethane
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DMF	Dimethyl formamide
EC	Ethylene carbonate
EG	Ethylene glycol
EIS	Electrochemical impedance spectroscopy
EO	Ethylene oxide unit
EO/Li ⁺	Ethylene oxide unit/lithium ion molar ratio
EV	Electric vehicle

GPE	Gel polymer electrolyte
HEV	Hybrid electric vehicle
HT-LiCoO ₂	High temperature LCO hexagonal structure
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
LMO	Lithium metal oxide
LT-LiCoO ₂	Low temperature LCO spinel cubic structure
LTO	Lithium titanium oxide
MCF	Micro carbon fiber
MCMB	Mesocarbon microbeads
MeOH	Methanol
mPEG	Polyethylene glycol monomethylether
MWCNT	Multi-walled carbon nanotube
NMP	N-Methyl-2-pyrrolidone
PAA	Poly(acrylic acid)
PAN	Poly(acrylonitrile)
PE	Polyethylene
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PVdF	Poly(vinylidene difluoride)
R _{CT}	Charge transfer resistance
SEI	Solid electrode interphase
SEM	Scanning electron microscopy
SiO _x NPs@PEG	Poly(ethylene glycol)-grafted silica nanoparticles
SiO _x NPs@N ₃	Azido-functionalized silica nanoparticles
SPE	Solid polymer electrolyte
SRC	Simplified Randles cell
SWCNT	Single-walled carbon nanotube
T _g	Glass-transition temperature
TBTA	Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine
TEM	Transmission electron microscopy

TGA	Thermogravimetric analyses
THF	Tetrahydrofuran
XPS	X-ray photoelectron spectroscopy
Z_W	Warburg impedance

CHAPTER 1

Objectives and methodology

Abstract

The aim of this thesis is the design of solid-state flexible high performance lithium batteries in a single step process. The general frame and the objectives of the project are presented in this chapter.

1.1 Context of the research

The inherent link between human development and energy management is overwhelming. Electrical energy has emerged as the unquestionable energy source to power equipments of everyday life. Home appliances, communication tools, laptops, GPS are all relying on electrical energy and more precisely on the lithium ion battery technology. Recently, development of intelligent clothes, flexible displays or electronics has created the need of new off-grid energy solutions. Safe, flexible batteries are now required to be seamlessly integrated to these devices. The next chapter of this manuscript will provide at best an overview of present lithium-ion technology, its limitations and future perspectives. Information provided in this chapter will help to understand the scope of this work.

1.2 The project

The ultimate aim of this work is the creation of a flexible lithium-ion battery in a single step. The creation of a flexible battery implies many constraints as it will be discussed in the next chapter. Every component of the battery has to be flexible as well as the entire assembled battery. Flexibility implies mechanical constraints inside components as well as at their interfaces. Aiming to design a battery in a single step is forcing us to investigate original design processes. Over the past few years, many methods were developed to create battery component. To design a flexible battery, a filtration process was selected to allow us to create the final device in a single step. Nevertheless, before considering the creation of a full battery, every component of the battery has to be individually designed and optimized. This thesis therefore implies a work on the different level of a battery creation. Positive and negative electrode will be created and their performances optimized in chapter 3. Separators will be produced by filtration and studied in the chapter 4.1.

Design and characterization of solid electrolyte will be covered in the section 4.2. Lastly, all the described components have to be assembled in a single step to produce a full cell with fair electrochemical properties. These results will be discussed in the chapter 5. The different parts of this project are briefly described in the following sections.

1.2.1 Current collectors and electrodes design

In chapter three, we will discuss the design of a simple process to create thin flexible electrodes. At first, conductive networks based on carbon nanotubes will be created via a filtration process and will be studied. Filtration process was retained as the best method to produce the different component of the battery. Carbon nanotubes were selected as base material for current collectors and electrodes due to their mechanical and electrical interesting properties (see section 2.3). The produced fabrics must serve as conductive scaffolds for electrodes. This kind of conductive network was previously reported as an excellent support for electronics.^[1] Previously, single walled carbon nanotubes and multi walled carbon nanotubes networks were created. A wide range of conductivities, from 12.5 S.cm^{-1} to 6600 S.cm^{-1} have been reported and these values will be targeted.^[2]

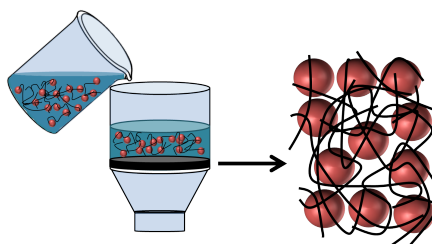


Figure 1.1 – Positive and negative electrode fabrication via filtration process: a dispersion of active materials and conductive MWCNTs are filtered to create electrodes.

Subsequently in the third chapter, negative and positive electrodes

will be created using the same filtration process. MWCNTs and active material particles will be mixed up together and filtered with the objective to form a conductive network entangling the particles (Figure 1.1). All the active materials used during this work are deeply described in the section 2.2. The complete understanding of their properties and behavior will help to interpret results. Electrode design using a filtration process has already been put to the test and resulted to the creation of high performing electrodes.^[3,4] Examples of electrodes composed of carbon nanotubes and conventional materials such as LiCoO_2 or graphite have already been reported. As example, Luo and coworkers created CNT- LiCoO_2 positive electrode.^[5] Gravimetric capacities recovered (151.4 mAh.g^{-1}) at low current densities ($< 0.1 \text{ C}$) were close to theoretical capacities of active materials. In addition, electrodes sustained current densities up to 2 C without major decay. Similar performances will be targeted. In their study, Park and coworkers tried to create highly free-standing flexible electrodes by removing aluminum current collector and adapting slurry composition.^[6] They proved that it was difficult to achieve similar performances to those obtained with metal current collectors. The mechanical performances of their PVdF - LiCoO_2 - Super P Carbon - CNT electrodes were superior to those of conventional electrodes. Unfortunately, the electrochemical performance was significantly lower (especially at high current densities). On one hand, gravimetric capacity was recorded at about 140 mAh.g^{-1} LiCoO_2 at 1 C rate for 50 cycles with less than 5% decrease. On the other hand, rate capabilities were significantly lower with about 82 mAh.g^{-1} LiCoO_2 at 5 C rate. Their explanation relied on the electronic conductivity 10 times lower than electrodes with traditional metallic current-collector. In this work, we hope that absence of insulating PVdF binder will provide electrodes exhibiting sufficient electronic conductivity to sustain high currents.

In this chapter, the impact of different parameters on electrode performances will be investigated. At first, the impact of multi-walled car-

bon nanotubes amount on the electrical conductivity and the electrochemical performances of the electrodes will be considered. Another studied factor is the pressure applied on the electrodes after their production to increase cohesion in the fabrics. Several studies demonstrated the influence of compactness of electrodes.^[7] On the one hand, the applied pressure improves the electronic conductivity of the electrodes. Nevertheless, applying pressure on electrode decrease thickness of electrodes and reduce voids available for electrolyte.^[8–10] A compromise has therefore to be reached to optimize electrochemical performances. Using commercial materials, we expect to reach cycle stabilities exceeding 100 cycles without significant capacity loss. In addition, the use of carbon nanotube as current collector and binder should reduce at the minimum the weight of non electroactive materials. A targeted value is 5 wt. %. Rate capabilities of 5 C corresponding to a full charge in 12 minutes will be targeted.

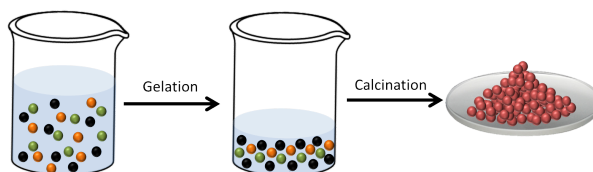


Figure 1.2 – LiCoO_2 particles synthesis based on lithium and cobalt salt precursors via sol-gel process.

Another part of this chapter is devoted to the the synthesis of nanoparticles of active materials via a sol-gel process (Figure 1.2). Controlling the size and morphology is of primary importance to design performing electrodes. Decreasing the dimensions of particles should lead to better electrochemical performances as diffusion paths decrease.^[11–14] However, size decrease of particles also increases the surface/volume ratio and can promote SEI formation. Electrochemical tests will allow us

to correlate particle size and electrochemical performances.

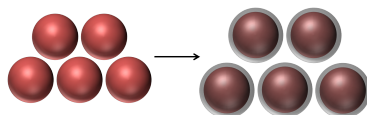


Figure 1.3 – Carbon coating of active particles via carbon precursor calcination.

Lastly, a carbon coating based on sucrose precursor will be envisioned on commercial particles to enhance their electrical conductivities (Figure 1.3). Since most of the active materials are semiconductors or insulators, this technique should promote charge collection at the surface of particles.^[15] Hopefully, these two materials improvements should enable us to improve rate capability of electrodes.

1.2.2 Separators and electrolytes design

Developing a filtration process to create batteries implies the use of dispersible nanomaterials to design separator. In this context, we will adopt cellulose as base material. In the first section of chapter four, cellulose nanofibers will be produced from fibers by oxidation and individualization. Creation of cellulose-based separator through filtration will later be implemented. Electrochemical characterization will be required to attest the compatibility with lithium ion technology. Using this method of separator production, we aim at performances at least equivalent to commercial separators in a liquid configuration. The electrochemical performances of the two types of materials will be compared by electrochemical characterization.

Solid polymer electrolytes are today considered as the best solution to design flexible electrolytes. Among them, poly(ethylene glycol)-based electrolytes display the highest ionic conductivities. Ionic conductivity of SPE is strongly correlated to their crystallinity at the expense of mechanical properties. The second section of chapter four is devoted to

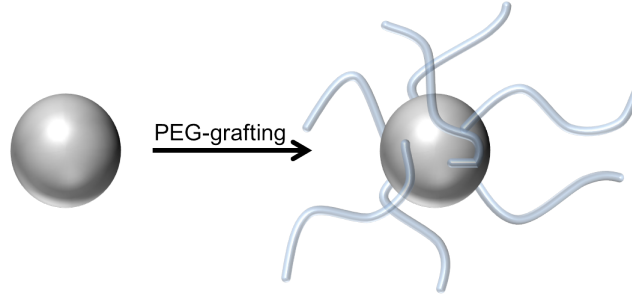


Figure 1.4 – Lithium ion conducting polymer grafting on silica nanoparticle core.

the inclusion of nanomaterials to PEG-based electrolytes with the objective to design a performing composite electrolyte with interesting mechanical properties. Silica nanoparticles as well as cellulose nanofibers will be envisioned as mechanical stabilizers (Figure 1.5). Inclusion of such nanoparticles has already proven its worth. In the best configuration, electronic conductivities up to $10^{-3} \text{ S.cm}^{-1}$ were measured.^[16] Poly(ethylene glycol) will be grafted on silica nanoparticles to highlight the impact of modified particles over free ones in electrolytes.^[17,18] Lastly, inclusion of cellulose nanofibers inside polymer electrolytes will be investigated (Figure 1.5). Mechanical properties of electrolytes will be assessed to underline the effect of nanomaterials inclusion.

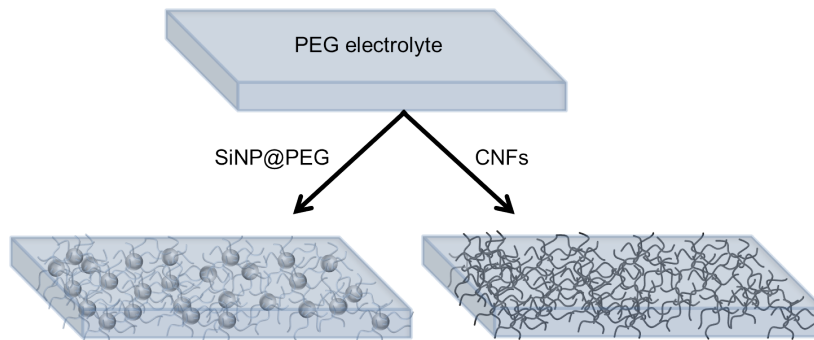


Figure 1.5 – Creation of composite solid electrolyte based on modified silica nanoparticles or on cellulose nanofibers

1.2.3 Design of full batteries

The last part of this thesis is devoted to the assembly of previously produced battery component. In the fifth chapter, positive electrode, separator/electrolyte and negative electrode dispersion have to be subsequently filtered to produce full batteries (Figure 1.6). Such a design process should ensure a good cohesion between layers.^[19–21] Moreover, a one-step process should considerably decrease time needed to produce a battery. In a first step, batteries will be created in a liquid configuration. Particular attention will be paid to the electrode balance. Indeed, this parameter has a great influence on performances. Successive filtrations to create a battery was previously reported by Leijonmarck *et al.*^[22] While batteries sustained current densities up to C rate, A significant decline was noticed on cycling stability after firsts cycles. They mainly attributed this drawback to parasitic side reactions with water. Special attention will be given to this point. By this process, we hope to produce a battery that can support a hundred cycles without major performance decay.

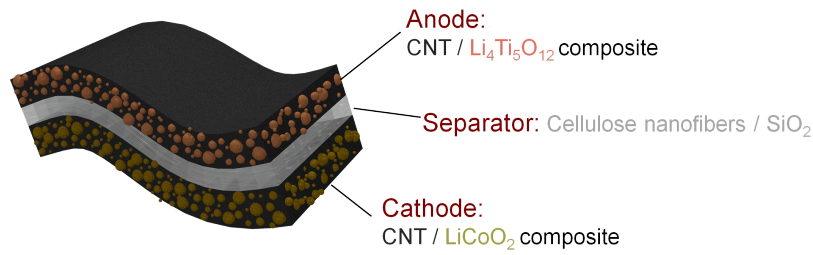


Figure 1.6 – Creation of lithium-ion battery in one step through filtration process.

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CHAPTER 2

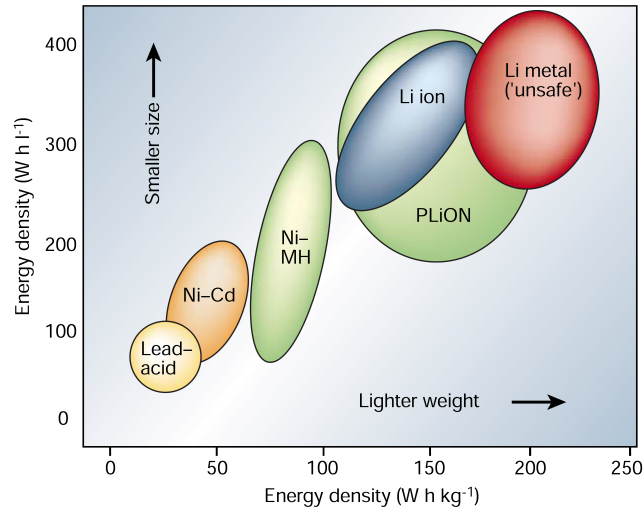
Lithium batteries : materials and concepts

Abstract

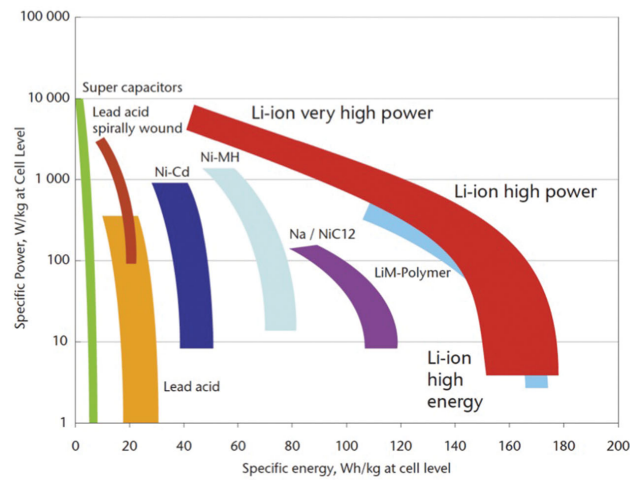
Behind their apparent simplicity, lithium-ion batteries are complex equipments and their operation is even more complex. Battery operation involves many electrochemical reactions. This implies many changes in compounds composition and in materials properties. The design of efficient lithium-ion batteries therefore requires advanced materials and a deep knowledge in fabrication processes. The creation of lithium-ion battery is a topic at the crossroads of chemistry, physics and engineering fields. This chapter unveils materials and principles of lithium-ion battery design.

2.1 Insight into lithium-ion batteries

The latest technology developed in the electrochemical battery field is the lithium-ion cell. Research started in the early 1970s with M. S. Whittingham's work. Unfortunately, his choice of electrode material (titanium sulfide) made it difficult to synthesize and extremely costly for practical reasons.^[1] In 1977, Samar Basu demonstrated the possibility to electrochemically intercalate lithium ions in graphite.^[2,3] This paved the way to use this material as a reliable negative electrode.^[4] In 1979, John Goodenough and Koichi Mizushima demonstrated the possibility to create a 4 V cell using lithium cobalt oxide (LiCoO_2) as positive electrode.^[5,6] Using solid electrolyte (poly(ethylene oxide)- lithium perchlorate) allowed Rachid Yazami to later demonstrate the reversibility of lithium ion intercalation in graphite in 1980.^[7] Akira Yoshino assembled in 1985 the first lithium-ion battery prototype using LiCoO_2 and carbon electrodes.^[8] In 1991 Sony released the first commercial batteries built on Akira Yoshino's scheme.^[9]



(a)



(b)

Figure 2.1 – Comparison of the different battery technologies: (a) Volumetric and gravimetric energy densities; Reproduced from^[10] (b) Power gravimetric density and gravimetric energy density. Reproduced from^[11].

Reasons of the growing interest for this new technology can be found in lithium chemistry. As the lightest and the least dense solid element on earth (equivalent weight 6.94 g.mol^{-1} and specific gravity 0.53 g.cm^{-3}), lithium can deliver high theoretical capacity up to 3860 mAh.g^{-1} .^[12,13] Lithium also possesses the most negative electrode potential (-3.01 V vs. SHE).^[12,14] These unique properties make it an excellent material for high energy and power batteries. Figure 2.1 clearly demonstrates this superiority over other technologies in terms of energy densities as well as in terms of specific power densities.^[10,11] In 2009, lithium-ion batteries already represented 37 % in market share in terms of revenue contribution (Figure 2.2). At this time, the biggest part of lithium-ion batteries were used in portable electronics such as cellphones, laptops. With the upcoming rise of electrical vehicle,¹ lithium-ion battery will certainly have its brightest days to come.

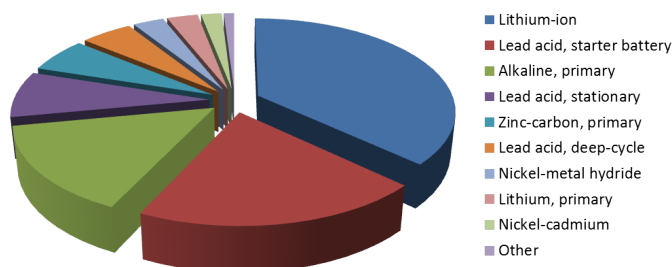


Figure 2.2 – Revenue contributions by different battery chemistries in 2009. Data from^[15].

¹According to Elon Musk, the Tesla CEO, 276.000 units of Tesla Model 3 were pre-ordered in the first 3 days of its release in the U.S.market in march 2016.

A typical commercial lithium ion battery is depicted in Figure 2.3. It consists in five major components: a positive electrode, a negative electrode, two current collectors, a separator, and the electrolyte.^[16] Redox reactions providing the electrical energy occur within the electrodes and more precisely, inside their active materials. In a commercial battery, the active material of the negative electrode is generally micro-porous graphite (equation (2.1)).^[9,17] On the opposite side of the battery, lithium cobalt oxide (LiCoO_2) remains the most common choice as positive active material (equation (2.2)).^[17,18] Combining these two electrodes produces 3.7 V batteries (equation (2.3)). Close to the electrodes, two metal foils act as current collectors to ensure proper charge collection from the surface of the electrodes to the external circuit. The two electrodes are physically separated by an insulating membrane called separator to prevent short-cuts. Lastly, electrodes and separator are generally soaked in liquid organic electrolyte to ensure lithium ions conduction.^[19]

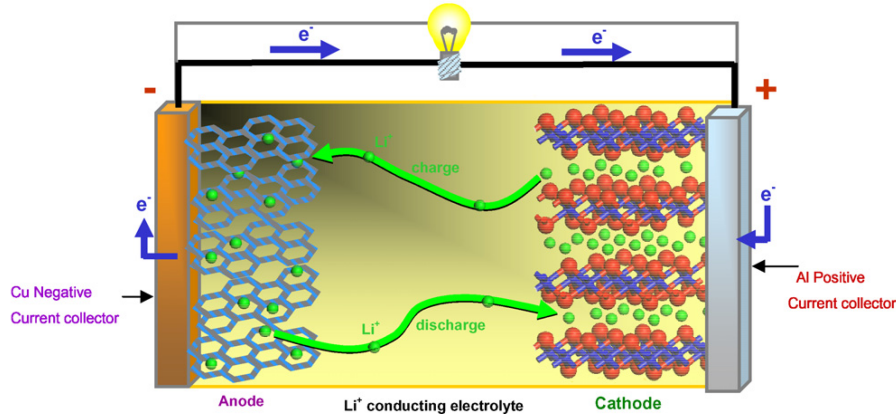
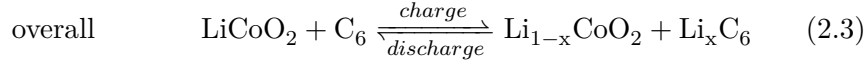
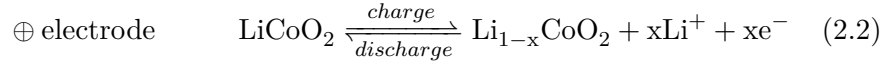
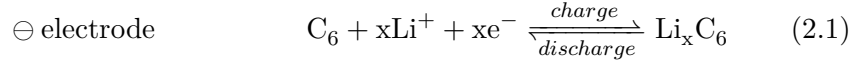


Figure 2.3 – Schematic representation of the commercial lithium-ion battery working principle. Reproduced from^[20].



During battery charge, the lithium cobalt oxide is oxidized and releases electrons and lithium ions. Electrons are collected by the metal current collector and travel through the external circuit. At the same time, lithium ions shuttle in the electrolyte through the separator to reach the graphite electrode. At this electrode, lithium is reduced on graphite by electrons from the external circuit. The discharge operation is the exact inverse process: lithium shuttles back to the lithium cobalt oxide electrode while electrons travel through the external circuit. This sums up the principle and composition of the majority of commercial lithium-ion batteries. Nevertheless, behind this apparent simplicity, things are more complicated. In addition to electroactive materials, conducting agents and binders are added to electrodes to ensure proper operation. Electrolytes are not just simple organic liquid, but a complex mixture of various liquids, lithium salts and additives. Figure 2.4 depicts a glimpse of the vast choice of materials available for each battery constituent. Moreover, this library is rapidly growing as the lithium-ion battery field constantly attracts more attention. Indeed, only few elements of the periodic table do not participate to the lithium ion battery design.^[21] The composition of lithium-ion batteries is thus highly complex and even more when those cells are being operated.^[12] Each component undergoes significant physico-chemical changes during operation: new chemical species are created, interfaces are modified,

conductivities changes... The battery design is therefore a real challenge and requires particular attention in the choice, the balance and the processing of materials. Cells manufacturing hence involves cutting-edge knowledge in various fields such as chemistry, physics, electronics and engineering.



Figure 2.4 – Lithium-ion batteries : composition and structure of conventional cells; constituents composition of Li-ion batteries. Underlined components: well established and commercially available chemistries; italic: some foreseen chemistries. Reproduced from [12].

2.2 Electrode active materials

Since the early stages of development of lithium-ion batteries in the late 80s, many kinds of electrode materials have been investigated. Ideal electrode materials have to fulfil the following conditions at best:^[22–26]

1. Anode materials have to exhibit the lowest electrochemical potential possible. The potential of this electrode should be as close as possible to the electrochemical potential of lithium metal. On the other side, cathode materials have to present the highest electrochemical potential versus Li/Li^+ . The voltage of the cathode should thus preferably be at around 4 V (generally limited by the electrolyte stability). Combined together, it provides a high cell voltage.
2. To maximize both gravimetric and volumetric energy densities, electrode materials should be densely packed and the lightest possible. To store the maximum energy, materials have to store a large amount of lithium ions per unit mass or volume. Combination of high voltage and high capacity leads to high energy storage. The gravimetric energy density can be estimated as followed :

$$Q_{\text{theoretical}} = \frac{nF}{3600 * Mw} \quad \text{mAh.g}^{-1} \quad (2.4)$$

with n the number of charge carrier, F the Faraday constant and Mw , the molecular weight of the active material.

3. Electrodes must react with lithium very rapidly in a fully reversible manner. This leads to high power density batteries.
4. Fast lithium ion diffusion in the material is required to sustain the high rate of redox reactions.
5. High electronic conductivity is required to sustain high currents during operation and provide high power electrodes.

6. Materials have to present a charge/discharge efficiency as close as possible to 100 %. A perfect coulombic efficiency also indicates the absence of side reaction, providing electrodes of long cycle life.
7. During operation, no significant change in the crystal structure should occur. Size swelling or structural changes induce strain in materials and hinder the reversibility of electrochemical reactions, leading to poor lifespan of materials.
8. Materials have also to present the lowest production cost possible. The matter of cost is somewhat relative; in high-end applications, cost is of secondary importance.
9. Materials have to present the best eco-compatibility. Most of lithium-ion systems contain transition metals such as nickel or cobalt which are toxic to various degrees. The recent introduction of nanomaterials in batteries also raises questions for their end of life treatment.

This summarizes the requirements for perfect electrode materials. As it is difficult to gather all these properties for a single material, nanostructuration of this material can help to palliate some weaknesses.^[27] Although developed materials are very different in nature, the majority of can be sorted in three main groups depending on their reaction mechanism: insertion materials, alloy materials and conversion materials (Figure 2.5).^[28,29]

In insertion materials, lithium ions intercalate into the lattice of bulk electrode without any major volume increase or host structural change. This insertion can be homogeneous or heterogeneous depending on interaction between guests and hosts. In alloys, lithium ions and electrons neutralize metalloids or semi-metals during charge whereas dealloying is the opposite process of returning lithium ions and the original metals. Conversion materials represent a new class where a reaction occurs between a binary transition metal compound MX and lithium to yield

metallic nanoparticles embedded in a matrix of LiX. During all these processes, the electrolyte and the conducting agents have the sole function of carrying charged species. They are not active in the electrochemical process of redox reaction of the active electrode materials.

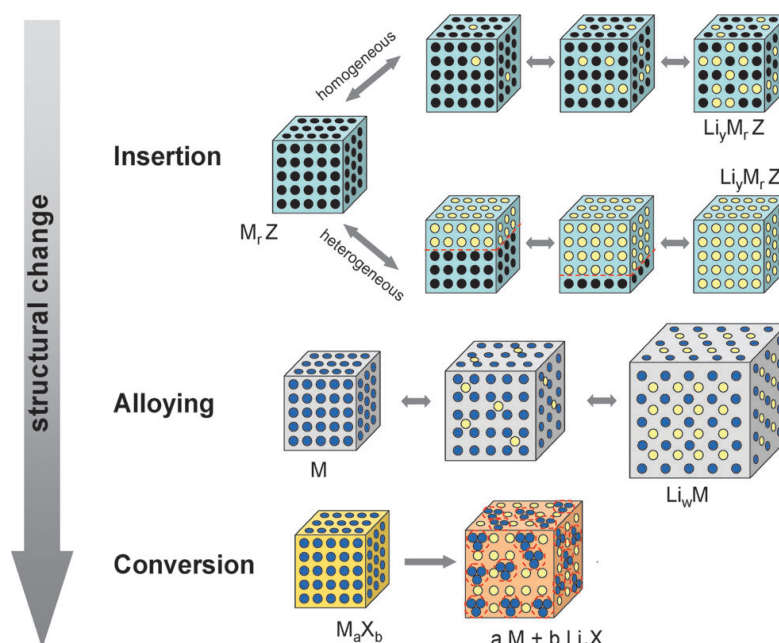
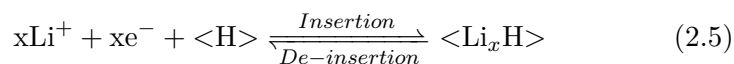


Figure 2.5 – Schematic representation of the different reaction mechanisms observed in electrode materials for lithium batteries. Black circles: voids in the crystal structure; blue circles: metal; yellow circles: lithium. Adapted from^[29].

2.2.1 Insertion materials

Insertion compounds represent the vast majority of commercial electrodes. One can find positive electrode materials as well as negative electrode materials in this class of compound. The fundamental mechanism remains the same, only the redox potential of insertion determines the appropriate side of battery.^[30] During operation, lithium ions (the guests, Li^+) insert or de-insert in the vacancies of the electrode matrix

(the host, $\langle H \rangle$) (equation (2.5)).



Insertion compounds can be classified according to the dimensionality of the passageway of guests into the host lattice (Figure 2.6).^[31] Examples of one-dimensional (1D) structures are materials crystallizing in the olivine structure (such as LiFePO_4). The most extensively investigated compounds are two-dimensional (2D) lattices such as graphite or transition-metal chalcogenides and oxides (such as LiCoO_2). Examples of three-dimensional (3D) structures are transition-metal oxides spinels (such as LiMn_2O_4 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$). One or two dimensional materials are particularly susceptible to intercalation reactions due to the presence of weak Van der Waals forces between either strongly bonded chains or layers. Three dimensional materials can also be host to insertion reactions if they provide interstitial sites that can be reached by the incoming guests.^[31] A common convention in literature is to name 2D materials as intercalation materials. Intercalation can be regarded as a special case of insertion. The term intercalation implies the restricting condition that a layered host takes up guests within its interlayer gaps, which may result in a volume change perpendicular to the layers, but which causes no other structural changes.^[32]

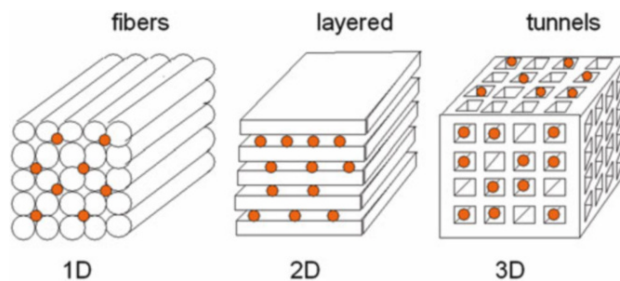


Figure 2.6 – Types of insertion compounds as a function of the dimensionality of passageway. Reproduced from^[31].

From a crystal chemistry point of view, insertion processes occurring during redox reaction involve a topotactic reversible insertion of lithium ions.^[33] This phenomenon happens without major structural change or volume expansion, promoting very good cycling stabilities.^[34] In return, topotactic reactions are usually limited to the accommodation of small amounts of lithium ions as the available interstitial empty sites in the hosts are limited. This limits greatly the specific capacities of insertion materials (graphite with 372 mAh.g^{-1} is considered the highest specific capacity).^[35,36] From a chemical point of view, insertion compounds can be classified in three different classes of materials depending on the presence or absence of limit compositions associated to structural or electronic properties modification due to host-guest interactions.^[37]

Type I: The perfectly non-stoichiometric compounds

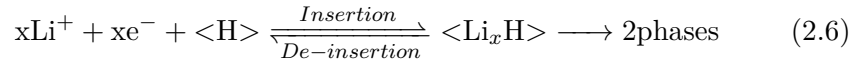
These compounds are defined by the intercalation reaction (equation (2.5)) where x can range from 0 to a maximum value x_{max} without any modification of initial properties. Steele defined this type of compound as solid-solutions prepared by electrochemical injection of ions into non stoichiometric chemicals.^[38] This class of materials is the ideal type of material for electrodes. These compounds undergo reversible electrochemical reactions and transport of matter occurs through a double flux of charged species (Li^+ and e^-). Ionic and electronic conductivities in the bulk of material remain constant whatever the concentration. These compounds are generally characterized by anisotropic structures such as lamellar structures of atomic or molecular layers. In this type of solid, it exists preferential diffusion paths for lithium ions as interplanar interactions are weak compared with intraplanar binding forces. Moreover, in type I compounds, guest-guest or guest-host interaction are generally weak.^[39] Examples of type I compounds are graphite or transition metal dichalcogenides such as MoS_2 .^[40,41]

Type II: The pseudo two-phase compounds

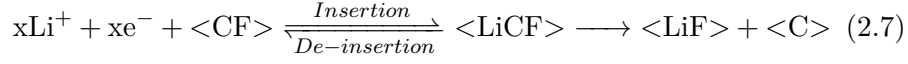
This classification includes compounds that undergo the same electrochemical reaction as type I compounds (equation (2.5)). The difference comes from the tendency of the guest species Li^+ to form an ordered sub-lattice with the host phase. Pseudo two-phase compounds result from the strong guest-guest or specific guest-host interactions. This property implies that only one type of conductivity (Li^+ or e^-) is needed in the starting material. The other conductivity can appear with the intercalation reaction and follows the reaction front. This modification of conductivity during operation can affect the reversibility of the electrochemical reaction as the intercalate $\langle \text{Li}_x\text{H} \rangle$ can become electrochemically insulating during the de-insertion process.^[39] In addition, in type II compounds, electrons injected during the intercalation process are distributed in the empty d-orbitals of the transition metals. The decrease of oxidation state of the metal results in a change of ionic radius of the coordination shell symmetry, inducing strains on the host framework.^[31] Lithium cobalt oxide is a good example of this type of compound.^[42]

Type III: The two-phase compounds

In this class of materials, compounds first undergo the same reaction as type I or II compounds but the formed intercalate compound $\langle \text{Li}_x\text{H} \rangle$ is unstable and dissociates (equation (2.6)).



During this phase separation, the two types of conductivities can be spread in the resulting two phases. A typical example of this phenomenon occurs in the poly(carbon fluoride) $\langle \text{CF} \rangle$ (equation (2.7)).



In this case, the formed intercalate $\langle\text{LiCF}\rangle$ decomposes in electron conducting carbon and lithium ion conducting lithium fluoride. For this reason, these materials cannot be reversibly cycled and thus are not suitable as electrode materials.^[26,39] Besides, other materials belonging to type III class such as the phospho-olivine LiFePO_4 or the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ give rise to two suitable phases for electrodes. During insertion, an unstable Li_xFePO_4 is formed. As a consequence, a rapid demixing occurs and a two-phase system forms, namely $\text{Li}_{1-\beta}\text{FePO}_4$ (Li-rich) and $\text{Li}_\alpha\text{FePO}_4$ (Li-poor).^[43-47]

These three types of insertion materials represent a vast and diversified library of chemicals. Among them, lithium cobalt oxide, lithium iron phosphate, graphite and lithium titanium oxide represent a large portion of active materials used in commercial applications. The latter will be described in short.

2.2.1.1 Lithium cobalt oxide layered material

Layered transition-metal oxides LiMO_2 ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}$ or a mix of different metals) have been the focus of considerable attention in the field of lithium batteries.^[48,49] This class of materials is often described as "ordered rocksalt" materials. Among these, lithium cobalt oxide (LiCoO_2 , LCO in short) is the most widely used in commercial lithium-ion batteries.^[50] First reported by John Goodenough *et al.* in 1981,^[5] LiCoO_2 has since been intensively studied and documented.^[23,51,52]

Depending on the synthesis conditions, lithium cobalt oxide can crystallize in many different forms according to the layer stacking order. For lithium-ion batteries purpose, the $\text{O}_3\text{-LiCoO}_2$ (Figure 2.7 (b)) form with an ABCABC stacking is the more appropriated.^[53-55] Unless otherwise

specified, only this $\text{O}_3\text{-LiCoO}_2$ crystal form will be described in the upcoming sections and will be simply referred as LiCoO_2 . As depicted in Figure 2.7 (a), this structure is based on a closed-packed network of oxygen atoms in which layers of Li^+ and Co^{3+} ions alternates on octahedral sites.^[56–58] In this two-dimensions material, lithium ions can reversibly be removed and reinserted between cobalt oxide layers, creating vacancies within the lithium planes.^[59,60]

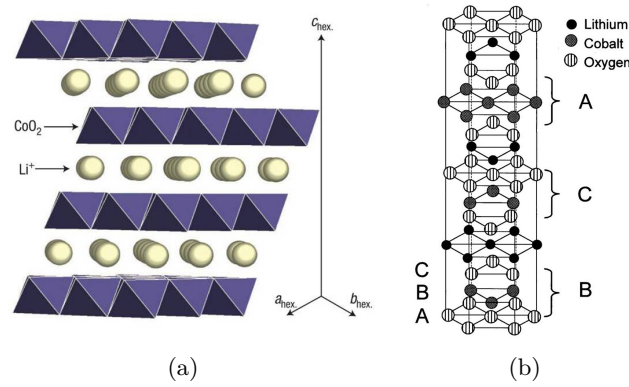
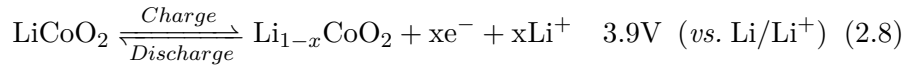


Figure 2.7 – Lithium cobalt oxide in its layered hexagonal structure: a) lithium ions layers between CoO_2 octahedra, b) projection along the $[110]$ zone axis shows lithium, cobalt and oxygen atoms in ABCABC stacking. Adapted from^[55,61].

During cell charge (equation 2.8), lithium ions are progressively removed from the LiCoO_2 lattice. The phenomena occurring during this process were deeply theoretically and experimentally described in the past decades.^[57,62–65]



While $x < 0.93$, the active material behaves as a solid state solution in a single phase (Li-rich phase) (Figure 2.8 (a)). As delithiation goes on,

in the region where $0.75 < x < 0.93$, the mechanism shifts to a two-phase process (Li-rich and Li-poor phases in a core-shell structure).^[42,66] This coexistence of the two phases gives rise to the large plateau at 3.93 V (Figure 2.8 (a)).^[57] It was shown that this phase transition is driven by the semiconducting-metal transition occurring during delithiation.^[67,68] Furthermore, the metallic behavior acquired by $\text{Li}_{1-x}\text{CoO}_x$ during the first delithiation does not revert to its original insulating state in the following redox cycles.^[69] As lithium ions are removed, the electrostatic screening of lithium ions decreases and electrostatic repulsion between CoO_2 sheets increases. Consequently, a subtle expansion along the c -axis of the hexagonal lattice is noticeable.^[70] As seen in Figure 2.8(b), in the range of $0.75 < x < 0.93$, the dependency of the parameter c of Li_xCoO_2 as a function of x splits into two parallel lines. These two values represent c -parameters of the two hexagonal phases that can be stable in this range.^[71] As the lithium concentration decreases, only the Li-poor phase subsists for $0.5 < x < 0.75$. If more than half of lithium ions are removed from the LCO lattice, binding effect of lithium ions between CoO_2 layers is too weak and the crystal undergoes an irreversible structure rearrangement. At the $\text{Li}_{0.5}\text{CoO}_2$ composition, the lattice undergoes a distortion from hexagonal to monoclinic symmetry. This reorganization is attributed to the formation of a lithium ion superlattice that involves alternating Li^+ ions in rows and rows of lithium vacancies.^[57,58,71,72] More accurately, Lu *et al.* demonstrated that O_3 -type of pristine LiCoO_2 is converted to O_1 -type Li_xCoO_2 ($x < 0.5$) after first lithium extraction. During the first lithium reinsertion, O_1 -type Li_xCoO_2 is converted to O_2 -type Li_xCoO_2 (ABCBAB stacking) (at $x = 0.93$) rather than O_3 -type (ABCABC stacking).^[73] Even worse, it was demonstrated that LiCoO_2 suffers from the dissolution of the metal ions in the electrolyte that induces oxygen release if delithiation exceed 0.5 (at potentials superior to 4.3 V).^[70,74,75]

Since this transition is irreversible, the cut-off voltage of LCO cath-

odes is in most cases set at 4.2 V and delithiation is limited to 0.5 Li^+ atoms per LCO unit in batteries. Therefore, practical gravimetric capacity is limited to 140 mAh.g^{-1} instead of 274 mAh.g^{-1} corresponding to the full delithiation of LiCoO_2 .^[76] Attempts have been made to improve LCO crystal stability of Li_xCoO_2 with $x < 0.5$.^[77] Metallic coatings on active particles were performed with success and it was proven that LCO particles could sustain a 4.5 V cut-off voltage.^[26,78] Cho *et al.* succeeded to cycle LCO coated particles up to 4.4 V with a gravimetric capacity reaching 170 mAh.g^{-1} .^[79,80] Nevertheless, such voltage cut-off increase bring us very close to the electrolyte stability window. As mentioned before, delithiation of LiCoO_2 is accompanied by a change in electrical conductivity. LCO is considered as a p-type semiconductor in its pristine state.^[81] While delithiation occurs, Co^{3+} are oxidized to Co^{4+} . Only a small concentration of Co^{4+} is necessary to increase electrical conductivity from 10^{-6} to $10^{-2} \text{ S.cm}^{-1}$.^[69,82] As most of the LMO layered materials, measured lithium diffusion coefficient in LiCoO_2 are pretty poor and values are reported to be comprised between $10^{-12} \text{ m}^2.\text{s}^{-1}$ and $10^{-11} \text{ m}^2.\text{s}^{-1}$ at room temperature.^[83–85] It is therefore essential to control size and morphology to limit diffusion path inside active materials particles.

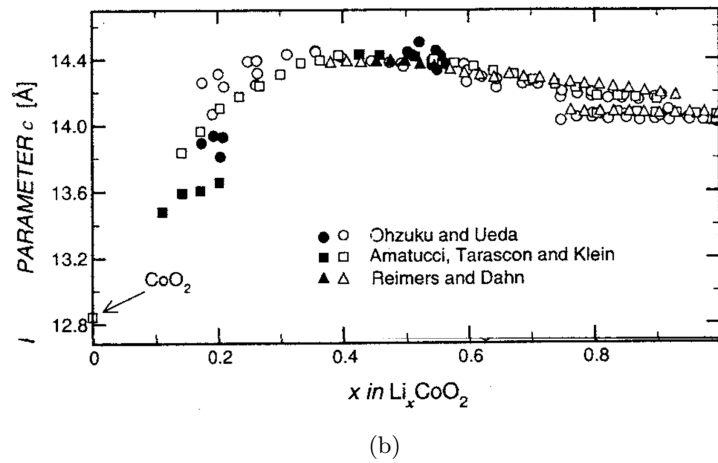
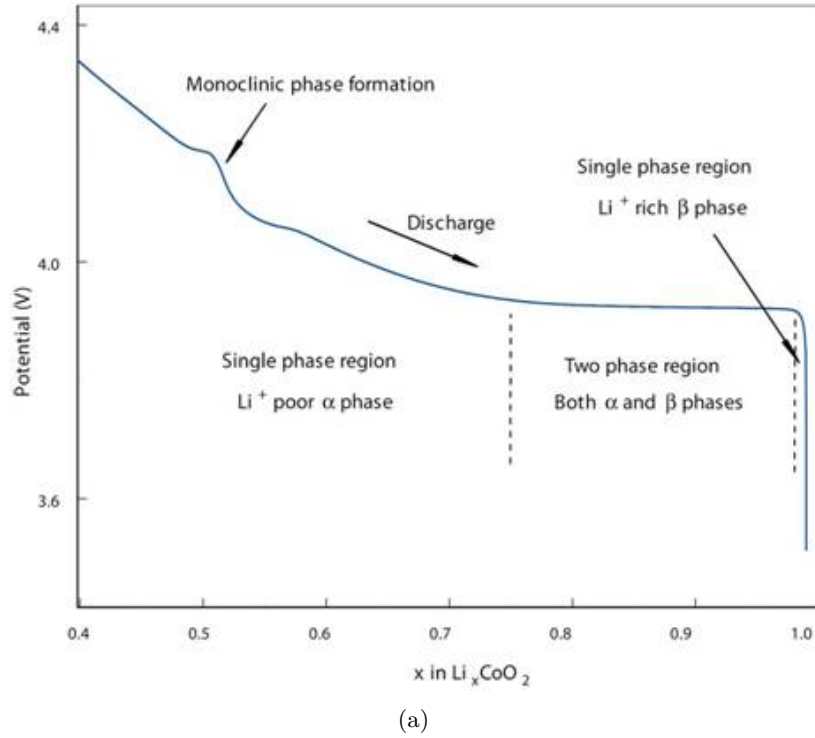


Figure 2.8 – Lithium cobalt oxide : (a) Voltage profile depending on lithiation degree and corresponding structural phases (b) lattice c -parameter of hexagonal unit cell (open symbols represent hexagonal phase and filled symbols represent monoclinic phase). Reproduced from [42,71].

In light of these features, LiCoO_2 exhibits many of the essential properties required to play the role of an active positive material in proper operation conditions. One of the major weakness of this material is its low practical gravimetric capacity. The voltage of lithium cobalt oxide with respect to metallic lithium or graphite is sufficient to guarantee high-power density cells.^[86] It is also important to note that the usual cut-off voltage of LCO cathodes is low enough to avoid electrolyte breakdown. Despite the optimized and well-controlled synthesis process, lithium cobalt oxide is still costly due to high raw materials price. Therefore, many other layered oxides based on other metals were envisioned to replace LiCoO_2 , but up to now, LCO remains a first choice material as positive electrode active material.

2.2.1.2 Lithium phosphate iron olivine

Goodenough and coworkers first reported lithium iron phosphate olivine (LFP, LiFePO_4) in 1996.^[87] The material structure consists of a distorted hexagonal close-packed oxygen framework where lithium and iron atoms occupy half of the octahedral sites while phosphorus atoms occupy one eighth of the tetrahedral sites (Figure 2.9 a).^[88,89] As it can be seen, LFP is thus a one dimension material. The purity and the size of crystals is therefore very important for diffusion phenomena (Figure 2.9 b)). In two or higher dimensions materials, points defect do not affect diffusion rates. In contrast, in one dimension material, the presence of defect in 1D diffusion channel has a drastic effect on diffusion rates.

The reaction corresponding to lithium iron phosphate insertion is described in equation 2.9. As it was previously mentioned, this compound is part of type III insertion materials. The intermediate formed insertion component is unstable and dissociate in two phases (Li-rich

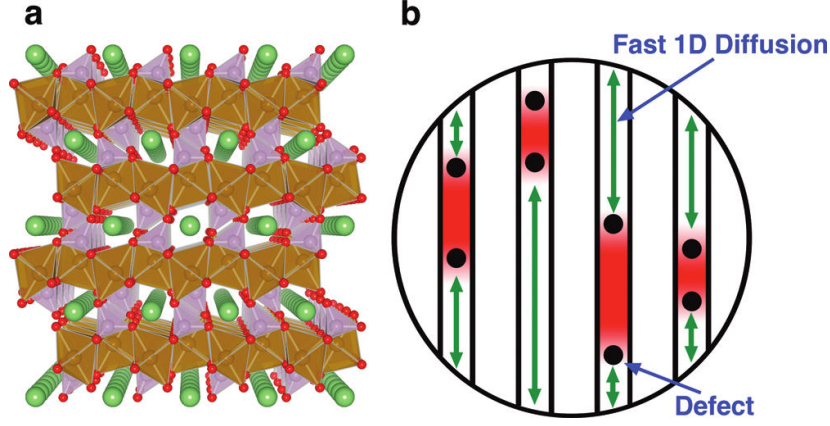


Figure 2.9 – Lithium phosphate iron: a) olivine structure where red spheres represent oxygen atoms, brown octahedron iron atoms, purple tetrahedra phosphorus atoms and green spheres lithium atoms and b) lithium ion diffusion along 1D channels. Reproduced from^[90].

and Li-poor phases).

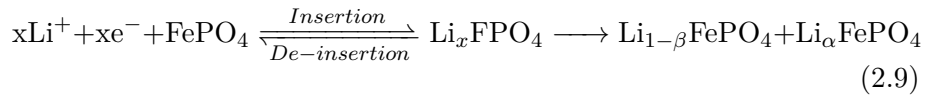


Figure 2.10 presents the typical voltage profile of a LFP electrode. The long flat plateau typical from a two-phase mechanism can be noticed. This plateau is located at 3.45 V, making it an excellent candidate for high-energy batteries. The theoretical capacity of this active material is evaluated at 170 mAh.g⁻¹ as LFP can be fully delithiated.^[91] Gravimetric capacity is therefore slightly better than lithium cobalt oxide. One of the major drawback of LFP is the very poor intrinsic electronic and ionic conductivities. Nevertheless, efforts on size-reduction to the nanoscale^[90] and carbon coating strategies,^[92] have enormously improved commercial LFP performances.^[91]

For the previous reasons, lithium iron phosphate is considered as one of the most promising cathode candidate for the next generation

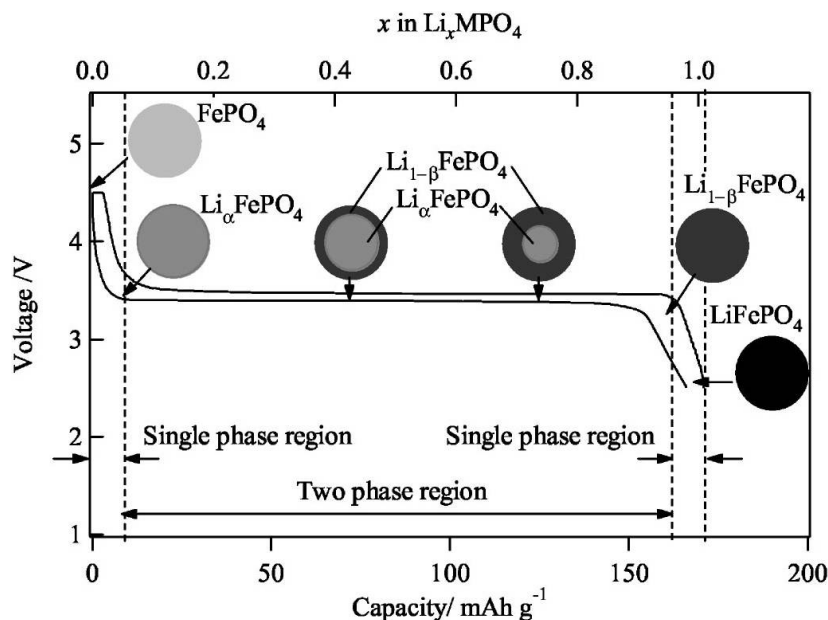


Figure 2.10 – Lithium Phosphate iron insertion/de-insertion process: voltage profile and two-phases mechanism. Reproduced from^[93].

positive electrode active materials. Not only, LFP meets pretty well the electrochemical requirements for cathode material but this material can be produced in a large amount at low cost and presents a low toxicity.^[94]

2.2.1.3 Graphite and carbonaceous materials

Carbonaceous materials are the best representative of insertion compounds. Historically, the first synthesis of lithiated carbons was reported by Hérold in 1955^[95] and a complete study of intercalation processes was described by Ebert *et al.*^[96] The first comprehensive reports on carbon anodes with practical relevance were published in 1989 by Mohri *et al.*^[97] and Kanno *et al.*^[98] Since this time and the commercialization of lithium-ion batteries by Sony in 1991, carbonaceous materials, and particularly graphite, dominate the market of negative electrodes.^[99] Therefore, they were intensely studied and optimized for the

The diagram illustrates the crystal structure of graphite, showing four layers of carbon atoms (A, B, C, and A planes). The layers are stacked in an ABAB sequence. The unit cell is outlined in red, showing the dimensions a_0 (0.246 nm) and c (0.6708 nm). The layer plane spacing is indicated as 0.141 nm. The axes are labeled: a-axis, b-axis, and c-axis.

