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Nanostructured silicon for advanced Li-ion storage systems

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For those who see the world in colors
and Patrick

Abstract

The interest in batteries, or more precisely, the interest in exploring beyond the current intercalation-type chemistry has been clearly catalyzed by the environmental concerns that became reality. On the one hand, transport electrification can considerably reduce the well-to-wheel emission through the use of renewable or low carbon electricity stored in efficient batteries. On the other hand, successful exploitation of intermittent energy production sources, such as solar or wind, requires energy storage capability, particularly in managing peak production and demand. Such storage systems would greatly increase the grid reliability while limiting the cost and the use of fossil fuel with their associated harmful products of combustion. Finally, our information-dependent and mobile society demands lighter, high capacity and cost-effective batteries. In this framework, considering the increasing energy demands and their broad spectrum of applications associated with their ubiquitous presence in our life, reducing the carbon-footprint of the battery manufacturing chain, in terms of material selection, production and disposal is also a pressing environmental concern. Currently, several Li-ion battery (LIB) chemistries are well established, however, they can not satisfy the energy demands nor the environmental policies associated with their production and disposal. Due to its high Li storage capability and low operating voltage, Si has been one of the anode contenders for the next generation of LIBs. Nonetheless, associated with its high Li storage capacity is the alloying chemistry with many challenges originating from the huge volume variation during Li-Si alloying and de-alloying reaction.

Herein, we explored several routes to alienate the key failure modes in Si cycling. First, we present a silicon nanowires (SiNWs) synthesis method based on a metal-assisted chemical etching scheme that allows for the reuse of the Si substrate via a sacrificial porous segment. This porous segment enables the efficient separation and transfer of SiNWs from their parent Si substrate. We further developed an accessible, room temperature synthesis method for the kinked SiNWs and discussed their potential as active electrode materials. Secondly, we explored an electrode design that is more realistic and suitable for alloying-type electrodes suffering from the volume variations. We report on the mechanical and electrochemical properties of a self-standing Si-carbon-based electrode design with optimized porosity to sustain the volume variations during Li-Si alloying reaction. In addition, Si surface passivation is discussed as a possible route for extending the cycling life of Si-based electrodes. We first address the electrochemical performance of thin Ni coated Si-based electrodes and discuss the benefits and drawbacks of such coating. Also, an aqueous conducting polymer is mechanochemically converted to a hydrogel that meets all the requirements as a binder for Si anodes. Not only it enhances the cycling life of Si anodes but also can deflect the current electrode manufacturing process towards a cleaner, safer path. Finally, this work evaluates possible routes to redirect LIB technology towards an environmentally friendlier, safer, and cost-effective direction by developing accessible material synthesis, with low energetic cost, and efficient use or reuse of raw materials as well as aqueous processing of battery electrodes. While many strategies have focused on a smooth carbon to Si transition without any alteration of the manufacturing process, here we challenge the conventional slurry-on-metal design and evaluate an alternative architecture.

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Symbols and abbreviations

δ	Phase lag between stress and strain
γ	Shear strain
G'	Storage modulus
G''	Loss modulus
ΔG^0	Standard Gibbs energy of reaction
ϵ	Dielectric constant of the medium
η	(Dynamic) viscosity of the medium
μ	Ion mobility
ϕ	Porosity
σ	Ionic conductivity
A	Si core radius
a_i	Activity corresponding to chemical specie i
C	Molar concentration
e	Unit of charge
E^0	Standard electrode potential
F	Faraday's constant, 96487 C/mole

h	Thickness of the Ni shell
I	Current
M	Molecular weight (kg/mole)
n	Number of charge carriers
N_i	Number of moles of species i
q	Specific capacity
R	Molar gas constant
r	Solvation radius
s	Catalyst mask opening diameter
s_i	Stoichiometric coefficient of species i
T	Temperature
t	Time
t_h	Thickness of the (Au) mask catalyst
z	Valence order of ionic species
AAO	Anodic alumina oxide
ALG	Sodium alginate
CB	Carbon black
CMC	Carboxy methyl cellulose
CVD	Chemical vapor deposition
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DME	Dimethoxyethane
DMSO	Dimethyl sulfoxide

DN	Donor number
DOL	Dioxolane
DWSiNTs	Double walled Si nanotubes
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
EMIM ⁺	1-Ethyl-3-methyl-imidazolium
EV	Electrical vehicle
FEC	Fluoroethylene carbonate
FSI ⁻	Bis(fluorosulfonyl)imide
IL	Ionic liquid
k-SiNWs	Kinked silicon nanowires
LA	Laser ablation
LCO	LiCoO ₂
LIB	Lithium-ion battery
LiPS	Lithium polysulfide
LISICON	LiM ₂ (PO ₄) ₃ , Li _{1+x+y} Al _x Ti _{2-x} Si _y P _{3-y} O ₁₂
LiTFSi	Lithium bis(trifluoromethanesulfonyl)imide
LTO	Li ₄ Ti ₅ O ₁₂
MACE	Metal-assisted chemical etching
MBE	Molecular beam epitaxy
Me-Im	1-Methylimidazole
MOF	Metal-organic frameworks
MWCNTs	Multi-walled carbon nanotubes

NCA Al-doped $\text{Li}[\text{NiCo}]\text{O}_2$

NMC $\text{Li}[\text{Ni}_{1-x-y}\text{Mn}_x\text{Co}_y]\text{O}_2$

NMP N-Methyl-2-pyrrolidone

OER Oxygen evolution reaction

ORR Oxygen reduction reaction

PAN Polyacrylonitrile

PANI Polyaniline

PC Propylene carbonate

PE Polyethylene

PEDOT:PSS Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

PEO Polyethyleneoxide

PMMA Poly(methyl methacrylate)

PP Polypropylene

PPO Poly(phenylene oxide)

PVDF Polyvinylidene fluoride

PYR_{1n}^+ Pyrrolidinium

$\text{PYR}_{13}\text{FSi}$ 1-Propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide

SBR Styrene butadiene rubber

SEI Solid electrolyte interphase

SEM Scanning electron microscopy

SHP Self healing polymer

SiGCNF Silicon and graphene/carbon nanofibers

SiNPs Silicon nanoparticles

SiNWs Silicon nanowires

TEGDME Tetraethylene glycol dimethyl ether

TEMPO 2,2,6-Tetramethyl-1-piperidinyloxy

TFSI[−] Bis(trifluoromethanesulfonyl)imide

TTF Tetrahydrofulvalene

VC Vinylene carbonate

VLS Vapor-liquid-solid

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Preface

On ne naît pas femme: on le devient.

Simone de Beauvoir

R. Feynman said “...in physics today, we have no knowledge of what energy is” and up to this point, this holds. The law of energy conservation, that governs all natural phenomena, states that energy is a constant quantity, regardless of the changes that nature undertakes. Thus, all we know about energy comes from thermodynamics that basically tells us that energy can not be created nor destroyed, only converted. In fact, we grasp the concept of energy due to the familiarity with the different energy forms and with the thermodynamics that mediates the relationship between these forms. Simply put, this work is about the reversible conversion of chemical energy into electrical energy of a Li-Si system. From another standpoint, the topic of energy resonates in connection to resource scarcity, the economics and social cost of migrating towards different energy forms, and the carbon footprint of these energies. We envisage the development and implementation of near-zero-emissions energy eco-systems to effectively reduce greenhouse emissions and limit the devastating effects of global warming. The efforts in this direction are expected to have an impact on the entire life cycle of the systems but are, nonetheless, depended one way or another on the sustainable advancement of the energy storage technology.

The energy density, or how much energy can be stored in a given volume or mass, has been the force guiding the research progress in the

battery technology. While there are several well-established lithium-ion battery (LIB) technologies, they can not satisfy the demands formulated by the applications, consumers nor the environmental aspects. Within this context, silicon has a comfortable position on all the levels due to the its high Li storage capacity at low voltage, availability, processing as well as the existing knowledge centered on Si. However, the huge Li storage capability also fuels the major challenges associated with Si electrodes. Nanostructured Si has been found to bring some relief in these challenges but its utility is shadowed by the inefficient, low-scale, synthesis processes.

This thesis aims at exploring several routes to limit the key failure modes of Si electrodes via material and electrode design. The general strategy is:

- (i) to provide fundamental knowledge on the behavior of nano-Si-based composites during Li insertion/deinsertion,
- (ii) to develop nano-Si-based active materials for the next generation of LIB in a sustainable manner by proposing a simple and optimized synthesis methodology,
- (iii) to fabricate viable Si-based electrodes that explore passivation strategies and unconventional design.