Figure 2.11 – Graphite crystallographic structure showing the hexagonal cell. Adapted from^[23].

Graphitic carbons are constituted of stacked graphene layers (Figure 2.11). Each of these layer is made of sp^2 hybridized carbon atoms arranged in a planar honeycomb-like network. The delocalized π electrons of sp^2 atoms are responsible for the electronic conductivity as well as the weak Van der Waals interactions between layers.^[23,109] The graphene layers can be arranged into a ABAB pattern (hexagonal structure) or less frequently following a ABCABC stacking structure (rhomboedral structure) along the c -axis. The term graphite is used for carbons having a layered lattice structure with perfect stacking order. As it can be seen in Figure 2.11, the structure of graphite crystal is anisotropic. The layered structure gives rise to two kind of surfaces: prismatic surfaces (edges) and basal plane surfaces.^[32] Obviously, properties along the basal plane and the edges are very different. For example, in-plane conductivity (along a and b -axis) reaches $2\text{--}3 \cdot 10^4 \text{ S.cm}^{-1}$ while conductivity along c -axis caps at 6 S.cm^{-1} .^[103] Reactivity of lithium electrochemical intercalation also highly differs. While the basal plane is relatively inactive for lithium insertion (in the absence of defects), edge planes show large amount of insertion. Properties of graphite particles are thus strongly determined by the ratio of basal and edge planes.^[110] Hence, the choice of active material morphology is of primary importance for electrode performances (Figure 2.12).

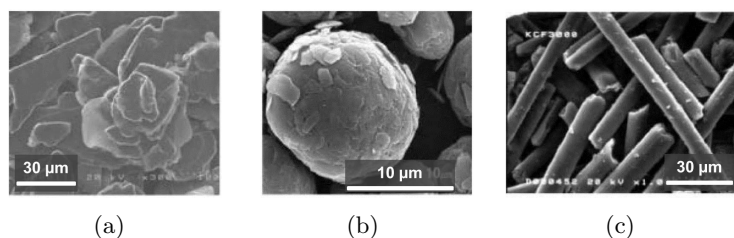


Figure 2.12 – Graphite particle morphologies: (a) natural graphite flakes, (b) natural graphite spheres and (c) artificial graphite microfibers. Adapted from^[23].

Besides perfectly crystalline graphite particles, the vast majority of

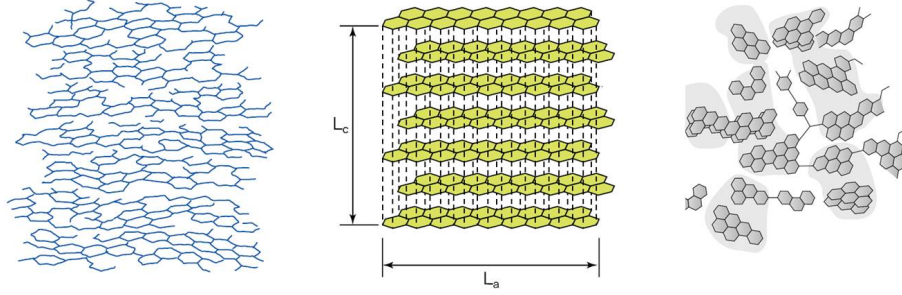
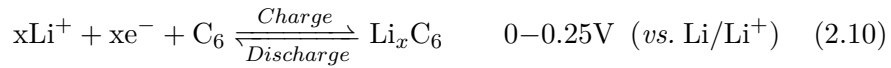


Figure 2.13 – Structure of carbons : (a) turbostratic graphitizable carbon, (b) perfect graphite and (c) non-graphitizable carbon. Adapted from^[23,85].

carbonaceous materials presents defects. Carbons that can be transformed in graphitic carbons via physical treatments are called graphitizable carbon or soft carbons, the others non-graphitizable are called hard carbons (Figure 2.13(a) and (c)). Under heat treatment (between 1000°C and 3000°C), defects of soft carbons disappear and planes become larger. The stacking of these planes is improved and the crystal structure expands in all directions while distance between planes decreases to produce almost perfect graphite particles (Figure 2.13(b)). Non-graphitizable carbons consists in small hexagonal networks and exhibit a highly disordered structure with crosslinking between domains. Due to this structure, it is difficult to reorganize the network even at high temperatures.



In graphite anodes, lithium ions react theoretically with six carbon atoms as described in the intercalation equation (2.10). Theoretical specific capacity exhibited by graphite is therefore evaluated at 372 mAh.g⁻¹. During the charge, lithium ions intercalate in the carbon ma-

terial. The voltage rapidly decreases from 3 V *versus* Li/Li^+ to reach 0.25 V, the potential at which intercalation begins.^[23,111] Lithium ions are intercalated through the edge planes or the structural defects in the basal plane via a mechanism called staging. While this phenomenon was intensively studied for years, two models of intercalation are still debated.^[112] The first one, which is commonly admitted, is the staging model of Rudorff (Figure 2.14 A). Lithium ions intercalate between two graphene layers to form a single lithium ion layer and lithium ions are not intercalated into adjacent layers. As lithium ion concentration increases in graphite, more layers are filled until lithium ion layers and graphene layers are arranged one after another.^[23,85] In the second model, the so-called Daumas-Hérol model, lithium ions can insert in any layers and rapidly form lithium island in the middle of graphene layers (Figure 2.14 B).^[113–116]

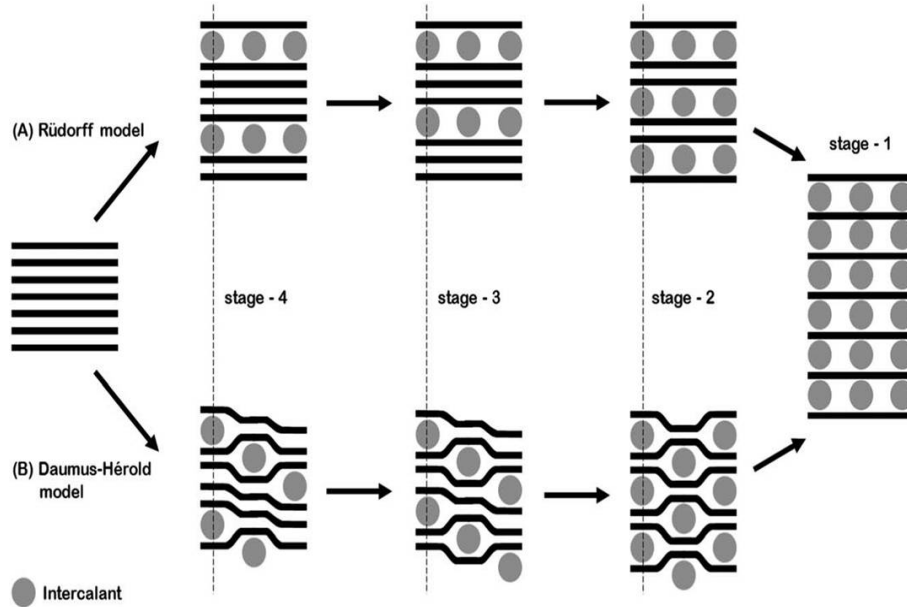


Figure 2.14 – Intercalation model in graphite: schematic of the (A) Rudorff and (B) Daumas-Hérol models of ion intercalation into graphite. Reproduced from^[23,115].

Appart from this difference, the two theories agree to describe transitions between stages and the coexistence of different phases during the lithiation process.^[117] These different stage transitions occur at precise voltage as shown in Figure 2.15. The last phase transition from LiC_{12} to LiC_6 is known to be as low as 0.065 V *versus* Li/Li^+ . This very low potential value implies that the maximum over-voltage for a graphite anode during discharge cannot exceed 0.065 V. Otherwise, reduction of lithium ions to metallic lithium (phenomenon known as lithium plating) inevitably occurs leading to solid electrolyte interphase (SEI) layer degradation and formation of lithium dendrites.^[118]

As described previously, few changes occur in perfectly non-stoichiometric compounds through insertion/de-insertion processes. During the intercalation, the structure of graphite shifts from ABAB to AAAA with a small increase of the interplanar distance. Volume expansion is limited to maximum 10 %, which prevents heavy strains in the structure.^[119] In a full state of charge (LiC_6), intercalated lithium ions have direct neighbours in adjacent layers but not in adjacent benzene ring of the interlayer.^[30,120] The electronic conductivity of the graphene layers slightly increases throughout the intercalation process but other properties change little.^[96,121]

Graphite is also greatly appreciated as negative electrode material for its ability to form a stable interphase with non aqueous electrolytes (Figure 2.16). In the case of graphite, the solide electrolyte interphase layer is mainly formed during the first cycle. This layer acts as a passivation layer, preventing further electrolyte reduction.^[122] As it is known, the volume expansion during cycling plays a major role in the SEI cohesion and growth.^[123,124] In graphite, the lattice mismatch is contained and the SEI layer does not have to endure too much strain.^[125] The composition of the SEI layer is influenced by the nature of the active materials on which it forms. In the case of graphite, the ratio between organic and inorganic compound in the SEI does not affect the conduc-

tivities too severely.^[126,127] The formation and influence of the SEI layer will be deeply described in section 2.6.5.

In light of these electrochemical considerations, graphite is considered as the top choice as active material for negative electrodes. Moreover, its low cost, eco-compatibility and abundance ensure it still has a bright future despite a limited capacity.

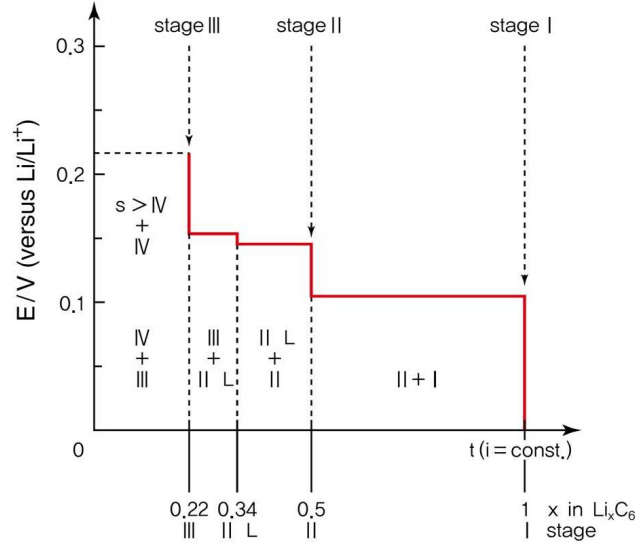


Figure 2.15 – Intercalation model in graphite: schematic galvanostatic curve. Reproduced from^[23,115].

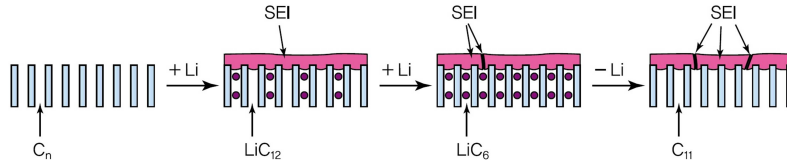


Figure 2.16 – SEI layer formation on graphite. Adapted from^[23].

2.2.1.4 Lithium titanate spinel

The $\text{Li}_{3+x}\text{Ti}_{6-x}\text{O}_{12}$ ($0 \leq x \leq 1$) solid solution family attracted a lot of attention in the past decades.^[128,129] Initially, lithium titanates were investigated for their interesting super-conductive properties at low temperature.^[130,131] Among these compounds, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO in short) structure was first reported by Jonker.^[132] In 1983, Murphy *et al.* demonstrated the reversible insertion of lithium ions in this spinel.^[133] Full cells with lithium titanium oxide as anode and various different positive electrodes were later reported.^[134,135] Lately, LTO spinel was even reported as a possible candidate for sodium-ion batteries.^[136–138]

Lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is part of the spinel group. Spinel is a class of material of general formula $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4^{2-}$ that crystallize in the face centered cubic crystal system. The oxide anions form a cubic close-packed lattice (32e) and the cations occupy some or all of the octahedral (16d) and tetrahedral sites (8a). All titanium atoms and one lithium atom are randomly distributed over the 16d octahedral vacancies (Figure 2.17(a)). The three remaining lithium atoms occupy tetrahedral 8a sites.^[139,140] Therefore, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is sometimes written as $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$, or even $[\text{Li}]_{8a}[\text{Ti}]_{16d}[\text{Li}_{1/3}\text{Ti}_{2/3}]_{16d}[\text{O}_4]_{32e}$.^[141,142]

During the charge process, lithiation occurs and lithium ions insert into the 16c octahedral vacancies (equation 2.11). This lithium insertion is accompanied by the transfer of lithium ions from 8a to the 16c vacancies. Hence, the spinel structure shifts to the rock-salt structure $[\text{Li}_2]_{16c}[\text{Ti}]_{16d}[\text{Li}_{1/3}\text{Ti}_{2/3}]_{16d}[\text{O}_4]_{32e}$.^[141,145] Besides this lithium insertion, three Ti^{4+} ions are reduced to Ti^{3+} ions during the two-phase transition.^[146] During this structural transition, only a slight contraction occurs. The volume of the lattice shrinks of about 0.2 %. Due to this negligible shrinkage, LTO is considered as a "zero strain" material for lithium insertion and removal.^[79,147] This property confers to the material a superior structural stability and guarantees the mechanical integrity of electrodes during the charge/discharge processes. The absence

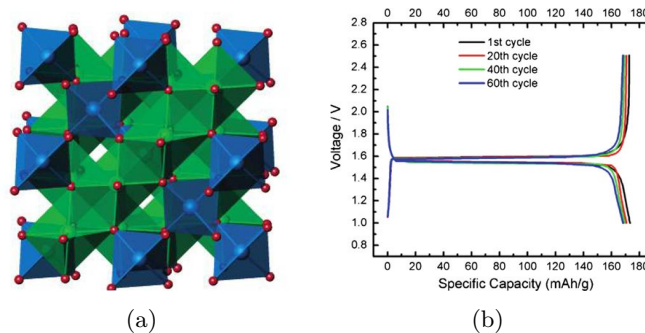
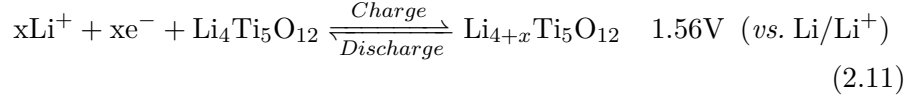


Figure 2.17 – Lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$: (a) spinel structure; red spheres represent oxygen atoms in a cubic closed-packed array, green octahedrons are filled with titanium and lithium atoms and blue tetrahedrons are partially filled with lithium atoms (b) typical voltage profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Reproduced from^[143,144].

of volume expansion helps to maintain a good contact between LTO particles, binder and conductive additives leading to extremely good cycle stability.^[148–150] The transition between the two structures occurring in $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ involves a two-phase equilibrium.^[45,140,141] This equilibrium is responsible for the very flat plateau at 1.562 V in the voltage profile for $0.09 < x < 2.91$ (Figure 2.17 (b)).^[151–153] The high voltage versus lithium exhibited by LTO allows it to be considered as negative or positive electrode material. Nevertheless, LTO is preferably exploited as negative active material for two main reasons. First, using LTO as cathode leads to full cells exhibiting a maximum of 1.5 V, while 3.2 V batteries can be designed with LTO as anode.^[154] Secondly, the high insertion potential is a great asset to avoid the lithium plating or SEI layer formation on the negative electrode. Side reactions are avoided since the decomposition of nonaqueous electrolytes occurs only below 0.8 V.^[155–157] The coulombic efficiency of the first cycle is therefore close to 100 %.



In LTO, only three lithium ions can be reversibly inserted and de-inserted in the framework of the spinel, limiting the theoretical capacity to 175 mAh.g^{-1} .^[158] Other titanium oxides with superior capacities (up to 335 mAh.g^{-1}) were studied but their cyclabilities are significantly worse or insertion voltage less suitable.^[159–162] Given the structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel, more lithium ions can theoretically be inserted in the remaining tetrahedral vacancies of the lattice. It was proven that the insertion of 1.5 or 2 lithium atoms was possible to reach the $\text{Li}_{8.5}\text{Ti}_5\text{O}_{12}$ or $\text{Li}_9\text{Ti}_5\text{O}_{12}$ compositions.^[163] This extra capacity is nevertheless impossible to reach without applying a negative potential for lithium insertion which directly leads to reduction of lithium ions to lithium metal. This undesired lithium plating on electrode therefore limits the capacity of LTO spinel to 175 mAh.g^{-1} . Unlike graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in its pristine form shows very low ionic or electrical conductivities.^[164–167] In its spinel form, ionic diffusivity is measured at $10^{-6} \text{ cm}^2.\text{s}^{-1}$ ^[168] and electrical conductivity of LTO is extremely low and evaluated at $10^{-13} \text{ S.cm}^{-1}$.^[169] Therefore, this material can be regarded as an electrical insulator. During lithiation, the spinel structure turns to a rock-salt configuration in a two-phase equilibrium and the $\text{Li}_7\text{Ti}_5\text{O}_{12}$ phase is electrically conducting.^[153,170] To circumvent these lacks of conductivity, various morphologies of LTO nanoparticles were reported with the aim of decreasing diffusion paths (Figure 2.18).^[129,142,171] Carbon^[172–175] or metal^[176,177] coating on micro-sized or nano-sized LTO nanoparticles also showed satisfactory results in the design of high cycling rate batteries. Heterogen atom substituted LTO particles were also prepared with substantial improvements in conductivities but unfortunately sometimes at the expense of the capacity.^[178–180]

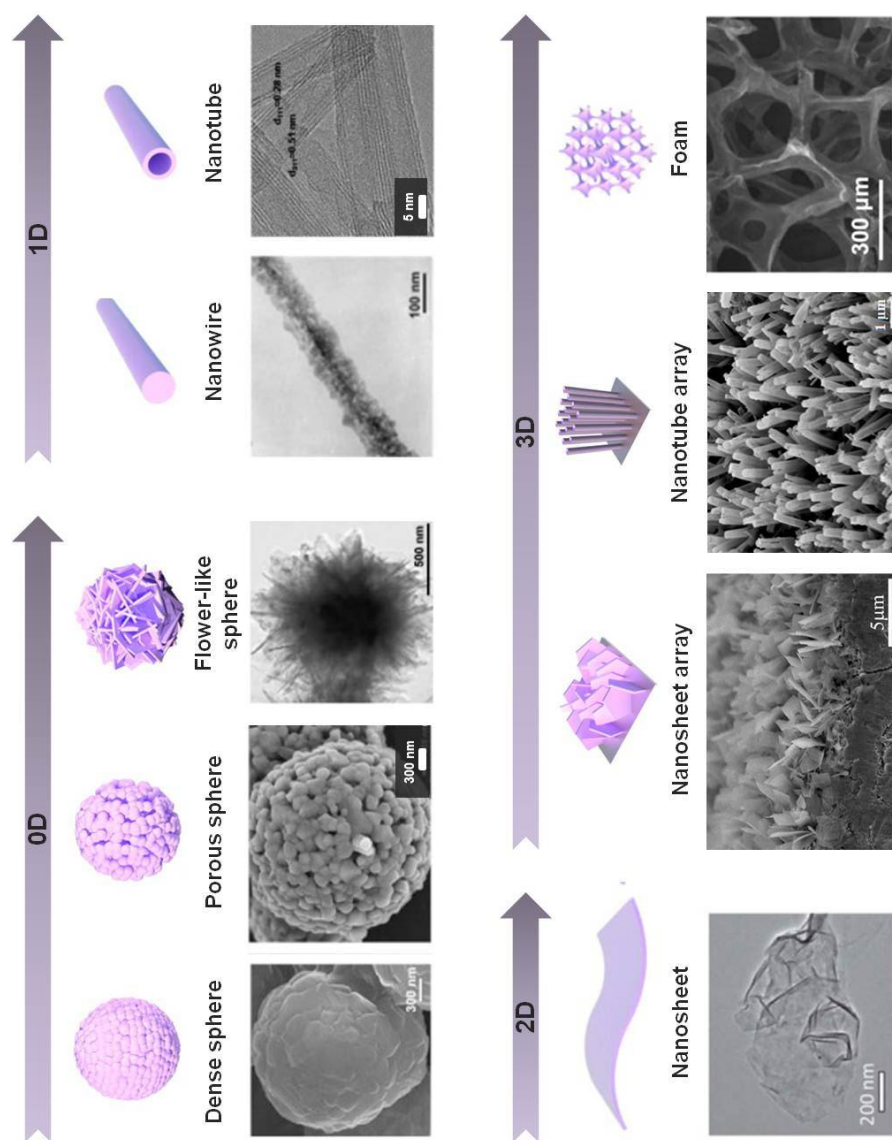


Figure 2.18 – Schematic illustration of various nanostructures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Adapted from [142].

From purely electrochemical point of view, LTO may appear less attractive than carbonaceous materials (372 mAh.g^{-1} and $0.25 \text{ V vs. Li/Li}^+$ for graphite). Nevertheless, LTO being a "zero-strain" material and the higher insertion potential are two substantial advantages. These properties are of paramount importance in the design of long-life batteries and LTO is considered as an interesting material for the conception of HEV or supercapacitors.^[146–148,181]

2.3 Passive electrode materials

In this section, we describe materials that do not directly provide energy but are nevertheless essential to lithium ion battery operation. Binders and conductive agents are only a small part of the electrode composition, but play a very important role in the cycling stability and rate capability. All these components play therefore vital roles in battery operation but their amount in the battery has to be minimized as they do not provide energy.

2.3.1 Binders

Although binders only reach 2–5 wt. % in a commercial electrode, binders are essential to the effective operation.^[182] As previously mentioned, the volume of most of active materials expands during lithiation. Therefore, binders are required to provide cohesion of active matter particles and to ensure mechanical stabilization of electrodes. In addition, binders have to meet other important criteria to be efficient.^[23]

First of all, they cannot dissolve in the highly polar carbonate organic solvent used as electrolyte. Nevertheless, suitable polymer binders have to swell by absorbing a proper amount of electrolyte to ensure lithium ion conduction within the electrode. Secondly, they have to be electrochemically stable in the voltage operation window of the battery. Binders must not be easily reduced at negative electrodes or oxidized

at positive electrode. Thirdly, binders have to be thermally stable since temperature can rise above 200 °C during the drying of the electrodes.

Fluorinated polymers such as poly(tetrafluoroethylene) (PTFE) or poly(vinylidene fluoride) (PVdF) meet all these requirements and are therefore especially suited to the binder task. Nevertheless, the solubility of these polymers is limited to only a few solvents and N-methyl-2-pyrrolidone (NMP) is the most frequently used. The use of this solvent is a disadvantage as it evaporates slowly in mild conditions. Therefore, demixing of binder, active material and conducting agents can occur during the drying process. Hence, water-soluble binders such as carboxymethyl cellulose,^[183] alginate^[184] or styrene-butadiene rubber^[185] are now considered as alternatives as they are easy to process while being cheaper and greener. Finally, conductive polymers acting at the same time as binder and conducting agent have been reported.^[186,187] However, production costs of these materials are far too high to be considered at industrial scale to date.^[23]

2.3.2 Conducting agents

To compensate the lack of intrinsic conductivity of active materials and the addition of insulating polymer binders, conducting agents are needed. Addition of a sufficient amount of conducting agents creates an electrical path within the electrode. Hence, it ensures the proper collection of electrons at the surface of the active material to the current collector. The most common conducting agents are nanosized carbon spherical particles, named nanocarbons. Lately, carbon nanotubes or nanofibers are considered as alternative conducting agents.^[106,188,189]

2.3.2.1 Nanocarbons

Nanocarbons represent the vast majority of conducting agents. Examples of these carbon fine powders include among others acetylene black (AB), Ketjen black (KB), super P or super C carbons. Depending

on their production method, these nanocarbons vary in size, morphology and degree of graphitization. These parameters have a direct impact on their properties.^[190]

Nanocarbons must meet the three following requirements in order to be used as conducting agents: electrical conductivity, dispersibility and wettability.^[23] While their graphitic structure ensures suitable electrical conductivity, the two other parameters are more challenging. A fine dispersion of nanocarbons within the electrode is nevertheless essential to secure a homogeneous electrical conduction. Modification of the nanocarbon surface is required to obtain wettability to ensure a good contact between the organic electrolyte and the particles.

2.3.2.2 Carbon nanotubes

Since the discovery in 1991 by Iijima,^[191] carbon nanotubes (CNTs) have attracted a growing interest. For the past 25 years, the number of publications or reviews involving these materials has continually increased.^[192,193] This success is due to the unique properties of these materials, as it will be briefly described below. Carbon nanotubes are cylinder-shaped materials composed of sp^2 -hybridized carbon atoms arranged in a honeycomb network. Therefore, they can be visualized as the result of a graphene sheet enrollment (Figure 2.19). Different types of CNTs can be distinguished based on the number of concentric graphene cylinders composing the material: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Figure 2.20).

As depicted in Figure 2.21, three different types of single-walled carbon nanotubes exist (i.e. zigzag, armchair and chiral), depending on the way the graphene sheet is enrolled, also known as helicity. As a result, electrical properties of CNTs can strongly vary from one nanotube to another, yielding to metallic and semiconducting CNTs. Since MWCNTs are composed of several concentric nanotubes in which helicity is known

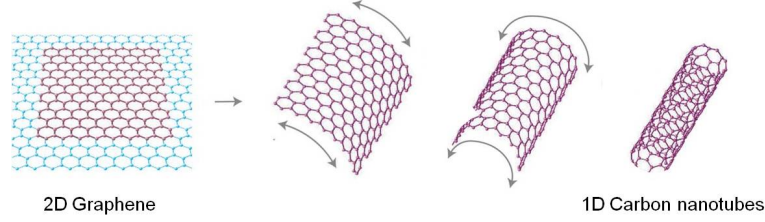


Figure 2.19 – Schematic representation of a carbon nanotube as an enrollment of a graphene sheet. Adapted from^[194].

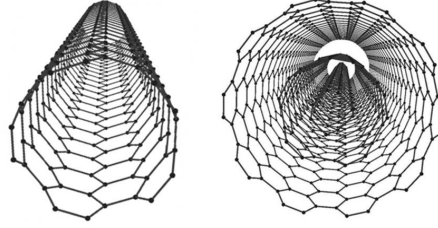


Figure 2.20 – Schematic representation of a SWCNT and a MWCNT. Reproduced from^[195].

to vary each layer, most of MWCNTs are statistically metallics.^[196] The structure of the nanotube is responsible for its impressive electronic properties. First, the sp^2 hybridization of the carbon atoms involves a complete delocalization of the π -electrons throughout the nanotube. This π -electron conjugated system allows a high mobility of the charge carriers along the nanotube. Due to their structure, carbon nanotubes exhibit remarkable electrical properties. With an electrical conductivity up to 10^6 S.cm^{-1} ,^[197] CNTs namely constitute excellent electrical conductors. Second, due to their quasi-one-dimensionality, electrons are confined in one direction, along the nanotube axis.

Besides these remarkable electrical properties, carbon nanotubes also exhibit outstanding mechanical and thermal properties. With a Young modulus (E) comprised between 1 and 5 TPa for SWCNTs,^[199] a tensile strength from 11 to 63 GPa^[200] and an elongation at break of 12 %, ^[200]

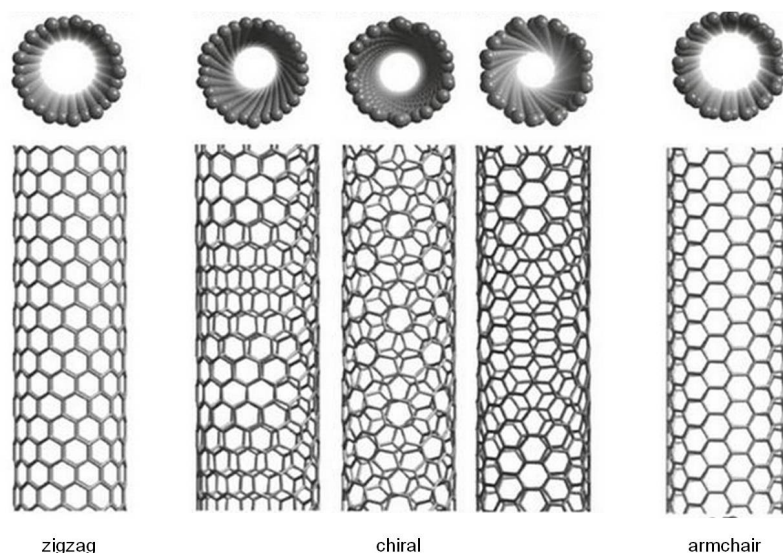


Figure 2.21 – Representation of zigzag, chiral and armchair carbon nanotubes. Adapted from^[198].

CNTs are one of the strongest and stiffest materials on earth, while being flexible.^[201] About 100 times stronger than steel for a considerably lower weight, CNTs can be useful components for the preparation of composite materials for diverse applications as varied as sports equipments, bulletproof jackets or transport vehicles. Carbon nanotubes also possess a thermal conductivity higher than diamond,^[197] which makes them good candidates for integration into polymer composites for the preparation of thermally conductive materials.^[202] The combination of all these unique properties make them a very interesting material for electronics.^[203] Applications in transistors,^[204] capacitors,^[205] sensors,^[206] flexible electronics,^[207] and lithium-ion batteries components^[176] have therefore emerged.^[208] During the last decade, the production cost of carbon nanotubes decreased from 45 000 to 100 \$.kg⁻¹, while their productivity reached several hundred tons per year.^[209] For this reason, they can now be implemented in practical applications.

2.4 Current collectors

Current collectors have the role to supply electrons to active materials or to withdraw electrons to the external circuits. Their conductivity is hence primordial and metals are a natural choice. Current collectors must also be electrochemically stable in the potential operation window of their electrode. Working potentials of negative electrode are comprised between 0.01 V and 3 V while working potentials of positive electrode are superior to 3 V. It is therefore important to avoid reduction of the current collector at the anode and oxidation at the cathode. The chemical nature of the metal is therefore different at each electrode and defined by its polarity.^[12,210] While taking into account financial considerations, copper is the most appropriate material for negative current collectors and aluminium for positive current collectors. These metals are processed in very thin foils to minimize their weight (10-20 μm) but show sufficient mechanical strength to be processed and ensure the structural integrity of the electrodes during operation.^[23] Lastly, metal foils have to present sufficient wettability to the electrode slurry and strong adhesion of the electrode after solvent removing. The surface state of metal foils is therefore critical and surface treatment can be required.^[211,212]

2.5 Separators

Separators do not participate in electrochemical reactions and have the sole role to physically separate the cathode and the anode. Nevertheless, they have to present particular properties and to meet some crucial requirements.^[213,214] The separator has the essential role to provide a pathway for lithium ion transport between electrodes. Wettability by liquid electrolyte is therefore an important property as well as their porosity (Figure 2.22). Separators have to absorb and retain a certain amount of electrolyte to ensure their lithium ion conduction role. In

addition, the separators must be chemically stable to the electrolyte and electrochemically inert under the strong oxidizing and reducing conditions when the battery operates. Most common used separators are 25 μm microporous polyolefin films such as poly(ethylene) (PE) or poly(propylene) (PP).^[213] These materials meet all requirements mentioned above in addition to outstanding mechanical properties and low cost.^[215]

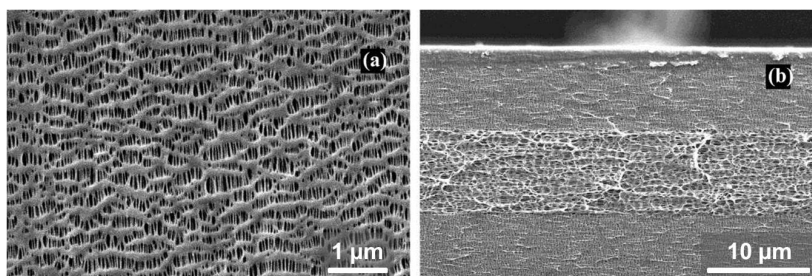


Figure 2.22 – Scanning electron micrographs of Celgard 2325 (PP/PE/PP) tri-layer separator used in lithium-ion batteries: (a) surface image and (b) cross-section. Reproduced from^[214].

2.6 Electrolytes

Beside electrodes, the electrolyte constitutes the third key component of batteries. Electrolytes are essential and ubiquitous in all electrochemical devices. The electrolyte acts as a medium for the transfer of charges, which are in the form of ions, between the two electrodes. The choice of electrolyte is of paramount importance as it can drastically change battery performances. Therefore, electrolytes have received considerable attention from the scientific community and were exhaustively documented.^[216,217] To be efficient, electrolytes have to meet the following minimal requirements:^[23,31,216]

1. The trivial role of electrolyte is the ion conduction between electrodes. Hence, electrolytes with superior ionic conductivity pro-

duce battery with superior performances. Rapid lithium ion diffusion within the electrolyte is especially important when batteries are rapidly charged or discharged.

2. Electrolyte have to be electronic insulator as no electrons should directly transfer between electrodes to keep self-discharge to a minimum.
3. Electrolytes should exhibit high chemical and electrochemical stabilities, especially at the charged surfaces of the electrodes. The range in volts between their oxidative and reductive decomposition limits quantifies the stability of an electrolyte. This concept is known as the electrochemical stability window of the electrolyte. Obviously, the redox potential of both electrode materials must fall within this electrochemical window.
4. The stability of an electrolyte has to be established for a wide range of temperature (e.g. -20 °C to 60 °C) to ensure safety during battery operation. Most of the electrolytes are flammable and may cause fire or explosions if heated or used improperly.
5. The electrolyte should be a low cost material as they represent not less than 22 % of the cost of materials to design a battery.^[218] In addition, it should be the more environmentally friendly possible.

Table 2.1 sums up the characteristics of different electrolytes referred for lithium-ion batteries. Liquid electrolytes consist of salts (electrolyte solutes) dissolved in organic solvents and exhibit high ionic conductivities. Ionic liquids consist in molten salts with a melting point below room-temperature. They do not contain flammable solvents and are therefore considered safer. Unfortunately, their production cost is very high. Solid polymer electrolytes consist in lithium salts dissolved in polymers of high polarity. Unfortunately, these electrolytes present poor lithium ion conduction. Gel polymer electrolytes consist in a polymer

matrix swelled with liquid electrolyte and show intermediate properties between liquid and polymer electrolytes. Besides these main electrolyte types, it also exists glassy and crystalline electrolytes^[219] but to date, these materials still did not show practical applications.

	Liquid electrolytes	Ionic liquid electrolytes	Solid polymer electrolytes	Gel polymer electrolytes
Composition	Organic solv. +lithium salts	RT ionic liquids +lithium salts	Polymer +lithium salts	Polymer +organic solv. +lithium salts
Ion conductivity	High	High	Low	Relatively high
Low-temp. perf.	Relatively good	Poor	Poor	Relatively good
Thermal stability	Poor	Good	Excellent	Relatively good

Table 2.1 – Electrolyte types for lithium batteries. Reproduced from [23].

2.6.1 Liquid electrolytes

Liquid electrolytes represent the majority of electrolytes in lithium ion batteries. Among all electrolytes listed previously, they present the best ionic conductivities with values up to $10^{-2} \text{ S.cm}^{-1}$.^[216] As previously mentioned, liquid electrolytes consist in lithium salts dissolved in a solvent. Hence, their ionic conductivity and other properties result from a complex choice of solvents, salts and additives.^[220]

2.6.1.1 Organic solvents

The choice of the solvent to design performing electrolytes is of major importance. The solvent has to meet several criteria.^[23] First, it should be able to dissolve salts to a sufficient concentration, in other words, its dielectric constant (ϵ) should be as high as possible. Second, solvent viscosity (η) should be low because a fluid solvent facilitates the ion transport. In addition, the solvent used for electrolyte design should remain liquid in a wide range of temperature. The solvent should also present a high flash point to ensure safety during battery operation. Lastly, as a result of the very active nature of the strongly reducing anodes and the strongly oxidizing cathodes, solvents with acidic protons are not appropriate.

A wide spectrum of polar solvents has been investigated and most of the appropriate ones fall in either one of the following classes: carbonates, ethers or esters. Among these solvents, the most commonly used for lithium ion batteries are listed in Table 2.2 and depicted in Figure 2.23. As it can be noted in Table 2.2, no liquid meets all the requirements perfectly and therefore, electrolytic solution formulations based on single solvents are very rare. Most liquid electrolytes are indeed based on a mix of two or more solvents in which lithium salts are dissolved. The combination of several solvents permits to attain various functional aims simultaneously.

Solvent	T_m [°C]	T_f [°C]	ϵ	η
Ethylene carbonate	39	248	89.6	1.86
Propylene carbonate	-49.2	241.7	64.4	2.53
Dimethyl carbonate	0.5	90	3.11	0.59
Diethyl carbonate	-43	126.8	2.81	0.75
Ethylmethyl carbonate	-55	108	2.96	0.65

Table 2.2 – Physicochemical properties of principal solvents for liquid electrolytes. Data from^[23].

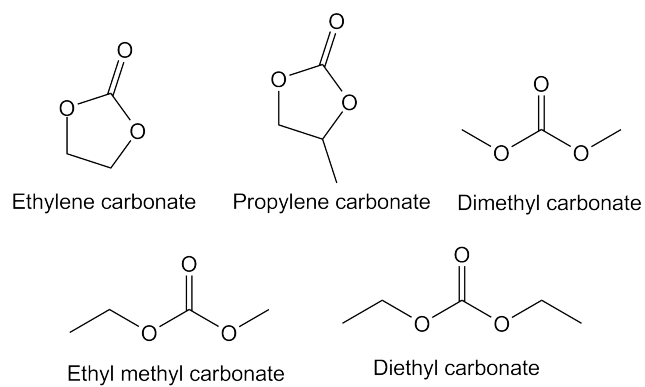


Figure 2.23 – Common organic solvents used for liquid electrolytes.

2.6.1.2 Lithium salts

Lithium salts have been extensively studied by many researchers as they constitute one of the most prospective way to enhance lithium cell performances.^[221] Lithium salts should meet the following prerequisites to be used as electrolyte salts. They should be able to dissolve in large amount and dissociate completely in organic solvents. Ionic mobility of both ions have to be as high as possible. Lastly, they have to exhibit high thermal and chemical stabilities.

The candidate that meets the requirements at best is lithium hexafluorophosphate (LiPF_6), although this compound presents serious problems when in presence of water. Indeed, moisture traces present in electrolyte react directly with LiPF_6 to generate the highly corrosive hydrofluoric acid (equation 2.12).^[222,223]



An alternative choice is lithium perchlorate (LiClO_4). It exhibits high solubility and good ionic conductivity in organic solvents. In addition, LiClO_4 is stable towards hydrolysis compared to fluoro-type salts. Nevertheless, the high oxidation state of chlorine makes him a very strong oxidant. At high temperature, it may be explosive in presence of organic species during battery operation.^[224,225]

2.6.1.3 Additives

The recent improvements in the fundamental understanding of lithium ion battery ageing phenomena are essential for improving battery electrochemical performance and safety. While many side-reactions at electrode interfaces can occur, the most economical approach to circumvent some of them is the use of electrolyte additives. Over the past several years, hundreds electrolyte additives with various functions have been reported. They can be used to enhance conductivity, battery lifespan or

safety. Hence, the majority of liquid electrolytes contains up to 5 wt. % of additives. Function and nature of these additives will be here briefly described.^[23,226,227]

SEI formation additives

It was demonstrated that during the first cycle of lithium ion batteries, a solid layer is formed at the interface between the electrolyte and the electrode. This formed solid electrolyte interphase will be described in depth in the next sections. The SEI formation is due to the reduction of carbonate-based solvents on the negative electrode. First the solvent is reduced into a radical-anion. The latter subsequently decomposes with two different mechanisms. One of them leads to the formation of undesirable gaseous species and Li_2CO_3 . The second one leads to the formation of an insoluble stable lithium alkyl carbonate layer. To promote the formation of this stable SEI film, SEI formation additives are added. They can be sorted in three groups:

- Reduction-type additives. This type of additives exhibits higher reductive potentials than the electrolyte solvents. Therefore, they are preferably reduced prior organic solvents. The formed radical anion subsequently polymerizes into an insoluble solid product covering the surface of the electrode. In the case of graphite anode, this protective layer deactivates the catalytic activity of graphite and prevent its exfoliation. Vinyl carbonates are great examples of this additive type.
- Reaction-type additives. This type of additives is not directly electrochemically reduced during the SEI formation process. However, those additives are able to either scavenge formed radical anions, or combine with the final products form more stable SEI compounds. One can find dioxide carbon precursors in this class of additives.

- SEI morphology modifiers. As previously mentioned, the stability of SEI layer is affected by the content of inorganic compounds. In a classic LiPF_6 -carbonate electrolyte, the major inorganic compounds are known to be Li_2CO_3 and LiF . The latter has been identified to be partly responsible of SEI instability. Electrolyte additives such as boron compounds were therefore developed as they are extremely efficient to dissolve lithium fluorides.

Overcharge inhibitors

Overcharge inhibitors are added to ensure safety of battery operation. Overcharging the battery results in chemical and electrochemical cathode degradation reactions but also in elevation of the temperature inside the battery. To circumvent this problem, redox-shuttle additives are added to electrolytes. These chemicals exhibit slightly higher redox potentials than the normal cut-off voltage of battery. When the cell exceeds its cut-off voltage, redox-shuttle additives are oxidized at the positive electrode to prevent overcharge. They are later transferred at the anode and reduced during the discharge process.

Ionic conductivity enhancers

As previously mentioned, the ionic conductivity of electrolytes deeply depend on the dissociation of lithium salts in the organic solvent. To promote this dissolution, ionic solvation enhancers are added to liquid electrolytes. Crown ethers were reported to be effective additives by isolating lithium ions from their anion counterpart. Nevertheless, this lithium complexation can impede battery performance by slowing down lithium ion diffusion.

Flame retardants

Safety concern has been a major priority in lithium ion battery development. To date, the flammability of the organic solvents in liquid electrolytes is still a major problem in lithium ion battery technology. Therefore, many researches have been focused on the development of fire-retardant additives to decrease the flammability of the liquid elec-

trolytes.

Besides these main electrolyte additives, one can also cite: cathode protection agent, salt stabilizers, corrosion inhibitors, wetting agents or viscosity modifiers. The design of performing electrolyte therefore relies on complex formulation and requires great attention.

2.6.2 Ionic liquids

Ionic liquids refer to salts in the liquid state. To be considered as electrolyte for lithium ion batteries, these salts have to be liquid in the temperature range of battery operation and to dissolve sufficient amounts of lithium salts. The unlimited combinations of cation/anion forming ionic liquids offer a broad library of chemicals. That allows to finely tune their physico-chemical properties as electrolyte candidates.^[228–231] Compared to liquid electrolytes, ionic liquids are more electrochemically stable and thermally resistant as well as less flammable. For these reasons, they are envisioned to replace liquid electrolytes.^[232] However, their performances in lithium ion batteries and their production cost is prohibitive for the development of commercial devices to date.^[233,234]

2.6.3 Solid polymer electrolytes

Solid polymer electrolytes (SPEs) can be viewed as a special variation of a solution-type electrolyte in which lithium salts are dissolved in polar macromolecules. Since Wright discovered in 1975 that ions can be transported within certain polymers,^[235] they became potential candidates for various applications, in particular lithium ion batteries electrolytes.^[236] The use of SPEs leads to solid-state batteries which have several added advantages over traditional liquid batteries:^[23,237]

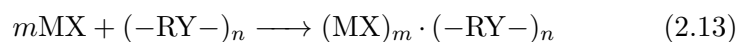
1. They produce higher energy density batteries.
2. Safety is enhanced as no leakage can occur.
3. SPEs do not release gases at high temperature and are not flammable.

4. No separator is required in all solid-state configuration.
5. Batteries can be manufactured in various shapes and designs including flexible or ultrathin batteries.

Such as for liquid electrolytes, in SPEs, the polymer should be able to dissolve sufficient amount of lithium salts to exhibit appropriate ionic conduction. Therefore, only polymers including polar elements such as oxygen, nitrogen and sulfur have been investigated.^[238] In addition, to exhibit appropriate ionic conductivity, polymers should display the following characteristics:^[23]

1. The polar group must include an electron donating group for cation solvation.
2. The polar group must exhibit ion coordination abilities.
3. Adequate spatial conformation of the chain to allow salt dissociation without steric hindrance.
4. A low glass-transition temperature (T_g) for an important flexibility of polymer chains to promote lithium ion conduction.

The most important characteristics for SPEs is naturally a high ionic conductivity. Ion transport in polymers was therefore heavily studied and documented.^[239–243] Solid polymer electrolytes consist in lithium salts dissolved in a polymer matrix and can be viewed as a solution of complexes of alkali metal salts (MX) with polymer hosts (RY) (Equation (2.13)).



Up to now, the commonly spread theory states that in a polymer matrix, predominating ionic conduction only occurs in amorphous regions.^[244] In this theory, the lithium ions can dissociate from polymers

segments and the polymer chain motion in the free volume space is responsible for the ionic conduction (Figure 2.24 a)). Hence, this mechanism called ion-hopping can only occur if polymer segments are free to undergo fairly large-amplitude excursions. Therefore, below the glass temperature transition (T_g), ionic conductivity drops dramatically as polymers are in a rigid glassy state. In this theory, crystalline regions of polymers are therefore an obstacle to lithium ion conduction.^[245] NMR studies tend to approve this theory and demonstrate that ionic conduction only takes place in the amorphous region of PEO, the crystalline complex only acting as a salt reservoir.^[246]

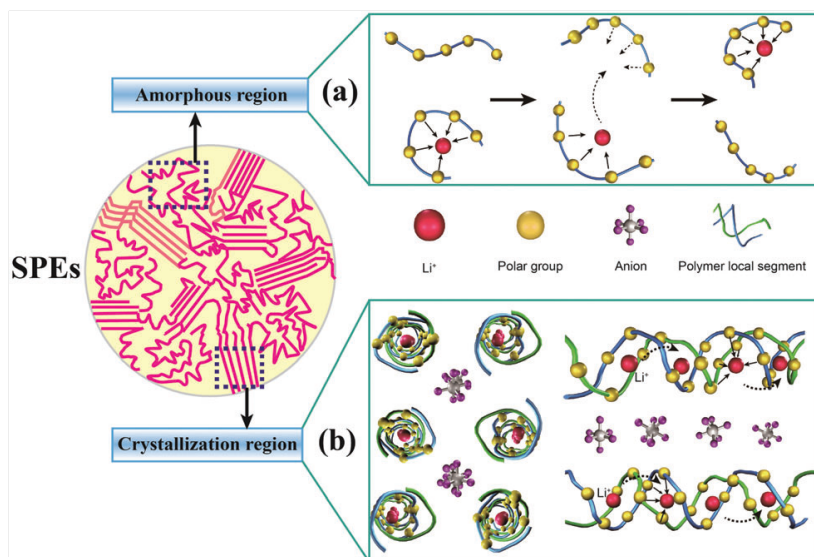


Figure 2.24 – Lithium ion conduction in polymers in a) amorphous region and b) in crystalline region. Reproduced from^[247].

A more recent theory defended by Bruce and co-workers introduces a different conduction mechanism for lithium ion motion in polymers.^[248] Here, crystalline regions of polymers can be viewed as channels for lithium ion conduction (Figure 2.24 b)). In this configuration, the lithium ions reside inside channels formed by interlocked polymer cylinders. The negative anions remain located outside and do not coordinate

lithium ions.^[249] Inside the polymer channels, lithium ions are free to move along the electric field. In addition, this theory demonstrates that ion transport in crystalline polymer electrolytes is dominated by the lithium cations, whereas both ions are generally mobile in the amorphous phase. Nevertheless, it is important to note that this type of conduction was demonstrated only for a specific type of complex with certain discrete compositions. While those theories are still debated,^[250] results tend to prove that ionic conductivity is higher in amorphous polymers than crystalline ones. Therefore, researches in SPEs strive to decrease at best crystallinity degree of polymers used in electrolytes.

Among researches conducted in the 40 past years, poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), polyphosphazene (PPhz) and polysiloxanes were the most studied polymers due to their superior ionic conductivities (Figure 2.25). For its interesting properties and for economic reasons, studies are particularly concentrated on PEO.^[251] Polyethylene oxides and polyethylene glycols have a similar chemical structure but are synthesized via two different ways. Polyethylene oxides are obtained by polymerization of ethylene oxide while polyethylene glycols are obtained by polycondensation of ethylene glycol molecules. Usually, low molecular weight polymers ($< 20000 \text{ g.mol}^{-1}$) are named PEG and high molecular weight ($> 20000 \text{ g.mol}^{-1}$) are named PEO. Nevertheless, generally both names are used interchangeably.