Our main findings are the following. First, we present a room-temperature synthesis of Si nanowires (SiNWs) that efficiently uses the Si resource via a material recycling scheme. Next, a similar procedure is developed for the room-temperature synthesis of kinked Si nanowires (k-SiNWs). Such nanostructures allowed us to evaluate the feasibility of a self-standing Si-C electrode design from mechanical and electrochemical standpoints and discuss the advantages and inconveniences of such unconventional designs. For instance, the optimized porosity of the electrode is certainly an advantage sacrificing, though, the volumetric capacity. We show that surface passivation is a possible route to extend the cycling life of Si-based electrodes. Related to this, we intimately investigated the effects of Ni coating on the lithiation behavior of Si

electrodes and use the knowledge to design optimized nano-Si to Ni coating configuration for high cycling stability electrodes. Finally, we show that passivation via conductive polymers mechanochemically converted to a hydrogel has additional benefits in terms of performance as well as environmental appeal. The manuscript is organized in 6 Chapters, as follows.

Chapter 1 provides an extensive description of LIB technology but also includes an overview of the past, present and promising battery technologies. It presents the relevant electrode materials as well as electrolytes, their limitations and the ongoing research strategies towards high energy density LIBs. Then, it discusses the implications of nanotechnology in LIBs, highlighting the benefits and the unknowns. Finally, we focus on the trends in LIBs from a technological standpoint and a sustainability perspective.

Chapter 2 places Si at the center of this work. We particularly describe the rich Si-Li electrochemistry and the related advantages and present the limitations. Next, we discuss the main degradation mechanisms related to the volume variations and the anisotropic swelling triggered by Li ions insertion. We then review major strategies and research directions to limit the detrimental effects and to extend the cycling life of Si electrodes with a focus on: material and electrode engineering, electrolyte systems, multi-functional binders and conductive additives. We stress on the importance of surface passivation of Si electrodes for the development of reliable, high performance LIBs. The chapter continues with an overview of the most common SiNWs synthesis approaches in the context of LIBs technology.

Chapter 3 offers an in depth analysis of the critical role of surface coatings for the Si electrodes. We used a Ni-Si system to gain understanding of the behavior of such coated structures during Li insertion. Based on the ratio of Ni coating thickness and the diameter of SiNWs, we identified two swelling and fracture regimes. Thicker coatings are found to reduce the overall anisotropic swelling, detrimental for Si electrodes as discussed in the previous Chapter, thus, promising better performing nano-Si electrodes. These findings are experimentally validated in Chapter 6.

Associated publication:

G. Sandu, L. Brassart, J.-F. Gohy, T. Pardoen, S. Melinte, and A. Vlad, "Surface Coating Mediated Swelling and Fracture of Silicon Nanowires during Lithiation," *ACS Nano*, vol. 8, p. 9427-9436, 2014.

Chapter 4 presents two optimized Si nanostructuring strategies based on metal-assisted chemical etching that enables the re-use of Si substrate by introducing a chemical peeling step. We first apply this procedure for the large-scale fabrication of vertically aligned SiNWs for LIBs electrodes. We found that the only limitation comes from the thickness of the Si substrate. Next, we propose a modified metal-assisted etching scheme that can be used for the synthesis of high-aspect ratio up to 200, mechanically stable, hybrid crystallographic orientation k-SiNWs. This method sustains high-etching rates and facilitates reproducible results. The protocol enables the control of the number, the location, and to a certain extent, the angle of the kinks via successive etch-quench sequences. We analyzed relevant Au catalyst parameters to assess their impact on the etched Si morphology.

Associated publications:

G. Sandu *et al.*, "Kinked Silicon Nanowires: Superstructures by Metal-Assisted Chemical Etching," *Nano Letters*, vol. 19, p. 7681, 2019.

G. Sandu *et al.*, "Kinked silicon nanowires-enabled interweaving electrode configuration for lithium-ion batteries," *Scientific Reports*, vol. 8, p. 9794, 2018.

Chapter 5 investigates the benefits of the developed nano-Si as active materials in LIB electrodes. We present a self-standing nano-Si-based architecture that seems more suitable for electrode materials that suffer from the volume variations. In terms of electrochemical performance, the k-SiNWs-based electrode stands as the best option compared with the vertical counterpart. Notably, the presence of kinks: (i) facilitates the homogeneous distribution of constituents as illustrated by elemental mapping as acquired with energy-dispersive X-ray spectroscopy, (ii) reinforces the electrode framework as revealed by tensile testing.

Associated publication:

G. Sandu *et al.*, "Kinked silicon nanowires-enabled interweaving electrode configuration for lithium-ion batteries," *Scientific Reports*, vol. 8, p. 9794, 2018.

Chapter 6 probes two multifunctional coatings in order to extend the cycling life of nano-Si electrodes. First, we iterate on the self-standing nano-Si assembly previously presented and design the Ni coated k-SiNWs structures as dictated by the findings from Chapter 3. We found that ionic liquid electrolyte systems associated with the integrated Ni current collector repress the detrimental effects related to the Si-Li alloying reaction, enabling high cycling stability with 80% capacity retention (1695 mAh/g_{Si}) after 100 cycles. Second, a conductive polymer is investigated as a lighter, functional coating option for nano-Si electrodes. Here, we emphasize on the stable cycling of nano-Si electrodes ($\approx$ 80% capacity retention after 200 cycles), the aqueous processing of nano-Si electrodes and the compatibility with the current manufacturing processes. This part as well as Chapter 3 is modulated by Prof.'s Alexandru Vlad vision for the LIB field. I thank him for the LIB initiation and valuable (life) insights.

Associated publications:

G. Sandu *et al.*, "Kinked silicon nanowires-enabled interweaving electrode configuration for lithium-ion batteries," *Scientific Reports*, vol. 8, p. 9794, 2018.

G. Sandu *et al.*, "Mechanochemical Synthesis of PEDOT:PSS Hydrogels for Aqueous Formulation of Li-Ion Battery Electrodes," *ACS Appl. Mater. Interfaces*, vol. 9, p. 34865, 2017.

Conclusions section gives an overview of what this work has accomplished, the aims and the current destination.

There are many aspects of this work that require further investigation and understanding. I compile a few in *Perspectives*. In addition, the section intends to inspire the reader toward future research directions and development prospects.

Associated author publication:

G. Sandu, A.Vlad, and S. Melinte, "Inkjet-printed paper battery," *E-MRS Spring Meeting*, Strasbourg 2017, poster presentation.

All the electrochemical data presented here was recorded in the Prof.'s Jean-François Gohy research facility. I am most grateful to him for his guidance and for always knowing how to ask the right questions. Chapter 3 also carries the analytical and inspirational touch of Prof. Laurence Brassart. I thank Dr. Sorin Melinte and Prof. Davide Bonifazi for their support and encouragements to look beyond batteries. Naturally, this work is the result of fruitful collaborations. I thank everyone for their energies and to Dr. Sorin Melinte for sharing my vision. At times, this patriarchal society weighted heavily on me and my work.

Many thanks to Prof. Roland Keunings for accepting to preside over the defence of this work as well as to Prof. Jonathan Coleman for his time and recommendations for improving this manuscript.

I am most grateful for everyone in my life. You are the ones that made all this possible! And, to Dr. Sorin Melinte for his extensive help in the elaboration of this book.

L'important n'est pas de convaincre, mais de donner à réfléchir.

Bernard Werber

Lithium-ion battery framework

Don't panic!

Douglas Adams in The Hitchhiker's Guide to the Galaxy

Electrochemical devices such as batteries convert chemical energy into electrical energy. If the process is reversible, the system is rechargeable. The drive in battery technologies has always been the energy density or how much energy can be stored or delivered per unit of weight or volume. Lithium-ion technology currently surpasses all the other battery chemistries with respect to their energy density, design flexibility or performance. This chapter briefly follows the timeline of battery development leading to LIBs and presents the fundamentals of batteries from thermodynamic considerations. Relevant electrode materials and electrolytes are discussed based on their performance and challenges as well as recent developments in electrode materials with highlights on the ongoing research strategies. This chapter continues with the development that nanotechnology unlocked in the LIB technology as well as the challenges and repercussion on the electrode design. Finally, we will introduce the possibility of greener and more sustainable electrical storage devices.