The interesting ionic conductivity displayed by PEO can be explained by its structure. Poly(ethylene oxide) is constituted of repeating $-\text{CH}_2-\text{CH}_2-\text{O}-$ units. Oxygen is a stronger electron donor than sulfur or nitrogen that helps for lithium salt dissolving. Moreover, the ethylene oxide unit (EO) represents the minimum steric requirement with an optimal spacing of the heteroatoms.^[252] In addition, PEO presents a low glass transition temperature (around -60°C), conferring its chains a good flexibility at room temperature. PEO is considered as a semi crystalline polymer with about 60 % of the bulk being crystalline and the reminder

present as an amorphous elastomeric phase at room temperature. The melting point of crystallites is known to be around 60°C . Therefore, the ionic conductivity strongly varies around this temperature. While values around $10^{-8} \text{ S.cm}^{-1}$ are commonly admitted at room temperature, ionic conductivities reach values up to $10^{-4} \text{ S.cm}^{-1}$ for temperatures higher than 65°C .^[253–255]

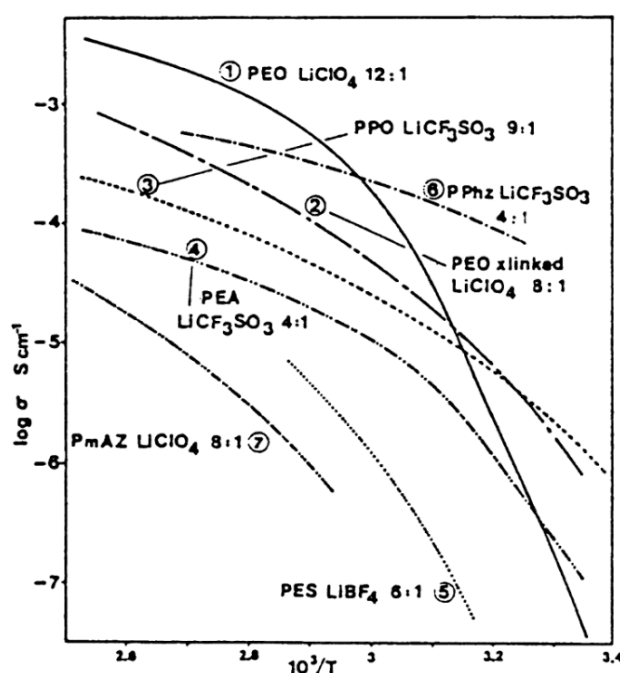


Figure 2.25 – Arrhenius plot of the conductivity of various polymer-salt adducts. (1) PEO; (2) cross-linked PEO; (3) poly(propylene oxide)(PPO); (4) poly(ethylene adipate)(PEA); (5) poly(ethylene succinate)(PES); (6) polyphosphazene(PPhz); (7) poly(N-methylaziridine)(PmAz). Reproduced from^[252].

The lithium ion conductance of electrolyte does not depend solely on ionic conductivity but also on geometry and size of battery since they influence ion pathways. Therefore, it does not exist a minimal ionic conductivity required for electrolytes. Nevertheless, a common value of $10^{-4} \text{ S.cm}^{-1}$ is generally admitted to be the strict minimum to produce

sufficient performing batteries even in the case of thin electrolyte layers. For this reason, the ionic conductivity of pure PEO is insufficient to design performing solid lithium ion batteries. Hence, particular attention is required to decrease its crystalline degree at room temperature. One of the most practical approach to enhance ionic conductivity is the addition of plasticizers such as small organic molecules, polar polymers or nanoparticles (Figure 2.26).^[256–259]

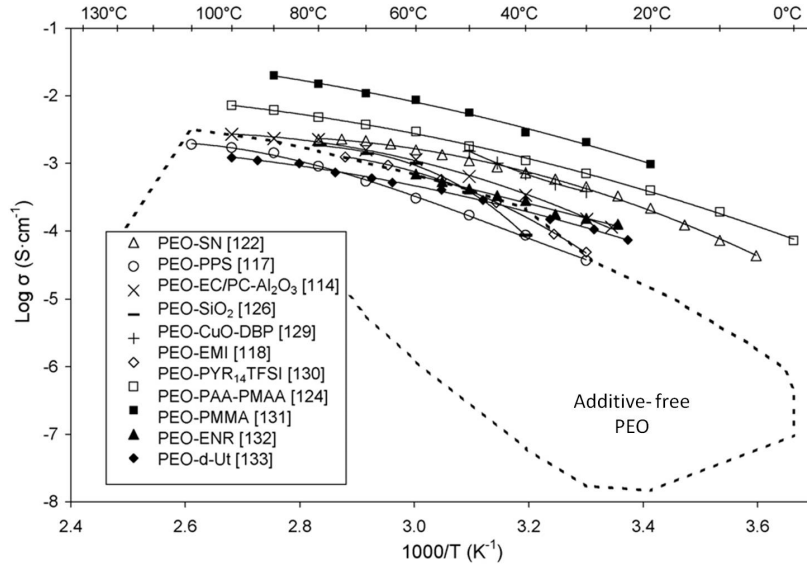


Figure 2.26 – Impact of additives on ionic conductivity in PEO-based solid polymer electrolytes. Reproduced from^[242].

Addition of small organic molecules such as liquid carbonates,^[257] succinonitrile,^[260] phthalates^[261] or citric acid^[262] as plasticizers was reported as an effective way to promote ionic conductivity. These plasticizers decrease crystallinity, and T_g but also promote lithium salt dissociation. Addition of liquid carbonates should be kept to a minimum so that the ion conduction mechanism does not change. In a large ratio, addition of liquid carbonates conducts to the formation of gel polymer electrolytes. Addition of polar polymers such as poly(ethylene glycol)^[263], poly(acrylic acid) (PAA) and poly(methyl methacrylate)

(PMMA)^[262] of low molecular weight was also investigated to enhance ionic conductivity with convincing results. Lastly, the addition of micro or nanoparticles in PEO-based electrolytes was reported as another effective way to promote ionic conductivity.^[256] This class of solid polymer electrolyte is commonly named composite polymer electrolyte (CPE). For the last decade, numerous studies reported that the dispersion of various particles such as SiO₂,^[264–267] TiO₂,^[267] Al₂O₃,^[262,268,269] ZrO₂ particles^[261,270] and molecular sieves^[271] in PEO-based electrolytes enhanced both ionic conductivity or mechanical properties.^[238,272] The characteristics of CPEs obtained by addition of stable ceramic nanoparticles depend on their size as well as their surface chemistry.^[273] Studies report that nano-sized particles that present a high-surface area are the most effective to inhibit crystallinity of PEO chains.^[274–276] It was demonstrated that the surface chemistry of added particles plays a significant role in the lithium ionic conduction.^[277] Polymer-particle interface can provide a preferential pathway for lithium on conduction at the ceramic surface that can enhance ionic conductivity.^[273] Moreover, a modification of the surface chemistry of silica can also improve the mechanical strength of CPEs.^[272,278,279] Reports showed that the use of ceramic nanoparticles as fillers for low and moderate-molecular weight PEO-based electrolytes yields to materials with the mechanical properties of solids, but having the processability of liquids.^[279–281] Lastly, crosslinking of SiO₂-PEO composite polymer electrolyte was demonstrated as a possibility to create dimensionally stable solid electrolytes.^[282]

2.6.4 Gel polymer electrolytes

Gel polymer electrolytes (GPE) are prepared by mixing polymers, organic solvents and lithium ion salts. This produces a gel where the solid polymer matrix is swelled by organic solvents. With the massive presence of liquid electrolyte in the GPE (up to 60 wt. %), the conduction mechanism is here close to the one encountered in classic liquid elec-

trolytes. Therefore, GPEs generally exhibit very high ionic conductivities (up to 10^{-3} S.cm $^{-1}$), close to the ones of pure liquid electrolytes.^[258] Organic solvents used to swell GPE are comparable to the ones described in the previous section. Traditionally, the polymer matrix is constituted by polyacrylonitrile, poly(vinylidene fluoride), poly(methyl methacrylate) or poly(ethylene oxide). While the ion conduction occurs mainly in the liquid, the polymer maintains the mechanical strength of GPE and stores the liquid. As a result of their composition, GPEs can be viewed as the best of both worlds: the polymer matrix provides mechanical resistance to the electrolyte while the organic solvent ensures a high ionic conductivity. Nevertheless, the properties offered by both elements are conflicting and GPEs can not present at the same time very high mechanical properties as well as very high ionic conductivities. Hence, incorporation of inorganic fillers into GPE is generally required to improve mechanical strength as well as transport and electrochemical properties.^[238] For the last decade, GPE have gone through considerable development in composition and performances.^[258,283] They represent undoubtedly an important breakthrough in lithium battery technology and are now referred as Li-po batteries. Nowadays, they are omnipresent and unavoidable in portable electronics. Nevertheless, safety of this technology still present risks as shown by recent Galaxy Note 7 battery issues.¹

2.6.5 Interfacial electrode–electrolyte reactions

Lithium-ion batteries are complex systems and their ageing processes are even more complicated. The decrease of performance originates from various causes and some of them are related to the reactions occurring at the electrode-electrolyte interphases.^[284] During battery operation, a layer presenting the properties of a solid electrolyte is formed at the surface of active materials.^[155] Rate capability, cycle stability, irreversible

¹Swiss credit analysts estimated that Galaxy Note 7 battery issues could cost Samsung a total of \$17 billion.

capacity loss, exfoliation of graphite and safety are therefore highly dependent of the quality of the formed interfaces. It is therefore imperative to have a fundamental understanding of the chemical and electrochemical phenomena at the interface between electrode and electrolyte to prevent capacity or power fading of batteries. As liquid electrolytes serve as a medium for lithium ion shuttling between electrodes, electrochemical reactions within active materials are promoted by an enlarged interface area between active materials and the electrolyte. Nevertheless, this increased surface also promotes electrolyte decomposition. Hence, many scientists deeply investigated and described the complex reactions of electrolytes alteration during battery operation.^[285] Ageing mechanisms occurring at the anode or the cathode are significantly different. At the negative electrode, electrolyte components undergo a reductive decomposition and form a layer refereed as solid electrolyte interphase (SEI). At the positive electrode, an oxidative decomposition of the electrolyte gives rise to a layer refereed as positive electrode/electrolyte interface (EEI).^[286]

Changes at the negative electrode/electrolyte interface are reported to be a major source for ageing of batteries and were deeply investigated in the last decade.^[155,287–290] Figure 2.27 depicts some of the various changes occuring at the interface between a common graphite electrode and a carbonate-based electrolyte. As it can be seen lot of those side reactions have negative effects such as gas formation, graphite exfoliation, lithium plating, precipitation of formed species. Obviously, these side-reactions represent a major cause of lithium battery decay. Nevertheless, if properly controlled, specific electrolyte decomposition reactions lead to the formation of a SEI, a stable passivating film on the surface of the active material (Figure 2.27 b)).

Lithium ion battery anodes generally operate at voltages outside of the electrochemical stability window of electrolyte components.^[290] The onset potential of SEI formation is not a fixed value and depends on

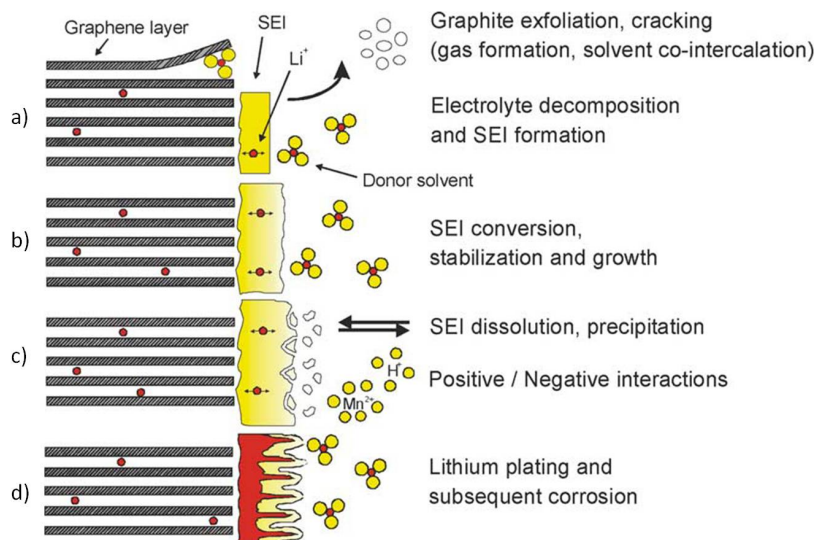


Figure 2.27 – Changes at the graphite/electrolyte interface.
Reproduced from^[291].

the nature of various factors such as the electrolyte and the nature of electrodes. Different values ranging from 0.8 V to 2 V can be found in literature^[292–294] but 0.8 V^[156,157] is the most widely adopted practical value for carbonates-based electrolytes with graphite anodes. At this voltages, liquid electrolytes are reduced on the surface of the electrode to form a vast library of negative or radical negative species.^[289] These decomposition products subsequently form solid lithiated species such as $(\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li})_2$, $\text{LiO}(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_2\text{OCO}_2\text{Li}$, $\text{Li}(\text{CH}_2)_2\text{OCO}_2\text{Li}$ and Li_2CO_3 . This electrolyte decomposition is therefore accompanied by irreversible consumption of lithium ions, decaying coulombic efficiency and battery performances.^[291] The solid electrolyte interphase formed by decomposition products acts similarly as a solid electrolyte layer. This SEI is electrically insulating but permeable to lithium ions.^[23] In addition, if properly formed, the porosity of SEI allows lithium ions to pass but no other electrolyte components.^[295] The solid electrolyte interphase therefore acts as a reasonably protective film on active material.

Its formation occurs in the first cycles of battery life and prevent further electrolyte degradation reactions.

On the other hand, oxidative decomposition reactions can occur at the positive electrode. This decomposition of carbonate solvents begins at a relatively high potential (generally above 4.5 V versus Li/Li⁺).^[216] For this reason, electrolyte degradation at the positive electrode is limited as the voltage of lithium ion battery cathode generally does not exceed 4.2 V. Therefore, few studies have reported surface electrode electrolyte interface layer formation on positive electrode materials.^[288,296–298] The composition of the positive EEI layer generally consists of similar solvent and salt decomposition products to those found on negative electrodes although their production mechanism is different. The oxidative decomposition at the positive electrode results mostly from chemical nucleophilic reactions driven by the lithium rich surface chemistry of the electrode material.^[286]

2.7 Battery Assembly

2.7.1 Conventional battery assembly

The commercial lithium-ion battery assembly itself is not very complex and has not changed significantly over past decades. The process is depicted in Figure 2.28. A slurry composed of the active material, the polymer binder, the conducting agents, solvents and additives is made up. The composition of the slurry has to be precisely controlled to produce electrodes with adequate properties.^[299] The slurry is later coated on current collectors for each electrode. The thickness of the coating is carefully defined by the manufacturer to maximise performances of the battery. Thicker electrodes increase electron paths to current collector and thus decrease their conductivity.^[300] Too thin electrodes decrease the capacity as current collector-electrode ratio increases. Typically, an electrode with a 50 μm thickness is coated on a 10 μm current col-

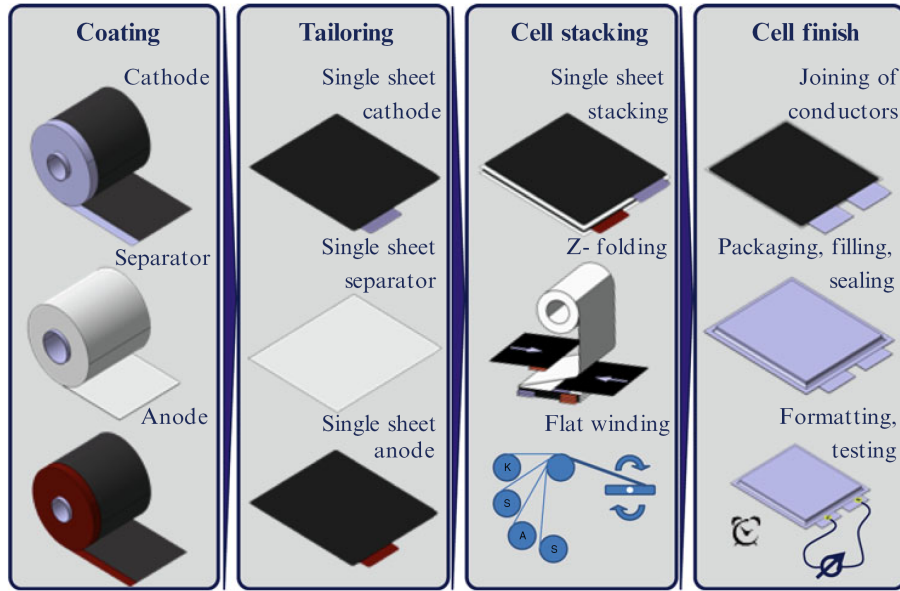


Figure 2.28 – Value chain for the conventional production of Lithium-ion cells. Reproduced from^[301].

lector (Figure 2.29).^[12,19] Cells are subsequently assembled by stacking anode-separator-cathode units. This process can be carried out through different approaches: Z-folding, flat winding or cylindrical rolling (Figure 2.28). This choice defines the shape and capacity of produced cells. Lastly, conductors are connected to current collectors, batteries are filled with liquid electrolytes and carefully sealed. This industrial process is now in its mature phase and it is possible to produce performing batteries in a large scale at a reasonable cost (total production cost has been divided by ten in the last decade to reach about 200 U.S. \$/kWh in 2015). Nevertheless, safety operation as well as performances still need to be improved to be considered in sensitive applications or electric vehicles. Moreover, their rigid enclosure in prismatic or cylindrical cells holds them back for further integration.

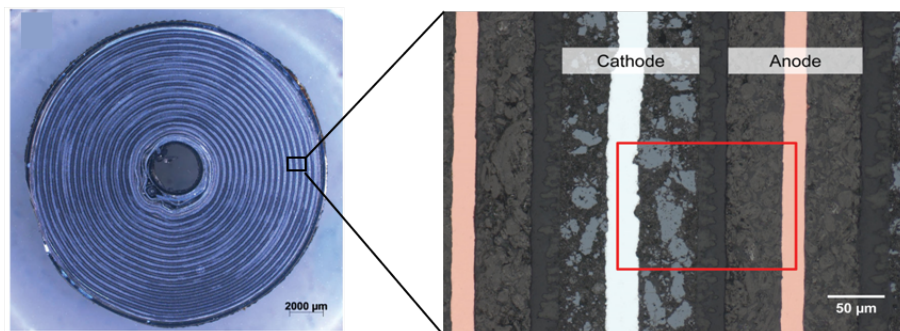


Figure 2.29 – Cross-section of a Li-ion 18650 cell: low magnification and high magnification highlighting the compact and dense structure with well-defined interfaces. The red square contains a complete unit cell of the battery. Adapted from^[12,302].

2.7.2 Flexible lithium batteries

In this ever-changing world, novel device forms such as curved cell-phones, flexible electronics or intelligent clothes continuously appear. These equipments require adapted power sources for a seamless integration, leading to the development of new battery configurations. Recently, paintable,^[303] flexible,^[304] stretchable,^[305] transparent,^[306] cable-shaped,^[307] 3D,^[308] ultra-thin^[309,310] or ultra-thick^[311] battery configurations were reported. The broad spectrum of possible unconventional configurations was already deeply and exhaustively detailed in literature.^[12,308] Therefore, this section only focuses on flexible configurations.

The recent development of flexible^[207] and wearable^[312,313] electronics attracted a lot of interest in the last years. While flexible electronics or display screens are now a reality, mass production of flexible power sources have not been implemented yet.¹ Nevertheless, in the last years, the scientific community have paved the way for such energy sources design.^[304,314–317] Flexible batteries are often associated with current

¹Samsung and Apple recently patented flexible configurations but they are based on connected rigid multi-case frame battery.

collector-free batteries. While the presence of copper or aluminum bulk metal foils enhance charges collection and mechanical stability of electrodes, their presence complicates the design of flexible configurations. Indeed, metal foils can suffer irreversible damages in stretchable or flexible configurations and there exists a strong risk of electrode delamination due to mechanical stress in such configurations.^[304] However, it is important to point out that the unit cell described in Figure 2.29 is flexible as it can be folded or winded during battery assembly.^[318] The stacking of a large number of units to provide more energy and the casing confers the battery its rigidity. To design flexible batteries, the electrodes as well as the separator have to be flexible. In addition, these three components have to sustain mechanical constraints without delamination of battery layers during operation.^[319–321] Several approaches are available to design flexible batteries. Today, flexible batteries are still in the development phase and most components are tested individually and assembled in liquid configuration. The design of flexible batteries with liquid electrolyte can be considered from two angles. A first possibility is to create separately the electrodes and the separator during a first step. In a second step, the different components are assembled to create the battery. A second possibility is the creation of the battery in one step during which the different constituents of the battery (electrodes and separator) are deposited successively layer by layer. Batteries produced according to these two methods are later filled with liquid electrolyte and sealed. Using liquid electrolyte guarantees a homogeneous distribution of the electrolyte within the battery. Presence of liquid electrolyte is a big safety concern because a large extent of mechanical deformation that is commonly exerted on flexible batteries. Producing a solid, flexible battery is a real challenge that adds considerable difficulty. Indeed, it is very difficult to add a solid electrolyte once the battery is assembled. The most feasible way is the use of polymer electrolyte. In this case it is possible to consider the addition of a polymer electrolyte precursor in its

liquid form and then proceed its polymerization in the assembled battery. However, this solution hardly guarantees electrolyte homogeneity and conductivity. The second possibility to create a solid flexible battery is the direct incorporation of the electrolyte inside electrodes and separator during the design of the different elements. The continuity of the properties of the electrolyte between the different layers must then be assured.

Regarding the choice of materials, a wide panel is also open to scientists. It is possible to move towards traditional compositions of materials (active materials, conductive additives and binders). Besides, it is also possible to focus on nanotechnology-based materials that combine several interesting properties. Since it is impossible to cover the whole range of flexible configurations developed by scientists, we will focus on paper-like configurations involving cellulose or carbon nanotubes. We will describe here the achievements of flexible batteries obtained by combining different approaches and choice of materials.

2.7.2.1 Cellulose-based electrodes and separators

One first possible approach to design flexible configurations is based on paper-electronics.^[322–326] Cellulose is a promising base material for the realization of flexible battery component. In addition to its interesting physical and chemical properties, this eco-friendly material is available worldwide and at a reasonable price.^[325] As raw material, it was demonstrated that commercial printing paper can be used to produce separators as well as scaffold for electrodes. Printing paper does not require heavy pre-treatment to be used in battery industry.^[327] For example, Yao *et al.* soaked commercial paper in 0.3 M HCl for ten minutes before washing and drying. This simple treatment is enough to remove mineral fillers and fluorescent whitening agents and result in a more porous open structure which is beneficial for paper-supported electrodes.^[328]

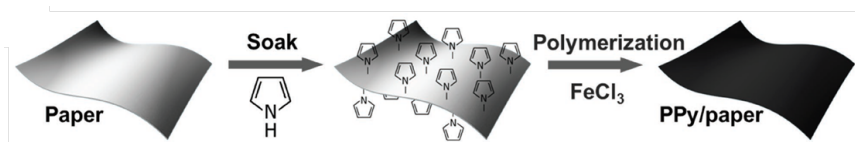


Figure 2.30 – Polypyrrole(PPy)-coated paper electrode fabricated by soaking and polymerization method. Adapted from^[329].

The creation of paper-supported electrodes can be achieved in different ways. As cellulose-based papers are insulating, it is mandatory to deposit a conductive layer on the surface. As example, a layer of graphite from pencil as conductive material can be deposited on the paper surface.^[330] Secondly, the active material is deposited on the paper-supported electrode. This step can be done by polymerizing the precursor of an active material. Using this method, Yuan *et al.* created graphite/poly(pyrrole) hybrid electrodes on paper for flexible solid-state supercapacitors (Figure 2.30).^[329] The active material can also be deposited by electrodeposition. Yao *et al.* demonstrated the creation of graphite/poly(aniline) paper electrodes by electrodeposition (Figure 2.31).^[328]

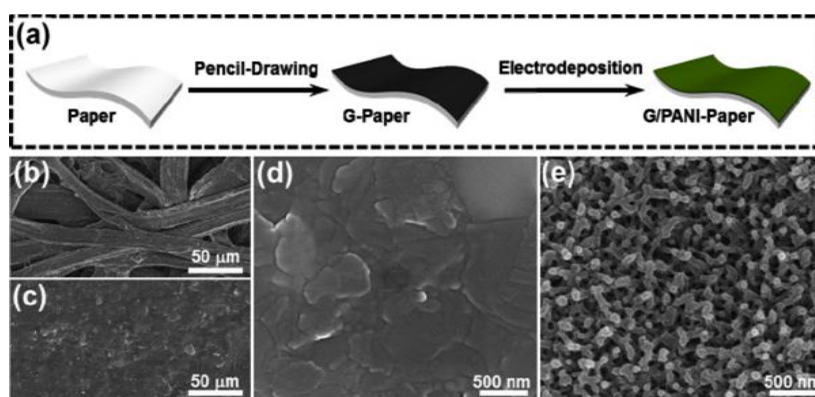


Figure 2.31 – (a) Schematic diagram of the fabrication of G/PANI-Paper. Scanning electron microscopy images of (b) blank A4 printing paper, (c,d) graphite paper, (e) G/Poly(aniline) paper. Adapted from^[328].

The active material can also be deposited on the paper electrode by a simple filtration method.^[327] It was reported that carbonaceous active materials such as graphene,^[331] graphite^[332] and carbon nanotubes^[327] were successfully used as active materials to create electrodes using this method (Figure 2.32).

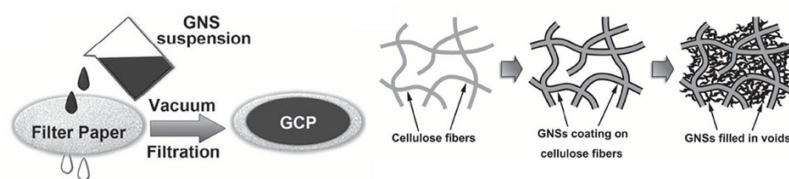


Figure 2.32 – Graphene-cellulose paper electrode fabricated by vacuum filtration method. Adapted from^[324].

Active materials as well as conductive layer can also be directly synthesized on the paper scaffold. Lately, Chen *et al.* reported the successful synthesis of MnO_2 nanosheets supported on cellulose based carbon papers. Cellulose filters were first carbonized in a tube furnace to provide conductive paper. In a second step, the carbonized papers were immersed in KMnO_4 . MnO_2 nanosheets are formed due to the reaction between MnO_4^- and carbon. The prepared electrodes presented high and constant capacitances over more than 6 000 cycles.^[333]

Electroactive materials and conductive agents can be incorporated directly into the electrodes directly during the creation of the cellulose fiber network.^[334] Jabbour *et al.* prepared paper-cathodes by filtration of an aqueous slurry containing cellulose fibers, carbon black particles and LiFePO_4 particles on a Buchner funnel. They demonstrated that such electrodes could sustain 200 cycles at $C/2$ rates delivery a capacity close to 100 mAh.g^{-1} .^[335] In the same way, they produced negative paper-supported electrode by filtering cellulose fibers and graphite powder. This time, the performance is more modest with load speeds not exceeding $1C$.^[332] With a similar method, Kang *et al.* produced performing electrodes by filtration of a mix of graphite nanosheet and

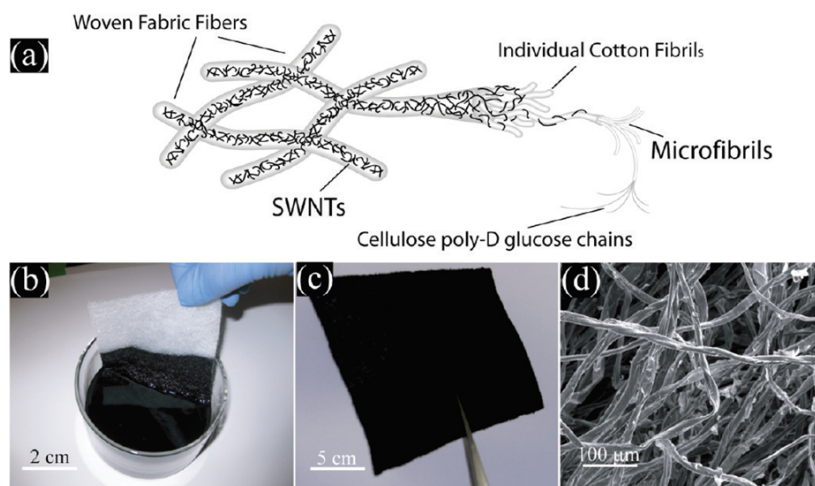


Figure 2.33 – Textile-based electrodes : (a) Schematic of SWNTs wrapping around cellulose fibers to form a 3D porous structure. (b) Conductive textiles are fabricated by dipping textile into an aqueous SWNT ink followed (c) textile conductor based on a fabric sheet with 100 % cotton (d) The schematic drawing of the stretchable supercapacitor with SWNT/fabric as electrodes and with stretchable fabric as the separator. Adapted from^[305].

cellulose fibers^[336]

Spray coating methods were also used to produce paper supported electrodes.^[337] Gerbadli *et al.* produced electrodes using air-spray coating.^[338] A cathodic aqueous slurry was prepared with LiFePO_4 as active material, carbon black as conductive additive and cellulose microfibril as well as CMC as binder. A commercial spray was used to finally deposit the slurry on a paper. Using the same method, they also produced negative electrodes based on carbon and graphite.^[338]

Textiles-based electrodes were also reported.^[305] Porous textile made of cotton fibers was dipped in a SWCNTs ink to produce highly conductive textiles with conductivity of 125 S.cm^{-1} (Figure 2.33). Such conductive textiles show great flexibility and stretchability. In addition it is possible to create supercapacitor from these electrodes.^[305]

Separators can be produced by the same filtration method inspired

from paper industry. With little adaptation such as inclusion of nanoparticles, modification of cellulose fiber surface or choice of length of fiber, it is easy to produce a broad range of specific cellulose fabrics with different properties.^[327,339,340] Depending on the conditions of its design, porosity and resistance can be tailored to the final application.^[341] A mix of cellulose nanofibers and nanoparticles is dispersed in an aqueous solution. The dispersion is later filtered to produce paper separator. The produced fabrics present similar electrochemical performances to those of traditional PE or PP-based separators.

2.7.2.2 Carbon nanotube-based electrodes

Flexible cellulose substrates are a very promising material and can be used as a scaffold to support conductive active materials to achieve high performance in many flexible energy storage systems. However, the addition of inactive cellulose paper substrate can considerably lower the energy density and power density of lithium ion batteries. Therefore, it is interesting to replace cellulose fibers with active charge storage materials.^[312] This can substantially enhance the electrical conductivity of electrode or the device specific capacity as well as energy density and power density.^[324] To replace the cellulose fibers, different materials have been tested: graphene, carbon nanotubes, carbon-fiber and carbon-free materials. To build flexible electronics, the use of carbon nanotubes is widely reported.^[342,343] Like cellulose nanofibers, carbon nanotubes are one-dimensional materials. This property allows them to be considered as a binder in a composite material. However, they have the great advantage to exhibit a very high electrical conductivity unlike cellulose nanofibers. The active materials can be integrated inside the scaffold by different methods such as co-deposition,^[344] or filtration.^[345–347] These methods produce highly conductive flexible electrodes embedding the electroactive materials (Figure 2.34).

As example, Du *et al.* created porous flexible electrode by filtering

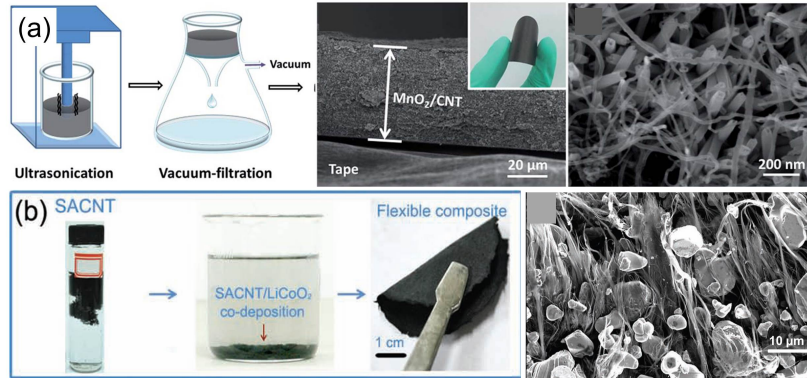


Figure 2.34 – Electrodes based on CNT conductive scaffolds : a) electrodes obtained by filtration and b) electrodes obtained by co-deposition process. Adapted from^[344,347].

a MnO_2 - CNT dispersion.^[347] They have demonstrated that their electrodes possess very good electrochemical properties by testing them in flexible solid-state supercapacitor configuration. Capacitance retention was almost constant over 6000 cycles and coulombic efficiency was close to 100 %.^[347]

Luo *et al.* produced composite electrodes made of LiCoO_2 and super aligned carbon nanotubes (SACNT) via a co-deposition method (Figure 2.34 (b)).^[344] The LiCoO_2 -SACNT composite displayed a high conductivity of $3.8 \times 10^2 \text{ S.m}^{-1}$ with only 1 wt. % of SACNTs, which is attributed to the great intrinsic conductivity ($3 \times 10^4 \text{ S.m}^{-1}$ for the pure SACNT film. As the amount of SACNTs increased to 5 wt. %, the conductivity of the composite rose to $2 \times 10^3 \text{ S.m}^{-1}$ which underlines the impact of carbon nanotube content. The LiCoO_2 -5 wt. % SACNT composite fabric presented the best cycling stability (151.4 mAh.g^{-1} at C/10 with capacity retention of 98.4 % over 50 cycles (Figure 2.35). The rate capability was evaluated at 137.4 mAh.g^{-1} at 2 C, corresponding to capacity retention of 90.8 % compared to C/10 rate.

Electrical properties of carbon nanotubes make them a first choice materials as flexible conductive support for electroactive materials.^[176]

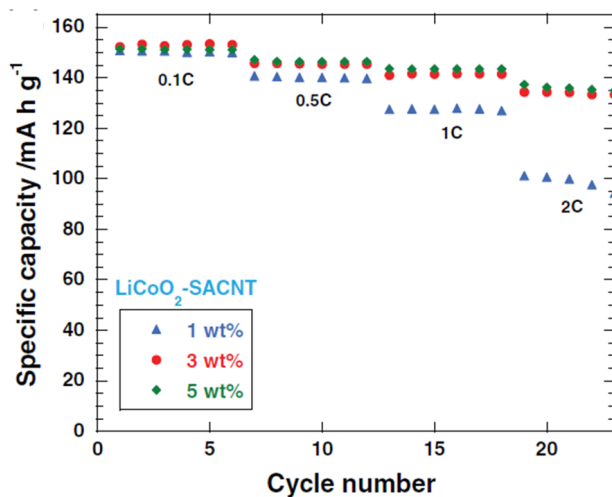


Figure 2.35 – Rate performance of the binder-free LiCoO_2 - SACNT composite cathodes produced by co-depositon process. Reproduced from^[344].

Another approach is therefore the direct functionalization of CNT with active materials. Silicon,^[348] FePO_4 ,^[349] SnO_2 ,^[350] TiO_2 ^[351] or organic polymer such as poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA)^[346,352] were already successfully deposited on the surface of CNTs to provide performing core-shell structure materials (Figure 2.36). These hybrid materials can subsequently be assembled through a filtration process to form electrodes without the addition of binder or conducting agents.

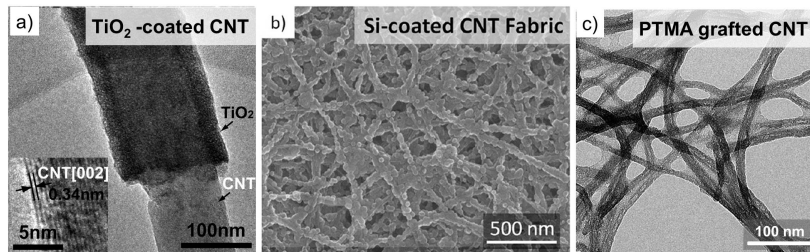


Figure 2.36 – Functionalized carbon nanotubes as composite materials for electrodes: a) TEM image of TiO_2 -coated CNT; SEM image of Si-coated CNT fabric; and c) TEM image of PTMA-functionalized CNTs. Reproduced from^[348,351,352].

2.7.3 Flexible battery assembly

As explained above, the creation of a complete battery can be achieved in one step, or by assembling the performed components.

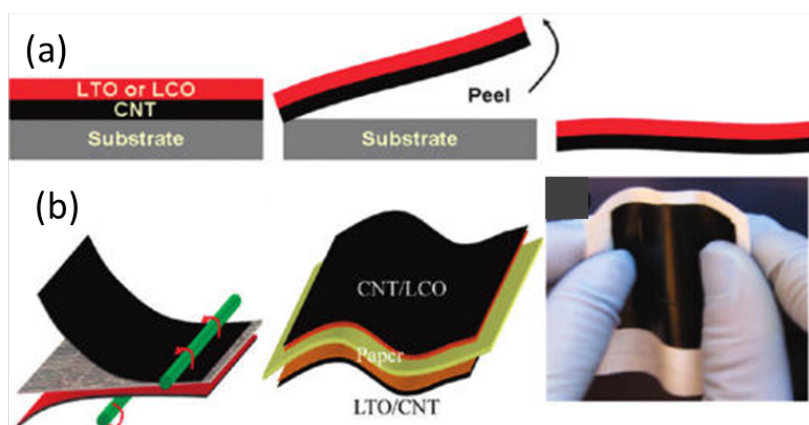


Figure 2.37 – (a) Schematic of fabrication process for free-standing LCO/CNT or LTO/CNT double layer thin films by doctor-blade coating. CNT can be easily peeled off due to the poor adhesion of CNTs to the substrate, (b) schematic of the lamination process: the freestanding film is laminated on paper with a rod and a thin layer of wet PVDF on paper. Picture of the Li-ion paper battery before encapsulation. Adapted from^[353].

In the first case, the different parts of the batteries are created separately and can be assembled in a rolling process. Cui and coworkers have produced a complete battery by this method (Figure 2.37).^[353] At first, they produced LTO-CNT and LCO-CNT electrodes by doctor blade method. The electrodes were then laminated to a paper sheet as a separator. A liquid electrolyte was then added before sealing the battery. The laminated Li-ion paper battery sustained 20 cycles at C/10 rate with no significant failure. After first cycle, coulombic efficiencies were evaluated between 94 % and 97 %.

To produce a solid state battery in a single step, Liu and coworkers have used successive doctor blade steps.^[354] The cathode was composed

of LiFePO_4 as active materials, nanocarbon as conductive agent and a PEO-lithium salt mixture as the electrolyte. The next electrolyte and separator layer was composed of the same PEO-lithium salt mixture. The last anode layer was of a composition similar to that of the anode with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the active material. Despite limited electrochemical performances, they proved that the concept worked.

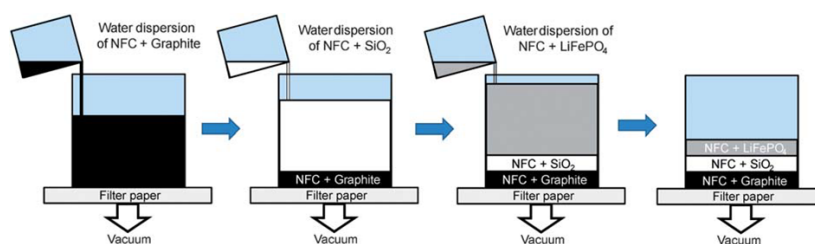


Figure 2.38 – Illustration of the sequential filtration steps during the production of a paper battery cell. Reproduced from^[341].

Last, different groups proved that successive filtrations of suspensions can allow the design of full-batteries in a single step.^[335,341] As example, Liejonmarck and co-workers made a full cell through a paper-making process by sequential filtration of water dispersions containing the battery components (Figure 2.38). Anodic layer is composed of cellulose nanofibers and graphite, separator is composed of cellulose nanofibers and silica nanoparticles and cathodic layer is composed of cellulose nanofibers and LiFePO_4 particles. A typical liquid electrolyte was used to fill battery. Under various current densities, the recorded cycling performances were promising with reversible capacities of 146 mAh.g^{-1} LiFePO_4 at C/10 rate and 101 mAh.g^{-1} LiFePO_4 at 1 C rate (Figure 2.39). Under constant density corresponding to C/2 rate, discharge capacities decreased fastly during the first 150 cycles to reach 60 mAh.g^{-1} LiFePO_4 .

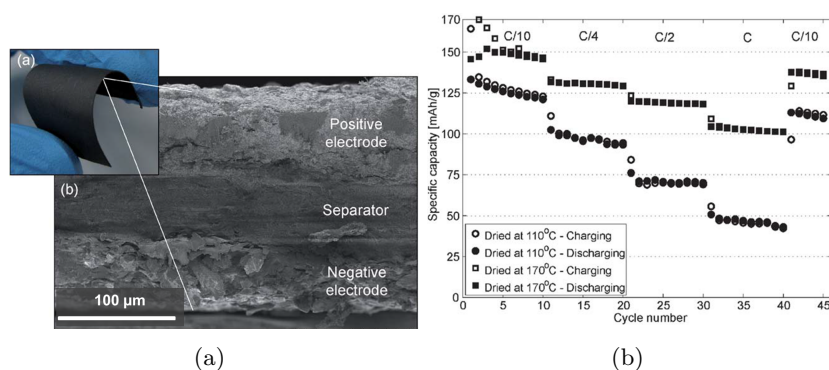


Figure 2.39 – Full cell produced by successive filtration steps: (a) Photograph and SEM image illustrating the flexibility of the paper battery. (b) Electrochemical results for paper battery cells. Adapted from^[341].

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CHAPTER 3

Current collectors and electrodes design

Abstract

In this chapter, the process to create thin flexible electrodes is described. Both anodes and cathodes were obtained via filtration process. Materials and compositions were carefully chosen to optimize performances and lifespan of electrodes. To improve rate capabilities, active materials particles were synthesized in an attempt to decrease their diameter and thus diffusion paths. Lastly, carbon coating was envisioned to increase electrical conductivity of the particles and to prevent overvoltage leading to degradation.

3.1 Current collectors

3.1.1 Carbon nanotubes buckypapers

Manufacturing processes for lithium-ion battery production have changed little for the past 20 years and metallic current collectors still represent 10 % of the total weight of the battery in most of the cases. While the number of scientific publications on lithium batteries is constantly growing, current collectors do not attract lot of attention. A flexible, lightweight and highly electron conductive current collector is nevertheless a key element to enable fabrication of high performance flexible lithium-ion batteries. Here, we describe the building up and characterization of conductive MWCNTs buckypapers via filtration process. Typically, 10 mg of MWCNTs were dispersed in 250 ml butanol and vacuum filtered on 0.22 μm PVdF filters (9.6 cm^2). This consistently leads to the production of 10-15 μm thick flexible buckypapers. This manufacturing process enabled us to create flexible conductive current collectors or conductive scaffolds for electrodes (Figure 3.1).

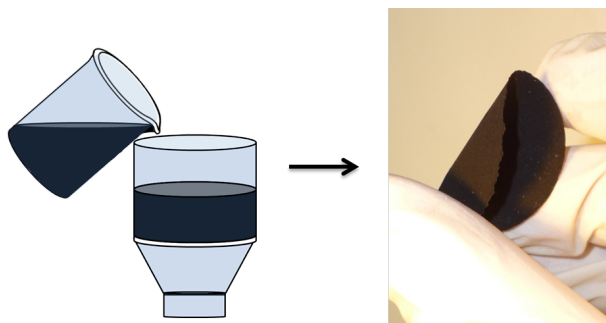


Figure 3.1 – MWCNTs buckypaper fabrication by filtration of a 10 mg MWCNT dispersion in butanol on 0.22 μm PVdF filter. This method repetitively produced 10-15 μm thick MWCNTs buckypapers.

Figure 3.2 presents SEM images of the surface of MWCNTs at different magnifications. With an average length over 1.5 μm , entanglement of CNTs confers cohesion to fabrics. In addition, images show the very

high porosity of fabrics due to random organization of tubes. The porosity of MWCNTs buckypapers prepared by the same filtration method was estimated between 87 % and 91 % by several groups by helio pycnometry or Hg porosimetry.^[1] These images (Figure 3.2) also reveal the absence of amorphous carbon as only one dimension objects are visible. This confirms a CNT loading close to 100 %. Energy dispersive X-ray spectroscopy (EDX) was performed on MWCNTs to assess the purity of CNTs. Analyses revealed the presence of 1.20 at. % of aluminum and some iron traces in MWCNTs. The presence of these elements is attributed to iron supported on aluminum oxide, a common catalyst for the chemical vapour deposition process for CNT synthesis. These two metals were eliminated by concentrated nitric acid washing. The success of this purification step was confirmed by EDX analysis which revealed the quasi absence of metal traces (only 0.02 wt. % of aluminum remaining). Nevertheless, this process is time consuming and takes us away from a green process to create lithium-ion batteries. Moreover this procedure can also create oxidized defects in MWCNTs deteriorating their electrical properties. This purification procedure was therefore abandoned as the presence of these transition metal traces does not interfere in lithium-ion battery as it will be confirmed by electrochemical analysis.

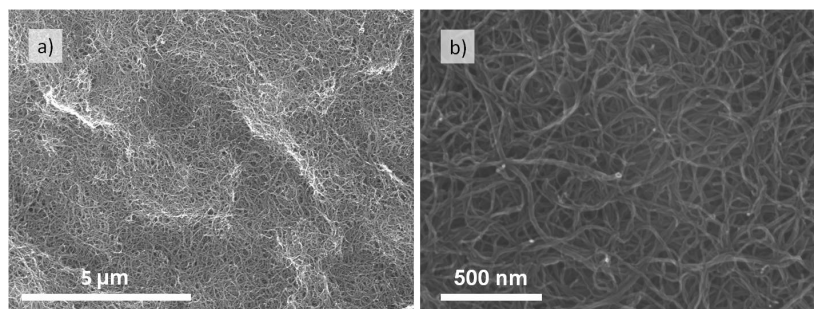


Figure 3.2 – SEM images of a MWCNTs current collector surface created by filtration process at different magnifications: a) 10,000 x, b) 60,000 x.

Electrochemical analysis of MWCNTs buckypapers were performed in Swagelock cell. This set-up is described in the experimental part of this chapter and in Figure 3.3. In this device, the two electrodes are placed on both sides of the insulating separator. In half-cell configuration, one of the electrode is replaced by lithium metal as reference electrode. Original Swagelock cells were modified by the addition of a spring to maintain the elements. On Cyclic voltammetry was operated on pristine MWCNTs fabrics at 1 mV.s^{-1} to demonstrate their stability at both positive or negative electrodes (Figure 3.4). Two electrochemical phenomena are visible. The reduction peak located in Figure 3.4 a) at 0.3 V during the first cycle can be attributed to two origins. The first one is the insertion of lithium ions in MWCNTs and the partial exfoliation of graphene layers of the tube. This reduction phenomenon was previously described by Zhang and coworkers.^[2] The second origin of this peak is the SEI formation on carbon substrates at potentials close to 0 V vs. Li/Li^+ . Carbonates are reduced on MWCNTs and form a passivating layer on their surface. These two phenomena are only visible during the first cycle.

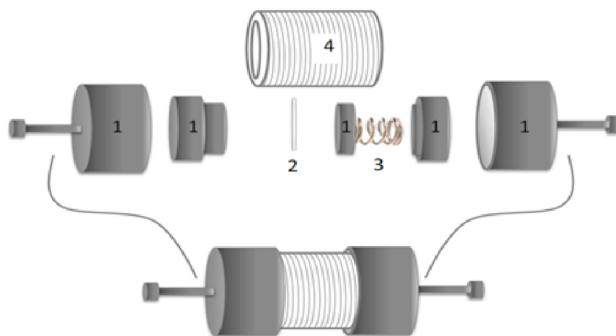
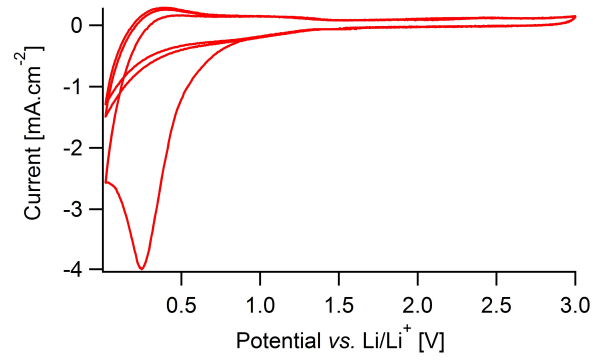


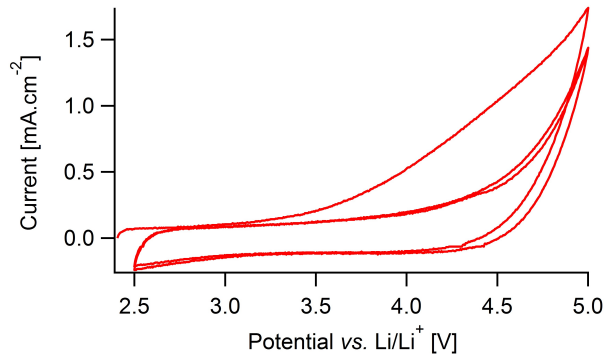
Figure 3.3 – Swagelock cell configuration: 1) stainless steel current collectors, 2) insulating separator, 3) spring and 4) teflon body.

The second peak is observed in Figure 3.4 b) when the potential increases beyond 3.7 V for the first cycle and when the potential increases

beyond 4.5 V for subsequent cycles. This well known phenomenon and is attributed to electrolyte decomposition on cathodic side of lithium-ion batteries. For carbonates electrolytes based on LiPF_6 , carbonates oxidizes into ROH species at voltages superior to 4.2 V during first cycle. This subsequently hydrolyzes the LiPF_6 salt and initiate a thermally activated autocatalytic electrolyte decomposition cycle involving POF_3 as a reactive.^[3,4] During the first cycle, MWCNTs are covered by a surface film from electrolyte decomposition. This passivation film formation seems to inhibit a massive solvent oxidation at potential below 4.5 V. Consequently, the electrolyte may be stable with very high specific surface MWCNTs buckypapers at potentials as high as 4.2 V.^[5,6] Except from these two peaks, no redox phenomena were observed in both voltammograms. This confirms the possibility to use these MWCNTs as current collectors or conductive scaffold in electrodes without supplementary purification.



(a)



(b)

Figure 3.4 – Cyclic voltammograms of MWCNTs buckypaper performed at 1 mV.s^{-1} in half-cell configuration versus lithium metal electrode : a) for negative current collector in the 0 V - 3 V range and b) for positive current collector in the 2.5 V - 5 V range.