1.1 The beginnings

Galvani had a revolutionary theory regarding the body movement. He thought that animals generate electricity and use it to power the motion of the body. At the time it has shaken the entire medical community and beyond. Until Galvani's theory, the field of the study of movement was sparse and guided by the pioneering work of Leonardo da Vinci centered on the anatomy and mechanics but explained by mostly myths. Galvani, with the help of his wife, observed that when the leg of a frog is touched with a knife, a twitch occurred. He reproduced the twitching in controlled experiments and published his findings in 1791 [1]. Finally, a theory grounded in physics rather than the mythology pushed the field further. His research had ripples in many scientific communities besides the kinesiology and captured the attention of an experimental physics professor, Volta. Volta's interest triggered a breakthrough in the field. He started by reproducing Galvani's experiments and observed two different metal wires used to connect the nerve with the spinal cord. Connecting the metals would make the leg twitch and Galvani simply assumed that the metals acted as electricity conductors, while the electricity was stored in the frog. However, Volta had another theory and thought that the two metals, in certain conditions, can generate an electric current. He then started evaluating different sets of metallic elements. Eventually, Volta published his bi-metal theory, where he describes his invention of an artificial electrical organ based on this principle, i.e. voltaic pile [2]. Later in 1859, Pb/H₂SO₄/PbO₂ (or lead-acid system) was assigned to Gaston Planté that built on the German physicist Wilhelm Joseph Sinstlenden discovery in 1854 [3]. This system included two spiral electrodes submersed in a glass containing H₂SO₄ electrolyte separated by a linen tissue. Further improvements to the system were implemented by Camille Alphonse Faure, in 1881, and it was used to power the first electric vehicle that reached the landmark of 100 km/h, the missile-shaped car 'La jamais contente' piloted by Camille Jenatzy. In fact, fuel-powered vehicles at that time were frequently disqualified for their high consumption.

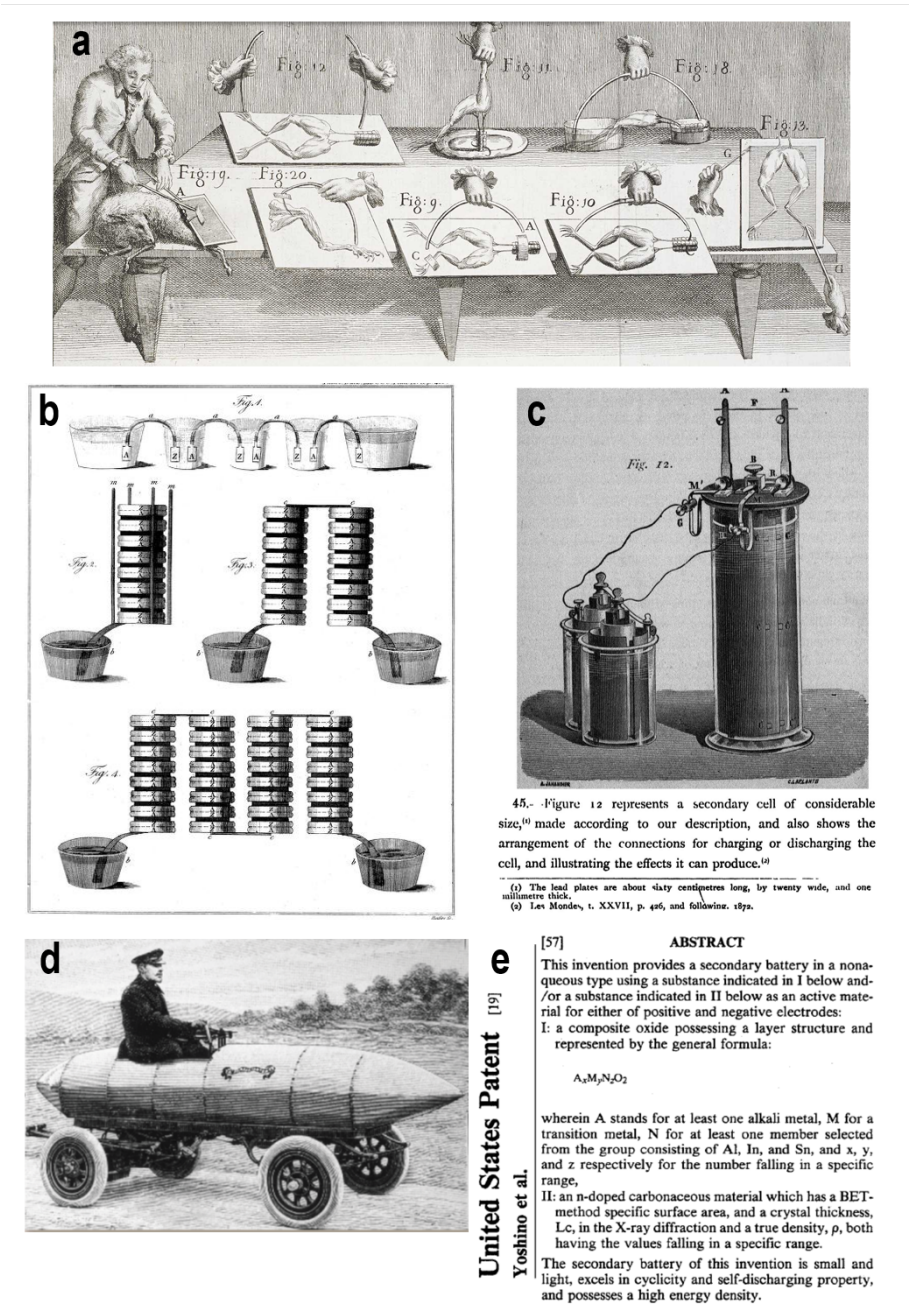


Figure 1.1: A journey through the past. (a) Galvani’s experimental setup taken from [1]. (b) Volta’s artificial electric organ as described in [2]. (c) Lead-acid secondary cell as developed by Planté [3]. (d) *La jamais contente* - the first electric powered vehicle and the first one to break the 100 km/h milestone [4]. (e) An extract from Yoshino patented methods [5].

Clearly, the idea of an electric car is not new but it was made obsolete by the steam technology and later by the internal combustion engine. Interestingly, the 1960's nickel-metal hydride rechargeable battery chemistry was sponsored by the giant automakers: Benz and Volkswagen. These reversible hydrogen-storage units have revolutionized consumer electronics, setting the trend for portable electronics. Along this, hundreds of other electrochemical couples or battery chemistries were proposed in the twentieth century but the 1990's Li-ion shuttling chemistry proposed by Sony surpasses all the previous chemistries in terms of voltage and storage capacity. It was a great achievement for the material scientist, nonetheless, insufficient nowadays for Moore's law-abiding electronics trend.

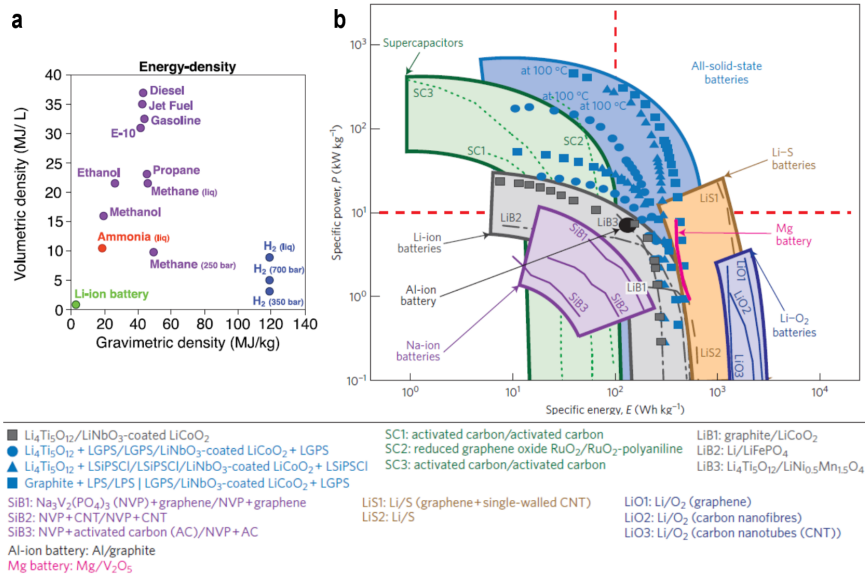


Figure 1.2: Energy sources vs LIB technology. (a) Energy sources for transportation. From [6]. (b) Ragone plot of current and future energy storage technologies. Adapted from [7].