To highlight the contribution of MWCNTs to the future electrode capacity, their gravimetric capacity was evaluated (Figure 3.5). MWCNTs buckypaper were evaluated in half cell configuration *versus* lithium. The absence of plateaus in the charge/discharge curves of MWCNTs buckypaper reveals a pure capacitive behaviour of the component. The capacitive response of pure MWCNT buckypapers was evaluated at 31.2 mAh.g^{-1} (in the potential range of $1 - 4.2 \text{ V vs. Li/Li}^+$). Such a small contribution will therefore be neglected in the subsequent electrode capacity evaluation. While every extra capacity is valuable for batteries, electrode contains less than 10 wt. % MWCNTs and current collectors represent less than 5 wt. % of the electrode weight. In this case, the impact of additional capacity is therefore minimal for a global lithium-ion battery. Nevertheless, the capacity of MWCNTs can reach much higher values in specific synthesis conditions (up to 225 mAh.g^{-1}) and find applications in supercapacitor configurations.^[7,8]

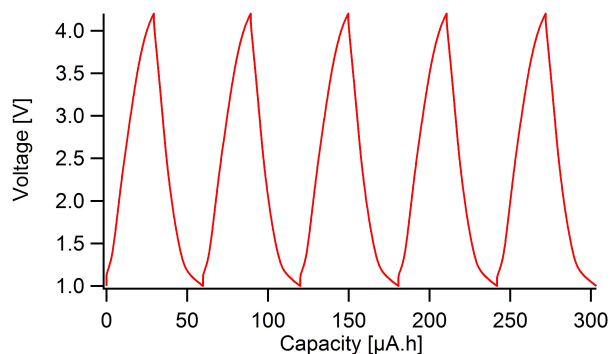


Figure 3.5 – Charge/discharge curves of a 1 mg MWCNTs buckypaper performed in half cell configuration versus lithium metal electrode under 0.1 mA current density.

Finally, the electrical conductivity of MWCNTs buckypaper was evaluated at 67 S.cm^{-1} via 4-point probe measurements performed at different positions on 5 different fabrics. This result is very close to similar fabrics made of oxidized carbon nanotubes which was evaluated at 40 S.cm^{-1} .^[9] By comparison, conductivities of metal foils of usual current collectors present much higher value ($0.58 \cdot 10^6 \text{ S.cm}^{-1}$ for copper and $0.37 \cdot 10^6 \text{ S.cm}^{-1}$ for aluminium). In the Swagelock configuration, this conductivity contrast is not too damaging for performances as the electron paths do not exceed microns. However, on longer distance, the lower electron conductivity can be a serious drawback. For our further electrodes studies, it was considered that conductivity of MWCNTs fabrics as sufficient to serve as conductive support for electrodes. It is also important to note that the 4-point probe method provides an evaluation of the lateral electrical conductivity in the x-y plane of fabrics but no information on the transversal conductivity. As the anisotropy of fabrics was not established, no conclusion on the transversal conductivity can be drawn.

In this first part of the work, flexible multi-walled carbon nanotube fabrics were successfully created via a filtration process. The electrochemical stability at both positive and negative electrodes was established and proved their possible use in lithium-ion batteries operational range. In addition, carbon nanotubes can also present better chemical stability than traditional metal foil current collectors. Indeed, most of usual carbonated electrolytes contains lithium hexafluorophosphate salt that can catalytically decompose into hydrofluoric acid in the presence of water traces. The latter was reported to cause major problems of metal current collector corrosion.^[10] Instead, MWCNTs are very stable in the same conditions. Therefore, MWCNTs fabrics used as current collector can be a great advantage. The use of these MWCNTs networks will now be used as conducting scaffold for electrodes.

3.2 Carbon nanotubes - active materials electrodes

As described previously, scientists have envisioned many different active materials and production methods for electrodes. In this section, we will focus on the most commercially used materials : lithium cobalt oxide (LCO, LiCoO_2) and lithium iron phosphate (LFP, LiFePO_4) for positive electrodes and graphite or lithium titanate (LTO, $\text{Li}_4\text{Ti}_5\text{O}_{12}$) for negative electrodes. Previously prepared MWCNTs buckypapers will be used as conductive scaffolds for electrodes. 11

3.2.1 Lithium cobalt oxide based cathodes

The first investigated active material is the lithium cobalt oxide. Its electrochemical properties and economic considerations make it one of the best compromise based on the criteria mentioned in section 2.2. Therefore, it remains today the most common active material for positive electrodes in commercial lithium ion batteries.^[11] As described previously, electrochemical performances of LCO are hindered by its layered hexagonal structure. It implies strong orientation effects as diffusion can occur in only two directions.^[12,13] Moreover, in their initial state LiCoO_2 crystals are electrical insulators. Although LiCoO_2 particles acquire semiconducting properties through delithiation, their electrical conductivity remains weak. Hence, particular care has to be taken to improve conductivities in LCO-based electrodes. In this study, we replace both polymer binder and conductive additives by multi-walled carbon nanotubes to provide well-performing electrodes. In this case, we take advantage of both MWCNTs morphology, structure and chemical composition. Carbon nanotubes will act within electrodes as a conductive scaffold. Many other advantages of the implemented process for electrode fabrication such as simplicity, cost and environmental considerations will be developed further.

3.2.1.1 Design of MWCNTs-LCO electrodes

The process implemented to create flexible electrodes is a vacuum filtration process. MWCNTs and LiCoO_2 particles are dispersed in variable amounts in 250 ml of butanol using sonic bath for at least 15 minutes. Dispersions are then directly vacuum filtered on PVdF filters. Nice fully flexible self-standing cathodes have been recovered by peeling after drying (Figure 3.6). The electrodes were later dried under vacuum at 60 °C for at least 24 hours.

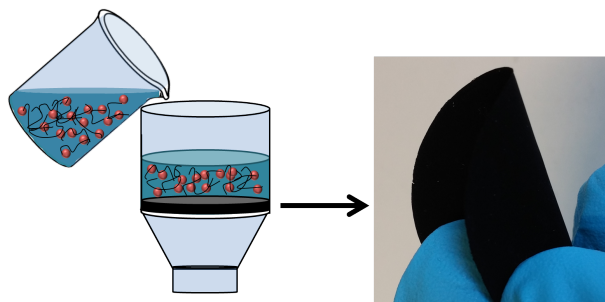


Figure 3.6 – Positive electrode fabrication by filtration of a 5 mg MWCNT and 45 mg LiCoO_2 dispersion on 0.22 μm PVdF millipore filter.

This vacuum filtration process presents several major advantages on other reported methods to create electrodes. As described previously, the conventional manufacturing process of lithium-ion batteries electrodes involves several steps and are costly.^[14] In most of the cases, the active material is dispersed with binder and conductive additives in N-methyl-2-pyrrolidone (NMP) to form a slurry. The used solvent is expensive and the recovery system is a large capital investment.^[15,16] Li *et al.* proved that replacing NMP by distilled water in their electrode production process leads to a decrease of 70 % of the manufacturing price and 12 % of the total cost of battery.^[16] Unfortunately, it is difficult to disperse MWCNTs in pure water. MWCNTs have tendency to assemble in bundles due to the strong van der Waals interaction en-

ergy estimated at $500 \text{ eV} \cdot \mu\text{m}^{-1}$ for tube–tube contact.^[17] Polymer or charged species are therefore often used as surfactants to secure stable MWCNTs dispersions.^[18,19] The introduction of these chemical species requires additional washing steps to ensure that no chemicals interfere in subsequent electrode operation. In our study, the use of butanol as dispersant does not require any surfactant addition or additional washing step.^[20] The drying step is also largely reduced in our filtration process. While it takes 12–24 hours at 120°C in the industrial process to remove NMP,^[15] our electrodes can be successfully dried after 6 hours at 60°C under vacuum. The vacuum filtration process described here only involves butanol as dispersant. Butanol is less expensive and more environmental-friendly than NMP. Moreover, after electrode filtration, butanol is easily recovered and reused several times without any supplementary purification steps. Nevertheless, the filtration process implies the use of large quantity of solvent. The fabrication process of a 1 cm^2 electrode in the common casting process require only few milliliters of NMP for the electrode slurry. In comparison, the fabrication of a cm^2 of electrode via our filtration process require 25ml of butanol. Dispersion of materials and especially MWCNTs always requires large quantities of solvents. As example, commercially stable MWCNTs dispersions generally do not contain more than 5 wt. % of MWCNTs.

While the use of conductive polymer binder was already reported,^[21–23] the vast majority of electrode implies the use of insulating PVdF for cost and practical reasons. Due to their morphology, MWCNTs act naturally as a binder. When added in a sufficient amount, they create a network entangling active matter particles and use of additional polymer binder is therefore unnecessary. The sp^2 -hybridized carbon atoms lattice ensure electrical conductivity along the carbon nanotubes and contact points between them ensure conduction through the whole network.^[24] Multi-walled carbon nanotubes were preferred over single-walled carbon nanotubes (SWCNTs) for many reasons. First of

all, MWCNTs can be produced by chemical vapor deposition in very large quantities at low cost.^[25] Secondly, it was reported that the electrical conductivity of MWCNTs is superior than the conductivity of SWCNTs.^[26] Indeed, depending on the orientation of the graphene sheet wrapping, individual CNT walls can be metallic or semiconducting. MWCNTs comprising many CNT walls, are therefore typically metallic and can carry currents of up to 10^9 A.cm^{-2} .^[27] Lastly, properties of MWCNTs are less susceptible to be altered during ultrasound-assisted dispersion.^[28]

SEM (Figure 3.7a)) proved that we obtained a composite presenting a constant thickness. That allows us to fully control the mass loading of fabrics during production. Electrodes with typical mass loading of 5.25 mg.cm^{-2} and a uniform thickness of $28\text{-}30 \text{ }\mu\text{m}$ were repeatedly produced for the purpose of this study. SEM images also confirmed that each active material particle is tightly entangled by a conductive MWCNTs network, efficiently binding the LiCoO_2 particles (Figure 3.7 b)). This intimate contact ensures a good charge transfer between electroactive LiCoO_2 particles and the MWCNTs network. As previously discussed, this effectively prevents local overvoltage and degradation of the active material.

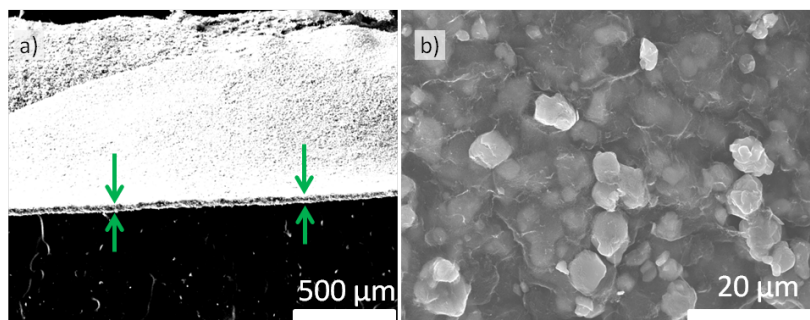


Figure 3.7 – SEM images of LiCoO_2 -MWCNTs fabrics: a) cross-section view of the electrode and b) high magnification view of electrodes surfaces.

To highlight the impact of the MWCNT content on electrode performances, cathodes with variable amounts of MWCNTs were created. Fabrics containing between 5 wt. % and 15 wt. % of carbon nanotubes were prepared. At 5 wt. % of MWCNTs, electrodes still presented a good mechanical integrity and this ratio can be envisioned for electrode production. Electrodes with up to 97.5 wt. % of active material were also successfully produced, however fabrics containing such low amounts of MWCNTs are becoming brittle and difficult to handle in a single electrode configuration. In usual electrodes, the amount of conductive additive is often superior to 5 % of the electrode weight.^[29] This amount is necessary to reach the percolation threshold in fabrics. It was demonstrated that the morphology of conductive additives strongly influences this percolation threshold and hence the electrical conductivity of electrodes.^[30,31] It is therefore not surprising that 1D materials such as carbon nanotubes offer better conductivities than particle-based electrodes.^[32,33] Theoretically, 0.5–1 wt. % CNTs can completely replace the commonly used conductive nanocarbons.^[34,35] Nevertheless, this amount of carbon nanotubes is insufficient to ensure cohesion within the electrode. For this reason, an insulating polymer binder usually required. In this configuration, 2 wt. % of NC7000 MWCNTs¹ are required to reach percolation threshold (electrical conductivity was evaluated at 1 mS.cm^{-1}). In our electrode filtration process, we obtain electrodes with excellent mechanical integrity with no added polymer binder and only 5 wt. % of MWCNTs.

In a first step, our electrodes were evaluated in half-cell configuration versus lithium metal as reference. Cycling between 3.0 V and 4.2 V was carried out at different current densities (from C/20 to 10 C) for 3 consecutive cycles to evaluate gravimetric capacity and the rate performance of the cathodes (Figure 3.8). At this point, it is important to note that electrode masses were evaluated with a balance capable of

¹NC7000 is the MWCNTs grade provided by Nanocyl during this study.

measuring within ± 0.1 mg. As our electrodes and fabrics are in the 1.5 mg - 4.0 mg weight range, the mass error can be significant and close to 6.7 %.

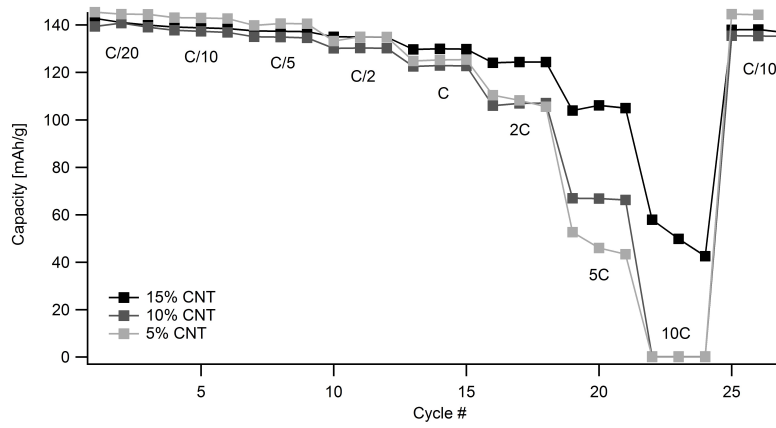


Figure 3.8 – Electrochemical performances of LiCoO₂-MWCNT electrodes containing different amounts of MWCNTs: charge capacity evaluated under various current densities in half cell configuration versus lithium metal electrode.

At low or intermediate current densities (≤ 1 C rate), electrodes present almost the same performances with a gravimetric capacity ranging from 123 mAh.g^{-1} to 145 mAh.g^{-1} . The error in calculated capacities is mainly related to mass measurement and is maximum 2.3 %. The impact of carbon nanotubes is barely noticeable. This result is fully satisfying considering that LiCoO₂ gravimetric practical capacity is 140 mAh.g^{-1} .^[36] At higher rates, the impact of the amount of MWCNTs on the electrochemical performances is noticeable. Cathodes containing 15 wt. % MWCNTs still present an acceptable capacity retention (106 mAh.g^{-1}) at 5 C but electrodes with lower MWCNTs content failed to sustain such rates, delivering less than 50 % of the theoretical capacity. Kanamura *et al.* studied the performances limitations of LiCoO₂ particles. They proved that at low or intermediate rate (< 30 C), the charge transfer control was predominant over solid state diffusion inside

the particles.^[37] The limited performances of our electrodes seem therefore due to a lack of connectivity between conductive scaffold and LCO particle. At 10 C rate, even the performances of 15 wt. % MWCNTs electrodes performances faded. Similar results were reported by Luo *et al.* with LiCoO₂-super-aligned carbon nanotubes electrodes obtained by co-deposition.^[38] At the twenty-fifth cycle, current density was set back at a C/10 rate to verify that electrode did not experience irreversible capacity loss. A gravimetric capacity of 135 to 144 mAh.g⁻¹ was evaluated and confirmed that the active material preserved its initial condition. As a comparison, Zang *et al.* evaluated the performances of a classic electrode made of 90 wt. % LiCoO₂, 5 wt. % carbon black, and 5 wt. % PVdF. The rate capability of their system was evaluated very similar to the performances of LiCoO₂-MWCNTs electrodes. The gravimetric capacity of electrode gradually fades to reach about 40 mAh.g⁻¹ at 8 C rate.^[39]

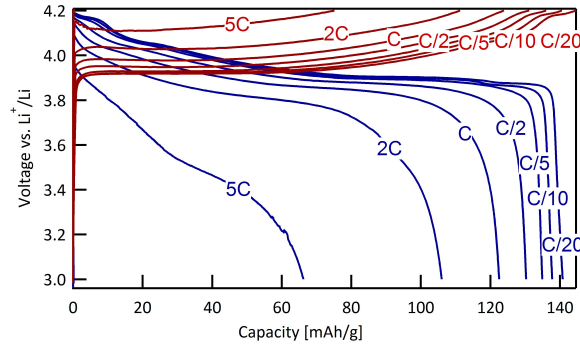


Figure 3.9 – Voltage profile of the first charge/discharge cycle under various current densities for LiCoO₂-MWCNTs electrodes (90:10 wt. %).

The charge/discharge curves of electrodes containing 10 wt. % MWCNTs reveal the loss of plateau at high rates ($> 2C$)(Figure 3.9). On the C/20 and C/10 charge profiles, inflexion of the curve can be identified at 4.18 V. This indicates the beginning of the transition from hexagonal

to monoclinic phase as described in Figure 2.8.^[37,40,41] It is therefore interesting to slightly decrease the cut-off voltage to prevent material degradation. Polarisation is also visible and increase with current densities. At 2C rate, a 0.25 V gap can be identified between charge and discharge curve. Such phenomena in the voltage profiles of electrodes can be partially explained by an insufficient electrical conductivity in the fabrics containing less than 10 wt. % of MWCNTs.

The electrical conductivity of fabrics was evaluated via 4-probe measurements for different electrode compositions (Figure 3.10). The homogeneity of the results was controlled by at least 5 measurements at different positions. Results show that the network of 100% pristine MWCNTs presents an electrical conductivity of 67 S.cm^{-1} , which is in good agreement with literature^[24] Electrical conductivities of cathodes containing between 5 wt.% and 15 wt. % MWCNTs were recorded between 4.4 S.cm^{-1} and 9.6 S.cm^{-1} which is in good accordance with literature.^[42] As before, the lateral component of electrical conductivity is here measured. By comparison, electrical conductivities of electrodes containing spherical nanocarbons are generally comprised in the range between $10^{-3} \text{ S.cm}^{-1}$ and 1 S.cm^{-1} .^[42-45] Electrical conductivities measured were compared to conventional electrodes produced by Doctor Blade deposition. Electrodes composed of LiCoO_2 , PVdF as binder and acetylene black and/or super P carbon in various proportions were produced. The polymer was dissolved in NMP solvent. Conducting agents and active material particles were dispersed homogeneously before casting the slurry on aluminum foil. Electrodes were peeled off the aluminum foil and dried under vacuum. Their conductivity was evaluated by the same 4-probe method as previously. The sample with the composition 80-5-7.5-7.5 (LCO-PVdF-AB-Super P in wt. %) presented the best conductivity evaluated at 0.67 S.cm^{-1} . Given this, we can assume that electrical conductivities of MWCNT-LCO electrodes produced by the filtration process are significantly better. Nevertheless, these fab-

rics failed to sustain high current densities during electrode operation. The variation of electrical conductivities is not important enough to explain the performance gap between fabrics at high current densities. The performance decay at high current density of electrodes containing less than 10 wt.% of MWCNTs was therefore attributed to the bad contact between carbon nanotubes and LCO particles. This contact is of paramount importance for charge collection at the surface of particles. Lastly, one can notice that the performances of our electrodes at 2 C rate can be considered satisfying. Indeed, at current densities higher than C rate, capacity gradually fades even for commercial batteries.^[46,47] Unless otherwise specified, only electrodes containing 10 wt. % of MWCNTs will be produced later in this manuscript.

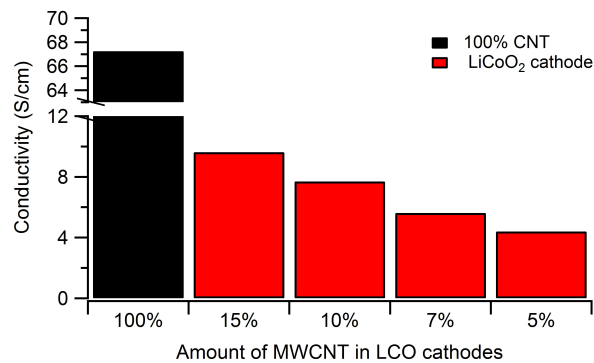


Figure 3.10 – Electrical conductivity of LiCoO₂-MWCNTs composite cathodes with various MWCNT contents (red bars). Pure MWCNTs buckypaper electrical conductivity is also evaluated (black bar). Four-probe measurement was realised under a 20 mV and current.

The lifespan of lithium cobalt oxide fabrics was subsequently evaluated. Cathodes containing 10 wt. % of MWCNTs and 90 wt. % of LCO particles were created. Their cycling stability was studied at C and C/2 rates. Best results over 3 attempts are presented in Figure 3.11. Electrode cycled at C/2 rate presented a 12.5 % capacity loss af-

ter 100 cycles while electrodes cycled at C rate showed a 31 % capacity loss. If a 12.5 % capacity loss is still acceptable after 100 cycles, that experiment proved that simple MWCNTs-LCO based electrodes cannot be envisioned as high performance cathodes due to the important capacity fade at intermediate or high C rates. With the exception from the 8 first cycles, coulombic efficiency readings were consistent and reached values over 99.5 %, indicating effective operation of the battery. A coulombic efficiency close to unity demonstrates limited faradic losses or parasitic side reactions that consume charges. This is of major importance as it hinders lifespan of electrodes. Studies identified time and heat as major factors hindering coulombic efficiency.^[48] In literature, two major reasons were identified for capacity decay of LCO-based electrodes.^[49,50] First of all, reactions between the electrolyte and lithium cobalt oxide can occur. These unwanted side reactions result in a constant growth of the surface layer leading to an increase of charge transfer resistance (R_{CT}). Secondly the degradation of LCO itself due to its structural transformation in the crystal. While LCO particles can tolerate some elastic strain, a major anisotropic strain will imply fractures in the crystal.^[36] The absence of polymer binder involves a risk of particles decohesion and a risk of disconnections between particles and conductive additives during cycling. In addition, during battery life, carbonates from electrolytes decomposes on the surface of MWCNTs, this can deteriorates the contact between carbon nanotubes and the active matter particle. In this case, contacts between MWCNTs and LCO particles can easily be lost. Moreover, MWCNTs present a very high specific surface area ($\sim 250 \text{ m}^2.\text{g}^{-1}$), increasing the risk of electrolyte degradation during battery life.^[51–55]

With the objective of collecting information about passivation layer formation on electrode, electrochemical impedance spectroscopy (EIS) was performed on LCO-MWCNTs half-cells at different times of the cycling stability test. EIS was conducted after cell assembly, after the

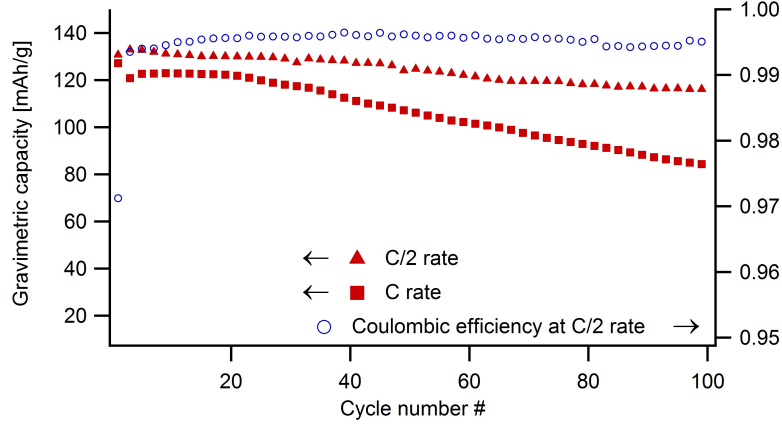


Figure 3.11 – Cycling stability evaluation of LiCoO₂-MWCNT electrodes (90:10 wt. %) under various current densities in half-cell configuration versus lithium metal electrode: evaluation of capacity retention and coulombic efficiency at C rate and C/2 rate over 100 cycles.

first charge and the first discharge and finally after the twentieth and hundredth discharge (Figure 3.12). As previously described, half-cells were cycled in a potential range of 3 to 4.2 V *vs.* Li/Li⁺. The observed pattern are typical for lithium battery half cells. The semi-circle is ascribed to charge transfer resistance R_{CT} , the straight line is attributed to diffusion properties of lithium ions in the solid material also called Warburg impedance Z_W .^[56,57] The impedance after the first and second charges show a small second compressed semi-circle. This second semi-circle can be attributed to the surface film impedance.^[56] A first observation is the large difference in impedance response between the initial step and subsequent measurements. As mentioned earlier, it was demonstrated that lithium cobalt oxide particles move from a semiconducting to a metallic behaviour during their first delithiation.^[58,59] This change of electronic conductivity explains that the imaginary part of the measurement tends to approach to the real axis Z' . Impedance spectra at the initial state, first, twentieth and hundredth discharge present a

semi-circle in the medium-high frequencies and a inclined straight line at lower frequencies. Figure 3.12 shows a significant increase of half-cell impedance throughout cycling, revealing an increase of the charge transfer resistance. This was attributed to the growth of a passivating film on electrodes. As previously mentioned, this increase in charge transfer resistance was reported as a major factor for capacity decay in LCO-based electrodes.^[49,50] Nevertheless, similar profiles of EIS performed at the twentieth and at the hundredth cycle demonstrate the stability of the passivating film.

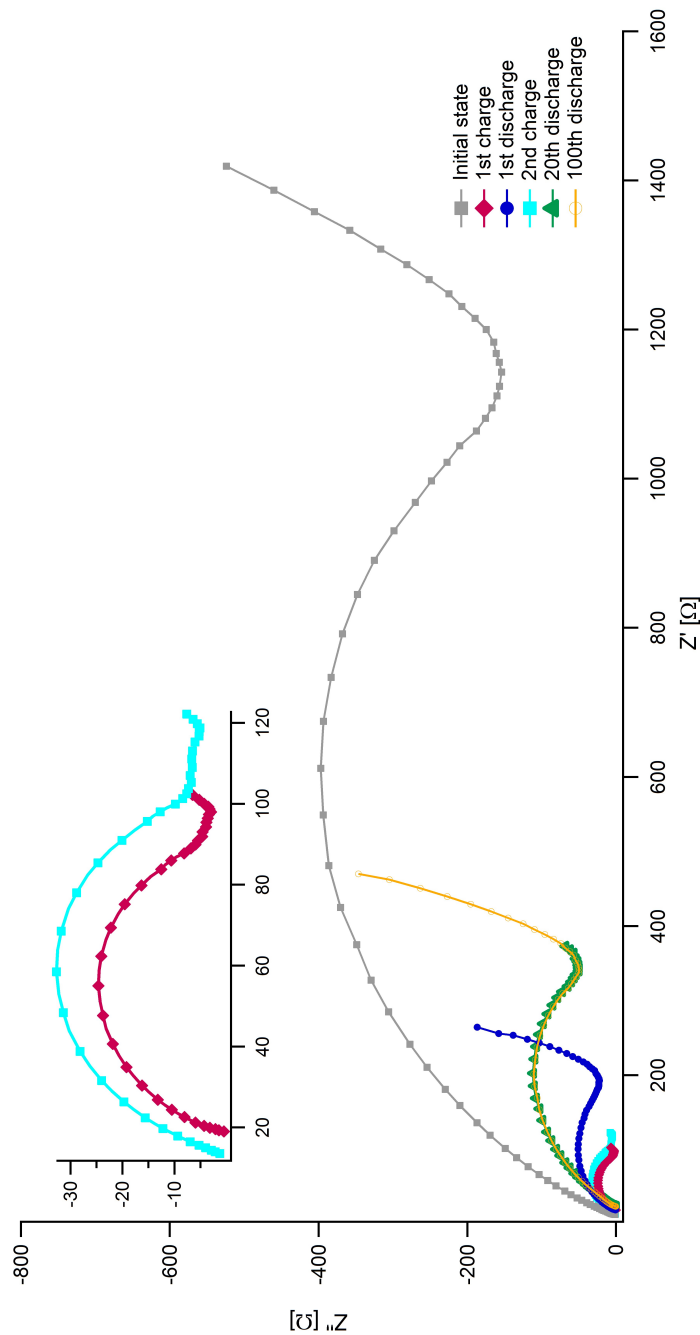


Figure 3.12 – Electrochemical impedance spectroscopy of LiCoO₂-MWCNTs electrodes evaluated in half-cell configuration versus lithium metal electrode. Measurement were performed under 5 mV perturbation at various cycling indexes. For clarity, the inset shows magnification of red and light blue curves.

With the objective of improving the lifespan of MWCNTs-LCO electrodes, fabrics have been pressed. The pressure applied on electrodes during their manufacturing is a well-known process used to improve cohesion and compactness in fabrics.^[60–62] A pressure of 3 t.m^{-2} or 6 t.m^{-2} was applied for 15 sec on electrodes. A similar electrode without post-production treatment was also evaluated for comparison. The electrode lifespan was evaluated at C rate for at least 200 cycles to gauge the impact of this post production process (Figure 3.13). A first cycle was performed at C/20 rate to allow passivation layer to be formed in good conditions. Results proved that applying pressure on electrodes after drying significantly increases cycling stability and performances of the electrodes. While the LCO reference electrode suffered a 57 % loss in capacity after 200 cycles, the decay in capacity of fabrics pressed under 3 t.m^{-2} was only of 13.1%. Electrodes pressed under 6 t.m^{-2} showed intermediate results with a capacity decay of 30 %. The results obtained for the 3 t.m^{-2} pressed electrode are satisfying since the decays of 4.1% and 13.1% after respectively 100 cycles and 200 cycles can be compared with literature.^[63] As a benchmark for comparison, Ning *et al.* indeed observed a capacity decay of about 6% and 8% after 100 and 200 cycles in Sony commercial batteries cycled at 1 C rate.¹ Improvement in cycle stability can be attributed to better cohesion in electrodes. Electrode thickness was measured before and after pressing operation. While pristine electrodes thickness was evaluated at 30 μm , thickness of 3 t.m^{-2} and 6 t.m^{-2} -pressed electrode thickness was evaluated at 18 μm and 13 μm . As previously mentioned, carbon nanotubes buckypapers contains approximatively 90 % voids. In this case, the majority of electrode mass is composed by LCO particles. In terms of volume occupation, we can estimate that LCO represent about 47.6 % of the total volume of a non pressed electrode. Therefore, voids still represent the vast majority of

¹Analyzed cells were commercial LCO/graphite Sony US 18650 (1.4 Ah) lithium-ion batteries. Cells were cycled at various current densities and voltage cut-off set at 4.2 V.

the remaining volume of electrode. With 3 t.m^{-2} and 6 t.m^{-2} -pressed electrodes the volume is reduced to 60 % and 43 % of the initial volume of electrode containing same LCO masses. Applied pressure enhances therefore considerably contacts between MWCNTs and particles. The better electrical conductivity between them helps to prevent local over-voltage and active material degradation. However, results presented on Figure 3.13 show that applying too much pressure on electrodes damages the lifespan of electrode. The explanation of this phenomenon probably lies in two factors. First, the applied pressure improve compactness of electrode and reduce voids available for liquid electrolyte. Lithium ion conduction can be hindered. Second, applying a high pressure on fabrics can weaken or fracture the crystal structure of LCO particles. The thickness of 6 t.m^{-2} pressed electrode was measured at $14 \text{ }\mu\text{m}$, a size close to LCO particles diameter. Building on this analysis, it is preferable to apply moderate pressure to improve electrode lifespan. To further improve electrode performances we investigated the synthesis of LCO nanoparticles.

3.2.1.2 LCO nanoparticles synthesis

To improve cathode behavior at high current densities, it was planned a home made synthesis of LiCoO_2 particles. Commercial LCO particles were measured on SEM images with a diameter of several microns. As previously explained, one of the major disadvantage of LiCoO_2 particles is their hexagonal layered structure. This implies that diffusion of lithium ions and electrons occurs in only two directions. Decreasing particle size and hence diffusion paths could greatly increase cathode performances. The reduced size of particles should also promote an intimate contact with MWCNTs. This section will focus on the synthesis of LiCoO_2 nanoparticles. Size of 100 nm will be targeted to improve electrochemical performances.

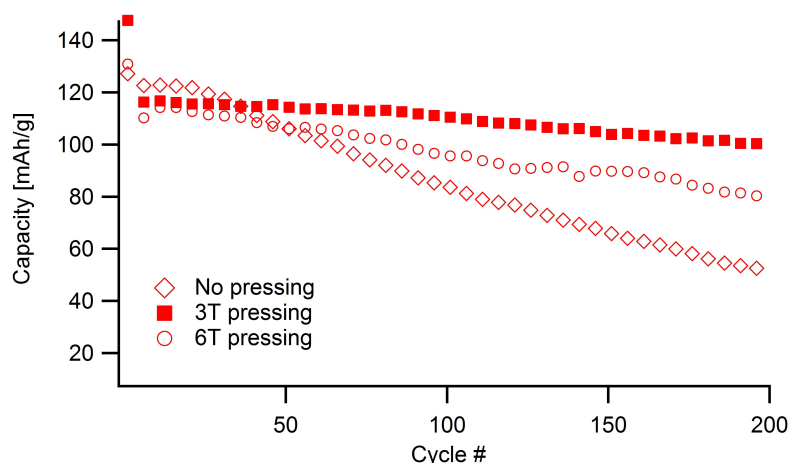


Figure 3.13 – Impact of different applied pressure on cycling stability of MWCNT-LiCoO₂ electrodes (90:10 wt. %): gravimetric capacities were evaluated in half-cell configuration versus lithium metal electrode at C rate over 200 cycles.

Among the numerous methods described in the literature,^[64,65] the sol-gel process was retained as the best way to create nanoparticles.^[66–68] In the appropriate conditions, this method can produce highly homogeneous nanopowders. Parameters of this process like stoichiometry, evaporation rate or calcination temperature are highly tunable. By controlling these conditions, we should be able to fully control size and shape of the synthesized particles. Other major advantages of this production method are its relative simplicity and short processing time. While traditional way to produce LCO particles sometimes imply high temperature or pressure for several hours, the sol-gel process can be conducted at atmospheric pressure and at lower temperature within a couple of hours. A large choice of lithium and cobalt precursors is available for sol-gel process. Lithium acetate and cobalt acetate were preferred for cost reasons. These salts were dissolved in different ratios in mQ water. The lithium/cobalt ratio is a very important parameter. During calcination at high temperature, a fraction of lithium can evaporate

leading to a cobalt excess. The latter excess leads to the formation of the Co_3O_4 spinel.^[69] Moreover, the synthesis of slightly overstoichiometric $\text{Li}_{1+\delta}\text{CoO}_2$ was reported as less susceptible to undergo transition to the monoclinic phase.^[70] Therefore 1.02, 1.04 and 1.06 lithium to cobalt ratio samples were prepared. Different amounts of ethylene glycol, citric acid and acrylic acid or poly(acrylic acid) were added to the solution to create the gel matrix. Table 3.1 provides an overview of the main gel composition calcined for LCO particles synthesis. These solutions were poured into aluminum or alumina ceramic pans and solvent was removed by gentle heating. Homogeneous red or purple gels were recovered. Gels were then heated and calcined under various thermal conditions (e.g. various annealing temperatures, annealing times or cooling rates). The typical set up for LiCoO_2 nanoparticles production is depicted in Figure 3.14. It implies a first step at low temperature (200 °C - 400 °C) to start the nucleation of an important amount of LCO crystal.^[67] In a second step, temperature is increased to 400 °C - 800 °C to allow the crystals growth. A final temperature superior to 700 °C is required to form the adequate crystalline phase. The variation of composition and calcination conditions generated a vast library of lithium cobalt oxide powders.

Entry	Lithium eq.	Cobalt eq.	Citric acid eq.	Ethylene glycol eq.	Acrylic acid/PAA eq.
1	1	1	1	1	0
2	1	1	1.5	1.5	0
3	1.02	1	1	1	0
4	1.02	1	1.5	1.5	0
5	1.06	1	1	1	0
6	1.06	1	1.5	1.5	0
7	1.04	1	0	1.5	2.5
8	1.06	1	1.5	1.5	0
9	1.06	1	0	1.5	2.5
10	1.06	1	0	1.5	5
11	1.06	1	1	1.5	2.5
12	1.06	1	1	1.5	5

Table 3.1 – Typical gel compositions for lithium cobalt oxide nanoparticles synthesis.

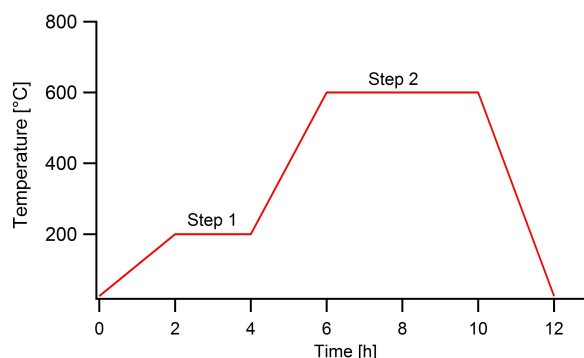


Figure 3.14 – Temperature profile of a typical LCO particles synthesis procedure. Adjustment in temperature and time of step 1 and 2 were evaluated.

Figure 3.15 shows diffraction patterns of LiCoO_2 powders synthesized in different conditions. Apart from the blue pattern corresponding to the entry 2 of Table 3.1, all other XRD patterns correspond to samples produced from entry 8. The blue curve differs from the others by the two marked peaks *. These peaks correspond to the Co_3O_4 spinel phase formed when a lack of lithium ions occurs during calcination. Besides, all the other peaks perfectly correspond to the commercial lithium cobalt oxide. All the other diffraction patterns obtained from powders corresponding to gel entry 8 in Table 3.1 differs by their calcination temperatures (400 °C - 700 °C). These patterns show the transition between the LT- LiCoO_2 cubic spinel-like structure (LT- LiCoO_2) to the rhombohedral layered LiCoO_2 (HT- LiCoO_2).^[71] The changes in the crystalline structure were identified in literature as the splitting of the 222 and 440 peaks (marked #). At 500 °C, we can assume that we have a mix of the two crystalline phases.^[68,72–75] A last piece of information can be obtained by analyzing the width of the peaks. One can see that the peaks of the home-made LCO sample are larger than the peaks corresponding to the commercial LCO. This indicates possible aggregation of nanoparticles in larger clusters. This transition between a cubic to an hexagonal layered phase can be tracked in cyclic voltammetry. Figure 3.16 shows

cyclic voltammograms of LiCoO_2 samples of entry 8 calcined at 500 °C and 600 °C. Both curves show a reversible redox process at 3.98/3.87 V, which refers to the oxidation and reduction of the layered HT- LiCoO_2 phase. Less pronounced peaks between 4.0 V and 4.2 V were attributed by Santiago *et al.* to order/disorder phase transitions.^[76]

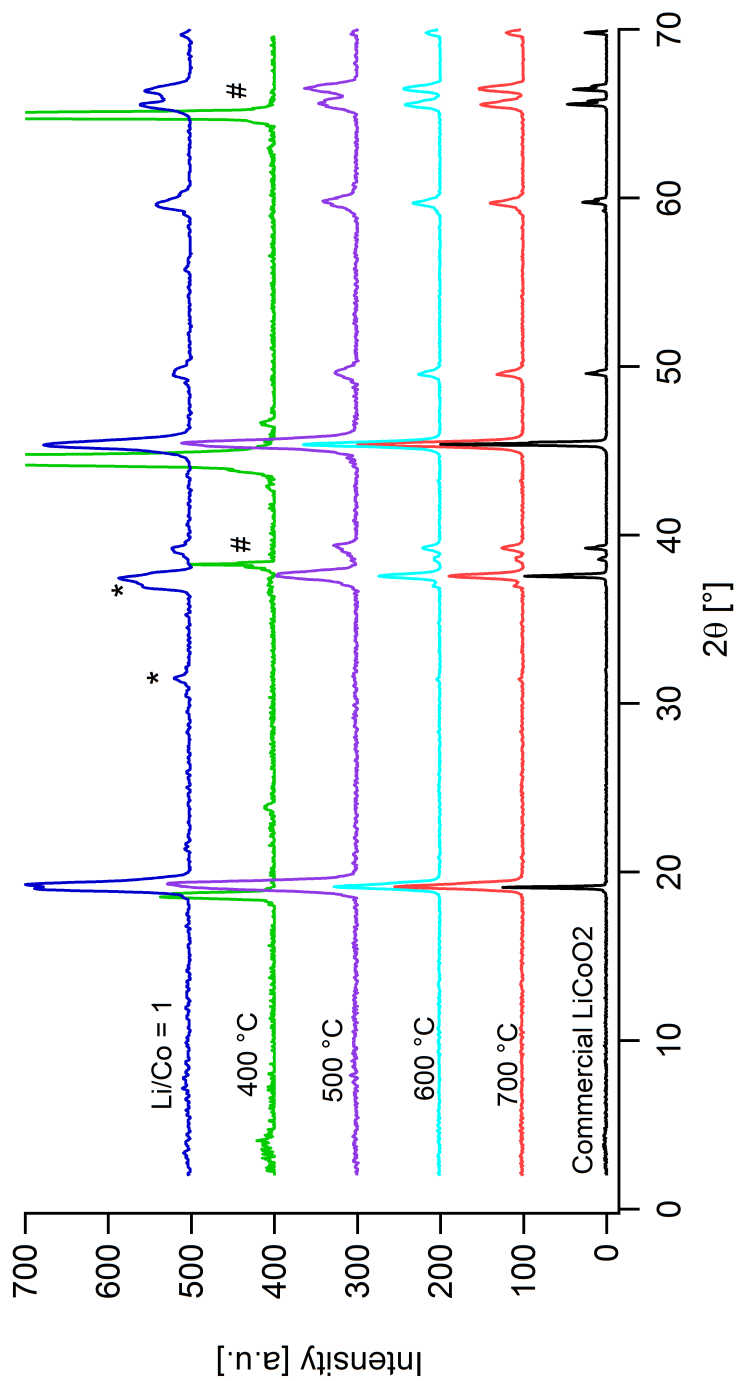


Figure 3.15 – XRD patterns of LiCoO_2 powders synthesized in different conditions: pattern a) corresponds to LiCoO_2 powder synthesized from gel with $\text{Li/Co}=1$ ratio calcined at 700 °C (entry 2 of table 3.1), pattern b) to e) correspond to LiCoO_2 powder synthesized from gel with $\text{Li/Co}=1.06$ ratio calcined at different temperatures (entry 8 of table 3.1) and pattern g) corresponds to commercial LiCoO_2 powder.

Concerning the LiCoO_2 synthesized at 500°C , an irreversible process at 3.37 V can be attributed to the LT- LiCoO_2 phase. In this structure Li^+ insertion/desinsertion is an irreversible process. This irreversibility can be related to the difference between the volume of the sites for Li^+ ions insertion in the layered and in the spinel structures. In the spinel structure, tetrahedral sites related to Li^+ are smaller than octahedral ones in the layered structure. This difference explains the poor reversibility of LT- LiCoO_2 spinel structure.

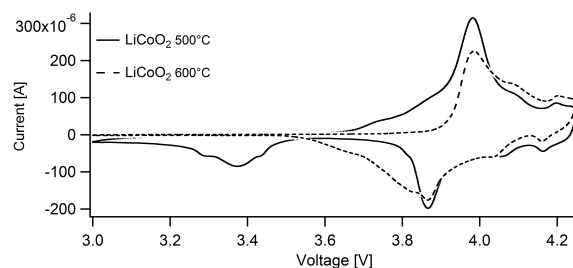


Figure 3.16 – Cyclic voltammograms of LiCoO_2 -MWCNTs electrode (90:10 wt. %) evaluated at $1\text{ mV}\cdot\text{s}^{-1}$ rate in half-cell configuration versus lithium metal electrode in the $3.0\text{ V} - 4.25\text{ V}$ range.

The morphology of particles created was investigated via scanning electron microscopy. Figure 3.17 presents the morphology of some LCO particles synthesized under various conditions. Figures 3.17 a) and b) show a sample of composition entry 5 calcined for 2 hours at 200°C and 10 hours at 600°C . Despite enjoyable size of individual particles, aggregation in this sample is clearly visible, particularly in Figure 3.17 a). Moreover, dispersion of particle size is really high. It was assumed that the organic/inorganic ratio was not appropriate and leads to aggregation of particles. In addition 10 hours calcination can induce aggregation of nanoparticles in bigger aggregates. Figures 3.17 c) and d) correspond to gel of entry 8 of Table 3.1 while Figures 3.17 e) and f) correspond to gel of entry 11 and 12, respectively, of Table 3.1. These samples were first heated at 200°C for 4 hours, followed by a step at 400°C for 2 hours and

finally 4 hours at 700 °C. After calcination, the powders were crushed using mortar and pestle to break biggest aggregates. More aggressive methods could have been employed but it could damage the crystal structure of particles.^[31] On Figure 3.17, it can be noticed that the size of the particles was much better controlled. Images d) and e) depict particles with average diameter of 300 nm. In image f), particles were sized at an average diameter of 150 nm. This reduced size (diameter of commercial particle is around 10 μm) should help to improve electrochemical performances as diffusion paths decrease. Unfortunately, these pictures also reveal the apparition of aggregation phenomena. Aggregation of particles will at the opposite hinder diffusion of lithium ion in the center of particle and affect the performances. Gel composition and calcination set up are therefore of paramount importance for morphology control. As previously said, the aggregation phenomenon can also be tracked on XRD patterns. On Figure 3.15, we can see that home made LCO sample present broader peaks than commercial samples. This enlargement of peaks is also a proof of crystal aggregation.

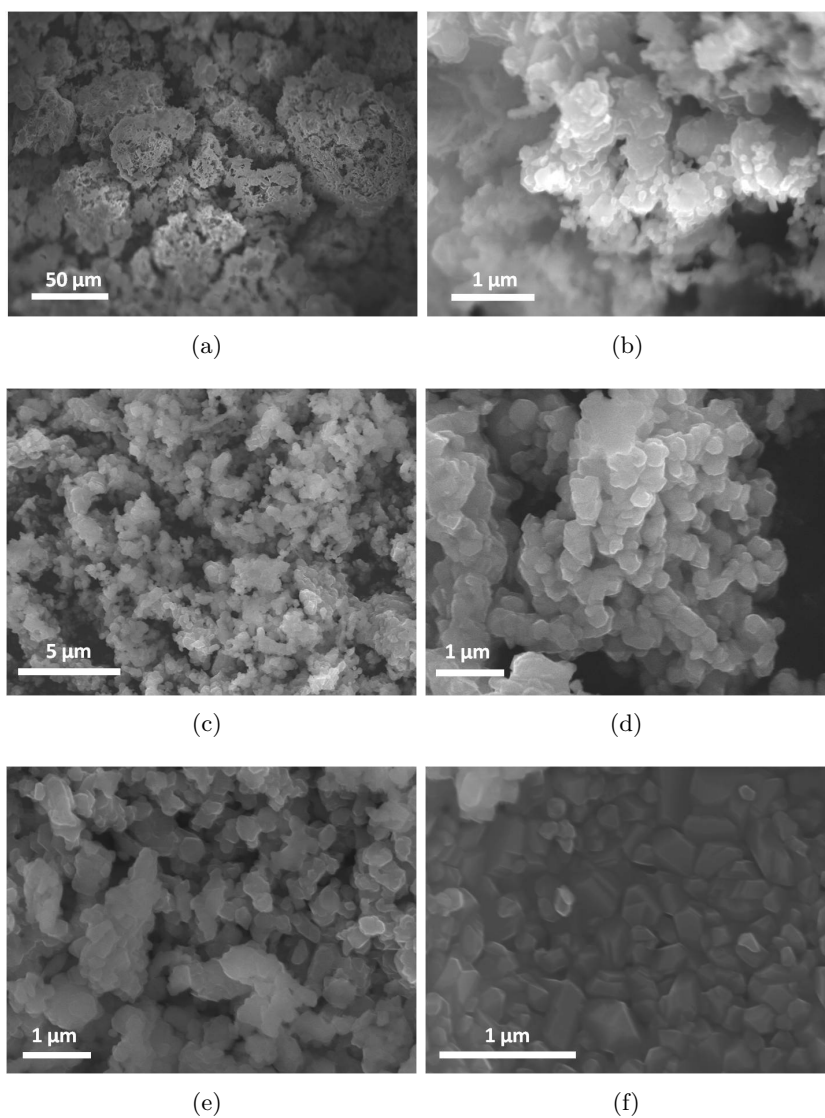


Figure 3.17 – SEM micrographs of synthesized lithium cobalt oxide particles with different composition: a) and b) correspond to entry 5; c) and d) to entry 8 and e) to entry 11 and f) to entry 12 of Table 3.1. These samples were first heated at 200 °C for 4 hours, followed by a step at 400 °C for 2 hours and finally 4 hours at 700 °C.

Electrochemical performances of home-made lithium cobalt oxide particles were then evaluated. At first, electrochemical performance of particles was evaluated in a traditional configuration. Active material particles, PVdF binder and carbon conducting agent were mixed together in NMP solvent to form a slurry. The latter was casted on aluminum foil to create electrodes. Unfortunately, most of these experiment were not conclusive as sample failed to successfully complete several cycles and reproducibility was difficult to achieve. The main reason was the inhomogeneity in thickness and composition of electrodes. Later, electrodes were designed using filtration process. Reproducibility of measurement was much better. The results presented in the following are reported for LCO particles prepared from gel of entry 8. These samples were first heated at 200 °C for 4 hours, followed by a step at 400 °C for 2 hours and finally 4 hours at 700 °C and 2 hours at 800 °C. Figure 3.18 depicts the typical behaviour of LCO-MWCNTs (90:10 wt. %) fabrics under various current densities. Experiment was repeated 3 times and the best results are here presented. The gravimetric capacity recovered at C/20 rate is evaluated at 105.5 mAh.g⁻¹. This recorded performance is not the one expected as the gravimetric capacity of LCO cycled between 3 V and 4.2 V should reach 140 mAh.g⁻¹. At higher rates, the gravimetric capacity rapidly drops to be close to zero at 5 C rate. At C rate, the recovered capacity was only 57 mAh.g⁻¹, barely the half of the capacity recovered for commercial LCO in the same fabrics. At the twentieth cycle, the current density was set back to a C/10 rate and a capacity of 82.5 mAh.g⁻¹ was recovered. This indicates that high current densities did not damage the material too severely. Nevertheless, one can notice that the active material loss 15 % of its capacity between cycle 5 and 25.

To improve cycle stability of these electrodes, a 3 t.m⁻² pressure was applied for 15 seconds to enhance the cohesion in fabrics. Capacity of home-made lithium cobalt oxide samples was then evaluated at

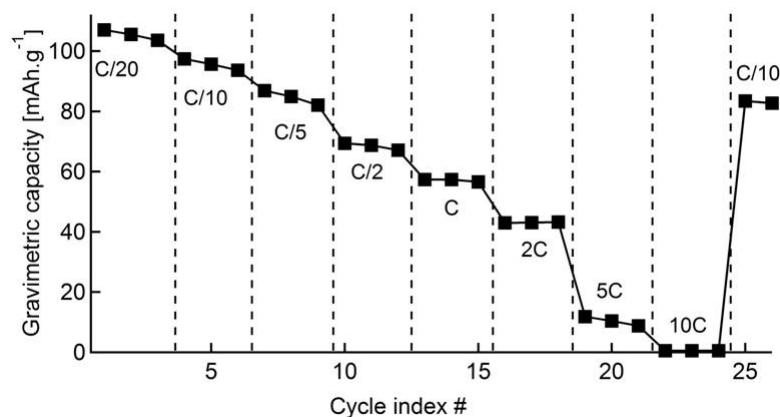


Figure 3.18 – Electrochemical performances of electrodes containing LiCoO₂ particles synthesized at 700 °C with composition of entry 8 of Table 3.1: charge capacity of LiCoO₂-MWCNT electrodes (90:10 wt. %) evaluated under various current densities in half cell configuration versus lithium metal electrode.

C rate for 100 cycles (Figure 3.19). During the first cycle at C/20 rate, the capacity was evaluated at 111 mAh.g⁻¹ which is consistent with the previous tests. However, gravimetric capacity recovered at C rate in the subsequent cycles was significantly better (93.5 mAh.g⁻¹ for cycle 2). Nevertheless the capacity decay over 100 cycle was evaluated at 42 % with 55 mAh.g⁻¹ at the hundredth cycle. This is significantly lower than the typical recorded values for commercial samples. Recorded coulombic efficiency was consistent over 99% (after cycle 6), which shows no significant problems of electrolyte degradation. The decrease of gravimetric capacity was therefore mainly attributed to the aggregation of nanoparticles of LiCoO₂ observed on XRD patterns and SEM micrographs. This causes local over-voltage that irreversibly damages the particles crystalline structure. Improvement of electrochemical performances compared to commercial particles is not noticeable. Nevertheless, little technical optimization of synthesis could certainly lead to the production of better performing nanoparticles. Indeed, particle

size is an important factor influencing diffusion path and SEI formation. These parameters have a direct impact on cyclability and rate capability. [65,77–79]

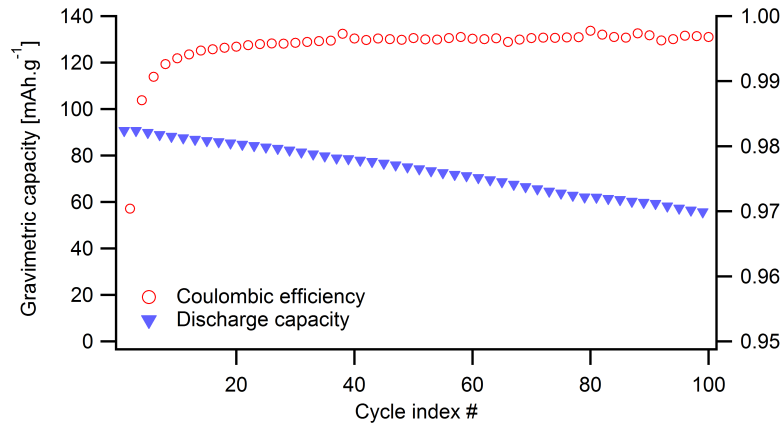


Figure 3.19 – Cycle stability evaluation of electrodes containing LiCoO_2 particles synthesized at 700 °C with composition of entry 8 of Table 3.1. Evaluation of LiCoO_2 -MWCNTs (90:10 wt. %) electrodes: capacity retention and coulombic efficiency at C rate over 100 cycles.

3.2.1.3 Carbon coating on LCO particles

Another method to improve electrochemical performances of electrodes containing LCO particles is the creation of a protective and/or conductive coating. A protective coating covers the active sites of active materials and therefore reduce the electrolyte decomposition so that its structural stability can be enhanced. A conductive coating can be designed to increase electrical conductivity on the surface of the particles of electrode active materials. As previously said, pristine LiCoO_2 particles present very poor electrical conductivity. Traditional electrodes are composed of a dispersion of active matter particles in a blend of polymer binder and conductive carbon nanoparticles. Electron transfer between the electrode and the particles is thus very dependent on the composition and the quality of the blend. As nanocarbons are difficult to disperse in solvents and in polymers, it is therefore likely that electrical contacts between the electrodes and the active matter particle occur in only a few regions of its surface. Replacing this blend of polymer and conductive additive by carbon nanotubes was a first step to improve electron collection on the surface of particles but it can still be improved. The next step was to create a conductive carbon coating on nanoparticles to improve further the electron exchange between carbon nanotubes and active materials.

Sucrose was chosen as carbon precursor for carbon coating for its abundance and low cost. Poly(acrylonitrile) (PAN) was chosen due to the absence of oxygen in its composition. LiCoO_2 particles were suspended in sucrose or PAN solutions of various concentrations. After evaporation of the solvent, coated particles were calcined at 600 °C in air for a reduced time lapse. Air was preferred to a reductive atmosphere to preserve LiCoO_2 particles. Indeed, reductive atmosphere can damage LiCoO_2 by reducing Co^{4+} to Co^{3+} . Particles with various LiCoO_2 weight ratios were prepared as described in the experimental part. Figure 3.20 represents different samples of carbon coated LCO particles.

Samples b) and c) containing sucrose were calcined for 10 minutes at 600 °C. Samples d) and e) and f) containing PAN were calcined at 500 °C for 30 minutes and 15 minutes respectively. As it can be seen, sucrose seems to provide a nice uniform coating on LCO particles while it was difficult to obtain convincing results with PAN. On Figure 3.20 d) e) f), it can be observed that the coating varies considerably from one particle to another. Moreover, the use of PAN leads to an important aggregation of LCO particles. Lastly, PAN involves DMF as solvent which increases ecological impact on the process.

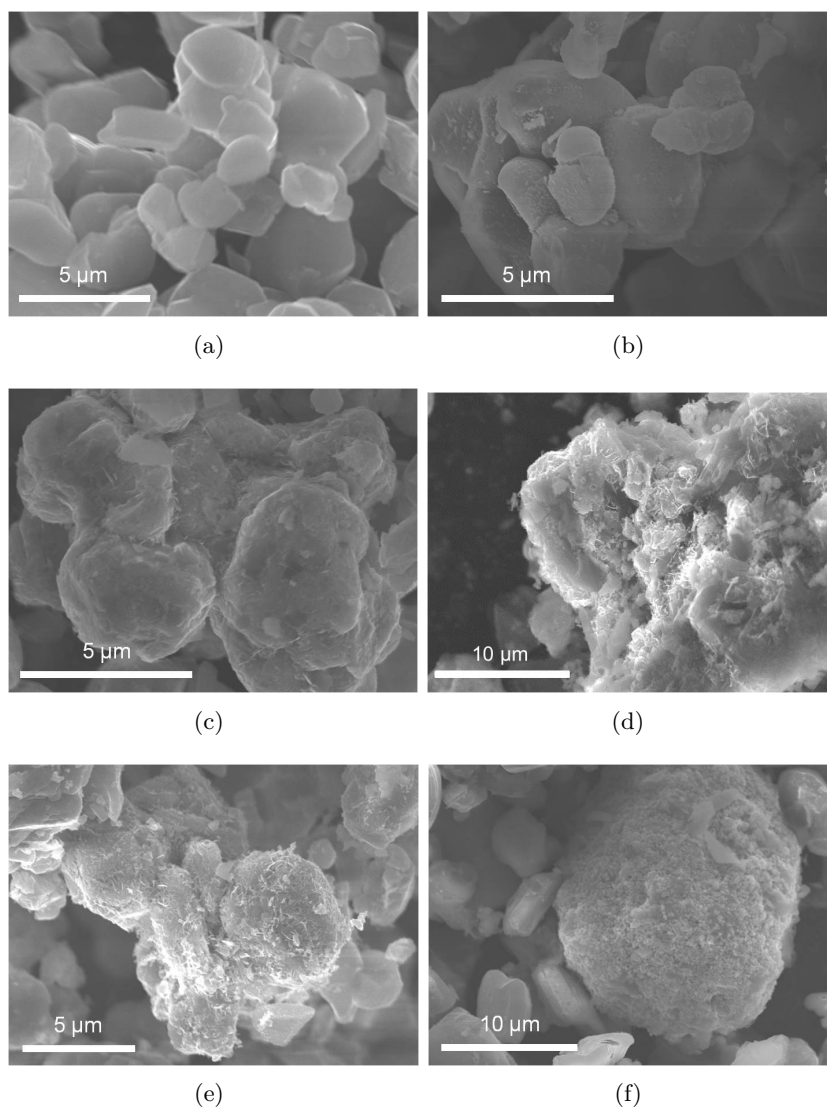


Figure 3.20 – SEM micrographs of different carbon coatings on lithium cobalt oxide particles: a) pristine LiCoO₂ particles; b) LiCoO₂ particles coated with a 0.16 wt. % sucrose solution; c) LiCoO₂ particles coated with a 2.1 wt. % sucrose solution; d), e) and f) LiCoO₂ particles coated with a 5 wt. % PAN solution.

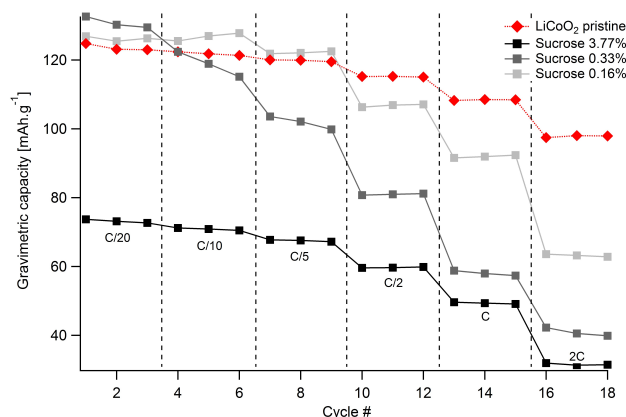


Figure 3.21 – Electrochemical performances of carbon coated LiCoO₂ particles for various carbon precursors contents calcined at 600 °C in air: charge capacity of LiCoO₂-MWCNTs electrodes (90:10 wt. %) under various current densities in half-cell configuration versus lithium metal electrode.

Only electrochemical performances of sucrose coated particles will be presented as no convincing results were obtained with carbon-coated LCO particles produced with PAN as carbon precursor. The inhomogeneity of coatings and particle aggregation are probably the main reason of failure in this case. Positive electrodes were cycled under different current densities to investigate the impact of carbon coating on electrochemical performances (Figure 3.21). For low carbon contents (0.16 and 0.33 %), at low C rate (below C/10), no significant influence of the carbon coating can be noticed. The electrochemical performances seem to be similar as for non-coated LCO particles. At intermediate cycling rates (starting from C/2 rate), the impact of carbon coating is quite noticeable and degrades electrochemical performances. At 2C rate, less than half of the gravimetric capacity could be recovered with such treated LiCoO₂ particles. For a higher carbon content (3.75 wt. % sucrose content), the cathode could not even sustain low cycling rate. At C/20, the LiCoO₂ gravimetric capacity was measured at 73 mAh.g⁻¹, half of the capacity recovered without carbon treatment. This damaged per-

formances proved that attempts to coat LiCoO_2 particles with effective conductive or protective carbon layer failed. The organic layer observed in SEM images is therefore probably non-conductive and degrades the electrochemical performances of LCO particles at intermediate current densities.

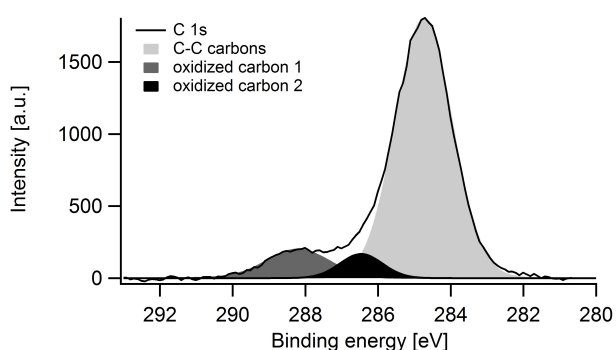


Figure 3.22 – Analysis of carbon forms at the surface of carbon coated LiCoO_2 particles by calcination of sucrose calcined at 500 °C: XPS C1s peak decomposition evidencing various oxidized carbon forms.

X-ray photoelectron spectroscopy was performed on these samples to determine the composition of the carbon layer on LCO particles. As it can be seen in Figure 3.22, the carbon 1s peak can be decomposed in three different peaks. Each of these components represents various degrees of carbon oxidation with the peak situated at the highest binding energy corresponding to the most oxidized form of carbon ($\text{C}=\text{O}$).^[80,81] The main peak located at 284.8 eV can be attributed to C-C bonds and represents 83.8 % of the total carbon content. These carbons present a sp^3 hybridization as there is no visible sign of shake-up between 291 eV and 292 eV.^[82] In addition, the presence of π bonds does not necessarily prove the conductivity of the carbon form. A good electrical conductivity is also related to the absence of defect in the structure of the material. The two other peaks located at 286.6 eV and 288.3 eV are attributed to oxidized forms of carbon and represent respectively 5.9 % and 10.3 %

of the carbon content. Such amounts of oxidized carbon forms on the coating of LCO particles creates a non conductive layer that can damage the electrochemical performance degradation.

Sucrose^[83] or cellulose from biomass^[84] were already indeed reported to be effective carbon precursor for graphitization. Unfortunately, attempts to create a conductive or protective shell on LCO particles with this method failed to improve performances. Several other methods or carbon precursors for conductive coating were already reported with success.^[85-87] However, they often imply significant increase of manufacturing costs of the active material.

3.2.2 Lithium iron phosphate based electrodes

Lithium phosphate iron is the second active material tested for the production of positive electrode via filtration method. As previously mentioned, LFP is a promising material but its 1D structure requires a highly conductive electrode matrix. Usually, LFP particles require conductive coating to produce effective electrodes.^[88,89]

LFP-MWCNTs (90:10 wt. %) fabrics were again tested in half-cell configuration versus lithium metal anode at various current densities (Figure 3.23). LFP-MWCNTs electrode were cycled in the 3.0 V - 4.0 V range. As it can be noticed, the electrode delivers only part of its capacity even at low or intermediate cycling rates ($\leq C$). A maximum of 132 mAh.g⁻¹ was recovered compared to the theoretical 170 mAh.g⁻¹. At higher rates gravimetric capacity faded gradually to zero at 10 C rate. The initial capacity was recovered after 35 cycles but the start of a decline is noticeable. This experiment has been repeated several times and the best results are presented in Figure 3.23. At first glance, the results can seem disappointing but they are indeed promising. It is well-known that performing cathode based on pristine LiFePO₄ particles are difficult to produce.^[88,89] LiFePO₄ particles present a good ionic conductivity in only one dimension but a very weak electrical conductivity in the matter. This drawback hinders the performances of electrodes and LiFePO₄ particles treatments are generally required.^[88,89] The behavior observed in Figure 3.23) is typical for electrodes prepared with pristine LFP particles. Nevertheless, with an appropriate preparation, it was proved that LiFePO₄-based cathode can deliver very good performances.^[90,91] Cheng and coworkers proved that by intergating nanosized LiFePO₄ particles in a porous carbon matrix cathode can retains 96.7 % of its initial capacity (over 80 mAh.g⁻¹ LiFePO₄/C composite) at 10 C over 1000 cycles. Moreover, their cathode could sustain high cycling rates such as 20 C and still delivering 60 mAh.g⁻¹ LiFePO₄/C composite.^[90]

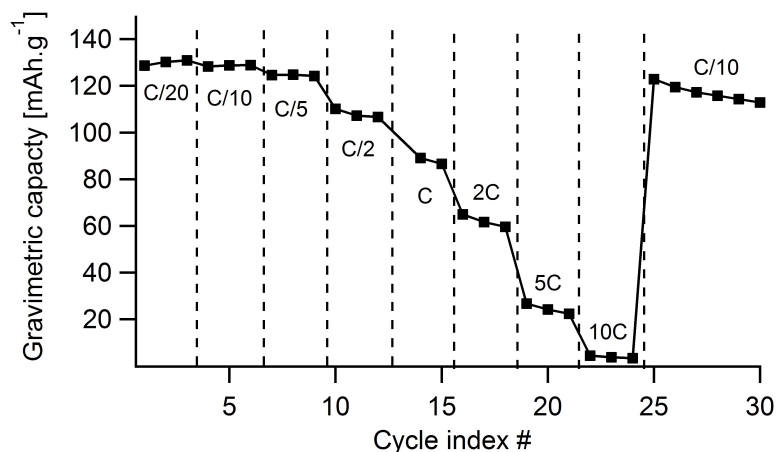


Figure 3.23 – Electrochemical performances of $\text{LiFePO}_4\text{-MWCNTs}$ electrode (90:10 wt. %): charge capacity evaluated under various current densities in half-cell configuration versus lithium metal electrode.

Subsequent tests were realized with electrodes pressed at 3 t.m^{-2} to increase cohesion in the fabrics and improve performances. Such a treatment has proved its effectiveness for LCO-MWCNTs cathodes. The cycling stability was evaluated over 100 cycles at constant C rate versus lithium metal anode in the 3.0 V - 4.0 V range for two different cells (Figure 3.24). In this case, the initial capacities were both evaluated at around 125 mAh.g^{-1} . This proved that pressing of electrode was a powerful tool to improve performances as capacity of electrode was previously evaluated at 84 mAh.g^{-1} for pristine electrodes at C rate. Unfortunately, one can notice that recorded gravimetric capacities declined constantly to reach only 79 mAh.g^{-1} after 100 cycles. That represents 37 % capacity lost which is not acceptable for electrodes. The recorded coulombic efficiencies are significantly low (between 0.9 and 1). This low coulombic efficiency was reported as an indicator of cycling degradation.^[92] Coulombic inefficiency relates parasitic reactions that occur in the cells at a reaction rate that is independent of the cell cycling

rate. That amount of parasitic reactions that occur for a given cycle is related to the time of cycle.^[48] These parasitic reactions can come from electrolyte, active matter or additive degradation (shortcuts in battery were excluded here as experiment was reproduced). In our study (Figure 3.24) charge/discharge were operated within one hour, which is pretty short time. The bad coulombic efficiency is therefore related to a very high parasitic reaction rate. On Figure 3.24, one can see that there is a strong correlation between the coulombic inefficiency and the loss of capacity rate. It could therefore be concluded that the LFP particles are degraded during battery operation. XRD analysis could be a tool to check the crystal structure of LFP particles after cycling and should be envisioned. One of the possibilities retained is the progressive obstruction of 1D channels of LFP structure with electrolyte degradation. The creation of a protective porous coating at the surface of LFP could prevent such degradation of electrochemical performances.

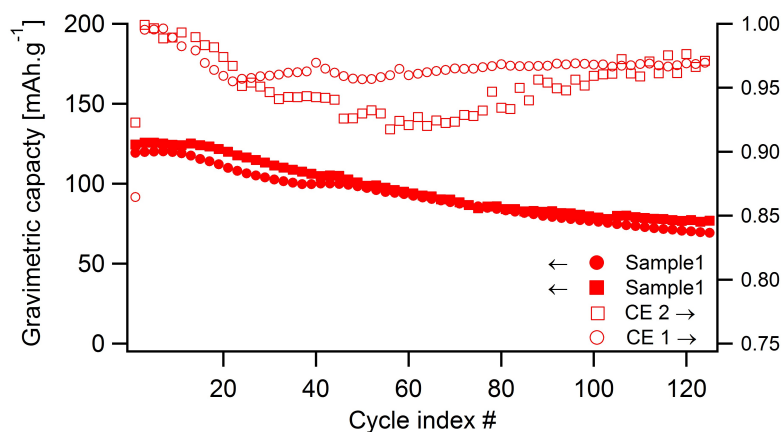


Figure 3.24 – Cycle stability evaluation of LiFePO₄-MWCNTs electrodes (90:10 wt. %) electrodes (3 t.m⁻² -pressed): evaluation of capacity retention and coulombic efficiency at C rate over 125 cycles.

The voltage profiles of a cycling stability test was analyzed (Figure 3.25). The typical flat voltage plateau of this two-phases compound can be observed. This charge plateau is located at 3.50 V for initial

charge and at 3.36 V for initial discharge. Electrode over polarization is therefore present and constant over time. During first cycle, the over-polarization was measured at a minimum of 69 mV. Polarization arises from the internal resistance of the electrode materials.^[93,94] It increases the charge potential above the redox potential and decreases the discharge potential. The overpotential is also known to be the driving force behind electrochemical phase transitions in insertion electrodes. This phase transformation is enhanced by increasing applied overpotential for lithium metal olivine phosphate. A complete study of overpotential effect on LFP crystals was realised by Tang *et al.*^[95] They proved that the crystalline-crystalline ($\Delta F_{c \rightarrow c}$) and crystalline-amorphous ($\Delta F_{c \rightarrow a}$) phases transitions are overpotential ($\Delta\phi$) dependent. Above $\Delta\phi = 16.6$ mV, the phase transition ($\Delta F_{c \rightarrow a}$) is promoted over the phase transition ($\Delta F_{c \rightarrow c}$). Moreover, above the critical $\Delta\phi = 28.5$ mV, the nucleation barrier for amorphous phase vanishes. Here is some serious clue of the gradual loss of capacity of electrodes. The overpotential observed on Figure 3.25 is directly linked to the poor electrical conductivity of LiFePO_4 particles and the insufficient electronic contact with MWCNTs.

This study of LiFePO_4 -MWCNTs proved that filtration process is an effective way to create electrodes. The measured performances are encouraging but underline the importance of modification of LiFePO_4 particles. This material is very promising but much higher performances can be reached by size-decreasing, ion doping, conductive/protective coating, or inclusion in a conductive matrix of the particles.^[96-99]

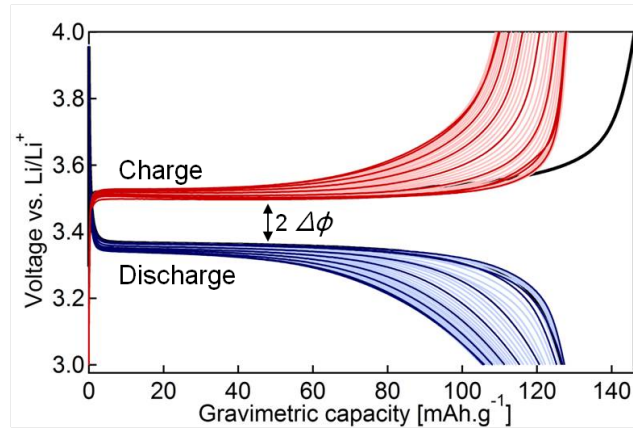


Figure 3.25 – Voltages profile of the LiFePO₄-MWCNTs (90:10 wt. %) 3t.m⁻²-pressed electrode evaluated on a half-cell configuration versus lithium metal at C rate during the first 100 cycles. Charge curves are depicted in red and discharge curves are depicted in blue.

3.2.3 Lithium titanate based electrodes

Lithium titanate oxide (LTO) was envisioned as the base material for our negative electrodes. As previously mentioned, this material is a promising candidate as anode active material for numerous applications despite its higher price than graphite. Its highly stable spinel-structure undergoes only very minor volumetric changes upon cycling and provides therefore a material with good cycling stability. Moreover, the solid electrolyte interphase formed at potentials below 1 V *versus* Li/Li⁺ is strongly reduced on LTO as its insertion potential is 1.6 V. This is of paramount importance since MWCNTs present a very high specific surface area and the SEI could significantly increase in this case the electrical resistance of the anodes.

In this section, anodes were created by the same vacuum filtration process as previously described. Dispersion of MWCNTs-Li₄Ti₅O₁₂ in various ratios were filtered to provide nice flexible self-standing electrodes. As for positive electrode fabrication, butanol was used as dispersive solvent to avoid the use of surfactants. Typical anodes were produced with a mass loading of 5.25 mg.cm⁻² and a uniform thickness of 32 μm. SEM images also confirmed that electrodes with homogeneous and constant thickness were created (Figure 3.26).

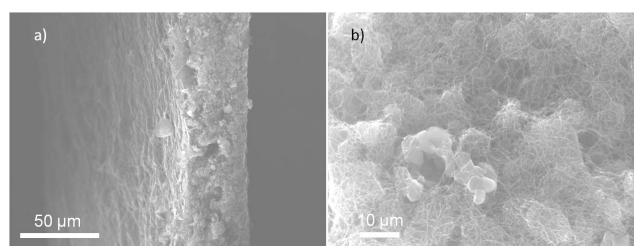


Figure 3.26 – SEM images of Li₄Ti₅O₁₂-MWCNTs fabrics (90:10 wt. %) a) cross-section view of the electrode and b) high magnification view of electrode surface.

The rate performance was investigated by cycling these anodes between 1.0 V and 2.0 V at different current densities (Figure 3.27). At

C/10 rate, a capacity around 162 mAh.g^{-1} was recovered for anodes containing 15 wt. % MWCNTs. This is in good agreement with the theoretical capacity of LTO (175 mAh.g^{-1}). At 1C rate, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ capacity was evaluated at 145 mAh.g^{-1} providing thus excellent performances. Here again, the error on calculated capacities is mainly related to mass measurement and is maximum 3.4 %. Above 2C rate, the capacity faded rapidly with no capacity retention at a 10 C rate. Electrical conductivities were similar to LCO-MWCNT fabrics and measured between 4.4 S.cm^{-1} and 9.6 S.cm^{-1} . With respect to LCO cathodes, the influence of the amount of MWCNT was less pronounced for LTO anodes. No significant differences were noticed between anodes containing 5 wt. % MWCNT and 15 wt. % MWCNT.

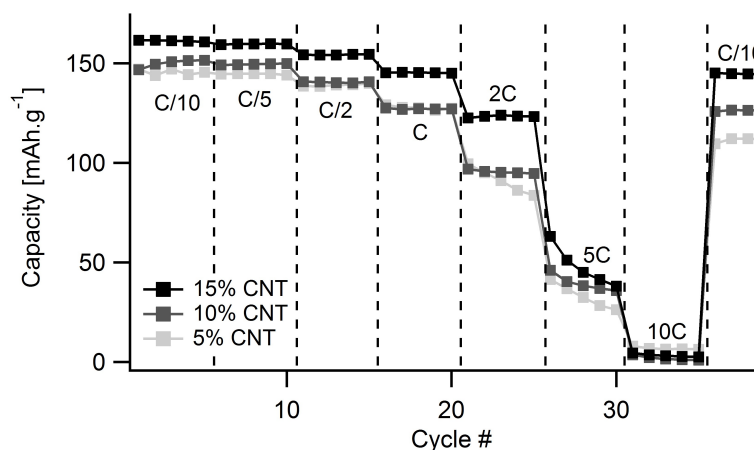


Figure 3.27 – Electrochemical performances of LTO-MWCNTs electrodes containing various amounts of MWCNTs: charge capacity under various current densities in half-cell configuration versus lithium metal electrode.

The cycling stability of electrodes containing 7 wt. % of MWCNTs was evaluated at 1C rate (Figure 3.28). The results showed impressive performances with the capacity evaluated at 142 mAh.g^{-1} dropping only at 98 % of its initial capacity after 100 cycles. Coulombic efficiency read-

ings were consistently over 98.5 %. These excellent results demonstrate the possible application of our manufacturing process for this kind of electrodes. With little technical optimization, LTO-MWCNTs will not only present extreme lifespan but also sustain higher current densities.

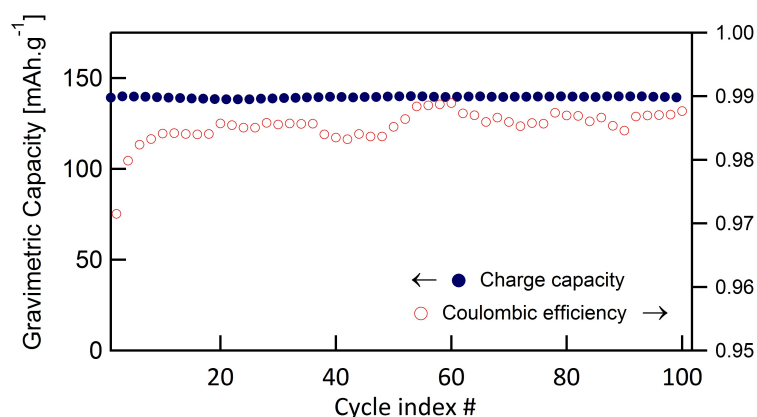


Figure 3.28 – Cycle stability evaluation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -MWCNTs electrode (90:10 wt. %) : evaluation of capacity retention and coulombic efficiency at 1C rate over 100 cycles in half-cell configuration versus lithium metal electrode.

Electrochemical impedance spectroscopy (EIS) was performed on a LTO-MWCNTs half-cell at various times of the cycling stability test. EIS was conducted after cell assembly and after first and hundredth charges (Figure 3.29). As before, half-cells were cycled in a potential window of 1 to 2 V *vs.* Li/Li⁺. One can notice a similar pattern as EIS performed on LCO-MCNTs electrodes. As previously, the semi-circle can be ascribed to charge transfer resistance R_{CT} . The straight line is attributed to diffusion properties of lithium ions in solid materials (Warburg impedance Z_W). Electrochemical impedance spectroscopy shows an increase in charge transfer resistance between cycles. This can be related to a modification of particles surface. Formation of SEI is not obvious on LTO-based electrodes. As previously mentioned, SEI layer is generally formed under a 1 V potential. Nevertheless, the morphology of

LTO particles or the presence of metal traces can catalyze and promote the SEI formation at superior potentials.^[2,100,101] While this increment of R_{CT} is clearly noticeable, it seems to have no consequence on cycling stability of LTO-MWCNT electrodes as shown in Figure 3.28.

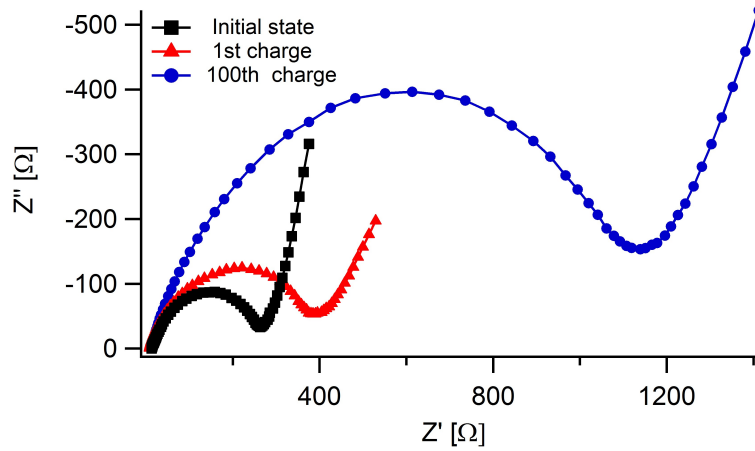


Figure 3.29 – Electrochemical impedance spectroscopy of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -MWCNTs electrodes evaluated in half-cell configuration versus lithium metal electrode at different cycling indexes. Measurements were performed under 5 mV perturbation at various cycling indexes.

Lastly, after 100 cycles, cells were dismantled to recover LTO-MWCNT fabrics. Figure 3.30 shows SEM images before and after electrochemical analysis to highlight the created passivating film. It can be noticed that individual particles of LTO as well as individual MWCNTs can be identified in Figure 3.30 a). After cycling, electrodes are covered by a passivating film and nor particles neither MWCNTs can be distinguished (Figure 3.30 b)).

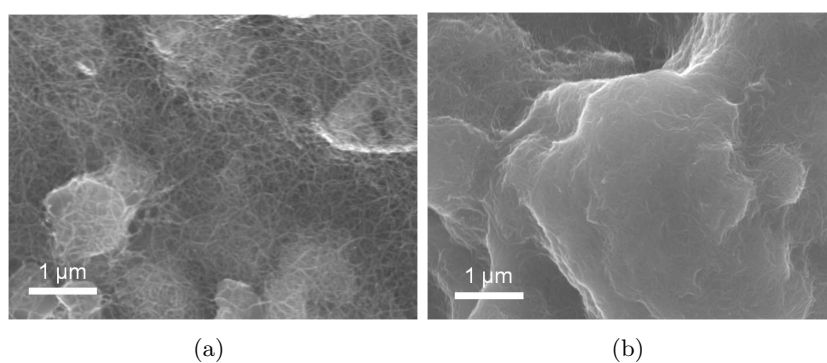


Figure 3.30 – SEM micrographs of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -MWCNTs electrodes surface: a) at initial state and b) after 100 cycles.

3.2.4 Graphite based electrodes

The last active material tested to design negative electrode by filtration is graphite. Graphite is undoubtedly the most studied and most commercially used material for negative electrodes. The numerous benefits of this material were deeply described in section 2.2.1.3. It was therefore important for us to apply our electrode manufacturing method to this material to prove its effectiveness. Therefore, we prepared meso-carbon microporous beads - MWCNTs fabrics with the same process as described previously. A dispersion containing 5 mg of MWCNT and 45 mg of MCMB was filtered through millipore device. Electrodes were peeled off and dried overnight at 60 °C under vacuum. As demonstrated in Figure 2.14 a), graphite delivers its full gravimetric capacity at very low potentials *versus* Li/Li⁺. It is therefore important to avoid over-potential leading to metal lithium plating on electrodes. Moreover, the low potential of graphite electrodes induces solid electrolyte interphase formation on the anode. The use of a large amount of carbon nanotubes presenting huge specific surface is therefore a risk. Figure 3.31 describes the behaviour of two MCMB-MWCNTs (90:10 wt. %) electrodes cycled at cut-off voltages of 10 mV. One of these electrode was pressed at 3 t.m⁻² for 15 seconds before electrochemical analysis. Electrodes performances were evaluated under various current densities in half-cell configuration *versus* lithium metal electrode.

Even at very low cycling rates (C/10), the pristine MCMB-MWCNTs fabric presents very low gravimetric capacity (57 mAh.g⁻¹) with respect to theoretical capacity (325 mAh.g⁻¹).^[102] According to the staging theory, at 10 mV, graphite base-anodes should almost deliver their full capacity, which is not the case here. At higher current densities, recovered gravimetric capacity faded quickly and can be considered as almost zero at C rate. The 3 t.m⁻² pressed MCMB-MWCNTs electrode presents a much better capacity at low current density. At C/10, a gravimetric capacity of 163 mAh.g⁻¹ was measured. Intimate contact between graphite

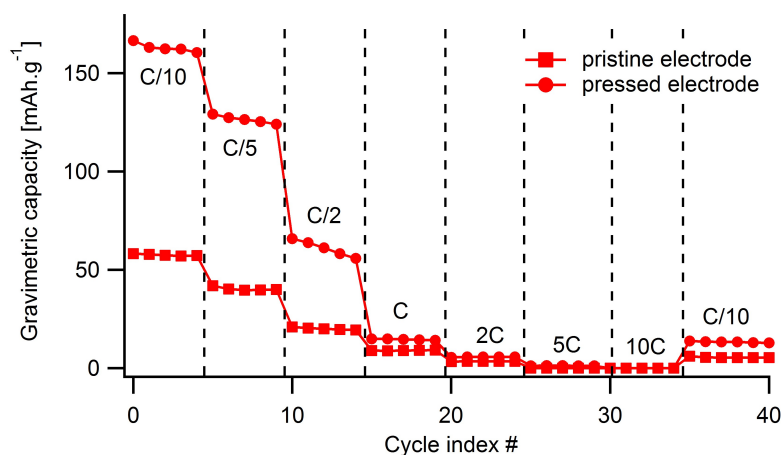


Figure 3.31 – Impact of a 3 t.m^{-2} pressure applied for 15 s on electrochemical performances of MCMB-MWCNTs electrodes (90:10 wt. %): charge capacity under various current densities in half-cell configuration versus lithium metal electrode.

particles and MWCNTs is a key factor for electrode performances. After 35 cycles, current density was set back to C/10 but unfortunately, the initial capacity of the active material was not recovered. Figure 3.31 demonstrates that electrodes suffered irreversible damages at moderate or high current densities. High current densities applied on graphite anode can lead to local overpotential. This was previously reported as a reason of irreversible gravimetric capacity loss.^[103,104]

Figure 3.32 presents the voltage profiles of MCMB-based electrodes. In the literature, it can be seen that the majority of MCMB capacity is recovered during a long flat plateau (Figure 3.32 a)). It implies that even a small polarization of electrode can dramatically hinder the capacity of electrodes. Figure 3.32 b) represents the voltage profile of our pressed fabrics. Here, the transition between stage IV, stage III and stage II can be clearly observed. One can also notice a polarization of electrodes, even at low current densities. This polarization is responsible for the weak recovered capacity through de lithium dendrite formation. It can

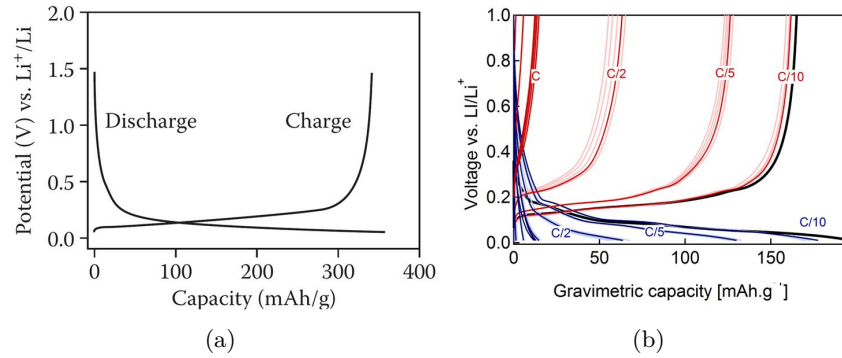


Figure 3.32 – Voltage profiles of MCMB-based electrodes: a) MCMB electrode as reported by^[105] and b) MCMB-MWCNTs fabrics (90:10 wt. %) pressed at 3 t.m^{-2} cycled at C rate versus lithium metal electrode with 10 mV cut-off voltage.

be assumed that the active materials undergoes a rapid degradation due to the formation of lithium dendrites. The phenomena of growth, and dissolution of lithium dendrites, and dead lithium residues occurs at potential close to zero vs Li/Li^+ and is mainly responsible of graphite electrode degradation.^[106]

Subsequent tests were realized with two electrodes pressed under 3 t.m^{-2} aiming to determine the lifespan of graphite electrodes. These electrodes were produced with the same composition as previously described. Electrodes were cycled at a 10 mV cut-off voltage at C rate (Figure 3.33). The first thing to notice is that an average capacity of 150 mAh.g^{-1} was recorded for five hundred cycles for both sample. That is not in accordance with the previous results (Figure 3.31) The recorded gravimetric capacity are significantly higher in the second experiment. We can therefore emit a doubt on reproducibility of experiments. At potential close to 0 V *vs* Li/Li^+ , just a small local overpotential on electrodes can drastically change recorded performances. Going back to results presented on Figure 3.33, we can observe that capacity remains constant over 500 cycles over 27 days. This proves the stability of

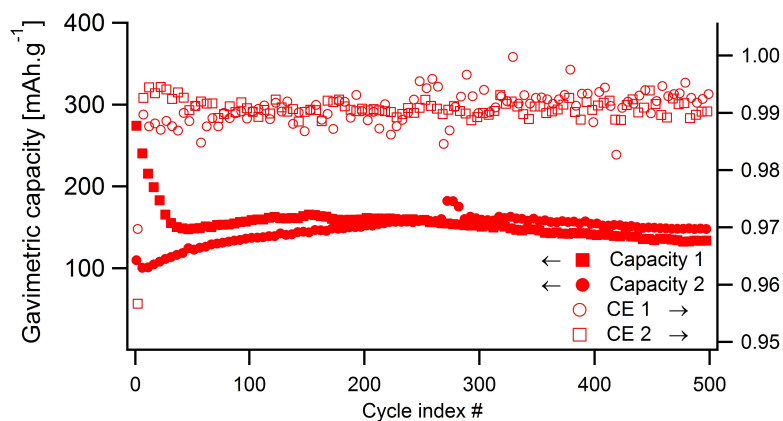


Figure 3.33 – Cycle stability evaluation of two different MCMB-MWCNTs electrodes (90:10 wt. %) pressed 6 t.m^{-2} : evaluation of capacity retention and coulombic efficiency at 1 C rate over 500 cycles in half-cell configuration versus lithium metal electrode.

MCMV-MWCNTs electrodes over time. The coulombic efficiencies were constant and recorded above 0.99. This traduces a good behavior of electrodes during operation with no major parasitic reactions. Nevertheless, the gravimetric capacities remains low compared to the theoretical capacity of MCMB that is 325 mAh.g^{-1} . On Figure 3.33, the capacity recorded for sample 1, rapidly decreases from 274 to 149 over the 42 firsts cycles. More experiments are needed to determine the exact cause of this lack of capacity. Nevertheless, it is likely that at low potentials, lithium plating occurs.^[106]

3.3 Conclusion

In this chapter, we have developed a fast and reliable method to repeatedly produce self-standing flexible electrodes.^[107] Unlike usual processes, this filtration method does not require toxic or costly solvents. Besides active material and MWCNTs, no chemicals are required to produce electrodes. Only butanol was used to produce electrodes and it can

be very easily recycled.

Electrochemical tests have proven that these binder-free electrodes present satisfying performances regarding rate capacity retention and cycle stability. Half-cell configuration tests have shown that both performing positive (LCO and LFP) and negative electrodes (LTO and MCMB) containing amounts of MWCNTs as low as 7–10 wt. % can be successfully produced. Several active materials were investigated in this section and all of them sustain at least hundred charge/discharge cycles without major degradation at low or intermediate current densities. However electrode performances at higher current densities have to be improved. The huge specific surface of MWCNT and the weak contact between active matter particles and MWCNTs must be taken into account. Post production treatment such as pressure applied on electrode is a very effective method to improve cohesion on fabrics.

In a second time, home-made synthesis of active matter particles was attempted. LiCoO_2 nanoparticles of high purity were successfully synthesized. Crystallographic and electrochemical analysis proved that the process envisioned to create such nanoparticles is reliable. Moreover, the size of the particles was found to reach requirements. Unfortunately, further optimization is required to avoid particle aggregation in order to enhance electrochemical performances.

Lastly, the creation of a conductive carbon-coating based on sucrose was investigated. Unfortunately, this low cost and abundant carbon precursor does not allowed to improve performances. It turned out that under mild conditions, the accordingly formed carbon layer can hardly be graphitized. Improvement of fabrics manufacturing is an easiest and less expensive way to improve electrochemical performances of MWCNTs electrodes and investigations should be pursued.

Experimental part

Materials

Lithium cobalt oxide (LiCoO_2 , LCO, 9 μm , 99.9 %), lithium iron phosphate (LiFePO_4 , LFP, 1.86 μm , 98 %), lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO, 1.9 μm , 98 %) and mesocarbon microbeads graphite powder (MCMB, 11 μm , 99.6 %) were purchased on their battery grade from MTIXTL. Butanol (HPLC grade, 99.7 % Sigma-Aldrich) was used without any further purification. Thin multiwalled carbon nanotubes NC7000 (MWCNT, av. diameter: 9.5 nm, av. length: 1.5 μm , carbon purity 90 %) were kindly provided by Nanocyl. Lithium foils (Alfa Aesar, 99.9 %) are used as reference electrode. Separator films (Celgard, 25 μm trilayer (PP-PE-PP)) are purchased from MTIXTL. A mixture of ethyl carbonate, dimethyl carbonate and diethyl carbonate 1:1:1 in volume (EC:DMC:DEC) with 1 M of lithium hexafluorophosphate was purchased from Novolyte and used as electrolyte. All components were stored under controlled atmosphere and used as received. Lithium acetate (Sigma-Aldrich, 99.95 %), cobalt(II) acetate tetrahydrate (Acros, 98 %), cobalt nitrate hexahydrate (Sigma-Aldrich, 98 %), citric acid monohydrate (Sigma-Aldrich, 99 %) ethylene glycol (EG, Fluka, p.a.) and acrylic acid (Sigma-Aldrich, 99 %). Dimethyl formamide (DMF, Sigma-Aldrich, 99.8 %), poly(acrylonitrile) (PAN, Sigma-Aldrich) and sucrose (Fisher, 99.9 %) used for carbon coating were used as received. Copper (II) nitrate trihydrate (Acros Organics, 99 %), ethylenediamine (Fluka, 99.5%), hydrazine (Sigma-Aldrich, 35 wt.%) used for copper nanowire synthesis were used as received.

Typical procedure for CNT buckypapers production

MWCNTs were dispersed in a large amount of butanol (typically 10 mg / 250 ml) using ultrasonic bath for 15 minutes. Dispersions were vacuum filtered on hydrophobic PVdF 0.22 μm filters using a Millipore

set-up. MWCNT buckypapers were first dried in ambient air at room temperature for 24 hours, then at 60 °C under vacuum for 48 hours.

Typical procedure for electrode production

Cathodes were prepared by dispersing variable amounts of MWCNTs and active matter particles (LCO or LFP) in 250 ml butanol using ultrasonic bath for at least 15 minutes. Anodes were prepared in the same way by dispersing variable amounts of MWCNT and active matter particles (LTO or MCMB) in 250 ml butanol using ultrasonic bath for at least 15 minutes. Dispersions were vacuum filtered on hydrophobic PVdF 0.22 μm filters using a Millipore set-up. Electrodes were first dried in ambient air at room temperature for 24 hours, then at 60 °C under vacuum for 48 hours. Electrodes were stored at 60 °C under vacuum for 48 hours and utilized in the days after production. For longer storage, fabrics were stored in argon-filled glove-box.

Typical procedure for LiCoO_2 particles synthesis

Lithium acetate (1 g, 15.16 mmol, 1.02 eq.), cobalt acetate tetrahydrate (3.7 g, 14.85 mmol, 1 eq.) and citric acid monohydrate (4.77 g, 22.74 mmol, 1.5eq.) were dissolved in a 20 ml vial containing 15 ml of mQ water. To help dissolution, the vial was sometimes heated at 50 °C. Ethylene glycol (1.265 ml, 22.74 mmol, 1.5 eq.) was added and the solution was stirred for 2 hours for a complete homogenization. The solution was poured in an aluminum pan and heated at different temperature to complete evaporation of solvent and gelation of the solution. The gel was then calcined at different temperatures for different times. Typically, samples were heated at low temperature (200 °C - 400 °C) for 1h to 2h to form solid particles. Then, samples were calcined at higher temperature (500 °C - 800 °C) for 1h to 5h to convert LT phase to HT phase. The obtained black solid was crushed using a planetary ball miller.

The same procedure was followed with cobalt nitrate hexahydrate as cobalt precursor and acrylic acid as gel precursor.

Typical procedure for carbon coating of LiCoO_2 particles

A stock solution was prepared by dissolving sucrose (500 mg) in 500 ml of mQ water. LiCoO_2 particles (1 g) were suspended in 10 ml of a mix ethanol/water (3:1). The appropriate amount of sucrose solution was added to reach the desired weight LiCoO_2 /sucrose ratio (0.1 - 5 wt. % sucrose). The solvent was evaporated under reduce pressure. The obtained black solid was milled and calcined at 600 °C for 10 minutes.

Swagelock cell assembly

Cells were assembled in Swagelock cells purchased from X2Labware (Figure 3.34). Metallic current collectors of Swagelock cells (item 1) were cleaned under ultrasound in acetone and RBS alkaline detergent successively. Teflon bodies of Swagelock (item 6) cells were cleaned in a piranha solution for 1 hour. All parts were dried under vacuum at 60 °C overnight. All cells were assembled under argon atmosphere (<0.1 ppm H_2O , <0.1 ppm O_2) in a MBraun glovebox. Cells were assembled in half-cell configuration with lithium metal foil as reference and counter electrode (item 5). Analyzed element (MWCNTs buckypapers or MWCNTs-active materials electrodes) are represented as item 3. Trilayer (PP-PE-PP) Celgard films were employed as separator (item 4).

Electrochemical characterizations

Electrical conductivities 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. Film thickness was measured using a Draper Expert digital micrometer.

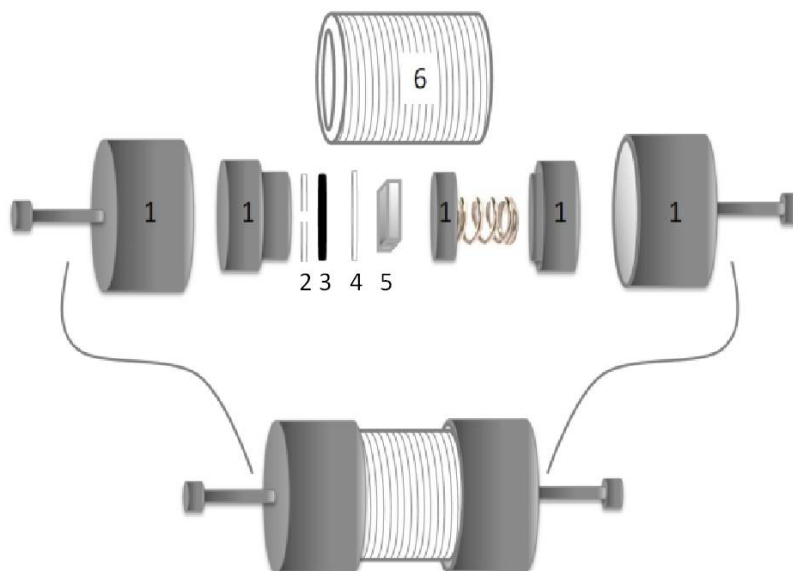


Figure 3.34 – Swagelock cell in half-cell configuration: 1) stainless steel current collectors, 2) optional insulating layer with a pinhole, 3) working electrode, 4) separator, 5) lithium reference electrode and 6) teflon body.