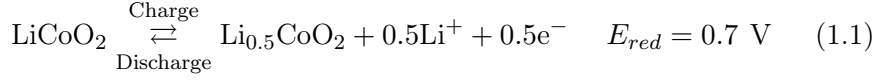
In addition, the interest in lithium-ion battery (LIB) today is also catalyzed by the current environmental concerns and the urgency of the C footprint reduction since they seem to be the best technologically avail-

able choice for powering the electric vehicles thus reducing or canceling the pollution related to C emissions of the fuel engine. However, their energy density is quite low compared to other energy sources used for transportation (Figure 1.2a). Nonetheless, there are some promising energy storage technologies that can tilt the balance towards batteries for a safer, economical and sustainable path to provide for human activities such as travel, communication, education (Figure 1.2b). Furthermore, to reduce the impact of the carbon footprint of the battery itself, the entire battery life is important: selecting sustainable materials as well as safe battery chemistries, implementing smart usage associated with renewable energy sources and finally the battery disposal, recycling or restoring at the end-of-life.

1.2 Fundamentals

A battery is made of one or more electrochemical cells giving a certain current at a nominal voltage over a period of time. An electrochemical cell relies on a set of reactions involving electrons. For a cell to be rechargeable, a reversible chemical reaction must take place at both electrodes. It is composed of two electrodes connected by an ion conduction material called the electrolyte and electrically insulated by a separator membrane. If these electrodes are connected to an external circuit, the charge transfer will be activated. Electrons flowing through the external circuit are balanced by the Li^+ flowing from the most negative to the most positive electrode. Thus, chemical energy is converted to electrical energy. Achieving this relies on a synergistic presence of simultaneous phenomena. To picture the general functioning of an electrochemical cell, we have to consider: the thermodynamics that is the responsible for the driving force of the reactions, the transport for the movement of ions, and the kinetics for the rates of the reactions. The key properties for energy storage devices are voltage and capacity. Both of them are dictated by thermodynamics. The voltage is given by the nature of chemicals involved in the reaction while capacity is directly related to how much of the reaction has occurred. Let's look at the reactions in the most conventional LiB cell. On one side, we have the electrode reaction

for the LiCoO_2 and the associated standard reduction potential, E_{red} :



On the other side, we have the electrode reaction for the carbonaceous material and the associated standard oxidation potential, E_{ox} :



The standard potential of the cell is given by:

$$E_{cell} = E_{cathode} - E_{anode}. \quad (1.3)$$

Thus, $E_{cell} = 0.7 - (-2.9) = 3.6 \text{ V}$. We can simply look-up the values for the standard electrode potentials in tables such as the one in Annex B from Linden's [8]. These values are experimentally determined in reference with the normal hydrogen electrode (NHE). If we need Li as reference¹, we have to consider $E_{cell} = E_{cathode} - E_{Li}$ thus the cell potential, for the carbonaceous electrode coupled with Li, will be: $E_{cell} = -2.9 - (-3.01) \approx 0.1 \text{ V}$ ². Finally, the voltage is directly related to Gibbs free energy of the chemicals via:

$$\Delta G^0 = nFE_{cell}, \quad (1.4)$$

where n is the number of transferred electrons and F is Faraday's constant. Thus, if the reaction proceeds without an external potential, spontaneous or thermodynamically favored ($\Delta G^0 < 0$), it is characteristic to a galvanic cell. During discharge, the anode (-) will undergo oxidation while the cathode (+) will be reduced. Thus, during charge, the electrolytic cell converts the electrical energy provided by an external source into chemical energy. The redox reaction is induced or forced ($\Delta G^0 > 0$). The anode (-) will be oxidized and the cathode (+) will be reduced with

¹This is the case for the Lithium (metal) battery or Li-ion half-cells discussed in this work.

²Throughout this work, we say low-working voltage vs Li/Li^+ is required for an anode material.

Li^+ flowing in the opposite direction. This is elegantly sketched in Figure 1.3.

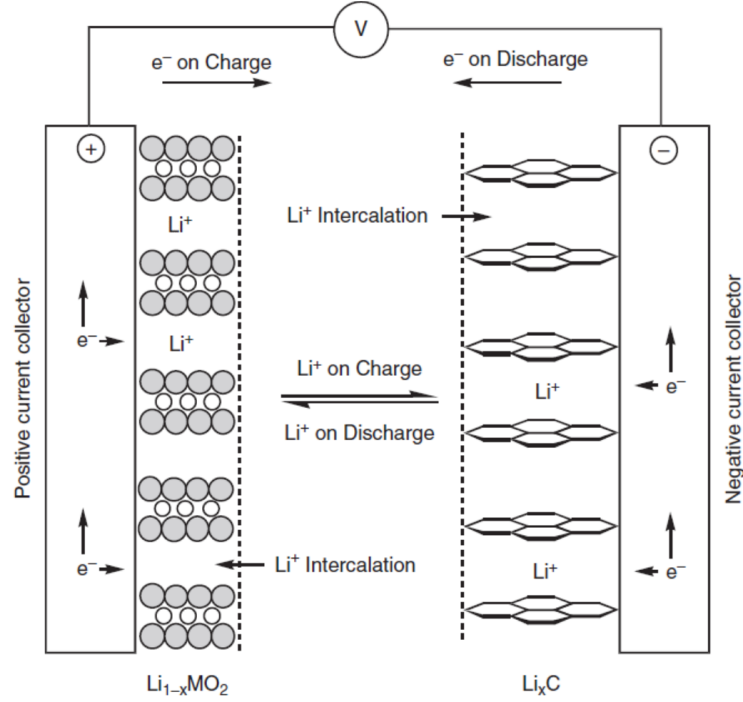


Figure 1.3: Schematics of the electrochemical processes in a conventional LIB cell with a carbonaceous anode and an alkali metal intercalation material such as LiCoO_2 . From [8].

Note that, in electrochemistry, oxidation reaction always occurs at the anode and the reduction at the cathode, thus the sign of the electrode is not important. Nonetheless, nomenclature convention allows using positive electrode for cathode and negative electrode for anodes, corresponding to the electrode state during discharge.

We said earlier that the electrons flowing through the external circuit have to be balanced by the Li ions transferred between the electrodes. The relationship between the number of electrons and the number of transferred moles is given by Faraday's law:

$$It = \frac{nFN_i}{s_i}, \quad (1.5)$$

where I is the current, t is time, N_i is the number of moles of species i and s_i corresponds to stoichiometric coefficient of species i . This gives us the amount of charge that the chemicals can store in Amper*hour. Let's compute it for a carbonaceous material, based on the reaction from 1.2. We will assume we have 1 g of carbonaceous material. From the reaction 1.2, we have one transferred electron, $n = 1$, $s_{carbon} = 6$ and 1 g of carbon equals to $\frac{1}{12}$ mol of carbon. Thus, we have:

$$It = \frac{1 * 96487 \frac{C}{mol} * \frac{1}{12} mol}{6} = 1.34 * 10^3 C. \quad (1.6)$$

We need to divide the result by $3600 \frac{C}{Ah}$ to get to 0.372 Ah for 1 g of carbonaceous material.

In general, the specific capacity of an electrode material reported to material load (mAh/g) is computed as:

$$q = \frac{nF}{3600 * M}, \quad (1.7)$$

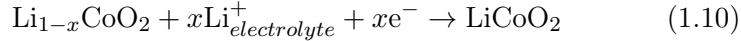
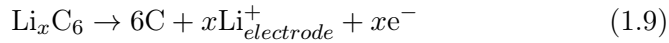
where M is the molecular weight (kg/mol).

For now, we only discussed standard conditions (1 atm, 25°C and molarity 1 mol/kg). For non-standard conditions, we have to consider Nernst equation as follows:

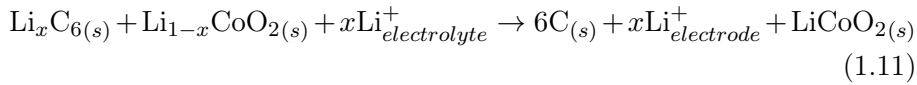
$$E = E_{cell}^0 - \frac{RT}{nF} \ln \left(\frac{\prod_j a_j^{s_j}}{\prod_i a_i^{s_i}} \right), \quad (1.8)$$

with a_j are the reaction products activities and a_i are the reactants activities. The s_j and s_i are their associated stoichiometric coefficients.