Cyclic voltammetry was carried out on a CHI660b potentiostat between 0 V and 5 V. Scanning rates were set as 0.1 mV.s^{-1} and 1 mV.s^{-1} .

Cycling stability and cycling performances were assessed using an Arbin BT2043 test station. LCO cathodes were cycled between 3.0 V and 4.2 V (**vs.** Li/Li^+) at various rates (0.05 C – 10 C). LFP cathodes were cycled between 3.0 V and 4 V (*vs.* Li/Li^+) at various rates (0.05 C – 10 C). LTO anodes were cycled between 2.0 V and 1.0 V (*vs.* Li/Li^+) at various rates (0.05 C – 10 C). MCMB anodes were cycled between 1.0 V and 0.02 or 0.01 V (*vs.* Li/Li^+) at various rates (0.05 C – 10 C).

Electrochemical impedance spectroscopy measurements were carried out on a CHI660b potentiostat by applying an AC voltage of 5 mV in

the frequency range of 0.1 Hz to 100 kHz.

Scanning Electron microscopy and EDX analysis

Morphologies of binder-free electrodes and carbon nanotubes bucky-papers were observed by scanning electron microscopy on a JEOL JSM-7600F microscope operated at voltages ranging between 5 kV to 30 kV. Energy dispersive X-ray spectroscopy analyses were performed on the same equipment operated at 30 kV.

Transmission electron microscopy

TEM images were obtained with a LEO 922 OMEGA energy filter transmission electron microscope operating at 200 kV. Nanowires samples were suspended in dichloromethane under ultrasonic treatment, then a drop of the supernatant was deposited on a holey carbon film supported on a copper grid, which was dried overnight at room temperature before analysis.

X ray diffraction

XRD patterns were obtained on a Siemens D-5000 powder diffractometer using Ni-filtered Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$). Measurements were performed at a rate of 0.02 deg.s^{-1} from 2 to 70 degrees.

X-ray phototelectron spectroscopy

XPS analyses were carried out at room temperature with a SSI-X-probe (SSX 100/206) photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocus Al X-ray source. The samples were held in place on small sample holders with double-sided adhesive tape and then placed on an insulating home-made ceramic carousel (Macor, Switzerland). Charge effects were avoided by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale was calibrated with reference to the Au 4f7/2 peak

at 84 eV and the binding energies were calculated with respect to the C-(C,H) component of the C 1s peak fixed at 284.8 eV. Data treatment was performed with the CasaXPS program (Casa Software Ltd., UK). The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

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CHAPTER 4

Separators and electrolytes design

Abstract

Herein, we designed and characterized separators and hybrid composite polymer electrolytes based on poly(ethylene glycol). At first cellulose nanofibers were produced by oxidation of fibers. Composite separators based on nanofibers and nanoparticles were designed and characterized. In a second time a series of poly(ethylene glycol) was grafted on silica nanoparticles. Electrolytes including modified silica nanoparticles as well as cellulose nanofibers were produced. Their electrochemical performances were evaluated and their mechanical behavior assessed.

4.1 Cellulose nanofibers-based separators

4.1.1 Cellulose nanofibers preparation

Developing a filtration process to create batteries in one single step involves the use of dispersable nanomaterials. In this context, use of commercial polyolefin-based separators is not possible. With the objective to stick to low cost and environmentally friendly materials, we adopted cellulose as base material. This material and its derivatives are an emerging viable route toward the development of green composite materials and processes for lithium ion battery manufacturing.^[1,2] Over the last 10 years, integration of nanocelluloses fibers in electrodes, electrolyte and separators has attracted an ever increasing attention.^[3–5] The search of abundant, renewable polymer sources available worldwide

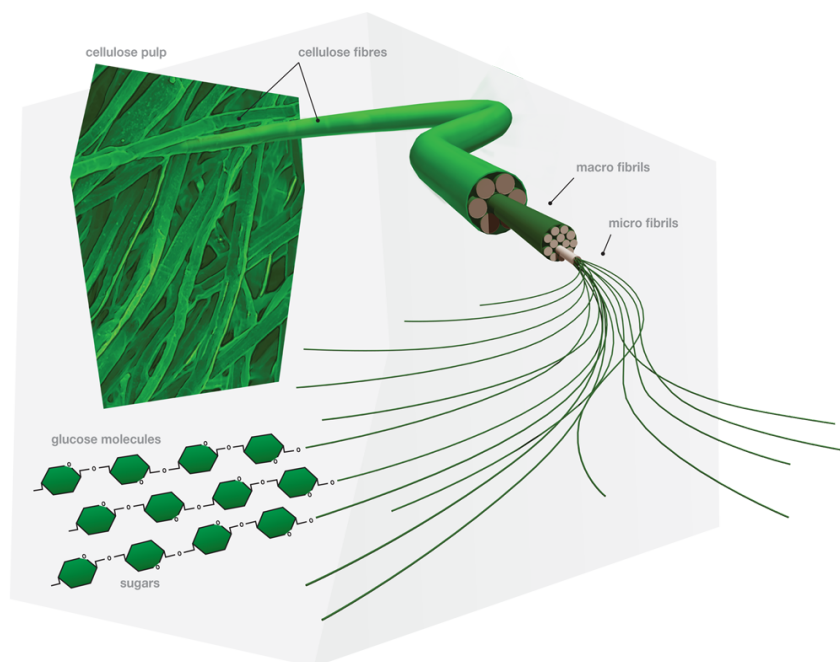


Figure 4.1 – Structure of cellulose: a) Cellulose fibers, b) macrofibers c) nanofibers composed of bundles of cellulose chains.

is the major reason. Cellulose is composed of fibers of different degree of organization. Therefore it exists many types of fibers: from cellulose micrometric fibers (CMFs) to cellulose nanofibers (CNFs) (Figure 4.1).

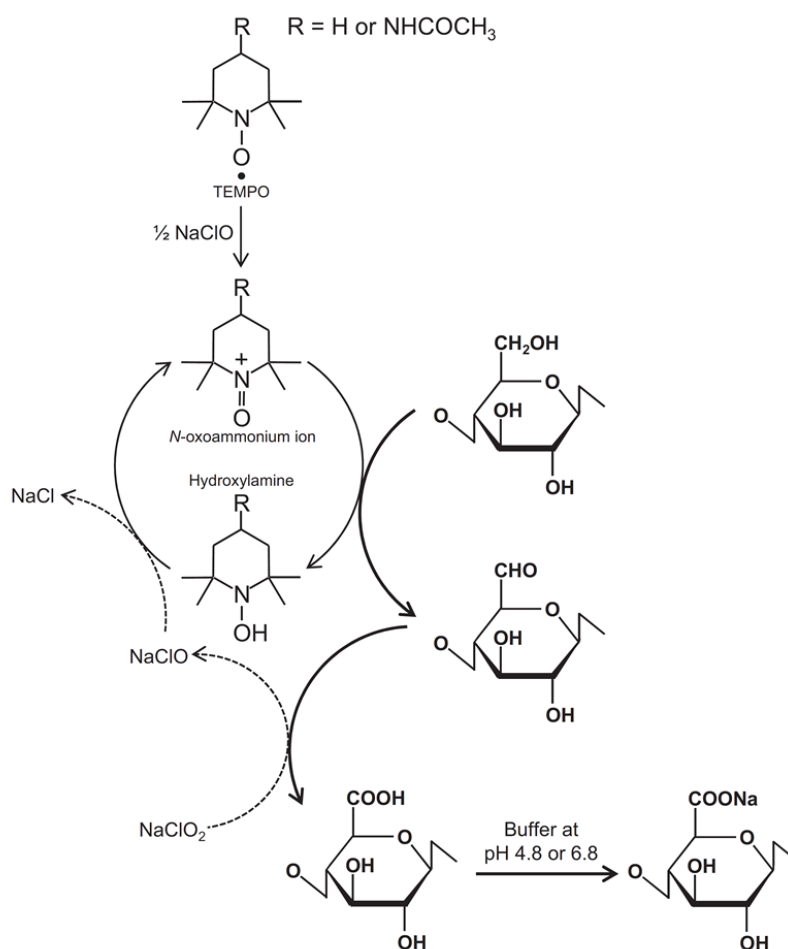


Figure 4.2 – Catalytic oxidation of cellulose hydroxyls groups to carboxylates by the TEMPO/NaClO/NaClO₂ system under neutral conditions. Reproduced from^[6].

First trials to produce cellulose nanofibers have been made with cellulose nanopowders from Sigma-Aldrich. This cellulose form is produced from cotton linters and was selected due to its high purity. Nevertheless we found that this microcrystalline cellulose was not appropriate for this experiment. Indeed, SEM analyses revealed that this material rather takes the form of cellulose microsphere than fibers. For this reason, it was preferred to choose a less purified cellulose source. Never dried soft wood pulp was obtained from Domsjö Fabriker AB in Örnsköldsvik, Sweden. This pulp is manufactured using mechanical, semi-chemical or fully chemical methods on softwoods. The moisture content of the pulps was evaluated by evaporation of 5 sample. The softwood pulp still contains more than 70 wt. % water. The latter is necessary to prevent aggregation of fibers which is difficult to subsequently break.

Cellulose nanofibers were produced by catalytic oxidation of cellulose fibers contained in never dried soft wood pulp (Figure 4.2). In a first step, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) is used as catalyst with NaClO as oxidant. Alcohol moieties of cellulose fibers are oxidized into aldehyde functions. Subsequently, NaClO₂ oxidizes the aldehyde functions into carboxylic acid groups while producing NaClO. These chemical reactions follow an optimal course in an aqueous phosphate buffer at pH 6.8. Under these neutral conditions, carboxylic acids are deprotonated to form carboxylates along the cellulose fibers. The reaction is allowed to continue for 72 hours at 60 °C to maximize the carboxylate content of fibers. Later, fibers are washed with distilled water and methanol. Oxidized fibers are later dispersed in water and pH was set at 10 with LiOH 1M. The oxidized cellulose nanofibers are finally individualized under sonication. Electrostatic repulsions of glucuronate units are responsible of this individualization of CNFs (Figure 4.3).

Cellulose nanofibers are finally collected by filtration and concentrated via successive centrifugations. The produced nanofibers can be stored for an indefinite period but should not be fully dried. Completely

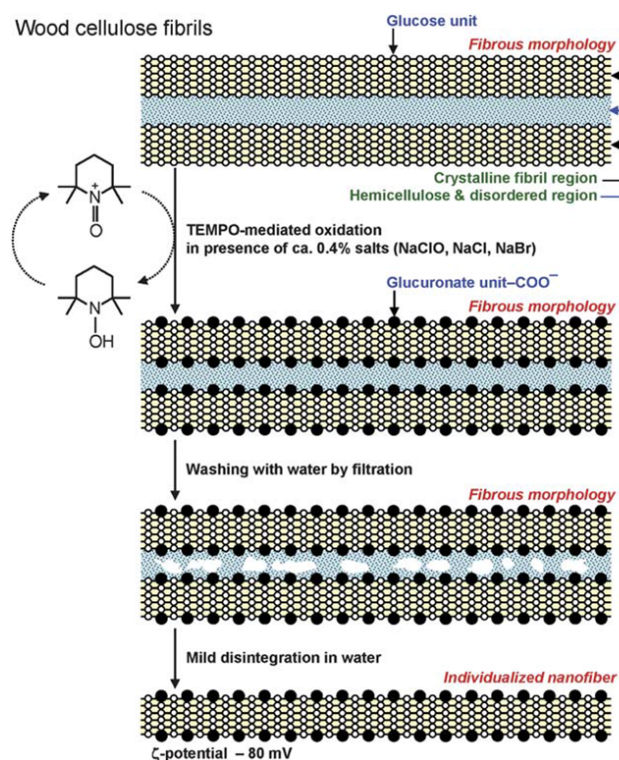


Figure 4.3 – Schematic model of cellulose nanofibers individualization by electrostatic repulsion of glucuronate units. Reproduced from [7].

drying the cellulose nanofibers leads to the formation of cohesive hydrogen bonds between neighboring fibers. The dried fibers are later very difficult to disperse. Therefore, it was decided to keep a minimum of water in the sample (approximately 300 % of the fiber weight). The production of cellulose nanofibers with this method was previously described in the literature.^[6–8] Mild reaction conditions are necessary to prevent depolymerization of cellulose fibers as the polymerization degree is an important factor to control the length, flexibility and resistance of the formed cellulose nanofibers.^[9] Cellulose nanofibers were dispersed in water and spin-coated on silicon substrate. Figure 4.4 shows AFM images of the prepared cellulose nanofibers. In this case, one can notice a

complete individualization of cellulose nanofibers. It is hard to evaluate the length and diameter of fiber based on this image but fibers length do not exceed a micron. It is difficult to get more interesting informations from the phase image. In some cases, it is possible to have mechanical informations of the analyzed sample. Unfortunately, the set-point amplitude ratio (r_{sp}) used for these images is 0.7. The (r_{sp}) corresponds to the ratio between set-point amplitude and the free oscillation amplitude. At such a light tapping, the hard and soft parts of materials show similar phase shift close to zero.^[10] To improve length of collected cellulose nanofibers, sonication time was later adapted to reduce cellulose nanofiber degradation. Figure 4.6 presents TEM images of the produced cellulose nanofibers. Analysis reveals that the individualized cellulose nanofibers display a width of 5 nm and a length of few microns.

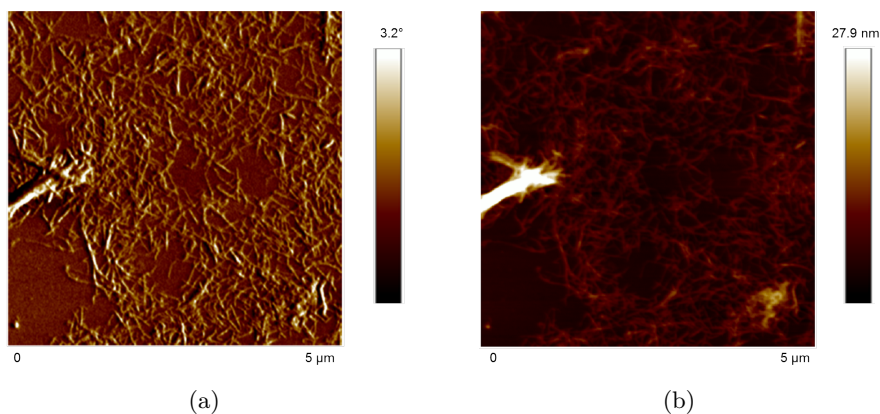
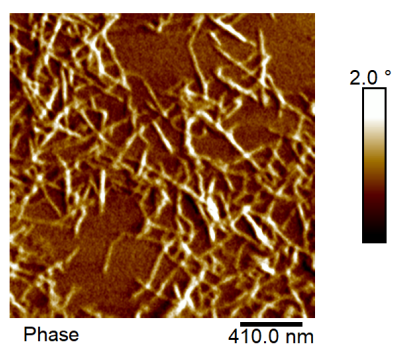
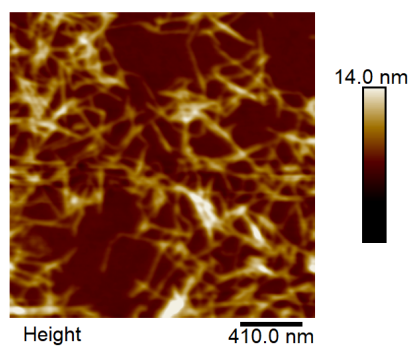


Figure 4.4 – AFM images of cellulose nanofibers produced by defibrillation of cellulose wood pulp by the TEMPO/NaClO/NaClO₂ system under neutral conditions : a) phase contrast image, b) topography image.



(a)



(b)

Figure 4.5 – Enlargement AFM images of cellulose nanofibers produced by defibrillation of cellulose wood pulp by the TEMPO/NaClO/NaClO₂ system under neutral conditions : a) phase contrast image, b) topography image.

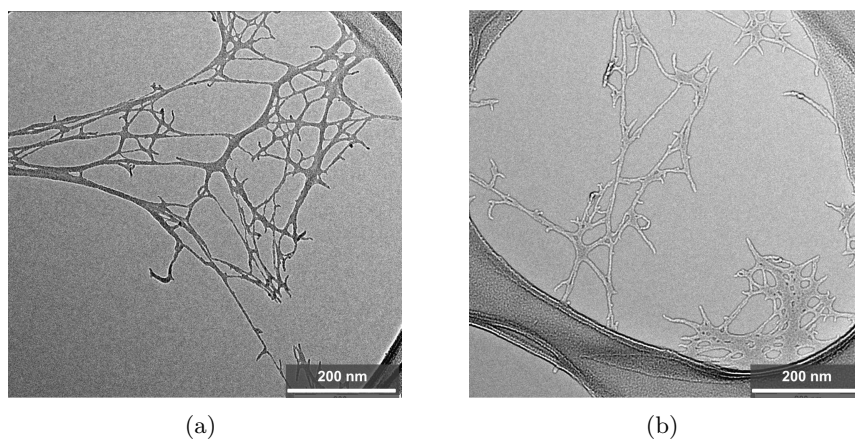


Figure 4.6 – TEM images of cellulose nanofibers produced by defibrillation of cellulose wood pulp by the TEMPO/NaClO/NaClO₂ system under neutral conditions.

4.1.2 Cellulose nanofibers composite separators

Separators were created by filtration under reduce pressure of a dispersion of cellulose nanofibers and silica nanoparticles in methanol. CNFs provide mechanical resistance to the separators while SiO_x NPs act as fillers and provide some porosity to separators.^[11] During the filtration process, nanofibers are able to form a network, which is consolidated upon drying by the formation of cohesive hydrogen bonds between neighboring fibers. The number of inter-fiber contact nodes and hydrogen bonds are therefore two important parameters that define the composite paper mechanical properties. Various compositions were investigated and a 50 % - 50 % weight ratio was preferred. The process produces flexible 25 μm thick composite separators (Figure 4.7). The equal proportion of CNFs and SiO_x NPs leads to fabrics that are easy to peel off from the PVdF filters and could be manipulated without any risk to break. Separators were then dried for 24 hours at 60 °C to remove solvent traces before further characterizations. AFM images of the separator surface were recorded to verify the homogeneity of fabrics (Figure 4.8). Individual silica nanoparticles or aggregates are not visible in the sample. This traduce a homogeneous repartition of components in the composite. As previously discussed, the phase shift between different part of the image is close to 0°. Therefore, it is difficult to draw conclusions about the soft and hard part of material.^[10]

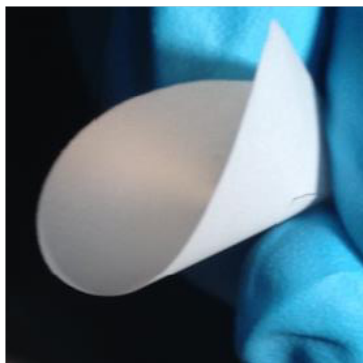


Figure 4.7 – Picture of a composite separator produced by the filtration of cellulose nanofibers and silica nanoparticles in equal proportions (10 mg: 10 mg).

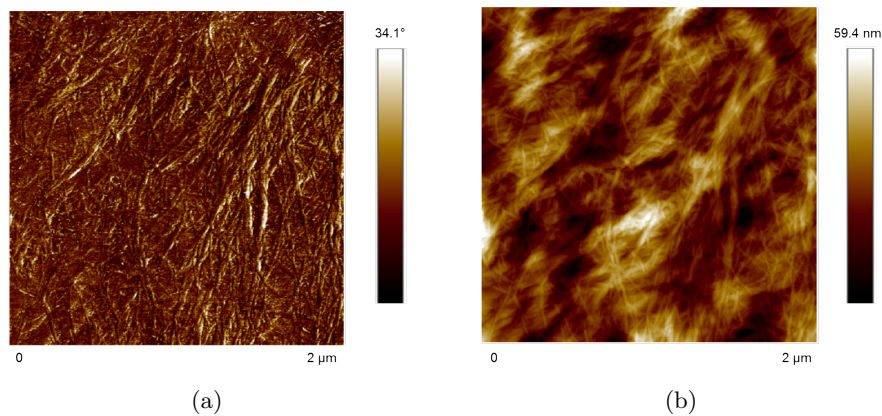


Figure 4.8 – AFM image of the surface of a composite cellulose nanofibers-based separator (CNF:SIO_xNPs 50:50): a) phase contrast image, b) topography image.

Electrochemical characterizations of cellulose-based separators were performed to assess compliance with lithium-ion battery technology. First, electrical insulating properties were verified via 4-probe measurements. Separators were then assembled in a half cell configuration in Swagelok cells. Electrochemical inertness of separators was verified in a 0.5 V - 4 V window using cyclic voltammetry (Figure 4.9). No major redox phenomena were detected during the first cycles. The only noticeable current elevation is a reduction peak located at 1 V. This corresponds to the formation of SEI on cellulose fibers. No redox peak was observed after first cycle, proving its compatibility with lithium-ion technology. Similar results were observed for bacterial cellulose separators developed by Jiang et al.^[12] The produced cellulose-based separator can therefore be used in the manufacturing of 4 V class lithium ion batteries.^[13–15]

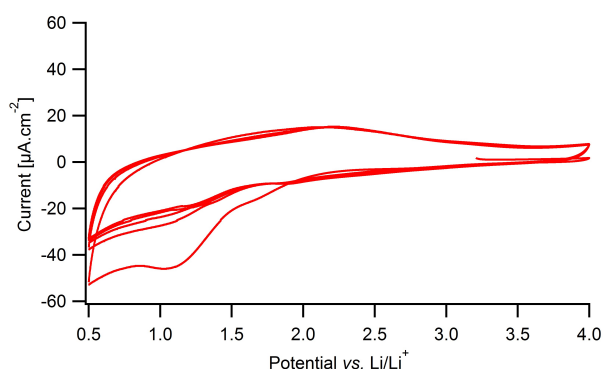


Figure 4.9 – Cyclic voltammograms of a composite cellulose nanofibers-based separator (CNFs:SIO_xNPs 50:50) recorded at 1mV.s⁻¹ in the 0.5 V - 4 V range.

Lastly, the compatibility with liquid electrolytes was verified to ensure the proper operation of future batteries. Separators were soaked in a mixture of liquid electrolytes (EC/DEC/DMC 1:1:1 in volume with 1M LiPF₆) and assembled in Swagelok cells. Electrochemical impedance spectroscopy was performed on these test cells as well as on cells containing commercial separators. The average ionic conductivity of cells

prepared with cellulose-based separators was evaluated at 2.83×10^{-4} S.cm⁻¹ while ionic conductivity of cells containing commercial separators was evaluated at 3.68×10^{-4} S.cm⁻¹. Therefore, no significant differences are noticeable which means that porosity is sufficient and wettability and compatibility with liquid electrolytes is established. Utilization of these composite cellulose nanofibers-based separators can therefore be considered for lithium-ion battery manufacturing.

4.2 Poly(ethylene oxide)-based electrolytes

As previously mentioned, among solid polymer electrolytes, poly(ethylene oxide) is the best material envisioned for lithium ion batteries. PEO can be seen as a soft, flexible solid while it still presents ionic conductivities up to 10^{-4} S.cm⁻¹.^[16] As previously explained, the ionic conductivity is strongly related to the molecular arrangement of PEO chains. Hence, everything should be implemented to decrease crystallinity of the polymer. As mentioned, a first way to break the crystalline is the doping by lithium salt addition. A second efficient way to promote the amorphous phase of PEO electrolytes is the addition of solid nanoparticles. These two strategies were investigated to develop a performing flexible solid electrolyte. Lastly, cellulose nanofibers were incorporated in composite polymer electrolytes to strengthen the structure and improve the mechanical behavior of composite electrolytes.

4.2.1 Poly(ethylene oxide) electrolytes

A high molar mass poly(ethylene oxide) was first selected to screen the ionic conductivity of PEO solid films. PEO_{400k} was selected to obtain self-standing films with good mechanical properties. An appropriate amount of PEO_{400k} was dissolved in acetonitrile for 48 hours at 50 °C to provide a 3.33 wt. % solution. Different amounts of LiClO₄ were dissolved into the solution to produce samples with the targeted ethylene oxide unit/lithium ion molar ratios (EO/Li⁺). Lithium perchlorate was

preferred to other lithium salts for its relative stability against water.^[17] A library of PEO_{400k}-LiClO₄ solutions was created, with EO/Li⁺ ratios varying from 30 to 5. Solutions were subsequently casted on aluminum pan and solvent was slowly evaporated under vacuum. Controlling the solvent evaporation rate was an important parameter to ensure film integrity and absence of bubbles and defects. This method provided a large collection of PEO_{400k}-LiClO₄ films. The samples presented different aspects regarding their salt concentration. Samples with the lowest salt concentration (EO/Li⁺ > 20) produced dry solid translucent films with good mechanical resistance and were easy to manipulate (Figure 4.10 (a)). Increasing the salt concentration produced solid polymer films that progressively turned to some sticky jelly transparent films (Figure 4.10 (b)). These films could hardly be manipulated without risks of breaking.



Figure 4.10 – PEO_{400k} films with different LiClO₄ concentrations obtained by evaporation of a DMF solution:

- (a) low LiClO₄ concentration (EO/Li⁺ = 20) resulting in highly crystalline translucent films,
- (b) high LiClO₄ concentration (EO/Li⁺ = 5) resulting in jelly-like transparent films.

The progressive loss of mechanical properties as well as transition between translucent to transparent optical properties is explained by the decrease of crystallinity. This transition between semi-crystalline PEO

films and amorphous PEO films can be tracked by optical microscopy imaging. Figure 4.11 clearly shows the evolution in the PEO film morphology and structure. Images of samples with high EO/Li⁺ ratio exhibit crystalline structures separated by amorphous regions (Figure 4.11 b)). The small pores visible on micrographs are caused by evaporation of acetonitrile during the film formation process. The increase of salt loading in samples induces a decrease of crystallization of PEO. This can be observed on Figure 4.11 c). This sample presents a relative smooth surface without major evidence of any crystalline structures. In Figure 4.11 d), PEO film is fully transparent and parallel stripes which are part of the structure of aluminum support are visible. The transition between the semi-crystalline state and amorphous state of polymer could also have been observed in DSC studies by the loss of a peak located in the 60 °C - 65 °C region. These results are coherent with previously studied PEO-lithium salt electrolyte films.^[18]

In order to evaluate the ionic conductivities of the SPEs, EIS is a powerful tool and was performed on PEO electrolyte samples. PEO films were punched at the appropriate size and inserted between two polished copper electrodes. EIS spectroscopy was conducted under a 20 mV perturbation in the 1 Hz - 1 MHz range. By sweeping a wide frequency range, different processes in the cell with different time constants can be observed and interpreted. To interpret the results of the electrochemical impedance spectroscopy, two equivalent electrical circuits were considered depending on the surface topography of the films (Figure 4.12). The difference of film surface smoothness is important in the electrochemical properties study. As described in Figure 4.12, films with a smooth surface do not interact the same way with electrodes as films with a rough surface. The first equivalent circuit is called simplified Randles cell (SRC) and is used in most of the cases to investigate electrolytes ionic conductivity. The second equivalent circuit integrates an additional capacitance C_{int} and an additional resistance R_{int} . These

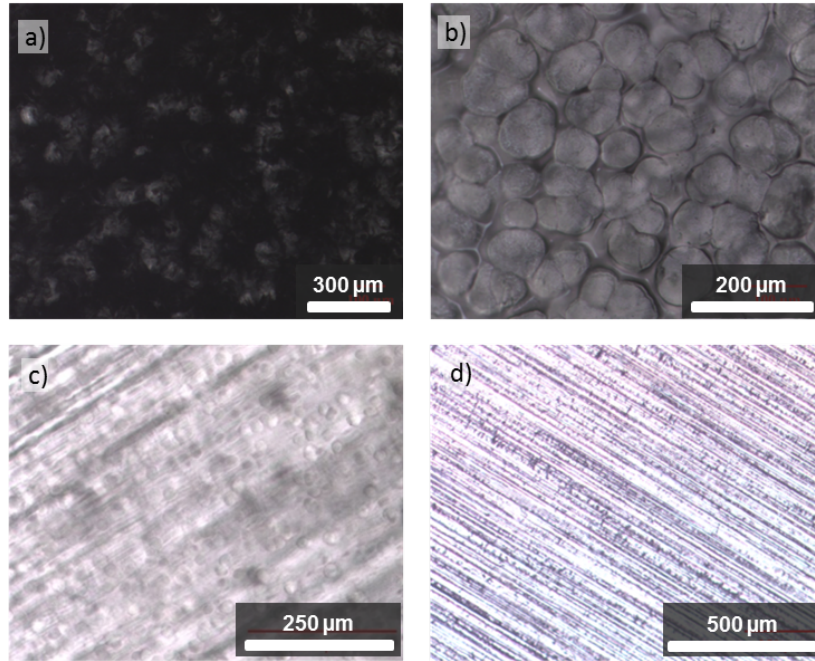


Figure 4.11 – Transition between solid PEO_{400k} film and jelly-like PEO_{400k} film by optical microscopy imaging:
a) $\text{EO}/\text{Li}^+ = 20$, b) $\text{EO}/\text{Li}^+ = 15$, c) $\text{EO}/\text{Li}^+ = 12$ and d) $\text{EO}/\text{Li}^+ = 10$.

additional components reflect the difference in cohesion between copper electrodes and electrolyte leading the creation of an interfacial capacitance.

Results of the EIS measurements for PEO_{400k} films are presented in the form of a Nyquist plot (Figure 4.14). In such a plot, the imaginary part (Z'') of the complex impedance of an electric circuit is plotted as a function of its real part (Z'). Figure 4.14 shows the recorded Nyquist plots of PEO films of different EO/Li^+ ratios. No significant difference can be noticed in the profiles. These profiles consists in a semi-circle and 45° slope. These are typical from a simplified Randles cell (SRC) and can be assimilated to this equivalent circuit (equivalent circuit 1 in Figure 4.12). Profiles corresponding to the second equivalent circuit

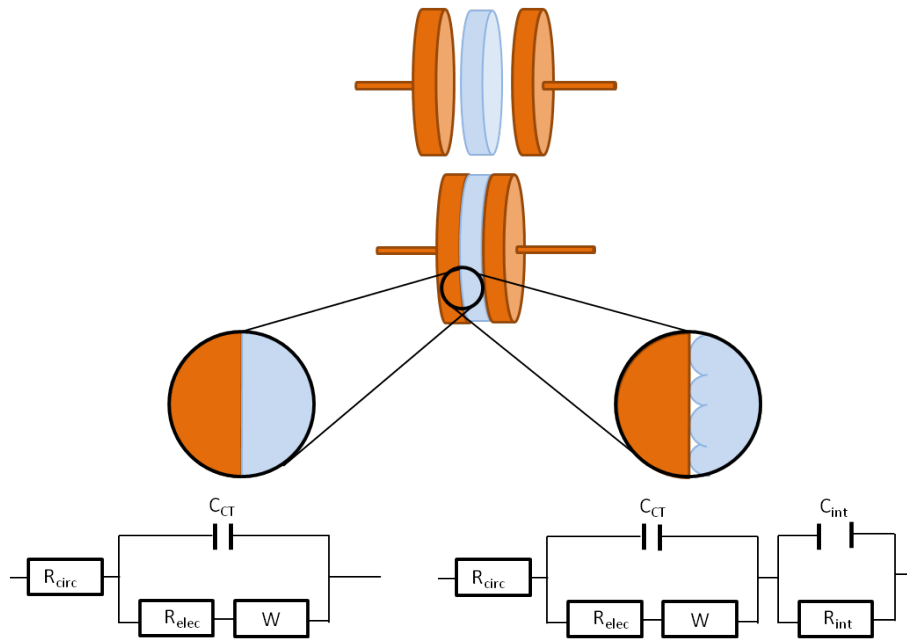


Figure 4.12 – Interface contact of PEO films with electrodes depending on their lithium salt concentration and the two resulting possible equivalent circuits : a) Simplified Randles Cell equivalent circuit, b) Modified Randles Cell equivalent circuit integrating interfacial capacitance.

should present a second semi-circle. Randles circuit is an equivalent electrical circuit composed of four elements. An electrical resistance (R_{circ}) that represents Swagelok cell and wire electrical resistance. A double-layer capacitance (C_{CT}) that can be assimilated to the charge transfer. A resistance (R_{elec}) representing ionic electrolyte resistance and a Warburg resistance (W) corresponding to the mobility of ions at high frequencies. This equivalent circuit is one of the simplest possible models use to describe response of electrolytes and the most often used in literature

In Figure 4.14 every pattern presents a semicircle ascribed to the ionic resistivity (R_{elec}) of the electrolyte. The diameter of the semicircle represents the value of ionic resistance (R_{elec}) (Figure 4.13). The ionic conductivity can be easily calculated using Ohm's law. Electrolyte samples were assimilated as discs of known diameter and thickness At high frequencies a 45° slope can be ascribed to Warburg impedance and represent the diffusion of lithium ions on a very short distance. R_{circ} represents the electrical resistance of the Swagelok set-up and is not visible on these Nyquist plots. R_{circ} values correspond to the first intersection of the semicircle with the x-axis. Introduction of a second capacitance corresponding to an imperfect interface would have resulted in the appearance of a second consecutive semi-circle due to the introduction of a second time constant. It was verified with simulation software such as Matlavl and Autolab frequency response analyser that the integration of an interfacial capacitance has an negligible effect. Therefore, all recorded curves can be assimilated to the first equivalent circuit suggested in Figure 4.12.

This study was reproduced for a poly(ethylene glycol) with a Mw = 2000 g.mol⁻¹. A polymer with a lower molar mass was selected to compare ionic conductivities in the same conditions. Samples with appropriate EO/Li⁺ ratio were created. The short length of the polymer chains makes the film even more difficult to manipulate. PEG-LiClO₄

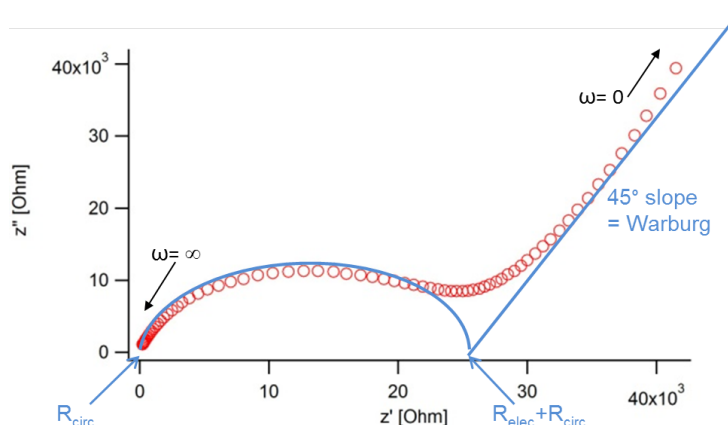


Figure 4.13 – Electrochemical impedance spectroscopy of electrolyte: interpretation of Nyquist plot by a simplified Randles cell equivalent circuit.

samples were therefore directly poured onto Swagelok electrodes. A ring made of polyethylene was used as spacer to prevent shortcuts and secure a constant thickness during measurements. Prior any further electrochemical characterization, electrolytes were controlled with a resistivity higher than $10^6 \Omega \cdot \text{cm}^{-1}$ using a multimeter.

Figure 4.15 present the average calculated ionic conductivities of PEO_{400k} and PEG_{2k} films with different lithium salt concentration. The measurements plotted in figure 4.15 represents the average of three consecutive measurements of the same sample. Dispersion of measurements was low with a maximum of $\pm 19\%$ for samples of high salt concentration. This amplitude corresponds to a maximum of $4.4 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. The higher dispersion of high salt concentration sample can be explained by their jelly-liquid behavior. The transition between semi-crystalline to amorphous PEO films visible in Figure 4.11 is here translated in terms of ionic conductivity. At EO/Li⁺ ratio higher than 20, polymer films exhibit ionic conductivities close to $10^{-7} \text{ S} \cdot \text{cm}^{-1}$. These values are clearly not sufficient to consider these samples as electrolytes despite their interesting mechanical properties. From EO/Li⁺ ratios between 20 and

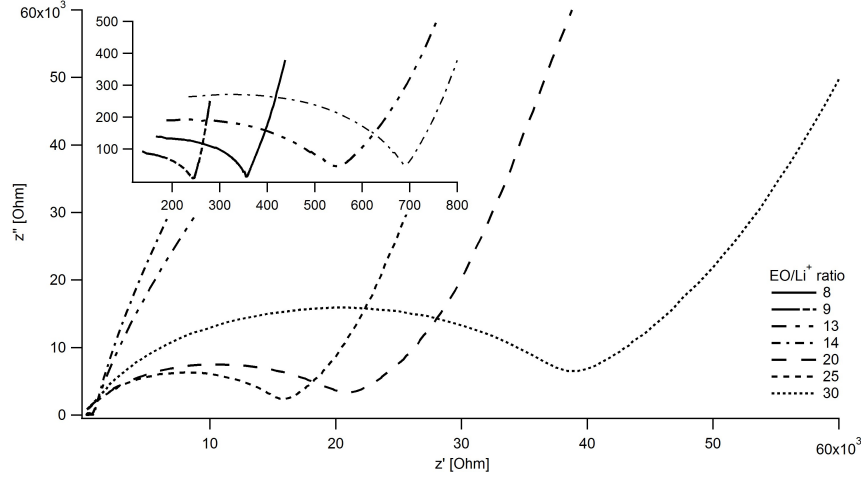


Figure 4.14 – Nyquist plot of EIS performed on PEO_{400k} film of different lithium concentration. Measurements were recorded under a perturbation of 5 mV.

15 EO/Li⁺, one can notice a gradual increase of ionic conductivity to reach values of $6.59 \times 10^{-6} \text{ S.cm}^{-1}$ for PEO_{400k} films and $9.98 \times 10^{-6} \text{ S.cm}^{-1}$ for PEG_{2k} films at a EO/Li⁺ ratio of 12.5. Ionic conductivities up to $2.37 \times 10^{-5} \text{ S.cm}^{-1}$ were recorded for samples with EO/Li⁺ ratio of 9. At higher salt load, the ionic conductivity tends to decrease due to the crystallization of lithium salt.^[19] No major differences in ionic conductivities could be noticed between samples made of PEO_{400k} and the ones made of PEG_{2k}. The recorded ionic conductivities are in good agreement with literature.^[20–23] At room temperature, it is difficult to reach fully satisfying ionic conductivities for polymer electrolytes. Ionic conductivities close to $10^{-3} \text{ S.cm}^{-1}$ can be reached at temperature higher than 65 °C.^[24] However, at these temperatures, mechanical properties are degraded and operation safety of batteries may be compromised.

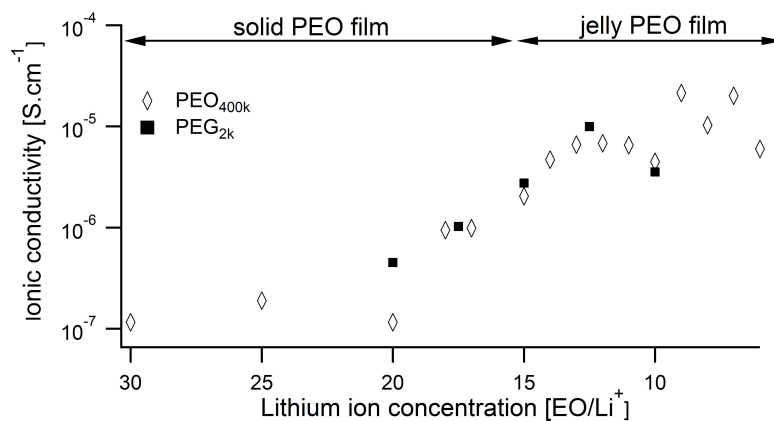


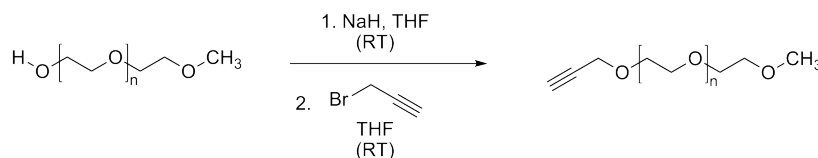
Figure 4.15 – Lithium ion concentration dependence of the ionic conductivities for PEO_{400k}-LiClO₄ and PEG_{2k}-LiClO₄ films.

4.2.2 Grafting of poly(ethylene glycol) on silica nanoparticles

With the objective to improve the mechanical behavior of polymer electrolytes while preserving ionic conduction properties, the incorporation of silica nanoparticles (SiO_xNPs) was investigated. SiO_xNPs can create a three dimensional network inside the electrolyte that prevents the viscous flow of polymer chains. That provides the required mechanical strength to design solid electrolyte for flexible batteries.^[25,26] Click chemistry was used to graft polymer on silica nanoparticles. Sharpless defines the term “click chemistry” as follows: click reactions as the reaction must be modular, wide in scope, give very high yields, generate only inoffensive byproducts that can be removed by nonchromatographic methods, and be stereospecific (but not necessarily enantioselective).^[27] During this thesis, the copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) was selected as a tool to graft alkyne-functionalized mPEG onto the surface of SiO_xNPs modified by azido groups. Grafting polymers on silica nanoparticles will help anchorage and strengthen mechanical properties of electrolytes.

4.2.2.1 Alkyne functionalization of poly(ethylene glycol)

Poly(ethylene glycol) monomethylether (mPEG) of various molar weight in masses ($M_w = 2000, 5000$ and 20000 g.mol^{-1}) were selected to be grafted on silica nanoparticles. These polymers are henceforth referred as mPEG_{2k}, mPEG_{5k} and mPEG_{20k}. In a first step, poly(ethylene glycol) backbones were tailored by an alkyne to form an appropriate partner of click reactions. The three different polymers (1 eq.) were allowed to react with propargyl bromide (4 eq.) in presence of sodium hydride (4 eq.) following scheme 4.1. All procedure details are reported in the experimental section.



Scheme 4.1 – Synthesis scheme of alkyne-functionnalized mPEG.

The strong base NaH is able to deprotonate the hydroxy end group of mPEG chains to form a highly nucleophilic alkoxide. The elater is allowed to react with propargyl bromide to form the corresponding propargyl ether. Alkyne-functionalized mPEGs were subsequently purified by double precipitation in cold diethyl ether. Functionalization and purity were assessed by ^1H NMR and FTIR characterizations.

^1H NMR spectra before and after alkyne-functionalization of mPEG are presented in Figure 4.16. Pristine mPEG_{2k} presents three typical signals: a multiplet centered at 4.05 ppm represents the 2 protons H_c of α -methyl, a multiplet centered at 3.85 ppm arising from the methylene represents protons H_d and lastly a signal centered at 3.59 ppm from the three H_e protons of the ω -methoxy group. After alkyne functionalization, peaks corresponding to protons of the mPEG backbones (H_c , H_d and H_e) are shifted to lower values. This was attributed to the change of solvent. Furthermore, two additional peaks corresponding

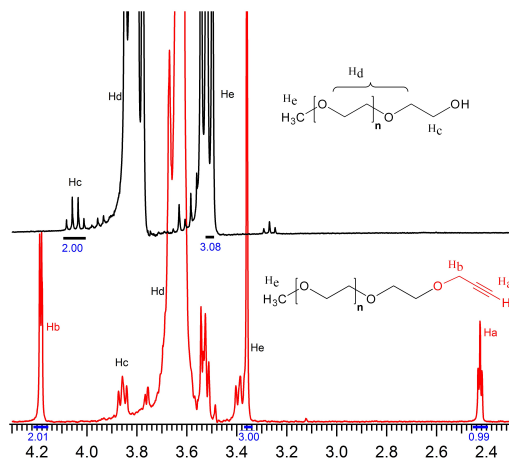


Figure 4.16 – ^1H NMR spectra of mPEG_{2k} and α -propargyl-mPEG_{2k} synthesized as previously described.

to the α -propargyl protons are observed in alkyne-functionalized mPEG. The triplet centered at 2.42 ppm corresponds to the H_a protons of the alkyne group while the doublet signal displayed at 4.19 ppm is attributed to H_b protons. Calculated ratios of tail groups demonstrate the complete functionalization of mPEG by propargyl bromide into α -propargyl mPEG.

The chemical structure of mPEG and of the corresponding α -propargyl mPEG was verified by FTIR analysis. Figure 4.17 presents the recorded traces of mPEG_{2k} and its derivative. In the later, the characteristic vibration band of the terminal alkyne $\equiv\text{C-H}$ appears at 3246 cm^{-1} . The disappearance of the absorption peak centered at 3468 cm^{-1} corresponding to the hydroxyl group confirms the complete transformation of mPEG_{2k} into alkyne-functionalized mPEG_{2k}.

Table 4.1 presents the yields of purified functionalized products obtained with respect to the three different types of mPEG. As it can be observed, there is a gradual yield increase as chain length increases. This noticeable increase can be explained by the lower solubility of longer

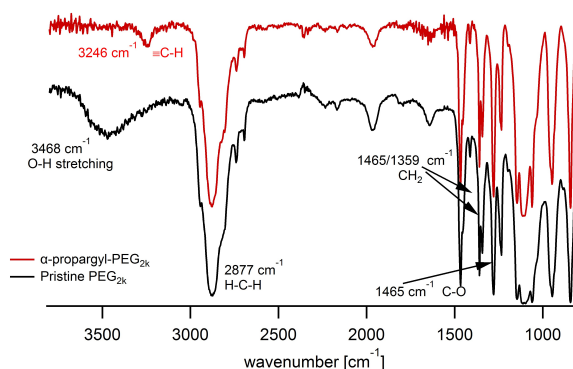


Figure 4.17 – FTIR spectra of mPEG_{2k} and α -propargyl mPEG_{2k} synthesized as previously described.

	Yield
α -propargyl mPEG _{2k}	73 %
α -propargyl mPEG _{5k}	75 %
α -propargyl mPEG _{20k}	85 %

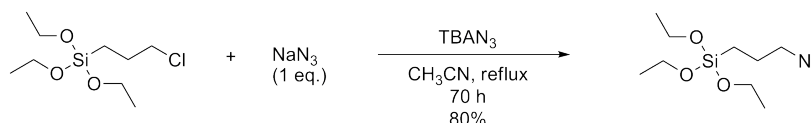
Table 4.1 – Yields for different α -propargyl mPEG synthesized as previously described.

polymer chains. As the purification process involves a double precipitation in bad solvent (cold diethylether), larger amounts of the longer polymer chains are collected.

4.2.2.2 Synthesis of (3-azidopropyl)triethoxysilane

The second clickable precursor prepared is the (3-azidopropyl)triethoxysilane (TEOSC₃N₃). This silane was preferred among others chlorosilanes or acetoxysilanes because of its higher stability to moisture.^[28] (3-azidopropyl)triethoxysilane was synthesized by a nucleophilic substitution reaction on (3-chloropropyl)triethoxysilane (TEOSCl) (1 eq.) by sodium azide (1 eq.), as described by Mader *et*

al.^[29] All procedure details are reported in the experimental section. TEOSC₃N₃ was prepared by reacting TEOSCl with sodium azide in refluxing degassed acetonitrile under inert atmosphere (scheme 4.2). The product was collected in the form of a colourless oil with a 80% yield.



Scheme 4.2 – Synthesis scheme of clickable silane (3-azidopropyl)triethoxysilane.

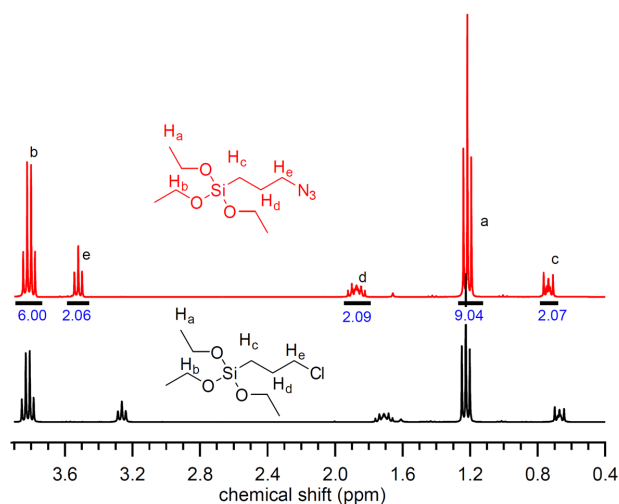


Figure 4.18 – ¹H NMR spectra of TEOSCl and the corresponding TEOSC₃N₃ synthesized as previously described.

Figure 4.18 compares the ¹H NMR spectra of the unreacted TEOSCl and the TEOSC₃N₃ product. This brings in light the shift of signal for protons H_c, H_d and H_e. Those three shifted signals correspond to protons of the hydrocarbonated moiety of the silane which are deshielded due to the presence of the highly electron withdrawing group N₃. This shows the substitution of chloride by azide which attracts electrons and

so deshielded the neighboring protons. Integration of the H_e and H_b protons gives a ratio of 0.34 indicating a total conversion of the TEOSCl to TEOSC_3N_3 .

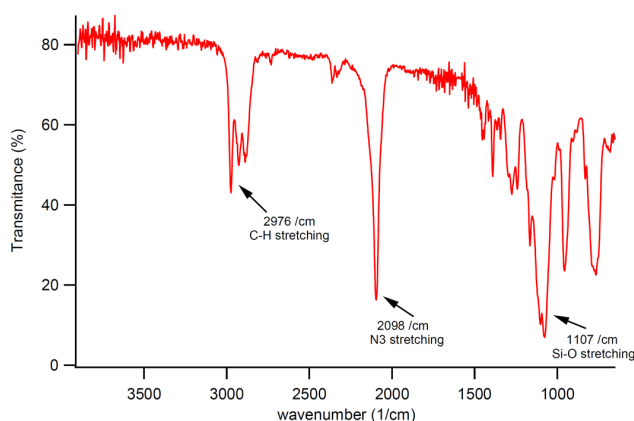
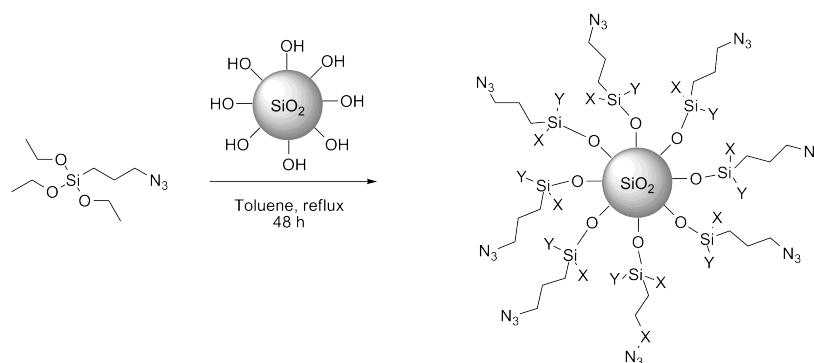


Figure 4.19 – FTIR spectrum of TEOSC_3N_3 .