Now let's put it into a friendlier LIB form. We take the conventional LIB cell at discharge and rewrite the reactions 1.1 and 1.2 as follows:



Taken together, we have:



The concentrations of solids never change, therefore, they are set equal to 1. Thus, Nernst equation for Li intercalation electrodes becomes:

$$E = E_{cell}^0 - \frac{RT}{xF} \ln\left(\frac{a_{Li^+}^{-1}{}_{electrode}}{a_{Li^+}_{electrolyte}}\right). \quad (1.12)$$

The activities of species are directly related to the concentrations and, in most situations, we can replace activities with concentrations, $C_{i,j}$. This directly relates the concentrations to the amount of charge that has passed using Equation 1.5. To sum up, Nernst formalism provides the tools to evaluate the state of the battery at a certain moment, certain concentration or certain potential. The reader is, however, advised to proceed with care when applying Equation 1.12 since not much is known about the activity of lithium in the electrolyte [9].

1.3 Redox active materials

Generally speaking, the electrode materials have to fulfill several requirements such as: good electronic and ionic conductivity, high specific capacity, low working potential (vs Li/Li⁺) for the negative electrode while a high potential (vs Li/Li⁺) for the positive electrode, high cycling stability, safety and availability. All these conditions are difficult to meet at once, as such conductive additives and binders are added to the electrode compositions. Based on how Li ions are accommodated, we can distinguish 3 types of active materials: insertion, conversion and alloy-type.

1.3.1 Positive electrode materials

Based on their reaction mechanism with lithium, the cathode materials are insertion type. A material can be used as a positive electrode material if the reaction with lithium is highly reversible and the host structure is not affected by the addition or removal of Li ions. The reaction with Li has to be fast, reliable and at high voltages. The materials contain redox metal ions and are ideally good electronic conductors providing efficient pathways for the electrons during the reactions. Li

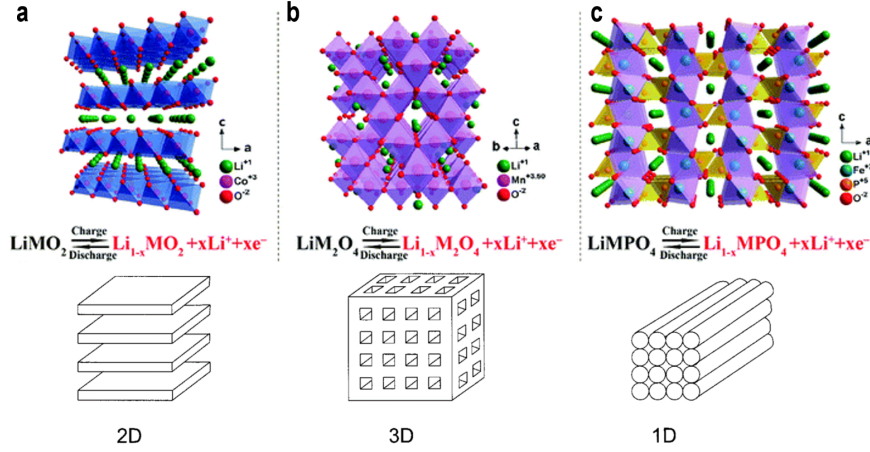


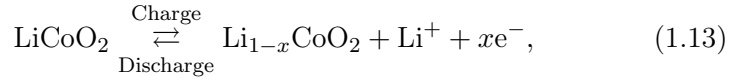
Figure 1.4: Positive redox active materials. (a) The layered crystal structures for LiCoO_2 . (b) The spinel LiMn_2O_4 structure. (c) The LiFePO_4 olivine structure. Below are presented the schematics with the void structure which represent the Li insertion channels. Adapted from [10, 11].

ions should easily access the host structure, i.e. the materials should also be good ion conductors. Finally, the host material should be stable without any damage to the lattice. Insertion type materials have several advantages over the other classes of materials such as a rather small volume change during cycling offering mechanical stability and, thus, long cycling life. Nonetheless, there are some limitations in terms of rate capability due to the sluggish Li ions diffusion, a challenge generalized to all solid-state materials as well as limited capacity since Li ions shuttling can affect the host lattice stability. Furthermore, lithiated cathodes are required which means that a limited amount of lithium is available. Parasitic reactions can consume the limited amount of lithium leading to cycling failure.

Nowadays, there are three types of structures, currently used as positive electrodes, that rely on an insertion mechanism for Li storage: the layered structure (LiCoO_2), spinel structure (LiMnO_2) and olivine structure (LiFePO_4). The structure type has an important effect on the Li diffusion, with important differences in Li insertion mechanism. Fur-

thermore, the host lattice stability that can be severely affected in the delithiated state. Interestingly, Professor John B. Goodenough showed the first clear demonstration of all these 3 types of structures and his work still governs state-of-the-art LIBs.

Layered structure. The most common layered structure material is LiCoO_2 (LCO) is similar to TiS_2 , a chalcogenide previously explored as cathode associated with a Li metal anode. It was common at the time for the cells to be assembled in the charged state and have to be subsequently discharged. Nonetheless, LiCoO_2 is synthesized in the lithiated state and Goodenough showed that lithium can be electrochemically removed, thus, the cell is assembled in the discharged state and has to be charged before use. The community was used with fabricating charged batteries and was reluctant to Goodenough's work. However, these results facilitated the exploration of other research directions for rechargeable LIB and eventually associate negative delithiated insertion materials such as C that represents the LIB as released by Sony in the '90s. The LCO cathode reaction follows:



where x is limited to 0.5 for practical applications to avoid the collapse of the delithiated structure. This means that only 50% of the theoretical capacity can be exploited. The LCO solid consists of stacked anionic cobalt and oxygen atoms build-up with edge-sharing octohedra with Li cations located in between (Figure 1.4a). Material scientists were aware of the issues related to cobalt in terms of price, availability, and toxicity and in an attempt to fully exploit the material, thus access more lithium, have tried to stabilize the structure by cationic substitution of Co^{3+} with Ni^{2+} and Mn^{4+} . Capacities greater than 200 mAh/g have been obtained for the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ material. Partial substitution of Co^{3+} with Ni^{2+} and Mn^{4+} resulted in the creation of $\text{Li}[\text{Ni}_{1-x-y}\text{Mn}_x\text{Co}_y]\text{O}_2$ or NMC class of layered oxides. Higher capacities are accessed in these Li-rich compounds as shown in Figure 1.5. Initially, LiNiO_2 was studied due to higher Li capacity, however, the drawbacks related to the instability of the delithiated Li_xNiO_2 structure leading to Li/Ni disorder since Ni tends to occupy the Li positions within the structure and ultimately blocking

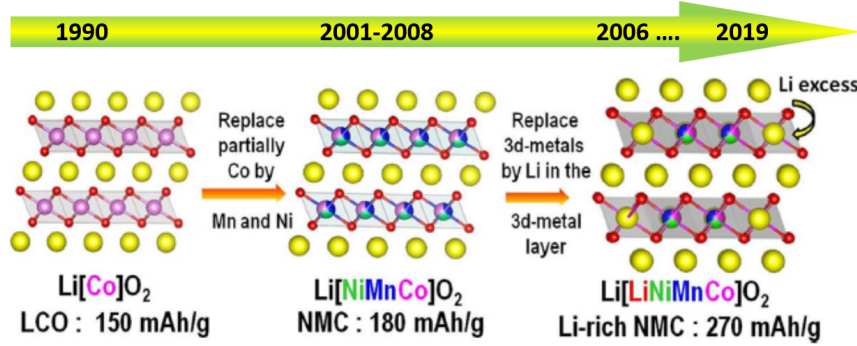
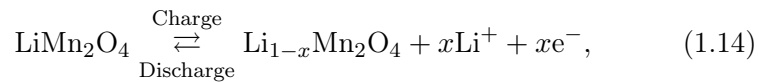


Figure 1.5: Technology evolution of the layered LiCoO₂. From [12].

the lithiation, required further investigations. Partial substitution of Ni with [Ni_{1-x}Co_x] managed to stabilize the structure but it fails to gain widespread adoption due to the diminished capacity. Interestingly, LiMnO₂ with the Mn⁴⁺/Mn³⁺ redox couple, was initially thought to be a layered material but the structural instability of the delithiated phase resulted in the collapse of the structure, transforming it into a spinel metal oxide. Finally, state-of-the-art cathodes are Al-doped Li[NiCo]O₂ with 15-20% Co, or NCA. Partial substitution of Ni or Co with fixed trivalent and divalent elements (such as Al or Mg) leads to a reduction of lithium that can be reversibly stored and extracted, but brings higher structural stability during delithiated state. As a matter of fact, NCA has the highest rate capability among cathode materials. Figure 1.5 shows the timeline in the development of layered oxide cathodes.