Figure 4.19 presents the FTIR spectrum of the prepared TEOSC_3N_3 . A strong absorption peak at 2098 cm^{-1} is visible. The latter is attributed to the azide function, confirming the formation of (3-azidopropyl)triethoxysilane.

4.2.2.3 Azido-functionalization of silica nanoparticles

The previously prepared TEOSC_3N_3 compound was subsequently grafted on pristine silica nanoparticles (SiO_xNPs) to produce azido-functionalized silica nanoparticles. The followed process was inspired from procedures described by Mader *et al.* and Ortega *et al.*^[29,30] Silica nanoparticles were dispersed in dry toluene and were allowed to react for 48 h under refluxing conditions with TEOSC_3N_3 following the strategy displayed on scheme 4.3. All procedure details are reported in the experimental section. Grafting of the clickable silane on SiO_xNPs produces azido-functionalized SiO_xNPs later referred as $\text{SiO}_x\text{NPs@N}_3$. The efficiency of the functionalization was verified by FTIR and XPS analysis.



Scheme 4.3 – Synthesis scheme of azido-functionalized silica nanoparticles.

Figure 4.20 presents the FTIR spectra of pristine SiO_xNPs and the corresponding $\text{SiO}_x\text{NPs@N}_3$. The appearance of peaks located at 2925 cm^{-1} and 2105 cm^{-1} respectively reveals the presence of hydrocarbons and azide functions in the structure of the product. The flat plateaus in the $1000\text{ cm}^{-1} - 1200\text{ cm}^{-1}$ region are attributed to saturation of the detector due to Si-O bounds. The proper azide moiety grafting on SiO_xNPs was confirmed by XPS characterization. The composition of the surface of pristine SiO_xNPs and their azide functionalized analogous $\text{SiO}_x\text{NPs@N}_3$ is compared in Table 4.2

Analysis of pristine SiO_xNPs reveals a slight amount of carbon (2.21 at. %) at the surface of nanoparticles. This presence was attributed to contaminants remaining after synthesis of SiO_xNPs . The Si/O ratio measured for pristine SiO_xNPs is close to the theoretical ratio. After reaction with the clickable azide, a peak centered at 402 eV appears. The later was attributed to the presence of 2.39 at. % nitrogen atoms at the surface of modified SiO_xNPs . Nevertheless, the carbon/nitrogen ratio recorded was 3.96/1. This is not in agreement with a total reaction of ethoxy groups of TEOSC_3N_3 . A C/N ratio of 1 would be expected if every ethoxy group reacted with the SiO_xNP surface. The structure of the formed functionalized SiO_xNPs is therefore difficult to describe

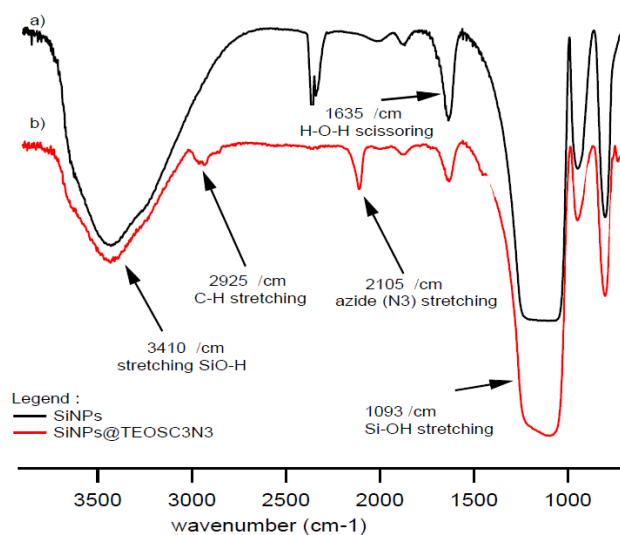


Figure 4.20 – FTIR spectra of a) pristine SiO_xNPs and b) azido-functionalized SiO_xNPs .

since a part of the carbon content can also be attributed to carbon of pristine SiO_xNPs or contamination from reactants.

	SiO_xNPs	$\text{SiO}_x\text{NPs@N}_3$
Si	32.98	31.29
O	64.81	56.94
N	0	2.39
C	2.21	9.39
O/Si	Exp.: 1.97 Th.: 2.00	Exp.: 1.82
C/N		Exp.: 3.96

Table 4.2 – Atomic concentrations (at. %) at the surface of silica nanoparticles and azido-functionalized silica nanoparticles evaluated by XPS analysis.

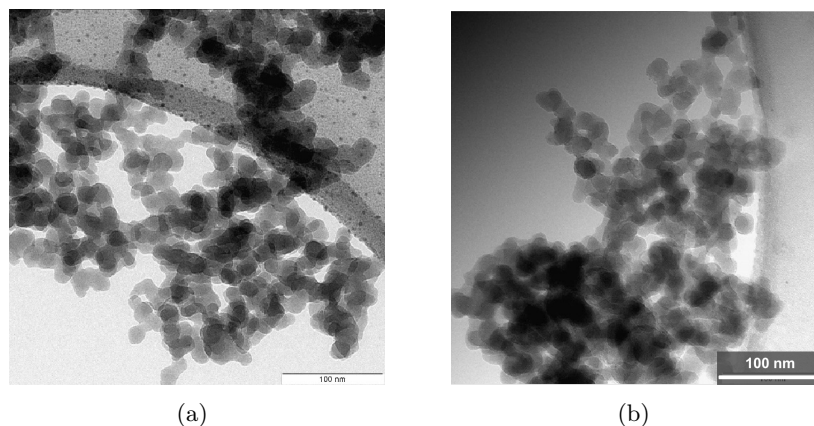


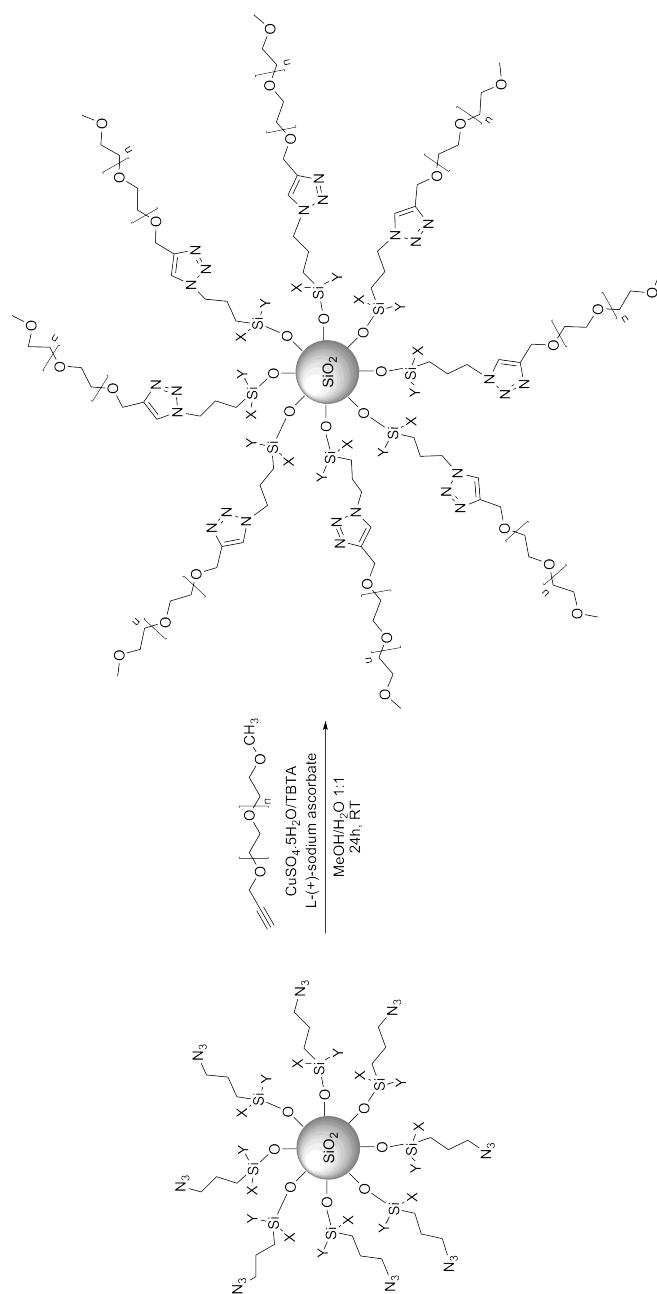
Figure 4.21 – TEM images of the evolution of silica nanoparticles morphology after functionalization: a) pristine silica nanoparticles and b) azido-functionalized silica nanoparticles.

TEM images of pristine silica nanoparticles and their azido-functionalized counterparts are presented in Figure 4.21. These images allow to confirm that the relatively strong experimental conditions used for functionalization do not alter the size or morphology of the nanoparticles. Size of 20 particles was measured using ImageJ software. The average particle size of pristine SiO_xNPs was measured at 16 nm (± 2.6 nm) while the size of their functionalized pendant was measured at 15.4 nm (± 2.2 nm). This analysis shows that particles are neither degraded nor aggregated during the synthesis process of azido-functionalized silica nanoparticles.

4.2.2.4 PEG grafting on SiO_xNPs using CuAAC

The click reaction between the two previously synthesized precursors was performed following a procedure established in the laboratory. Previously, this copper-catalyzed azide-alkyne cycloaddition reaction (CuAAC) was intensively described in literature.^[31] This cycloaddition reaction allows to create covalently bound molecules to solid surfaces^[32] as silica nanoparticles.^[33] Alkyne-functionalized polyethylene glycol (1

eq.) and azido-functionalized silica nanoparticles were allowed to react together in presence of catalyst. In this procedure, copper (II) sulfate pentahydrate (0.8 eq.) was used in combination with sodium ascorbate (1.6 eq.) to produce *in situ* the copper(I) catalyst. Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.8 eq.) was selected as the copper ligand.^[34] The reaction described on scheme 4.4 was carried out in different solvent mixtures at different temperatures in order to optimize grafting yields. PEG-grafted silica nanoparticles ($\text{SiO}_x\text{NPs@PEG}$) were subsequently collected by centrifugation and extensively washed with water and methanol. Particles were later characterized by TEM, FTIR, TGA and XPS analysis.



Scheme 4.4 – Synthesis scheme of mPEG-grafted silica nanoparticles.

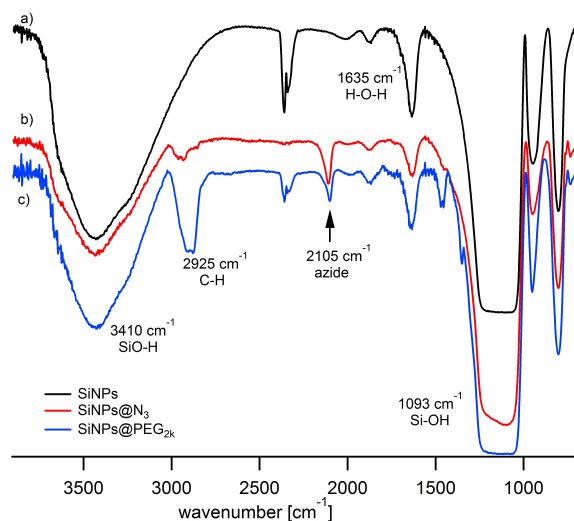


Figure 4.22 – FTIR spectra of a) pristine silica nanoparticles, b) azide-functionalized silica nanoparticles c) PEG_{2k}-grafted silica nanoparticles.

FTIR is an interesting technique to investigate the evolution of a CuAAC reaction.^[35–37] Indeed, azide and alkyne bands are easy to track by FTIR analysis, providing a way to evaluate the efficiency of the reaction. The reaction was first carried out at room temperature in a solvent mixture of water and methanol (1:1 in volume). Figure 4.22 shows the stacked spectra of pristine SiO_xNPs, azido-functionalized SiO_xNPs and PEG_{2k}-grafted SiO_xNPs prepared in these conditions. After the click reaction, one can notice the strong increase of the C-H bond stretching band observed at 2925 cm⁻¹. Simultaneously, the absorption band corresponding to azide stretching located at 2105 cm⁻¹ decreases. These observations suggest the efficient reaction between the two CuAAC partners. Nevertheless, the trace recorded for PEG_{2k}-grafted SiO_xNPs still shows evidence of unreacted azide functions. The flat plateaus in the 1000 cm⁻¹ - 1200 cm⁻¹ region are again attributed to saturation of the detector due to Si-O bounds.

To highlight the absence of non-covalently bound poly(ethylene gly-

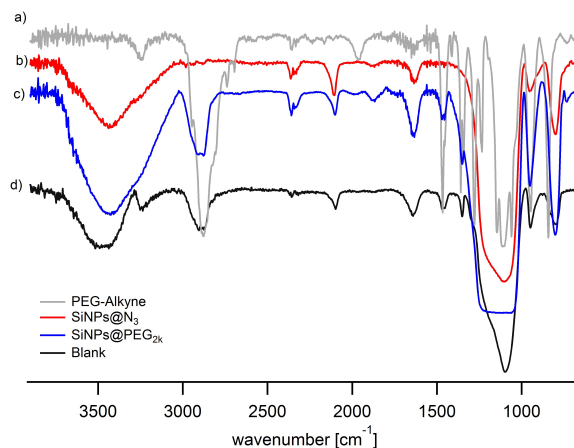


Figure 4.23 – FTIR spectra proving the absence of non-covalently bound mPEG at the surface of SiO_xNPs : a) alkyne-functionalized PEG_{2k} ; b) azido-functionalized silica nanoparticles; c) PEG_{2k} -grafted silica nanoparticles; d) blank sample.

col) at the surface of silica nanoparticles, a blank sample was prepared as control test. Alkyne-functionalized mPEG was mixed together with azido-functionalized SiO_xNPs in a 10:1 weight ratio. The recorded traces of the unreacted partners of the click reactions, PEG-grafted SiO_xNPs and the blank are presented in Figure 4.23 to bring to light the effectiveness of the reaction. Figure 4.23 clearly shows that the band at 3246 cm^{-1} attributed to alkyne is identified in the blank sample but is not visible in the PEG-grafted particles. This test demonstrates and validates the hypothesis of covalent grafting of PEG to SiO_xNPs .

Since FTIR traces on Figure 4.22 highlighted the presence of remaining azide functions on SiO_xNPs , the CuAAC reaction conditions were optimized in order to increase the grafting yield. Figure 4.24 presents the FTIR traces of PEG_x -grafted SiO_xNPs synthesized in a mixture of water, methanol and acetone (1:1:7 in volume) at 40°C . According to the recorded spectra of mPEG-grafted SiO_xNPs , no evidence of remaining azide function was detected this time. This improvement in grafting yield was attributed to a better solvation of polymer chains

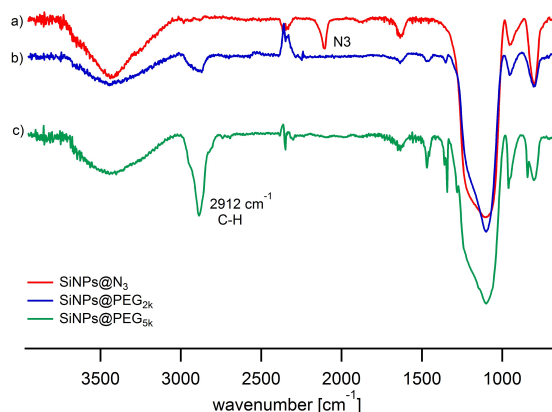


Figure 4.24 – FTIR spectra in improved reaction conditions: a) azido-functionalized SiO_x NPs, b) PEG_{2k} -grafted SiO_x NPs, c) PEG_{5k} -grafted SiO_x NPs.

in the reaction medium. In poor solvents, polymer chains grafted on the silica nanoparticles tend to create an impenetrable layer on the surface of the particle.^[38,39] Conversely, the grafted polymer chains tend to swell in good solvent and form an extended layer of stretched tethered chains (Figure 4.25).^[40] The configuration resulting from the expansion of polymer brushes maximizes the exposure of SiO_x NPs surface. Therefore, the azide sites can be more easily reached by new incoming alkyne-functionalized mPEG chains.

Thermogravimetric analysis was later conducted to evaluate the grafting yield of polymer brushes on silica nanoparticles. The collected results allowed us to compare the efficiency of grafting according to reaction conditions. TGA experiments were conducted on washed PEG-grafted silica nanoparticles. This is what allows us to think that the amount of polymer measured by TGA corresponds to grafted polymer on the surface rather than adsorbed polymer. Figure 4.26 presents the TGA records of different PEG-grafted silica nanoparticles samples as well as pristine or azido-functionalized silica nanoparticles. The recorded TGA

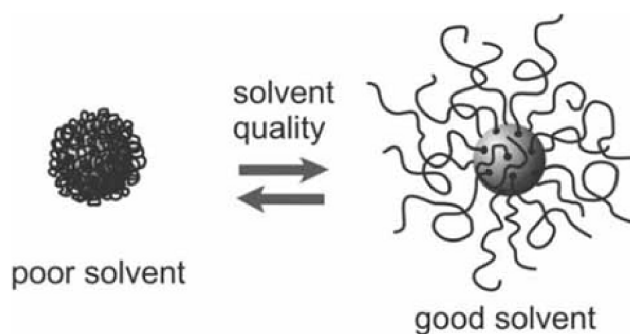


Figure 4.25 – Configuration of polymer brushes on silica nanoparticles depending on the quality of polymer solvent. Reproduced from^[40].

trace of pristine SiO_x NPs reveals a loss of 1.4 wt. % between 25 °C and 100 °C. This weight loss can be attributed to desorption of moisture or organic solvents at the surface of nanoparticles. A second weight loss of 2 % was recorded between 100 °C and 250 °C. This can be attributed to the presence of small organic molecules at the surface of nanoparticles. This analyze confirms previous XPS analysis revealing the presence of carbon traces in pristine silica nanoparticles samples. From the TGA trace of azido-functionalized SiO_x NPs, one can notice a similar weight loss at low temperatures followed by a second slow weight loss at temperature higher than 300 °C. The latter was attributed to degradation of covalently bound organic molecules at the surface of SiO_x NPs. The TGA traces of PEG-grafted SiO_x NPs samples display a major weight loss between 300 °C and 450 °C. This weight loss is attributed to grafted polymer on the surface of the nanoparticles. Table 4.3 recaps yields of grafted polymer measured by TGA analysis. For PEG_{2k} , the grafted mass of polymer was estimated at 12.2 wt. % when CuAAC was performed in the water/methanol mixture at room temperature. In contrast, the grafted mass of the same polymer was estimated at 18.5 wt. % when CuAAC was performed in a mixture of water, methanol and acetone at 40 °C. The impact of improved reaction conditions is again

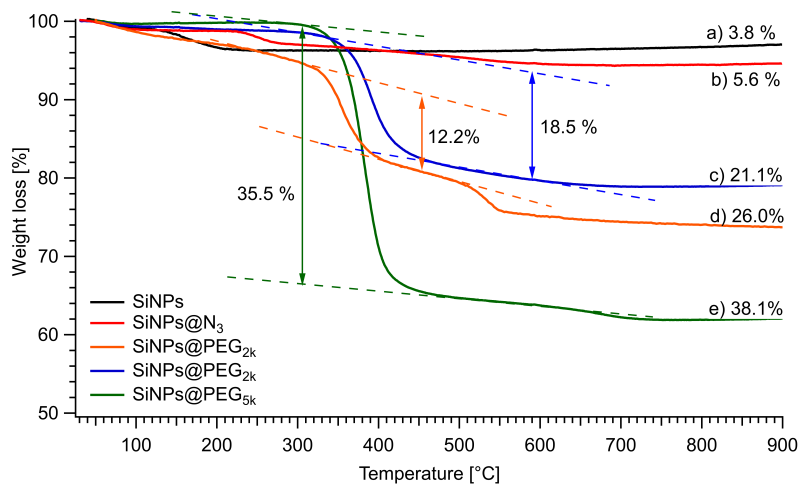


Figure 4.26 – Thermogravimetric analysis of: a)pristine SiO_x NPs, b)azido-functionnalized SiO_x NPs, c and d) PEG_{2k} -grafted silica nanoparticles and e) PEG_{5k} -grafted silica nanoparticles.

clearly noticeable. In addition, it is not surprising that the PEG content evaluated for PEG_{5k} grafted nanoparticles (35.5 wt. %) in these conditions is superior to the PEG_{2k} grafted nanoparticles. Nevertheless, the weight loss ratio between $\text{SiO}_x\text{NPs@PEG}_{5k}$ and $\text{SiO}_x\text{NPs@PEG}_{2k}$ is close to two, indicating a higher grafting yield for PEG_{2k} .

	Solvent	Temp.	Reac. Time	PEG wt. %
PEG_{2k}	$\text{H}_2\text{O}/\text{MeOH}$ 1:1	20°C	24h	10.2
PEG_{2k}	$\text{H}_2\text{O}/\text{MeOH}/\text{acetone}$ 1:1:7	40°C	24h	18.5
PEG_{5k}	$\text{H}_2\text{O}/\text{MeOH}/\text{acetone}$ 1:1:7	40°C	48h	35.5

Table 4.3 – Grafting yield of PEG on SiO_x NPs according to CuAAC reaction conditions.

Lastly, XPS analyses were exploited to access the composition of sil-

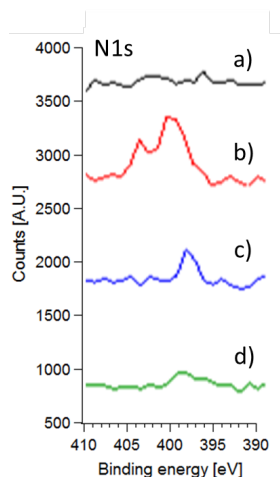


Figure 4.27 – XPS spectra of nitrogen 1s peak: a) pristine SiO_xNPs , b) $\text{SiO}_x\text{NPs}@N_3$ c) $\text{SiO}_x\text{NPs}@PEG_{2k}$ and d) $\text{SiO}_x\text{NPs}@PEG_{5k}$.

ica nanoparticles surface. The completion of the reaction can be evaluated by the evolution of nitrogen 1s peak (Figure 4.27). The double-peak structure visible in $\text{SiO}_x\text{NPs}@N_3$ is indicative of the azide group.^[41,42] A smaller peak is seen at 404.0 eV and a larger peak is observed at 400.5 eV with a ratio of 1:2 in agreement with previously reported results for azide peak location. XPS spectra of $\text{SiO}_x\text{NPs}@PEG_{2k}$ and $\text{SiO}_x\text{NPs}@PEG_{5k}$ show a single peak located at 398.9 eV. This indicates a complete reaction of azide groups during CuAAC.^[41,42] The carbon content was evaluated at 43.0 at. % and 53.8 at. % at the surface of $\text{SiO}_x\text{NPs}@PEG_{2k}$ and $\text{SiO}_x\text{NPs}@PEG_{5k}$ respectively (Table 4.4). This confirms the presence of an important organic layer at the surface of nanoparticles. The ratio of grafted PEG_{5k} compared to PEG_{2k} differs to the one calculated according to TGA analysis. XPS being a local surface analysis technique, the polymer grafting yield is difficult to establish. In addition, neither TGA analysis, nor XPS analysis allow us to assess that the grafting is completely homogeneous on particle sample.

Figure 4.28 shows TEM micrographs of the pristine SiO_xNPs and PEG-grafted silica nanoparticles. A first remark to be made is that the

silica cores of PEG-grafted particles maintain their original spherical shape. While the PEG shell is not clearly visible in the PEG_{2k}-grafted SiO_xNPs sample (Figure 4.28 b)), the presence of a polymer matrix is clearly identifiable in the PEG_{5k}-grafted SiO_xNPs sample (Figure 4.28 c)). The contrast between samples containing PEG_{2k} and PEG_{5k} is explained by the different amount of grafted polymer. Sample represented in Figure 4.28 c) contains 15 wt. % more polymer than sample represented on Figure 4.28 b). In addition, polymer chains are longer in the PEG_{5k}-grafted SiO_xNPs and they can entangle more easily with chains from other particles. The better individualization of PEG_{5k}-grafted SiO_xNPs brings in light a broader distribution of silica cores. This disparity was probably already present in previous samples but particles individualization makes it more visible. These synthesized PEG-grafted silica nanoparticles were subsequently used to prepare composite polymer electrolytes. The electrochemical performances and the mechanical behavior of these prepared CPEs were subsequently characterized.

	SiO _x NPs	SiO _x NPs@N ₃	SiO _x NPs@PEG _{2k}	SiO _x NPs@PEG _{5k}
Si	32.98	31.29	16.18	9.44
O	64.81	56.94	39.68	35.99
N	0	2.39	1.15	0.75
C	2.21	9.39	42.99	53.83

Table 4.4 – Atomic concentrations (at. %) at the surface of PEG-grafted silica nanoparticles and their precursors evaluated by XPS analysis.

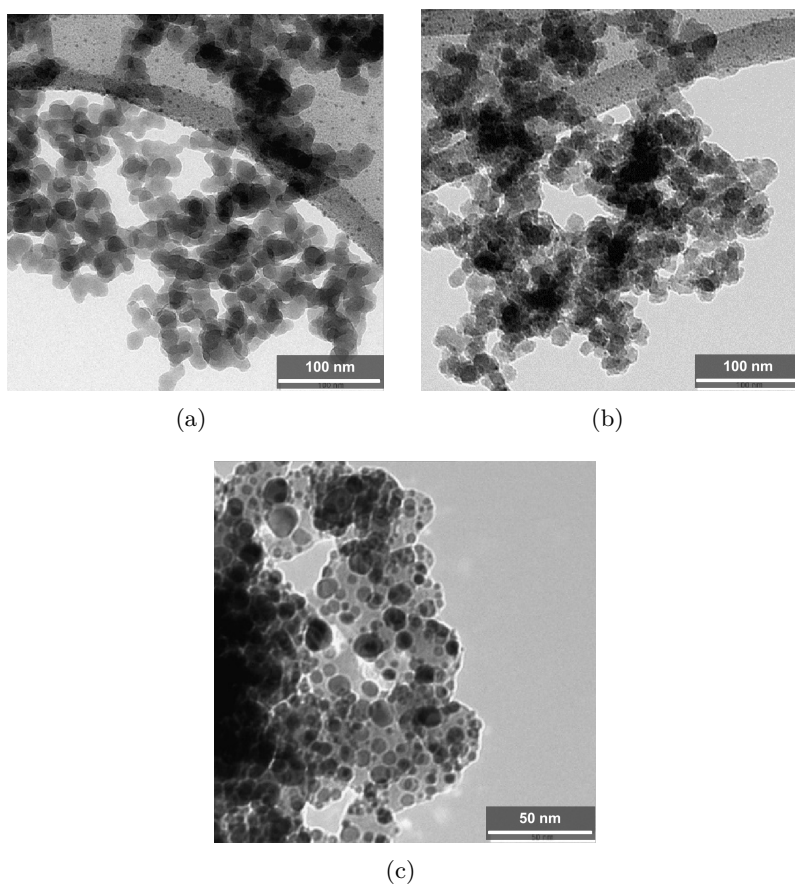


Figure 4.28 – TEM images of the evolution of silica nanoparticles morphology after PEG grafting: a) pristine silica nanoparticles, b) PEG_{2k}-grafted silica nanoparticles and c) PEG_{5k}-grafted silica nanoparticles.

4.2.3 Electrochemical characterization of PEG CPE

The previously synthesized PEG-grafted silica nanoparticles were used to prepare composite polymer electrolytes. In an ideal situation, additives should represent only a small fraction of the electrolyte. Since, the best grafting yield reached was about 36 wt. %, free PEO had to be added to reach more than 95 wt. % of PEG. Free poly(ethylene glycol) chains ($M_w = 2\,000\text{ g.mol}^{-1}$) were melted at 50 °C under stirring. An appropriate amount of pristine silica nanoparticles or PEG-grafted silica nanoparticles was added and samples were homogenized for 15 minutes at 50 °C. Samples could later be re-heated at mild temperatures to facilitate the shaping for analyses. A Swagelock setup was used as described previously to perform electrochemical impedance spectroscopy measurements. Swagelock cells were assembled, sealed and left in a vertical position for at least 3 hours to allow CPEs to relax.

Entry	EO/Li	type of SiO _x NPs	Amount of SiO _x NPs/CNFs	Ionic conductivity 10 ⁻⁶ S.cm ⁻¹
1	12.5		0	9.98
2	10		0	35.5
3	12.5	pristine	2	2.66
4	10	pristine	2	10.2
5	12.5	PEG _{2k} -grafted	2	6.4
6	12.5	PEG _{5k} -grafted	2	4.9
7	12.5	pristine	4	2.9
8	10	pristine	4	25
9	12.5	PEG _{2k} -grafted	4	8.26
10	12.5	PEG _{5k} -grafted	4	4.5
11	12.5	CNFs	2	66.8
12	12.5	CNFs	4	8.26

Table 4.5 – Compositions and measured ionic conductivities of prepared composite polymer electrolytes based on poly(ethylene glycol).

Table 4.5 summarizes the compositions of the prepared composite polymer electrolyte and their measured ionic conductivities at 20 °C. Ionic conductivities of CPEs containing pristine silica nanoparticles were evaluated for a LiClO_4 load of $\text{EO}/\text{Li}^+=12.5/1$ and $\text{EO}/\text{Li}^+=10/1$. Ionic conductivities of CPEs containing PEG-grafted SiO_x NPs were only evaluated for a LiClO_4 load of 12.5/1. The analysis of ionic conductivities for samples containing a lithium salt load of 12.5/1 reveals no significant impact of the addition of SiO_x NPs in CPE. Such a low amount of silica nanoparticles (between 2 wt. % and 4 wt. %) does not impact positively or negatively the ionic conductivity. Measured ionic conductivities of the CPE range between $2.9 \times 10^{-6} \text{ S.cm}^{-1}$ and $8.26 \times 10^{-6} \text{ S.cm}^{-1}$. This is in good agreement with literature data which report ionic conductivities between $10^{-5} \text{ S.cm}^{-1}$ and $10^{-7} \text{ S.cm}^{-1}$ for composite polymer electrolytes at room temperature. For a similar system of CPE based on silica nanoparticles and poly(ethylene oxide) (5wt. % SiO_x NPs), Shen *et al.* reported ionic conductivities of $6 \times 10^{-6} \text{ S.cm}^{-1}$ at 30 °C.^[43,44] It is important to note that the ionic conductivity can drastically increase with temperature. For example, Shen *et al.* measured ionic conductivity of $10^{-4} \text{ S.cm}^{-1}$ at 50 °C.

The electrochemical stability of electrolytes over the operating potential window of battery is of crucial importance to design electrolytes. Therefore, oxidative and reductive decomposition limits of the prepared composite electrolytes were quantified by means of cyclic voltammetry in a window of 0 to 5V (Figure 4.29). Below 0.5 V, a drop of the current can be observed on the voltammograms, especially during first cycles. This was attributed to the complex reduction reactions due to formation of a solid electrolyte interface on the lithium anode.^[45] The opposite phenomenon occurs at voltages over 4.5 V during the first cycles. No other relevant electrochemical redox process is observed between 0.5 V to 4.5 V. This analysis indicates that the PEG_{5k}-grafted SiO_x NPs based CPEs can be successfully employed for Li-ion batteries.

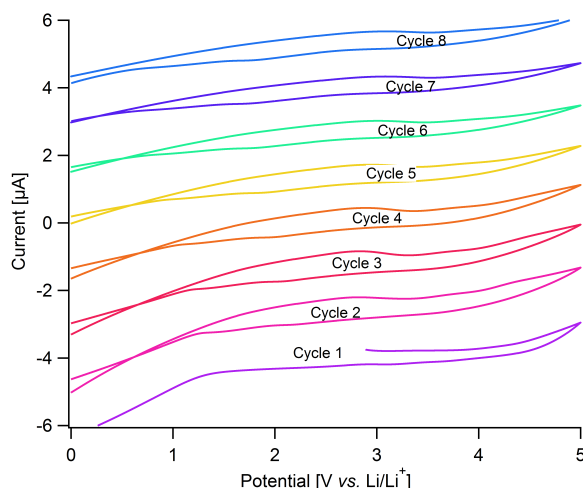


Figure 4.29 – Cyclic voltammograms of mPEG_{5k}-grafted SiO_xNPs composite polymer electrolytes (Entry 10 of Table 4.5) evaluated in half-cell configuration versus lithium metal electrode in the 0 V - 5 V range at 1 mV.s⁻¹. The curves are shifted by 2 μA for clarity

4.2.4 Mechanical behavior of PEG CPEs

Shear rheological experiments were performed on previously described composite polymer electrolytes at a controlled temperature of 20 °C. Normal forces were checked to be relaxed prior any measurement. The dynamic response of analyzed samples can be divided into two constituents: the storage (or elastic) modulus G' and the loss (or viscous) modulus G'' . The storage modulus is related to the elastic energy stored in the system on deformation. The loss modulus is linked to the viscous dissipation of energy in the system. In order to assess the mechanical properties of a polymer material in terms of the viscoelasticity behavior, it is usual to study the spectrum showing G' and G'' as a function of shear frequency.^[46] The relative magnitudes and shapes of the G' and G'' curves indicate the type and the extent of microstructure present. A profile where the G' values are higher than G'' represents a sample which possesses a strong resistance. In the ideal case, the phase lag δ

(i.e. the lag between the applied stress and the resulting deformation), is 0° . Otherwise, the system is viscoelastic, and the G'' values become greater than G' with a δ of 90° for purely viscous liquid systems.^[47]

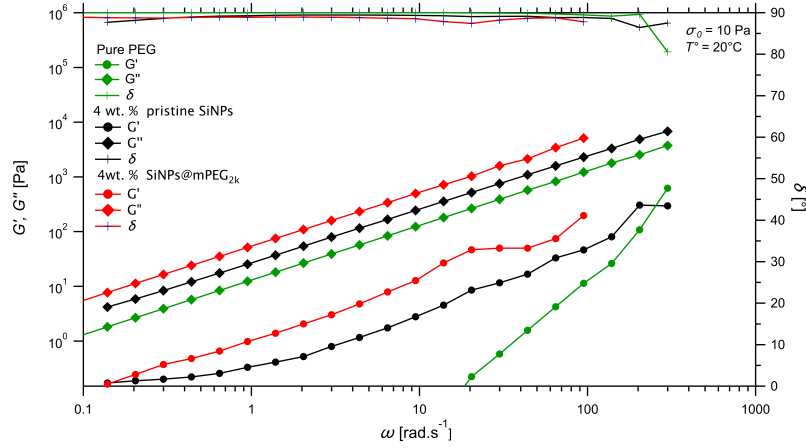


Figure 4.30 – Loss and storage moduli versus frequency of composite polymer electrolytes : a) pure poly(ethylene glycol), b) poly(ethylene glycol) with 4 wt. % of pristine SiO_xNPs and c) poly(ethylene glycol) with 4 wt. % of pristine SiO_xNPs and $\text{SiO}_x\text{NPs@mPEG}_{2k}$.

The plots of G' , G'' and δ versus shear frequency ω that are presented in Figure 4.30 compare the dynamic rheological response of pure PEG_{2k} , composite electrolytes containing 4 wt. % of pristine SiO_xNPs and composite electrolytes containing 4wt. % of PEG_{2k} -grafted SiO_xNPs . Green curves represent the pure poly(ethylene glycol) sample (Entry 1 of Table 4.5), black curves represent the sample comprising pristine silica particles (Entry 7 of Table 4.5) whereas the red symbols indicate the response of the sample involving PEG_{2k} -grafted SiO_xNPs (Entry 9 of Table 4.5). In every cases, the response is highly viscous and liquid-like, as the viscous modulus (G'') significantly exceeds the elasticity modulus (G') with both G' and G'' being frequency dependent. This tendency is in agreement with the phase lag (δ) whose value is constant over the investigated frequency range and close to 90° , characteristic of a liquid.^[47] Nevertheless, one can notice the significant increase of elastic modulus

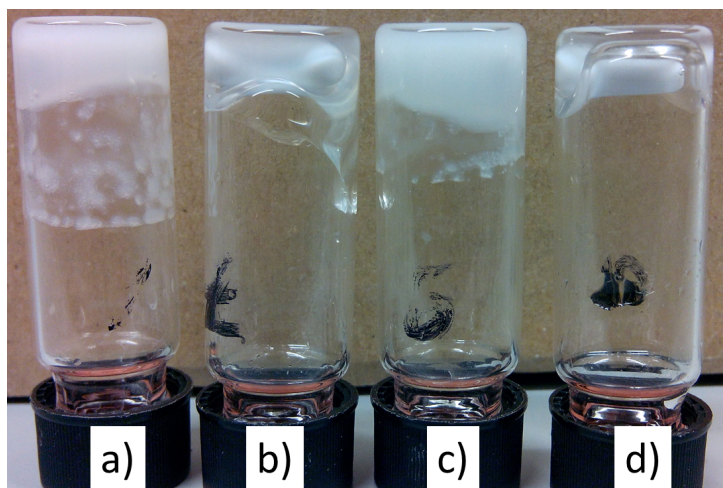


Figure 4.31 – PEO-composite electrolyte macroscopic aspect : pictures were taken 15 seconds after we turned-upside down the vial. CPE present a EO/Li ratio of 12.5 : a) CPE containing 4 wt. % of CNF , b) CPE containing 4 wt. % $\text{SiO}_x\text{NPs@PEG}_{2k}$, c) CPE containing 4 wt. % of $\text{SiO}_x\text{NPs@PEG}_{5k}$ and d) PEG electrolyte without nanoparticles.

throughout SiO_xNPs addition which is an indication of the improvement of mechanical behavior. Comparing samples reveals that PEG_{2k} -grafted SiO_xNPs CPE bears higher storage and loss moduli over the experiment than free silica nanoparticles CPE. This clue is a sign of a reinforcing effect due the grafting of PEG at the silica surface. However, the prepared composite electrolytes still exhibit a pure liquid behavior. Other studies also reported that well dispersed surface-functionalized nanoparticles influence positively the dynamics of polymers in nanocomposite materials.^[48] Macroscopically, samples sample containing 4 wt. % of $\text{SiO}_x\text{NPs@PEG}_{2k}$ and the one containing no silica particles do not behave differently (4.31 b) and d)). Once vial is turned upside-down, they rapidly start to flow on the edges of the vial. The only difference is the turbidity that can be observed in the sample containing silica nanoparticles.

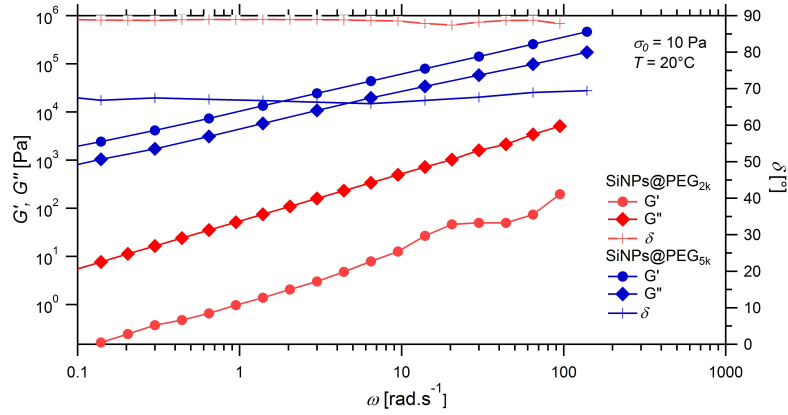
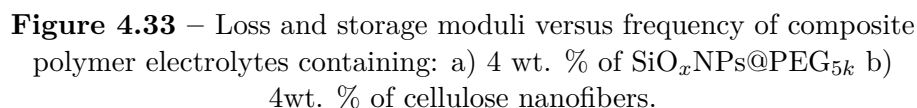


Figure 4.32 – Loss and storage moduli versus frequency of composite polymer electrolytes : Effect of chain length of PEG-grafted SiO_xNPs on rheological measurements: a) 4 wt. % of $\text{SiO}_x\text{NPs@PEG}_{2k}$ and b) 4 wt. % of $\text{SiO}_x\text{NPs@PEG}_{5k}$.

Figure 4.32 compares the dynamic rheological responses of composite electrolytes containing 4 wt. % of $\text{SiO}_x\text{NPS@PEG}_{2k}$ and 4 wt. % of $\text{SiO}_x\text{NPS@PEG}_{5k}$. In the case of PEG_{5k} -grafted nanoparticles, phase

lag was measured at a constant value of 70° . Therefore, the CPE still exhibits viscoelastic properties dominated by a liquid-like behavior due to a lack of structuration. Nevertheless the flow resistance is higher than previously prepared CPEs. Measured viscous modulus of electrolytes containing $\text{SiO}_x\text{NPS@PEG}_{5k}$ were recorded significantly higher than electrolytes containing $\text{SiO}_x\text{NPS@PEG}_{2k}$. The measured viscosity modulus is approximately three orders of magnitude higher while the measured elastic modulus is four orders of magnitude higher. These analyses indicate that a structuration is appearing but the formed network in the material is too weak to prevent polymeric flow. Nevertheless, the parallel G' and G'' curves suggest that the flow is constrained. The observed improvement of mechanical stability attests the presence of entanglements inside the composite polymer electrolyte. The explanation lies in the increased chain length of the grafted polymers. Poly(ethylene glycol) is known to exhibit a critical molar mass for chain entanglement around 1850 g.mol^{-1} .^[49,50] The strength of the structure is due to the presence of these connectivity points between the constituents.^[51–54] To exhibit elastic properties, a PEO-based material requires a minimum of 3 to 4 entanglements per strand.^[55] It may be therefore more cautious to talk about hydrodynamic effects than a real nanostructuration of material for this composite polymer electrolyte.^[56] An increase in the number of entanglements should lead to a more structured material.^[53] This can be achieved by an increase of the grafted PEG chain length or an increase of the PEG-grafted particles proportion. Figure 4.31 c) presents the macroscopic behavior of the CPE containing 4 wt. % $\text{SiO}_x\text{NPs@PEG}_{5k}$. At the opposite of the previous samples, CPE does not flow as easily on the edge of the vial. The traces of CPE on the edges of the vial are due to the *préparation* of CPE and its cooling. This time, CPE is completely opaque.

Composite polymer electrolytes were also created by addition of cellulose nanofibers into a poly(ethylene glycol) matrix (Entry 11 and 12



of Table 4.5) The dynamic rheological response of cellulose fiber-based composite is displayed on Figure 4.33. This time, the behavior expressed by the CPE is typical from a rubbery material with a strong structuration as the elastic response dominates at low frequencies. The material still undergoes irreversible deformations as the polymer strands are free to move but chains are more constraint in their movements. At higher deformation frequencies, a more intense response can be observed as the material does not have the time to adapt to constraint. This CPE can therefore be assimilated as a soft matrix supported by a robust scaffold. Integration of CNFs that possess superior mechanical properties^[57] created a structuration inside the material thanks to their morphology. The charge density at their surface helped their dispersion and decreased their clogging tendency.^[58] Figure 4.31 presents the macroscopic behavior of the CNF-based CPE. Once again, we can see that after 15 seconds, the CPE does not flow on the edges of the vial. The traces of CPE on the edges of the vial are still due to the préparation of CPE and its cooling. Use of cellulose nanofibers as mechanical reinforcement can be considered as a promising concept to build composite electrolytes.^[59]

4.3 Conclusion

In a first step, cellulose nanofibers were successfully individualized from soft wood pulp. The selected process allowed us to produce a reasonable amount of CNFs. The produced nanofibers were successfully integrated in composite separators using a filtration process. The produced fabrics were subsequently electrochemically characterized. It has been established that composite separators fully meet the requirements of lithium-ion battery separators.

In a second step, poly(ethylene glycol) of different molar masses were successfully grafted on silica nanoparticles. The efficiency of PEG grafting was verified by different characterization techniques. The obtained $\text{SiO}_x\text{NPs@PEG}$ were later included in the preparation of composite polymer electrolytes. Electrochemical characterizations of composite polymer electrolytes allowed us to establish their compatibility with lithium-ion battery technology. The prepared CPEs are electrochemically stable and their ionic conductivities are sufficient to integrate them in 4 V class battery.

Lastly, mechanical behavior of composite polymer electrolyte was investigated. It was demonstrated that the incorporation of a slight amount of $\text{SiO}_x\text{NPs@PEG}$ in polymer electrolyte improved their mechanical properties. It has been highlighted that the length of the polymer chain grafted on silica nanoparticles was an important factor to strengthen the electrolyte. Later, CPE including cellulose nanofibers were prepared. In this case, CPE can therefore be seen as an ion conducting polymer matrix supported by a cellulose nanofibers scaffold. It was established that 4 wt. % of cellulose nanofibers improved drastically the mechanical behavior of prepared electrolytes. Nevertheless, prepared CPE are still subject to flow because polymer chains are still free to move. Therefore, application in flexible batteries are comprised as this kind of batteries suffer severe mechanical stress. Reticulation of CPE of inclusion of a solid separator is hence required.

In order to improve further mechanical properties of and synthesize a fully solid state electrolyte able to sustain intense mechanical stress, a three dimensional network of PEG can be envisioned. This aim could be reached by condensation of difunctional poly(ethylene glycol) and multi-functional molecules. A three dimensional network across the whole electrolyte should lead to a substantial increase of mechanical properties while ionic conductivities should be preserved. Nevertheless, this approach hardly seems to be compatible with the filtration process.

Experimental part

Materials

Polyethylene glycol monomethylether (mPEG, Aldrich), sodium hydride (NaH, Aldrich, 60 wt. % in mineral oil), propargyl bromide (Acros Organics, 80 wt. % in toluene), magnesium sulfate (VWR, 98 %), (3-chloropropyl)triethoxysilane (TEOSCl, Aldrich, 97 %), tetrabutylammonium azide (TCI, 95 %), sodium sulfate (VWR, 98 %), silica nanoparticles (SiO_x NPs, Aldrich, 99.5 %), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Acros Organics, 98 %), Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA, TCI, 97 %), sodium ascorbate (Aldrich, 98 %), lithium perchlorate anhydrous (LiClO_4 , Alfa Aesar, 99.99 %), sodium hypochlorite solution (Sigma-Aldrich, 10-15 %), Sodium chlorite (Sigma-Aldrich, 80 %) (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, Sigma-Aldrich, 98 %) and lithium hydroxide (Aldrich, 98 %) were used as received. Tetrahydrofuran (THF, VWR, HPLC grade) and toluene (VWR, HPLC grade) were distilled on CaH_2 before use, dichloromethane (DCM, VWR, HPLC grade) acetonitrile (ACN, VWR, HPLC grade) were used as received.

Never dried cellulose soft wood pulp was kindly provided by Domsjö Fabriker AB, Örnsköldsvik, Sweden.

Cellulose nanofibers preparation

In a round-bottom flask, 10 g of never-dried cellulose pulp were added (this corresponds to 2 to 2.4 g of dried cellulose fibers). Phosphate buffer (180ml, pH 6.8) was added and temperature was elevated at 60 °C. Sodium hypochlorite 15% in water (1.24 ml) was diluted in 20 ml of phosphate buffer then added to the reaction mixture. Sodium chlorite (2.26 g; 25 mmol) and TEMPO (40mg; 0.25 mmol) were then added. The mixture was stirred for 72 hours before cooling at room temperature. Oxidized cellulose fibers were filtered and thoroughly washed with

water and methanol. The oxidized cellulose fibers were then dispersed in distilled water and pH was set at 10 with LiOH 1M. The dispersion was sonicated for 15 mins - 30 mins using ultrasonic bath. Cellulose fibers and cellulose nanofibers were then separated using a nylon cloth filter (25 μm). The process was repeated to recover a larger amount of cellulose nanofibers. Cellulose nanofibers were then concentrated using centrifugation for 15 mins at 4 000 RPM.

Separator production

Variable amounts of cellulose nanofibers and silica nanoparticles (typically 10 mg of each) were dispersed in 100 ml ethanol. Dispersions were vacuum filtered on hydrophobic PVdF 0.22 μm filters using a Millipore set-up. Separators were first dried in ambient air at room temperature for 24 hours, peeled off and finally dried at 60 °C under vacuum for 48 hours.

Electrochemical characterization of CNF-based separators

Electrical conductivities were measured by a 4-point probe station (Lucas Lab L320) coupled with a Keithley 2410 monitor. Current was adjusted to keep a constant voltage of 10 mV. Film thickness was measured using a Draper Expert digital micrometer.

Separator were soaked in liquid electrolyte between two stainless steel electrodes in Swagelock cells. All cells were assembled under argon atmosphere (<0.1 ppm H_2O , <0.1 ppm O_2) in a MBraun glovebox.

Cyclic voltametry was carried out on a CHI660b potentiostat between 0 V and 5 V. Scanning rate were set as 0.1 mV/s and 1 mV/s.

Electrochemical impedance spectroscopy measurements were carried out on a CHI660b potentiostat by applying an AC voltage of 5 mV in the frequency range of 0.1 Hz to 100 kHz.

TEM and AFM imaging

Images in transmission electron microscopy were recorded on a LEO 922 microscope, operating at 120 kV accelerating voltage in bright field mode. Samples for TEM experiments were prepared by drop casting a dispersion of cellulose nanofibers or silicon dioxide nanoparticles in water on TEM grids (SPI, Lacey carbon on 200 mesh Cu grid). Grids were carefully dried under vacuum at room temperature. Particles measurements were executed with ImageJ 1.49 software (Wayne Rasband, National Institute of health).

Atomic force microscopy was performed on a Digital Instrument Nanoscope V scanning force microscope in tapping mode using NCL cantilevers (Si, 48 N/m, 330 kHz, Nanosensors). Samples for AFM experiments were prepared by spin-coating nanoparticles and nanofibers dispersions on silicon wafers. Silicon wafers were previously washed in acetone, Piranha solution and MilliQ water.

Chemical characterizations

Proton nuclear magnetic resonance (^1H NMR) spectra were acquired on a 300 MHz Bruker Advance II.