Spinel structure. Spinel structures are a class of minerals obeying A²⁺B₂³⁺O₄⁻² which crystallize in a cubic crystal system with oxygen anions arranged in a cubic closed packed lattice and A and B cations occupy octahedral or tetrahedral sites. Perhaps the most significant metal oxide from this class is LiMn₂O₄, a 3D Li ion conductor as shown in Figure 1.4b. The electrochemical reactions associated with Li removal/insertion within the host lattice follows:



with $0 \leq x \leq 1$.

The mechanism of capacity fading results from a concentration of several elements. LiMn_2O_4 presents some important issues at a low state-of-charge (low x values) with structural changes, manganese decomposition reaction and dissolution of Mn^{2+} in the electrolyte due to the HF traces that probably results from the PF_6 decomposition. A high state-of-charge (high x values) affects the stability of the structure in the delithiated phase, site exchange between Li and Mn can occur and also electrolyte oxidation. It also suffers from volume changes and Li ordering during cycling. While the spinel LiMn_2O_4 has a lower capacity than LiCoO_2 , it has important advantages in terms of cost, toxicity, and material availability. Thus, numerous efforts have been redirected to annihilate the issues associated with LiMn_2O_4 . To suppress the structural distortions, manganese ions were partially replaced by trivalent or divalent cations such as Co, Cr, Al, Ni or Mg. This strategy managed to improve the cycling life of manganese-based spinels. Perhaps the most important is $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ with $x=0.5$, a '5 V' class material with a redox action at 4.7 V that presents a capacity of 130 mAh/g. Li-rich spinels have also been studied despite of their low associated Li storage capacity. Finally, mixed layered-spinel structures have also been evaluated.

Olivine structure. Olivine structure of lithium metal phosphates, LiM(II)PO_4 with $\text{M}=\{\text{Fe, Mn, Co, Ni}\}$, are the most promising class of cathodes for rechargeable LIBs. In particular, LiFePO_4 demonstrates a capacity of 170 mAh/g and a potential to reversibly cycle Li at 3.4-3.5 V vs Li/Li^+ . In addition, LiFePO_4 presents many advantages with regards to cost, toxicity, and safety in functioning. The olivine structure consists of a 3D framework with PO_4 occupying the tetrahedral positions and the magnetic metals M the octahedral as shown in Figure 1.4c. In olivine structure, Li ions move along 1D channels. Thus, any defects in these channels lead to poor rate capability. In fact, this class of material suffers from poor electronic conductivity in the crystal lattice (electron hopping between Fe(II) and Fe(III)) associated with slow Li transport in the lattice. Therefore, a functional conducting coating is usually applied to sustain the charge transport.

Due to $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple, LiMnPO_4 has a higher working potential similar to LiCoPO_4 . Nonetheless, the former has many benefits such as availability, environmental safety, higher voltage compared with LiFePO_4 but is at the limit of the electrolyte stability window (around 4 V vs Li/Li^+) and suffers from poor electron conductivity as well. Finally, cathode compounds based on mix mixed lithium transition metal phosphates have also been evaluated to enhance the rate capability and the specific capacity. Polyanionic-types of structures having XO_4 with $\text{X} = \{\text{Si}, \text{Ge}\}$ have also received attention in the light of promising results for the olivine.

Other cathode materials. Incredible amount of effort has been directed in the development of materials beyond the traditional cathodes. For instance, a new class of conversion type materials has been developed, transition metal halides. Among them, FeF_3 has the highest theoretical capacity known for a cathode material with the exemption of sulfur, 712 mAh/g and the redox activity at 2.7 V vs Li/Li^+ . However, more effort is needed to overcome the crystal structure instability and low electrical conductivity. Furthermore, besides the inorganic cathodes, organic cathodes have also been investigated as emerging materials with a great variety of polymeric redox-active materials classified as conjugated polymers, non-conjugated redox-active polymers, and radical compounds. One of the most intensively studied conjugated polymer is polypyrrole. An extensive report with the most promising organic materials is presented in [13].

1.3.2 Negative electrode materials

While a variety of cathode materials are available, the progress with the anode materials has always been sluggish. For instance, cathodes were developed in the '80s and they did not find a reliable negative match until later. At first, Li metal was intensively explored but the dendritic lithium shortage associated with unpredictable cell explosion encouraged the community to look for an alternative. Early research on carbonaceous materials showed that Li intercalation was possible but it

was concurrent with the intercalation of solvent molecules which resulted in carbonaceous structure collapsing. Dahn *et al.* eventually showed that petroleum coke, a C-rich oil refining by-product, performs much better than graphite if ethylene carbonate (EC) replaces propylene carbonate (PC) solvent [14]. However, Yoshino had all the right elements at the time to show the true potential of carbonaceous materials. First, he used pure starting material rather than the by-product that Dahn used. In Japan, LiPF_6 and LiCl_4 were commonly used electrolytes for primary cells vs LiAsF_6 at the time the best electrolyte for rechargeable Li metal that Dahn employed. Also, Yoshino selected a separator based on polyethylene (PE) rather than polypropylene (PP), which was more common at the time. These elements gave Yoshino the title of the LIB inventor based on the concept of Li shuttling developed by Armand with the cathodes developed by Goodenough.

Based on their reaction mechanism with Li, negative materials can be classified as insertion, conversion, and alloy-type. Carbonaceous materials are by far the most adopted insertion type active material in LIBs. They can be distinguished as ordered or with crystallographic long-range order such as graphite and disordered or amorphous carbon. Li insertion behavior depends greatly on the type of carbon as it will be discussed in the following. Li titanates are the second class of material and the most interesting nowadays for commercial adoption. As alloy type, the focus is on abundant materials such as Si, Sn, and Al, as discussed later in this Chapter; generally, metals that form an alloy with Li. Finally, lithium storage oxides (based on Si, Sn, Al) and transition metal oxides (based on Mn, Fe, Co, Ni, Cu) have also been evaluated.

Lithium metal. Lithium metal suffers from the electrolyte instability at the low working potential thus resulting in the formation of the solid electrolyte interphase (SEI). However, this SEI, as well as Li re-deposition, occurs inhomogeneously at spots with higher intensity of the electric field or lower impedance, thus, with advanced cycling, the surface will change the morphology and dendrite will form. This usually results in internal short circuits that are responsible for the limited cycling life and occasional explosions. The problems related to discharge are due to Li dissolution that does not occur uniformly resulting in dendrite discon-

nection from the main electrode, loss of electrical connection, thus Li is trapped and charge/discharge efficiency is low (Figure 1.6a). Nonetheless, today primary Li metal cells use Li metal safely and avoid this dendrite formation process. However, in terms of sustainability, these types of cells will be limited, with Li resources more likely directed towards reusable systems, such as rechargeable Li-metal. For Li-metal, one research direction involves the use of polymer electrolytes such as polyethyleneoxide (PEO) with a lithium bis(trifluoromethanesulfonyl)imide (LiTFSi) salt. Such systems are attractive due to their safety features since they do not include flammable compounds and there is no leakage risk. While Li metal is a promising anode alternative due to its extra high capacity (3860 mAh/g) it has been under the loop of material scientists for over 30 years, yet the usage was limited to a few applications requiring polymer or solid electrolytes since their performance in liquid electrolytes is hazardous and limited. Furthermore, Li metal is a charged anode, therefore it must be combined with a cathode in a charged state. Usually, LIBs are assembled in the discharged state, thus other cathode materials are exploited with Li metal such as V_2O_5 or MnO_2 . Nonetheless, Li metal is still under intensive study by the community as a negative electrode for the Li-S and Li-air technologies. If these emerging Li-based technologies become available in the future, Li recycling will also be mandatory. These aspects will be discussed later in this Chapter.

Graphite. Graphite spheres or mesocarbon microbeads have been the materials of choice. The anode shows reliable cycling and a capacity of 300-350 mAh/g with a low surface area and consequently a low irreversible capacity due to SEI, while proved a decent safety in association with liquid electrolytes. As previously mentioned, the type or structure of carbon will greatly impact Li intercalation capacity and potential. The basic unit block for carbonaceous materials is graphene. The stacking of graphene layers follows a well know order to form the graphite. The hexagonal graphite A-B-A is a very common, thermodynamically stable phase. In a less common polymorphic form A-B-C-A stacking forms homohedral graphite. Nonetheless, all materials contain some sort of disorder. As a matter of fact, various carbonaceous materials have been developed with induced stacking disorders.

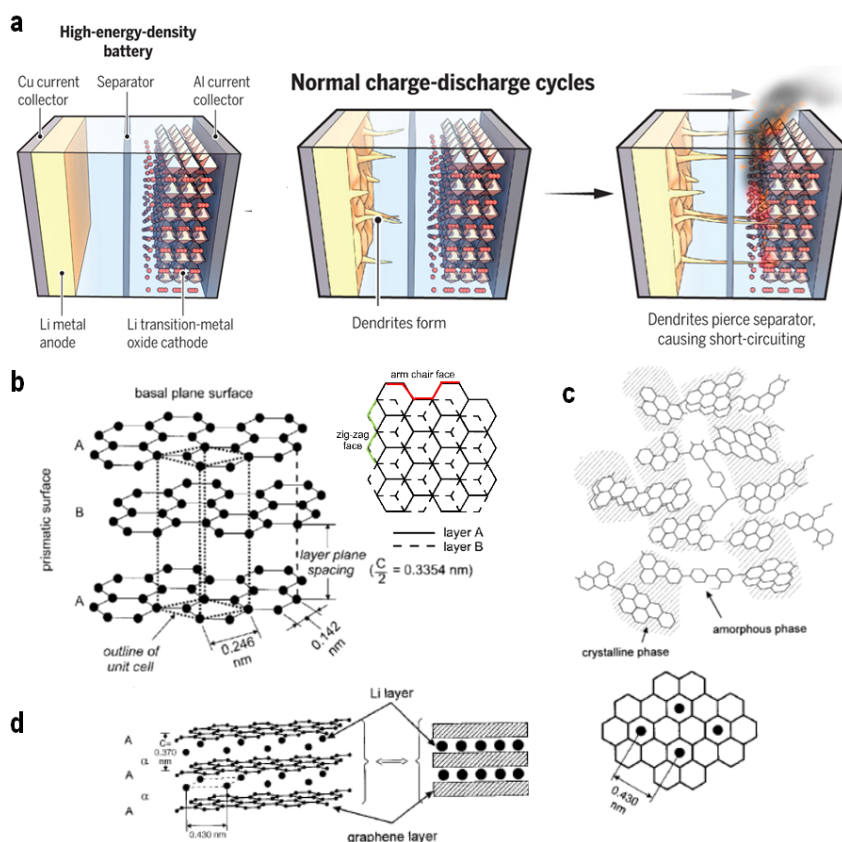


Figure 1.6: Negative redox active materials. (a) Lithium metal and the dangers associated with dendrite growing. Adapted from [15]. (b) Schematic of the hexagonal graphite with the three types of surfaces. (c) Non-graphitic (disordered) carbon. (d) Expected LiC_6 structure. From [11].

For instance, turbostratic disordered carbon includes those where the graphitic parallel planes are shifted or rotated. All types of carbon are dependent on the nature of the precursor material (solid, liquid or vapor) and require graphitization at extremely high temperature, greater than 1000°C .

Graphite exhibits three types of surfaces with different reactivity towards Li as shown in Figure 1.6. Basal planes are usually saturated, present low reactivity, and are the most prone to defects. Prismatic planes (zig-zag surface and armchair surface) present the highest Li re-

activity consequently forming thick SEI. Surface functional groups may be tailored to improve the quality of the SEI. The Li intercalation occurs only through prismatic surfaces while with the basal surfaces the intercalation is only possible if defects are present. Highest Li content at room temperature corresponds to the LiC_6 or 372 mAh/g (760 mAh/cm³). The lithiation mechanism follows a stage formation with different possible LiC_x phases before the fully lithiated LiC_6 . Li transport occurs along the grain boundary. The expected LiC_6 follows the structures sketched in Figure 1.6d. There are some intrinsic advantages for this insertion type mechanism such as reduced volume variation, only 10% for graphite, and as a consequence, the electrode provides good mechanical stability and a relatively long cycling life, around 1000 cycles. The only drawback is related to the rate capability. Graphite working potential or Li insertion occurs at a potential below the stability window of the electrolyte thus, it will be reductively decomposed and a SEI will form. A good quality SEI will be critical for a good cycling life. For graphite, in particular, this SEI prevents solvent intercalation and therefore, graphite exfoliation.

Solid electrolyte interphase: One side of the interface. Solid electrolyte interphase is electronically insulating, transparent to Li ions, increases the electrode impedance and limits the rate capability of the electrode. SEI was found to grow during rest times and at high temperatures and the growing rate slows down with the increase of thickness. The SEI formation depends on the electrolyte (salt, solvent, additives), electrode material (surface chemistry, structure, morphology, volume variations) and the formation process. In the electrolyte, the Li^+ are solvated (or converted) by the solvent in $\text{Li}(\text{solv})_n^+$. When passing through the SEI the $\text{Li}(\text{solv})_n^+$ are desolvated and intercalated as pure Li^+ . Thus, without the SEI or an ineffective one the solvent co-intercalates with Li. If $\text{Li}(\text{solv})_n^+$ is intercalated, it would be further reduced during potential decrease and results in gas formation that leads to graphite exfoliation.

Therefore, the solvent selection for the electrolyte is critical for the formation of an efficient SEI. For graphite, EC shows an efficient SEI formation and reversible Li^+ intercalation. The type of graphite is also critical since it can influence the capacity by variation of thermal or mechanical treatment. Mechanical treatment can lower the surface area,

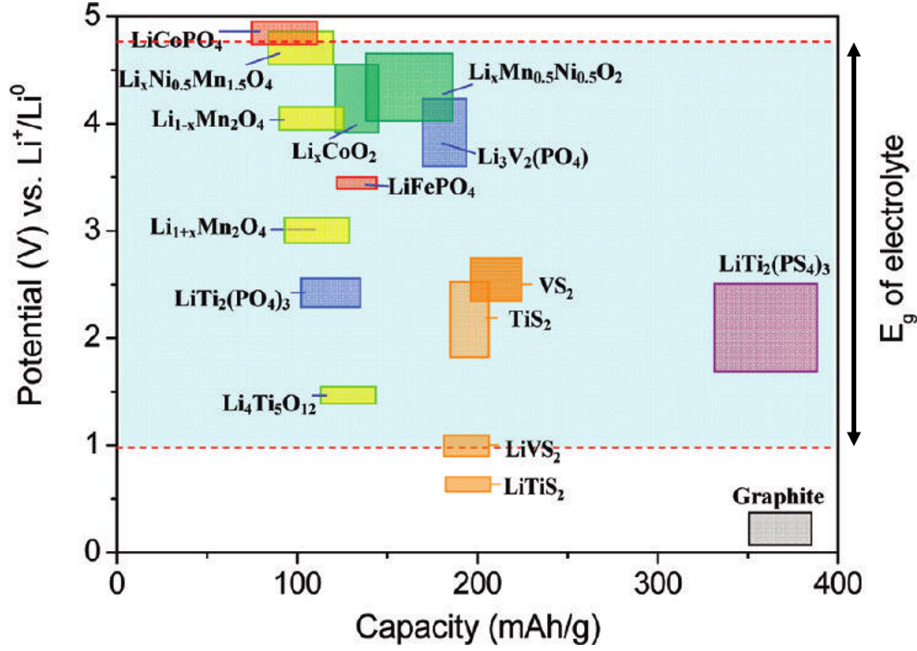


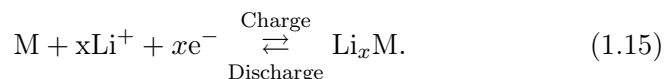
Figure 1.7: Electrolyte stability window from [16].

smooth surfaces, thus, decreases the exfoliation tendency and can introduce structural defects, supporting the formation of stable SEI. One possible research direction for the formation and anchoring of effective SEI is via surface functionalization. Functional amorphous C coatings have been found to positively influence the cycling life by providing an effective barrier towards co-intercalation of solvent molecules, lower surface area (low irreversible capacity) and increased rate capability. Chemical modifications of graphite using functional groups have also been explored. Higher Li storage is related to higher graphitic order but is not related to faster Li kinetics or rate capability. Therefore, there are major differences in rate capability as a function of the structure. Amorphous C can sustain faster Li kinetics due to the multiple access points for Li but at the same time is also more prone to Li trapping that can occur at the defect sites. Thus, besides the SEI, Li trapping also contributes to the irreversible capacity from the formation cycle. Due to disorder, solvent co-intercalation is not favorable in amorphous carbon thus SEI is

no longer desired but nevertheless will form due to the working potential and the electrolyte instability. The electrolyte stability window for some common electrode materials is shown in Figure 1.7.