Infrared (IR) spectra were recorded on thin films deposited onto sodium chloride plates or in bulk into potassium bromide pellets with a FT-IR Shimadzu 8400S spectrometer.

Typical procedure for alkyne functionalization of the polyethylene glycol monomethylether

Sodium hydride (800 mg; 20 mmol; 4eq) was added to a solution of mPEG_{2k} (10 g; 5 mmol; 1eq.) in dry tetrahydrofuran (50 ml). After stirring at room temperature for 1 hour, a solution of propargyl bromide (80 wt. % in toluene; 2.23 ml; 20 mmol; 4 eq.) was introduced drop-wise to the medium and the reaction mixture was stirred overnight. The solvent (THF) was removed under reduced pressure. The obtained product

was dissolved in dichloromethane, extracted 3 times with deionized water (25 ml) and lastly with brine solution (25 ml). The organic phase was collected, dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by precipitation in cold diethyl ether to afford 7.3 g of a white solid. The same procedure was followed to functionalize mPEG_{5k} and mPEG_{20k}. Time was the only parameter varying.

¹H NMR (300 MHz, CDCl₃) mPEG_{2k} δ(ppm): 2.43 (t, J 3 Hz, 1H, C≡C-H), 3.36 (s, 3H, CH₃O), 3.39-3.87 (m, 45H, CH₂), 4.18 (d, J 3 Hz, 2H, O-CH₂-C≡C)

¹H NMR (300 MHz, CDCl₃) mPEG_{5k} δ(ppm): 2.42 (t, J 3Hz, 1H, C≡C-H), 3.36 (s, 3H, CH₃O), 3.39-3.86 (m, 562H, CH₂), 4.17 (d, J 3 Hz, 2H)

¹H NMR (300 MHz, CDCl₃) mPEG_{20k} δ(ppm): 2.43 (t, J 3Hz, 1H, C≡C-H), 3.37 (s, 3H, CH₃O), 3.38-3.88 (m, 2023H, CH₂), 4.19 (d, J 3 Hz, 2H)

FT-IR: 3247 cm⁻¹ C-H stretching of alkyne, 2877-2694 cm⁻¹ C-H stretching in methylene groups, 1486-1454 cm⁻¹ C-H scissoring in methylene groups, 1234-1278 cm⁻¹ C-O stretching in CH₂-O-CH₂.

Typical procedure for the synthesis of (3-azidopropyl)triethoxysilane

(3-chloropropyl)triethoxysilane (10 ml; 41.5 mmol; 1 eq.) was introduced in a 100 ml round bottom flask under argon atmosphere. The medium was filled with freshly distilled acetonitrile (45 ml) and stirred for 10 min. Afterwards, tetrabutylammonium azide (116.6 mg; 0.41 mmol, 0.01 eq.) was added to the medium and the mixture was refluxed for 76 hours. The reaction was allowed to cool and acetonitrile was removed under reduced pressure. The resulting product was dissolved in dichloromethane and extracted 3 times with water. The organic fractions were collected, dried on sodium sulfate, filtered and concentrated to afford a colorless oil (8.66 g).

Typical procedure for the functionalization of silica nanoparticles with (3-azidopropyl)triethoxysilane

Silica nanoparticles (2 g) were placed in a Schlenk flask and dispersed in of dry toluene (200 ml). (3-azidopropyl)triethoxysilane (4 ml) was added and refluxed for 76 hours under stirring. The obtained $\text{SiO}_x\text{NPs@N}_3$ were separated from solvent by centrifugation (15 mins, 4 000 tr/min), washed 6 times alternating water and acetone and dried at 35 °C under vacuum for 24h. The particles were afforded as a white solid.

Polyethylene glycol grafting on silica nanoparticles

Alkyne-functionalized mPEG_{2k} (200 mg; 0.1 mmol; 1 eq.) was introduced in a Schlenk flask containing a water and methanol mixture (1:1 in volume, 10 ml) and stirred at room temperature until the total dissolution of the polymer. Azide-functionalized silica nanoparticles (160 mg) were introduced in the Schlenk and dispersed by sonication for 15 minutes.

Afterwards, an equimolar solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (23 mg; 0.08 mmole; 0.8 eq.) and TBTA (42 mg; 0.08 mmol; 0.8 eq.) in 2 ml of 1:1 solvent mixture $\text{H}_2\text{O}/\text{MeOH}$, was added. The medium was degassed by bubbling argon for 20 minutes. Sodium ascorbate (33 mg; 0.16 mmol; 1.6 eq.) was added, the medium was degassed for 10 additional minutes and the reaction mixture was stirred for 24 hours. The resulting product was collected by centrifugation (15 min, 4 000 rpm), rinsed 6 times (45 ml) alternating water and ethanol and dried over vacuum oven at 35 °C.

The same procedure was followed to graft mPEG_{5k} on $\text{SiO}_x\text{NPs@N}_3$. Only parameters varying were solvent mixture and temperature.

X-ray photoelectron spectroscopy of grafted silica nanoparticles

XPS analyses were realized at room temperature by means of a SSI X-Probe (SSX 100/206) photoelectron spectrometer from FISONS equipped with a monochromatized microfocus Al X-ray source. Samples were 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 was set at $800\ \mu\text{m} \times 1200\ \mu\text{m}$. Charge effects were suppressed by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale was calibrated with reference to the $\text{Au}_{4f7/2}$ peak at 84 eV. Data treatment was performed with the CasaXPS software (Casa Software Ltd., UK). The peaks were decomposed into a sum of Gaussian/Lorentzian (85/15) after subtraction of a Shirley type baseline.

Thermogravimetric analysis

Thermogravimetric analysis were recorded on a TGA/SDTA 851e instrument from METTLER TOLEDO. Samples (from 3 to 10 mg) were introduced in 70 μL alumina containers. Analyses were carried out with a heating ramp of $10\ ^\circ\text{C}.\text{min}^{-1}$ and under a nitrogen flow ($50\ \text{ml}.\text{min}^{-1}$).

Electrochemical Impedance Spectroscopy of $\text{PEG}_{400k}\text{-LiClO}_4$

PEG_{400k} was dissolved in dry acetonitrile at $50\ ^\circ\text{C}$ for 2 days to produce a 3.33 wt. % solution. 10 grams of that solution were mixed with an appropriate amount of LiClO_4 to reach the right EO/Li^+ ratio. That mixture was poured in an aluminum pan and the solvent was evaporated under vacuum at $40\ ^\circ\text{C}$. The samples were finally dried for 48 hours at $30\ ^\circ\text{C}$ and stored in a glovebox under controlled atmosphere. The $\text{PEG}_{400k}\text{-LiClO}_4$ films were introduced between two copper plates with area of $\sim 7.07\ \text{cm}^2$. The setup was connected to a three electrodes

potentiostat. Electrochemical impedance spectroscopy measurements were carried out on a Metrohm Autolab potentiostat by applying an AC voltage of 5 to 10 mV in the frequency range of 0.01 Hz to 1 MHz.

Electrochemical Impedance Spectroscopy of PEG_{2k-35k}-LiClO₄

PEG (500 mg) was melted at 65 °C in a vial under stirring. LiClO₄ wt. 65% in THF was added to the vial to reach the right Li⁺/O ratio. A ring made of polyethylene was used as spacer to prevent shortcut and secure a constant thickness during measurement. The melted PEG-LiClO₄ mixture was directly casted on pre-heated stainless steel electrodes and the solvent was evaporated under reduced pressure. Once dried, electrodes were assembled in a swagelock cell system. Electrochemical impedance spectroscopy measurements were carried out on a Agilent 4284A potentiostat by applying an AC voltage of 5 mV in the frequency range of 1 Hz to 1 MHz.

Rheological measurements of PEG_{2k-35k}-LiClO₄

Shear rheological experiments were performed on a Kinexus Ultra (Malvern Instrument) rheometer equipped with a heat exchanger. Measurements were carried out at given temperatures, using a 8 or 20 mm plate-plate geometry. The gap was adjusted between 50 and 250 μm so that the geometry was completely filled. Normal forces were checked to be relaxed prior any measurement.

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CHAPTER 5

Design of full batteries

Abstract

In previous chapters of this work, we demonstrate that our previously described positive and negative electrodes are compatible. Electrode balance is analyzed and performances are correlated. In a second step, the incorporation of cellulose nanofibers separators is realized. Performances of the corresponding full cells are assessed. Finally, we demonstrate that filtration process can be used to produce lithium-ion batteries in a single step.

5.1 Capacity-balancing of electrodes

In this chapter, we designed full cells with lithium cobalt oxide-based cathodes and lithium titanate-based anodes. The voltage of this battery is determined by the voltage of the two corresponding half-cells. In this case, battery voltage is therefore around 2.4 volts. The capacity of full-cells is determined by irreversible capacity of both electrodes (Figure 5.1).^[1] During the first charge (Figure 5.1 a)), lithium ions are transferred from the cathode to the anode through the electrolyte. Most of lithium ions are reversibly intercalated in the anodic material. Nevertheless, part of lithium ions supplied by the cathode are consumed in the initial irreversible reaction of SEI layer formation at the anode. During the first discharge, the part of lithium ion not involved in irreversible reaction shuttle back to the positive electrode. As for the first charge, a part of the lithium ions are consumed in irreversible reactions at the cathode. Two cases may arise. In the first case (Figure 5.1 b)), reversible positive capacity is larger than reversible negative capacity. The reversible capacity of the full cell is here determined by the reversible capacity of negative electrode. In the second case, the reversible capacity of positive electrode is smaller than the reversible capacity of negative electrode (Figure 5.1 c)). In this case, the full cell reversible capacity is equal to the reversible positive capacity. These two cases are respectively called anode-limited design and cathode-limited design battery. They are attributed to the difference in the amount of lithium supplied to the half cell with lithium metal as the reference electrode and a full cell with a counter electrode. This is because lithium ion is limitless in half-cell configuration but restricted by counter electrodes in full-cell configuration. Cathode/anode capacity ratio is therefore one of the most important criterion to design full-cells.^[1,2]

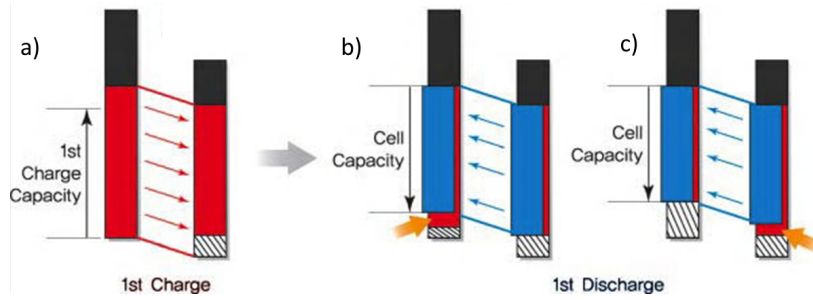


Figure 5.1 – Irreversible capacity of a cathode and an anode: a) lithium is transferred from the cathode to the anode, b) and c) lithium from reversible anode capacity is restored to cathode. Adapted from^[1].

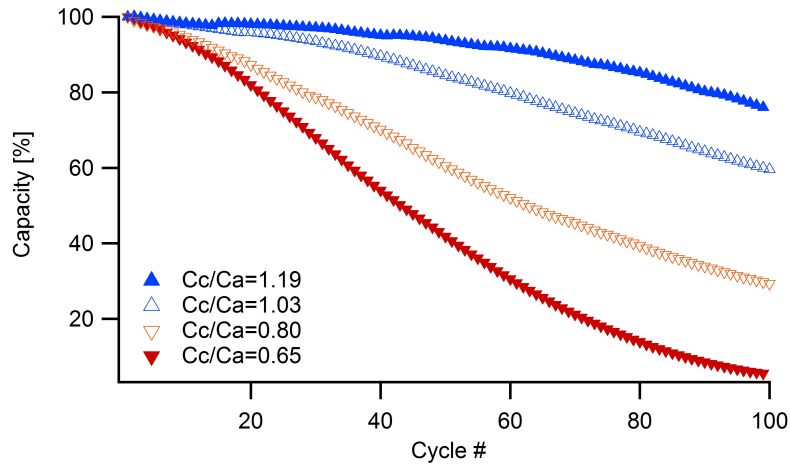


Figure 5.2 – Impact of capacity balancing on capacity retention of full batteries (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes). Capacity of batteries is evaluated in the 1V - 2.7 V range at 1 C rate with respect to the in debt electrode.

Tests performed on half-cell configurations showed that active materials-MWCNT-based fabrics meet the expectations for quality electrodes. Electrode containing 10 wt. % MWCNTs showed satisfying performances with lithium as counter electrode. Gravimetric capacity recovered for both electrode was close to the theoretical gravimetric capacity. Therefore, MWCNT-LiCoO₂ cathodes and MWCNT-Li₄Ti₅O₁₂ anodes containing both 10 wt. % MWCNTs were assembled in a full cell configuration with a porous Ceardllgard separator soaked with liquid electrolyte. Full cells with different cathode - anode capacity ratios were prepared and tested (Figure 5.2). Experiment was reproduced twice with very similar results. Current was set at C / 20 during the first cycle and at C over the next 100 cycles. Current densities were set according to limited electrode. Voltage cut-off was set at 2.7 V during charge and at 1 V during discharge. During charge, if delithiation exceeds half of the lithium amount present in MWCNTs-LiCoO₂ electrodes, LiCoO₂ particles undergo structural change from hexagonal to cubic spinel structure.^[3] This leads to an irreversible capacity loss for the cathode material. In a cell with an excess of positive material, Li₄Ti₅O₁₂ reaches its saturation (Li₇Ti₅O₁₂) before reversible delithiation of LiCoO₂, preventing thus LCO degradation. Results showed that a small excess of cathode material (1.2 ratio in term of capacity) presented the best results with capacity retention of 76 % after 100 cycles (Figure 5.2). Battery with a cathode/anode capacity ratio of 1.2 were therefore further investigated. Voltage profiles of these batteries during the first hundred cycles are presented in Figure 5.3. Current density during the first cycle was set at 0.1 C to allow passivation layer creation. The first cycle therefore presents higher capacity due to the irreversible capacity of the first cycle. The other curves show no significant differences for the 50 first cycles. However, the voltage profile of the hundredth cycle shows an inflexion point in charge and discharge curves at around 2.5 V that could suggest degradation of LCO particles. In

addition, it can be seen that voltages are slightly higher than previous cycles at the same state of charge. Progressive loss of electrical contact between carbon nanotubes and active material particles is probably due to the formation of passivation layer and decohesion of particle. This is partly the cause this observations and the progressive loss of capacity of the battery. A change of the voltage cut-off from 2.7 V to 2.5 V could help to further improve the lifespan of electrodes but at the expense of the battery capacity.

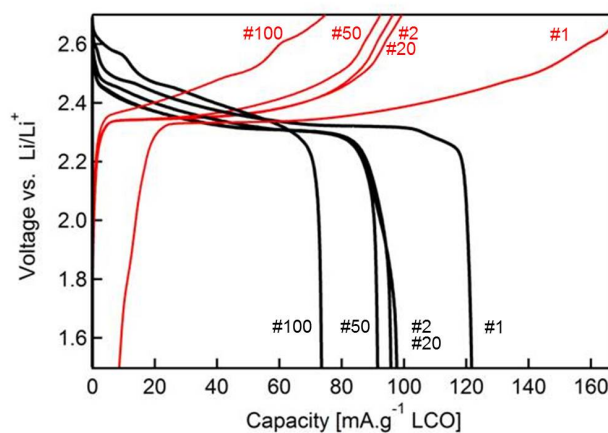


Figure 5.3 – Voltage profiles recorded in the 1 V - 2.7 V range at 1 C rate for full batteries (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes) with a $C_c/C_a = 1.2$ ratio. Cycles 1, 2, 20, 50 and 100 are represented.

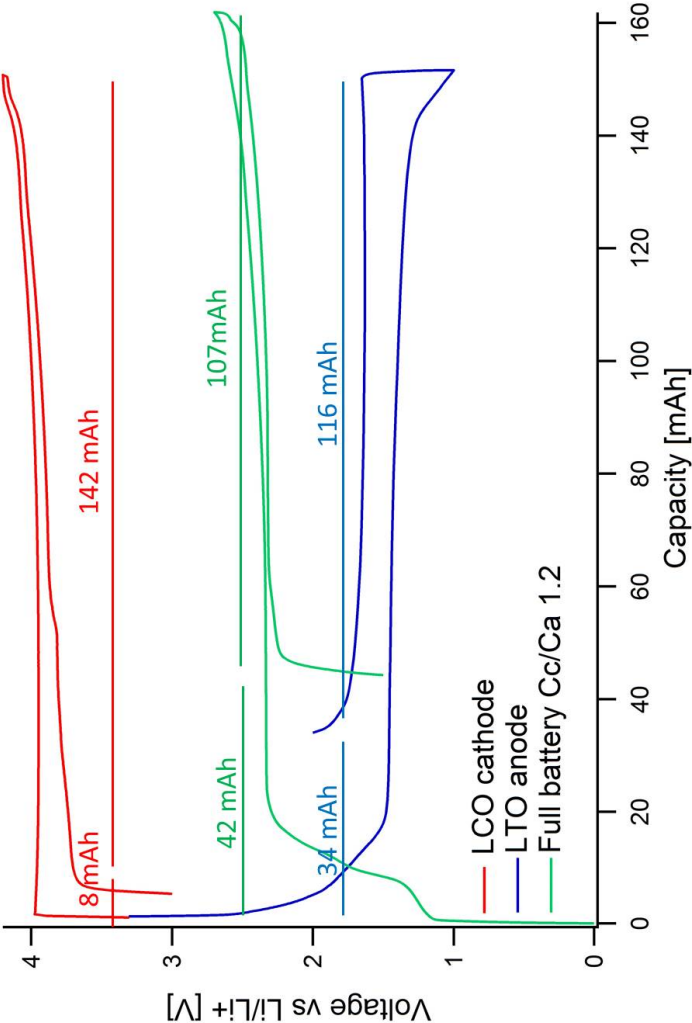


Figure 5.4 – First cycle voltage profiles recorded of LCO electrodes, LTO electro design half cell configuration and full battery range (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes) with a $C_c/C_a = 1.2$ ratio.

The phenomena taking place during the first cycle were analyzed more deeply (Figure 5.4). This graph depicts the voltage profile of a LCO-MWCNTs electrode (90:10 wt. % - 1 g LCO) and a LTO-MWCNTs electrode (90:10 wt. % - 0.78 g LTO). The mass were chosen to respect the cathode-anode reversible capacity ratio of 1.2. The green curve depicts the voltage profile of a full-cell designed with the corresponding electrodes. Figure 5.5 depicts the phenomena taking place inside the full-cell. During first charge, a certain amount of LiCoO_2 is delithiated (corresponding to 150 mAh). Lithium ions shuttle through the electrolyte and the anode is lithiated. A certain quantity of the lithium ions undergoes irreversible reaction forming passivation layer. This quantity was evaluated to 34 mAh from the Figure 5.3. Only 116 mAh of lithium ions are now able to shuttle back to the LCO cathode during the first discharge. This is very different from the case of half cells. In half cells, capacity of lithium counter electrode is limitless. During first discharge, 116 mAh of lithium ions insert in LCO material. A part of these lithium ions undergoes irreversible reaction on their turn. This was estimated to 8 mAh of lithium ions from the Figure 5.3. After first cycle, lithium cobalt oxide is therefore not fully lithiated and some cathode capacity is therefore lost. We estimate the composition of positive active material close to $\text{Li}_{0.88}\text{CoO}_2$ after the first cycle and the reversible capacity of the cathode represents around 107 mAh. The full-cell voltage profile is depicted on Figure 5.3. After the first cycle of full cell, 114 mAh.g^{-1} LCO were recovered which is close to the predictions. We are in this case in an anode-limited configuration. During the first 25 cycles of the battery life, capacity is almost constant (2 % decay) ($C_c/C_a=1.19$ full-cell of Figure Figure 5.2), Nevertheless, over time, LCO cathode capacity will slowly be reduced as it was observed in half-cell configuration. At one point, cathode capacity falls below anode capacity and full cell is in a cathode-limited configuration. The decline in battery capacity then accelerates as delithiation can exceed $\text{Li}_{0.5}\text{CoO}_2$.

In traditional graphite/lithium cobalt oxide batteries, a cathode/anode ratio smaller than 1 is recommended. In this case, larger negative anode capacity prevent safety issues that can arise due to lithium deposition at the anode during charging. In our case, graphite is not used to design full-cells. Selected active material for negative electrode is lithium titanate. On this material, lithium metal deposition should not occur on LTO electrodes as intercalation potential is about 1.6 V vs Li/Li⁺. As previously demonstrated in half-cell configuration, lithium titanate-based electrodes are very stable. On the other hand, we previously demonstrated our difficulties to design very stable MWCNTs-LCO electrodes. Results presented on Figure 5.2 proved that a cathode to anode capacity ratio of 1.2 showed the best results. Batteries with electrodes of capacity ratio $C_c/C_a = 1.2$ were therefore repeatedly produced for further analyses.

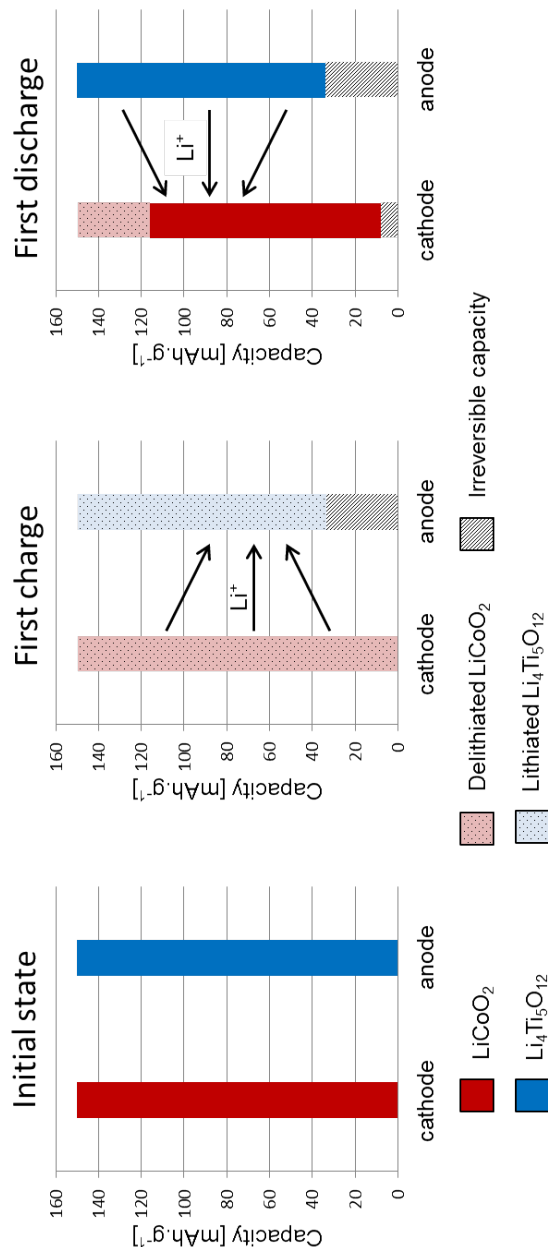


Figure 5.5 – Initial irreversible capacity of a full cells : MWCNTs-LiCoO₂ cathode (10:90) vs. MWCNTs-Li₄Ti₅O₁₂ (10:90). Cathode to anode capacity ratio was set to 1.2.

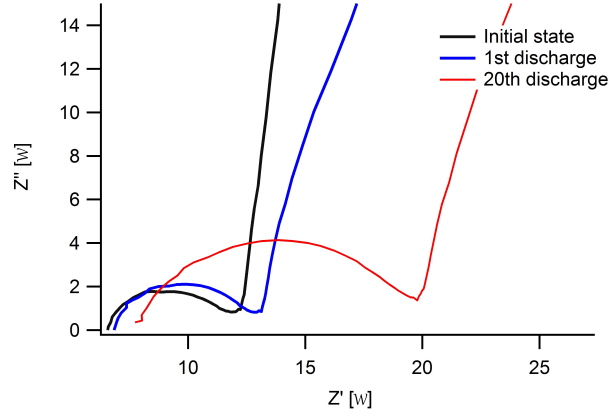


Figure 5.6 – Electrochemical impedance spectroscopy of full batteries (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes - $Cc/Ca = 1.2$) during the first 20 cycles. Measurements are recorded under a 5 mV perturbation.

Electrochemical impedance spectroscopy analysis was also performed during cycling of the battery to investigate solid electrolyte interface creation and closely monitor the cycling degradation (Figure 5.6). For the freshly assembled cell (initial state), the EIS trace in the Nyquist plot presents a single semi-circle that can be ascribed to the interfacial resistance. It also presents a straight line with an angle of 45° with respect to the real axis (Z') in the low frequency region corresponding to a Warburg diffusion of ions in solution. After the first and twentieth cycles, Figure 5.6 shows an increase of the arc diameter, corresponding to the solid interface layer formation, which increases the internal resistance of the cell.^[4] This increase of internal resistance is partly responsible for capacity degradation over time. Internal resistance increase can cause local overvoltage and degrade active material. It also leads to loss of contact between the conductive network and active matter particles.

5.2 Cellulose nanofibers-based separator integration

The next step in the design of the flexible lithium-ion batteries is the integration of the previously described cellulose nanofiber-based composite separator. Full cells were assembled in the same configuration as previously described with a cathode to anode capacity ratio of 1.2. Commercial PE-PP-PE separator was replaced by home-made filtered CNF:SiO_x NPs composite separator (50:50 wt. %ratio). Figure 5.7 shows the comparison of cycle stability between a cell with commercial separators and two cells with CNF-based separators. In each case, capacity retention calculated after the first 40 cycles is close to 95 % and coulombic efficiency above 98 %. Moreover, one can observe no significant differences between batteries with commercial separator and batteries with cellulose nanofibers separator. As previously described, in a positive to negative capacity ratio of 1.2, the degradation of LCO is not very important at the beginning. After cycle 40, while the capacity retention of cells with commercial separator slowly declines, the phenomenon is even more pronounced for batteries with the home made separator. After 40 cycles, the positive to negative capacity ratio drops below 1 and we switch to a cathode-limited configuration. Therefore, the capacity fade accelerates. Nevertheless, these results are very encouraging as it proves that our cellulose separator can be used in this full cell configuration. Performances of batteries with cellulose-based separator are not so different from the batteries with commercial separator. To explain decay in the capacity retention, it must also be taken into account the time elapsed between the first and the hundredth cycle. In this case, the elapsed time represents about 10 days of analysis. During this time, many phenomena can occur as a loss of contact between MWCNTs and active matter particle or electrolyte degradation.

Figure 5.8 shows the voltage profiles of a full-cell with CNF-based

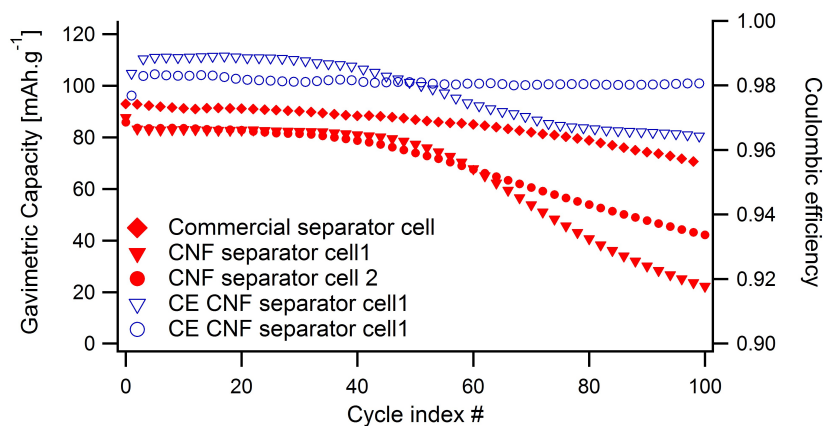


Figure 5.7 – Impact of CNF-based separator integration: evaluation of cycle stability for full cells with commercial separators and full cells with CNF-based separators. All batteries were designed with a LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes in a $C_c/C_a = 1.2$ ratio. Gravimetric capacity and coulombic efficiency were evaluated at 1 C rate in the 1 V - 2.7 V range.

separator. The curves exhibit no significant differences with cell with commercial separator (Figure 5.3). As noted above, an inflexion point can still be observed at 2.5 V during charge. Changing the cut-off voltage should probably improve capacity retention over time but at the expense of capacity.

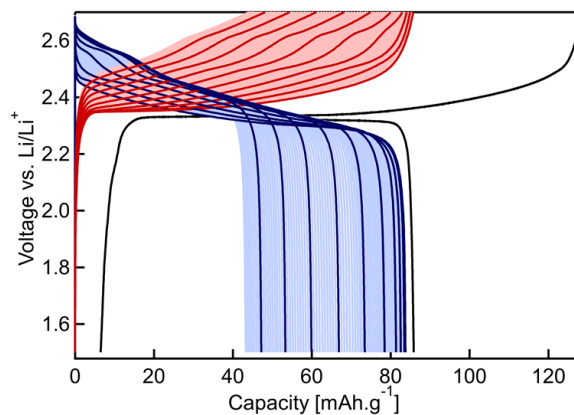


Figure 5.8 – Voltage profiles recorded in the 1 V - 2.7 V range at 1 C rate for full batteries (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes) with a Cc/Ca ratio = 1.2 and cellulose-based composite separator. Cycles 1 to 100 are represented.

5.3 One-step fabrication of batteries

The last part in the design of the flexible lithium-ion battery in one step was the sequential filtration of each layer: MWCNTs-LCO positive electrode, cellulose-based separator and MWCNTs-LTO negative electrode. Filtration produced flexible robust batteries several times (Figure 5.9). However, the sequential filtrations required much more time than separate filtrations. The increase in time to complete the filtration is mainly due to the difference of difference of hydrophobicity of each layer and the nature of dispersion solvents. The filter is composed of hydrophobic PVdF. The first filtered layer is mainly composed of MWCNTs that are hydrophobics. The second filtration is the separator layer which involves methanol. This filtration is therefore very slow as methanol percolates hardly through the MWCNTs network due to its polarity. This second filtration creates a layer of cellulose and silica nanoparticles layer. The filtration of last layer involves butanol as dis-

persant on a hydrophilic layer. This explain the slow process of battery filtration in one single step. Each sample was later carrefully dried for 48 hours at 60°C under vaccum to remove every solvent traces.

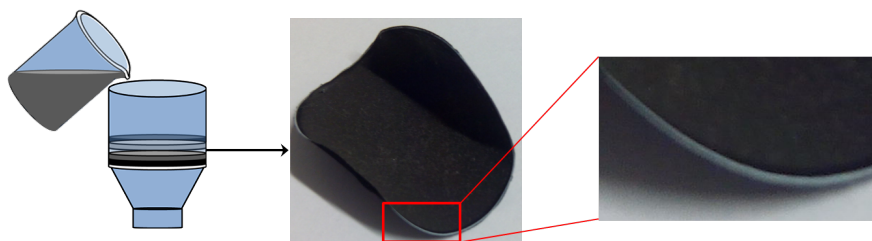


Figure 5.9 – One step battery via filtration process. Each layer is sequentially deposited.

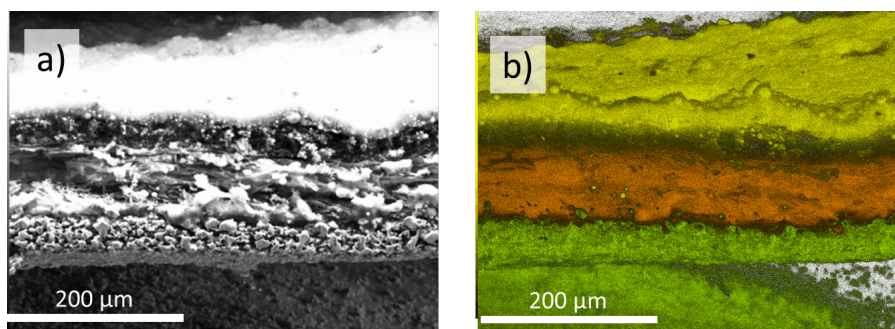


Figure 5.10 – Cross-section a full cell produced successive filtration step: a) SEM image and b) EDX mapping performed at 15 kV with Ti in yellow, Si in orange and Co in green.

After drying, diverse methods were investigated to punch test batteries at the appropriate size. All of the traditional cutting methods failed to produce working batteries. Conventional tools to cut batteries lead to the creation of shortcuts between the two electrodes whatever the thickness of separator was. A laser cutting method was eventually employed. Figure 5.10 shows the cross-section of a battery cut by laser. EDX mapping shows the clear separation between the three components of the battery. From this image, we can evaluate the thickness of sep-

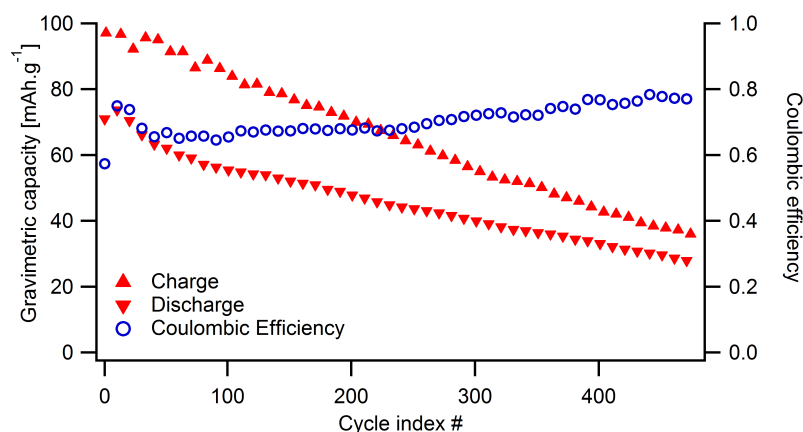


Figure 5.11 – Impact of the one step battery fabrication process on performances: evaluation of cycle stability for full cells with cellulose-based composite separators. Batteries were designed with a LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes in a $C_c/C_a = 1.2$ ratio and all battery component were successively filtered. Gravimetric capacity and coulombic efficiency were evaluated at 1 C rate in the 1 V - 2.7 V range.

arator to 67 μm . Thickness of commercial separators is 25 μm . In our battery, lithium ions have to cover more than twice the distance. This can have a direct influence on performances.

Even with this method, only one test battery over eleven samples sustained several cycle. The results are presented in Figure 5.11. Gravimetric capacity is here expressed in terms of mAh per gram of LiCoO_2 . The first observation is the relatively low coulombic efficiency observed. The latter was recorded constant between 60 % and 80 %. The explanation lies in the presence of a very small short-cut between the two electrodes. These short-cuts could have two possible sources. They can come from the filtration process itself. During the filtration of the anode, MWCNTs can infiltrate the separator layer and make connections with the cathode. This explanation is unlikely. Separator layer is about 67 μm thick and MWCNTs are few μm long. The second possible source

of short-cuts is the punching method and preparation of Swagelock cell. During these steps, it is very likely that short-cuts are created at the edge of battery. On Figure 5.11, one can notice that only 77.07 mAh^{-1} could be recovered during the discharge in first cycles. This is only a little bit more than half of the theoretical capacity. Nevertheless, it is important to note that the battery produced by sequential filtrations sustained 500 cycles with only a 62 % capacity loss. In this case, the 500 cycles represent about 45 days of measurement. This result is therefore very encouraging. It proves that the filtration process is a very interesting method to create batteries in a single step. Figure 5.12 shows the voltage profile of the full-cell designed by sequential filtrations. Again, these voltage profiles are similar to the previous one. We can observe inflexion point at 2.5V on each curve. Experiments with different cut-off voltage should be carried on to assess the impact on lifespan of batteries.

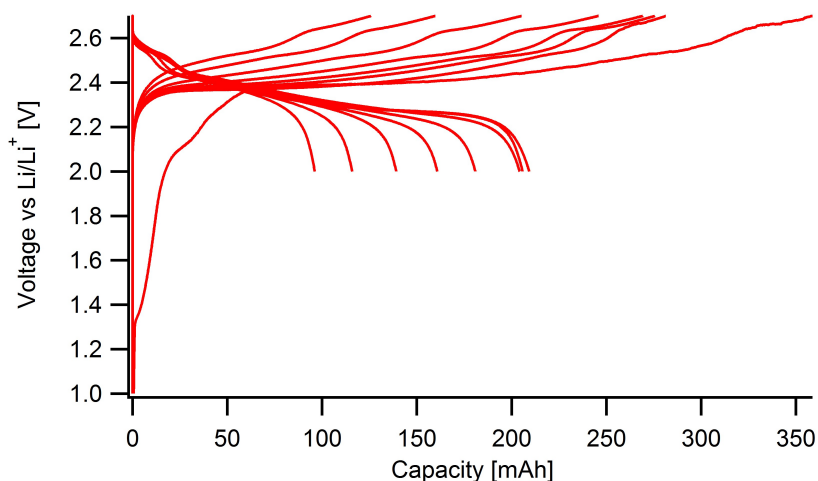


Figure 5.12 – Voltage profiles of full-cell made by filtration Voltage profiles recorded in the 1 V - 2.7 V range at 1 C rate for full batteries produced by sequential filtration of components (LCO-MWCNTs (90:10 wt. %) *vs.* LTO-MWCNTs (90:10 wt. %) electrodes - cellulose separator (10 mg CNF - 10 mg SiO_x Nps) with a Cc/Ca = 1.2 ratio. Cycles 1, 2, 20, 50, 100, 200, 300 and 400 are represented.

5.4 Conclusion

In this chapter, we first demonstrated that negative electrodes and positive electrodes based on carbon nanotubes networks are compatible. We investigated the electrode balance and the impact of limited-electrode configurations. Full-cell configurations are very different from half-cell configurations. In full-cell configuration, the amount of lithium ions is not limitless. Special attention should therefore be paid to electrode balance and on irreversible capacity during first cycle. Recorded performances of our batteries show that a slight excess of cathode material produces batteries with better cycling stabilities.

In a second phase, we replaced commercial polyolefin-based separators by the cellulose nanofiber-based separator. Recorded performances showed no sign major differences. Very encouraging results were recorded during the 40 firsts cycles. After the 40 firsts cycles, capacity gradually fades as lithium cobalt cathode is depleted

In a third phase, we proved that a filtration process can be implemented to create batteries in a single-step. The analysis shows that the battery sustained 500 cycles on a period of about 45 days. Coulombic efficiency analysis highlighted the presence of short-cuts between anode and cathode. These short-cuts are created during the battery assembly and with little technical optimisation, we should be able to create full-cells in a single step that present very good performances.

Experimental part

Materials

Lithium cobalt oxide (LiCoO_2 , LCO, 9 μm , 99.9 %) and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO, 1.9 μm , 98 %) were purchased on their battery grade from MTIXTL. Butanol (HPLC grade, 99.7 % Sigma-Aldrich) was used without any further purification. Thin multiwalled carbon nanotubes NC7000 (MWCNT, av. diameter: 9.5 nm, av. length: 1.5 μm , carbon purity 90 %) were kindly provided by Nanocyl. Lithium foils (Alfa Aesar, 99.9 %) were used as reference electrode. Separator films (Celgard, 25 μm trilayer (PP-PE-PP)) were purchased from MTIXTL. A mixture of ethyl carbonate, dimethyl carbonate and diethyl carbonate 1:1:1 in volume (EC:DMC:DEC) with 1 M of lithium hexafluorophosphate was purchased from Novolyte and used as electrolyte. All components were stored under controlled atmosphere and used as received.

Mass balancing electrodes

Positive and negative electrodes were created using the method described in chapter 5. Combination of electrodes with different capacities provided a large collection of a full batteries with various electrode balances. Batteries were created with electrode capacity ratios comprised between 0.65 and 1.4. Cycling stability and cycling performances were assessed using an Arbin BT2043 test station. Current densities were calculated on the basis of default electrode capacity. Full batteries were cycled between 1.0 V and 2.7 V. Electrochemical impedance spectroscopy measurements were carried out on a CHI660b potentiostat by applying an AC voltage of 5 mV in the frequency range of 0.1 Hz to 100 kHz.

CNF-based separator integration

Full batteries with an electrode balance $C_c/C_a = 1.2$ were produced. Cellulose nanofibers-based separator were produced as described

in chapter 5. Standard Cellgard separator was replaced by cellulose home-made nanofibers-based separator. Cycling stability and cycling performances were assessed using an Arbin BT2043 test station. Current densities were calculated on the basis of default electrode capacity. Full batteries were cycled between 1.0 V and 2.7 V. Electrochemical impedance spectroscopy measurements were carried out on a CHI660b potentiostat by applying an AC voltage of 5 mV in the frequency range of 0.1 Hz to 100 kHz.

One-step batteries

Cathode, cellulose-based separator and anode were sequentially vacuum filtered. Batteries were dried at room temperature for 24 hours and for 48 hours at 60°C under vacuum. Batteries were cut to the required dimensions by means of an Oxford Lasers industrial system using a 355 nm UV Talisker picosecond laser ULTRA 355-4 system with a diode-pumped solid-state amplifier. Cycling stability and cycling performances were assessed using an Arbin BT2043 test station. Current densities were calculated on the basis of default electrode capacity. Full batteries were cycled between 1.0 V and 2.5 V or 2.7 V.

Scanning Electron microscopy and EDX analysis

Morphologies of binder-free electrodes and carbon nanotubes buckypapers were observed by scanning electron microscopy on a JEOL JSM-7600F microscope operated at voltages ranging between 5 kV to 30 kV. Energy dispersive X-ray spectroscopy analysis were performed on the same equipment operated at 30 kV.

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CHAPTER 6

Conclusion and perspectives

In the recent years, the need of transportable energy sources has significantly risen. In this field, Li-ion battery technology has become a key technology in everyday life. Solutions were already successfully implemented for cell phones, laptops or even electric vehicles. Recently, technological breakthroughs in flexible electronics paved the way for wearable electronics and flexible screens. In this context, it is difficult to integrate the current portable energy solutions into future devices. Nevertheless, the design of new flexible portable energy sources introduces security constraints. Every component has to be flexible as well as the assembled battery. During operation, strong cohesion between components is also required in a flexible configuration. Therefore, separately creating the different components and assembling them together at the end of line is not the most appropriate production process. In addition, commercial lithium ion battery technologies are based on liquid organic electrolytes to maximize performances. Since the flammability of liquid electrolytes is known to be the main cause of failure, a flexible battery

needs to integrate new kind of electrolytes. In this context, poly(ethylene oxide) is a promising candidate. If properly prepared, PEO-based electrolytes exhibit sufficient ionic conductivity while standing solid. All these considerations let us conclude that the traditional design process had to be rethought for a flexible configuration. Therefore, this thesis was devoted to the implementation of solutions for the design of battery in a single filtration step including a solid electrolyte.

The first part of this work was dedicated to the creation of electrodes through filtration. A filtration process implies the use of battery components in the form of suspension. Most of the commercial battery electrodes being made of active materials, nanocarbons and polymer binders, their composition had to be adapted. In a first step, carbon nanotube buckypapers were created by filtration of homogeneous suspensions of multiwalled carbon nanotubes. After optimization of parameters such as the solvent choice and filtration conditions, we were able to reproducibly produce CNT-based robust conductive networks. Electrical conductivity and electrochemical inertness over a 0-5 V potential window were established to assess compatibility with lithium ion technology. In a second step, electrodes containing various amounts of active materials and multi-walled carbon nanotubes were reproducibly created. Cathodes were evaluated with lithium phosphate iron and lithium cobalt oxide as positive materials while mesoporous carbon beads and lithium titanium oxide were chosen as negative active materials. The performance of prepared electrodes as well as their durability were established by means of electrochemical characterizations. It was demonstrated that the filtration of a suspension containing electrochemical active materials and conductive carbon nanotubes is a very effective way to produce performing electrodes. Despite showing very promising results, electrochemical performances can still be improved. The major risk in configurations involving only MWCNTs and active matter particles is the loss of contact between them. Applying pressure on electrodes allows

the improving of cohesion inside the fabrics was improved as well as the electrochemical performances.

The second part of this work was devoted to the creation of flexible separators through a filtration process. Traditional microporous polyolefin separators can be produced at low cost and exhibit very good performances. Unfortunately, they are not adapted to be implemented in a filtration process. In this part of the thesis, we created cellulose fibers by oxidization and individualization of fibers from cellulose wood pulp. The produced fibers allowed us to create separators by means of filtration. Measured properties proved that the produced cellulose-based separators can be utilized in lithium ion battery without hampering performances.

In a third phase, we attempted to create a composite polymer electrolyte based on poly(ethylene glycol) and silica nanoparticles. With the objective to be integrated in a filtration process, silica nanoparticles were successfully grafted with poly(ethylene oxide). After synthesis condition optimization, composite electrolytes based on PEG and lithium perchlorate were produced. Their ionic conductivities were evaluated and considered satisfactory. Then, the positive impact of grafted silica nanoparticles and cellulose nanofibers on mechanical properties of composite polymer electrolytes was assessed. Despite showing very promising conduction properties, the designed composite polymer electrolytes are not in a solid state. Therefore, there is a risk of short-cut apparition in a flexible battery configuration if there is no fully solid separator. A fully solid state electrolyte able to sustain intense mechanical stress can be designed through the conception of a three dimensional network of PEG. This aim could be reached by condensation of difunctional polymers and multi-functional molecules. A three dimensional network across the whole electrolyte should lead to a substantial increase of mechanical properties while ionic conductivities should be preserved. In this configuration, separator is no longer required.

The last part of this thesis was dedicated to the creation of batteries in a single step. At first, the previously developed positive electrodes based on LiCoO_2 and the negative electrodes based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were integrated in a full cell. Their compatibility and the optimal electrode balance was established. Electrode capacity balance was proved as a crucial parameter in the design of batteries. Secondly, commercial polyolefin based separators were replaced by home-made cellulose-based separators to assess the impact on electrochemical performances. The measured performances were very convincing as no major differences with commercial separator were noted. In a third step, these three key components were sequentially filtered to create a battery in a single step. Tailoring the battery at the right size without creation of short-cuts was found to be the critical step in this process. The designed batteries were later filled with traditional liquid electrolyte. Recorded performances showed that the produced battery was able to sustain 500 cycles on a period of about 45 days, which is very encouraging. The decay in battery capacity was largely attributed to LCO degradation over time. We are therefore confident to claim that cathode performances improvement is expected to have a large beneficial effect on the full lithium ion cell. In a future work, integration of designed composite electrolyte should be investigated. Suspensions of Poly(ethylene glycol)-grafted silica nanoparticles as electrolyte can be filtered to create flexible solid electrolyte. The PEG-grafted silica nanoparticles can also be mixed with electrode components to create the solid electrodes. Heating the fabrics will ensure the cohesion and homogeneity of battery components.

The filtration process developed in this thesis was proven to be an effective, fast, reliable method to produce electrodes. This method is non costly as dispersion solvents can be recycled and no additives are required. In addition this process can be adapted for various other active materials or conductive agents/binders. Every traditional materials such as metal oxides or carbonaceous particles can be used to create

electrodes. Moreover, organic materials such as electroactive polymers can be grafted on the conductive scaffold to be filtered and to design electrodes. The size of the electrodes and their thickness can be easily adapted to the need of the manufacturer. All of these elements prove the huge potential of this process. The developed method to create battery components is not far from the process used in paper making industry. To produce paper, a soft wood pulp solution is injected at high pressure directly into the space between two continuously rotating wires. These carry the pulp into the gap former, which rapidly drains the excess water from both sides. This immobilises the pulp within milliseconds turning into a continuous web of paper. The delicate paperweb is then carried into the press section by continuously looped wet felts which carry away most of the water. This process allows paper-making industry to create tons of finished products in a very short lapse of time. Adapting this performing equipment to electrode materials should be possible with little technical optimisation. The chosen raw material can also be tuned to improve mechanical properties of fabrics. In this thesis, only one kind of multi-walled carbon nanotubes was used but it exists a very broad range of materials with different properties. For example, use of very long carbon nanotubes can be a method to adapt the process and create stronger fabrics. One can also think about functionalized carbon nanotubes and a post production cross-linking step. The principal ingredient used in paper making industry is water. Producing 1 kilogram of paper requires 100 liters of water. The later is recycled at 95 %. In this thesis we used butanol as dispersant for filtration. Large quantities of butanol were required to produce square centimeters of electrode. Nevertheless, the recycling rate of butanol was here close to 100 % with no purification step or major evaporation step. For these reasons, there are a large number of similarities between our experiments and the paper making industry. Hence, it should be no surprise if battery industry turns to this kind of process to create battery components in the future.

Scientific contributions

Scientific publications

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- **J.-P. Bourgeois**, Q. Hang, J. Rolland, A. Vlad, J.-F. Gohy and M. Skorobogatiy, Flexible fiber batteries for applications in smart textiles. *Physics*, **2013**, 1-10
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- J. Rolland, J. Brassinne, **J.-P. Bourgeois**, A. Vlad and J.-F. Gohy, Chemically anchored liquid-PEO based block copolymer electrolytes for solid-state lithium-ion batteries. *J. Mater. Chem. A.*, **2014**, 2, 11839-11846
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- **J.-P. Bourgeois**, A. Vlad and J.-F. Gohy, Design of Flexible and Self-Standing Electrodes for Li-Ion Batteries. *Chin. J. Chem.*, **2017**, 55 (1), 44-47
- E. Poggi, W. Ouvry, B. Ernould, **J.-P. Bourgeois**, S. Chattopadhyay, F. Du Prez and J.-F. Gohy, Preparation of Janus nanoparticles from block copolymer thin films using triazolidione chemistry. *RSC Adv.*, **2017**, 7, 37048–37054

Scientific communications

Oral communications

- PhD student's day 2014 - Design of flexible solid-state lithium-ion batteries
- Winfab's day 2013 - High performance solid-state flexible lithium-ion batteries

Poster communications

- BPG annual meeting 2012 - Design of flexible carbon nanotube-based electrodes for lithium-ion batteries
- BPG annual meeting 2013 - Design of polymer electrolyte for flexible lithium ion batteries
- BPG annual meeting 2014 - Flexible solid-state lithium-ion battery
- PhD student's day 2013 - Design of flexible carbon nanotube-based electrodes for lithium-ion batteries
- Winfab's day 2013- Design of flexible carbon nanotube-based electrodes for lithium-ion batteries
- Precision polymer Materials 2011 - Multi-stimuli responsive behavior of block copolymers