Titanates. Titanates are a class of spinel structures, including the most important $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) that has a theoretical capacity of 175 mAh/g (practical 150 mAh/g) and a Li insertion potential at 1.5 V vs Li/Li⁺. The capacity is lower and the insertion potential is higher than graphite which results in a cell with a lower nominal voltage while the energy density of the LTO cell is significantly reduced than the graphite counterpart. The Li insertion in LTO follows a two-phase mechanism and shows high thermal stability with excellent mechanical and cycling stability with less than 1% volume variation. The higher Li insertion potential means that the electrolyte decomposition is avoided, thus the electrode impedance remains low and high rates are achievable. Furthermore, other electrolyte formulation can be used to enhance the performance at low temperature and expand the temperature range that graphite offers. Gas formation is, nonetheless, the problem with LTO electrodes that occurs at high temperature or after long storage or idle periods. The reasons are still under intensive study but the electrolyte decomposition catalyzed by LTO is assumed to be responsible.

Lithium storage metals or alloys. This class of materials relies on reversible alloy formation or formation of intermetallic compounds that follows:



This class can provide the highest Li storage capacity at the exchange of high volume changes that eventually cause problems with mechanical stability and, ultimately, with cycling life. This section is continued in Chapter 2, taking Si as case study.

1.4 Electrolyte systems

The electrolyte is a transport medium for Li ions, thus the most important parameter for the electrolyte is how fast Li ions move. The electrolytes available today can be divided into three categories: liquid

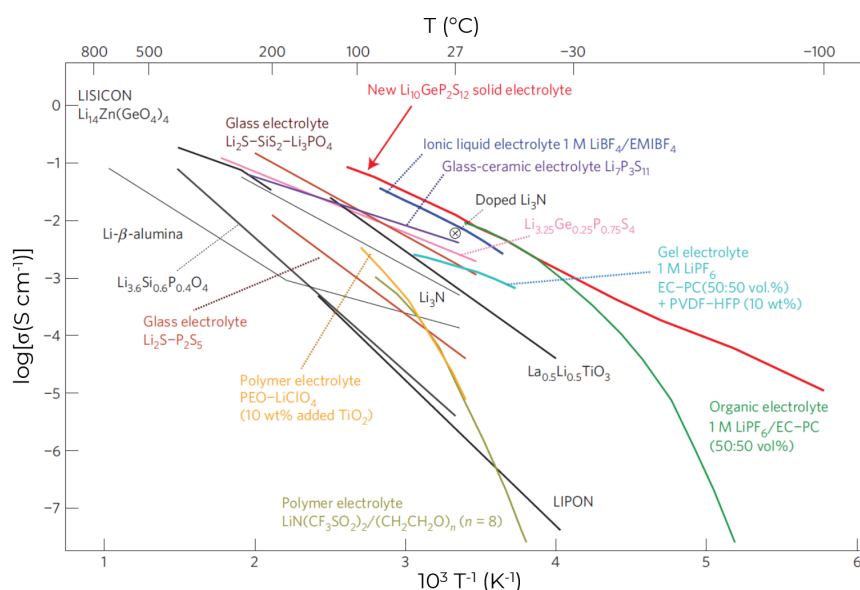


Figure 1.8: Ionic conductivity of different types to electrolyte systems. From [17].

electrolyte, polymer electrolyte, and solid electrolyte. Ideally, the electrolyte would be a good ionic conductor to facilitate Li transport, an electronic insulator to prevent self-discharge, chemically inert as well as electrochemically inert in a large window of potential, safe during electrical, thermal, mechanical abuse. Water, alcohols or acids are prohibited as it will result in H_2 gas formation. Ideally, the electrolyte system would be safe, from renewable sources, bio-degradable, and cost-efficient. Reality is quite far from the ideal electrolyte systems. State-of-the-art liquid electrolyte formulations do not meet most of these technical requirements and they are corrosive and quite toxic. Thus, a lot of effort goes into developing new, safer electrolytes with a larger stability window.

Liquid organic electrolytes. Liquid organic electrolytes are based on one or more aprotic solvents that solvate the electrolyte salt, typically LiPF_6 . In a conventional cell, the electrolyte has to completely wet the electrode and the separator surface. To facilitate the Li ions shuttling,

the most important property of the electrolyte is the ionic conductivity, σ :

$$\sigma = \sum_i n_i \mu_i z_i e, \quad (1.16)$$

where n represents the free ion number or charge carrier number, z is the valence order of ionic species, e is the unit of charge and μ is the ion mobility as given by:

$$\mu_i = \frac{1}{6\pi\eta r_i}, \quad (1.17)$$

with η (dynamic) viscosity of the medium and r is the solvation radius. Thus, based on Equations 1.16 and 1.17 increase of σ is only possible if the ion mobility increases by, for instance, a low viscosity solvent. Another possibility requires the association of large stabilized anions such as PF_6^- or 'imide⁻' which will alter n . In addition, Li ions are preferentially solvated by solvents with high dielectric constant while dissociation is favored when anions are well stabilized (e.g. by electron-withdrawing groups). Thus, an electrolyte requires a solvent with high dielectric constant, ϵ , such as EC, associated with dimethyl carbonate (DMC) or diethyl carbonate (DEC) to reduce the viscosity. Cations are preferentially solvated by high ϵ components. On the other hand, ion dissociation is important since only dissociated ions, unpaired ions, can migrate in the electric field. Ion triples are also allowed as they contribute to the ion conduction. Besides, the choice of solvents for a LIB electrolyte is also dictated by the temperature requirements of the application. Thus, up to 5 solvents can be included in the electrolyte formulation to increase performance, ion conductivity, range of functioning temperature and electrolyte stability. Ionic conductivity of relevant electrolyte systems is shown in Figure 1.8. LiTFSi has received a lot of attention lately since its use results in reduced gas formation.

Solid electrolyte interphase: The other side of the interface. For the proper functioning of the cell, the electrolyte has to work in the range of 0 to 4.4 V vs Li/Li⁺. The electrolyte stability window for some common electrode materials is shown in Figure 1.7. Furthermore, no solvents are stable around 0 V but some display limited reaction such as EC, resulting in a passivation layer, transparent to Li ions that protects the electrolyte from further decomposition. This film protects the graphite surface and

allows stable cycling without degradation. The SEI formation consumes lithium and since the process is irreversible, a loss of capacity is observed. The SEI depends on the electrolyte formulation and electrode materials, for instance, the type of carbonaceous material. As a matter of fact, since the reaction occurs at the surface of the active materials, the materials with low specific surface present a lower capacity loss. A good quality SEI is therefore crucial since it will dictate the cycling life, storage life and can impact the safety in functioning. For instance, a poorly formed SEI will continue to consume the electrolyte showing poor capacity retention and high electrode impedance due to the SEI deposit. To establish a uniform and stable SEI film, commercial cells are going through a 'formation' cycle that involves charging/discharging at lower rates or sometimes at elevated temperature for several times. For graphite, EC was found to form the most stable SEI with a minimum amount of Li. The SEI is critical for Li alloy-forming material such as Si, S, or Ge, which undergo important volume expansion during Li alloying reaction. De facto, the failure mechanism for these materials is the constant SEI formation that consumes Li and the electrolyte resulting in a rapid capacity decay. Much research is currently directed at developing a stable SEI on these types of materials. Finally, additives can be incorporated in the electrolyte formulation to specifically alter the chemistry of the SEI and promote the formation of a stable SEI. On the cathode side, the SEI formation is less studied, however, with the development of the '5 V' class of cathodes, the electrolyte stability at high potentials has also become a subject of interest.

Additives. Parasitic reactions in LIB cells can ultimately lead to capacity loss or, in some extreme situations, to explosions. Usually, to prevent such events, role assigned additives are added in the electrolyte composition to improve the general performance or the safety of the cell. Information of additives present in the electrolyte is scarce and highly proprietary but the additives should not go above 10%. From the literature, additives are known for anode passivation film-forming agent, such as vinylene carbonate (VC) or fluoroethylene carbonate (FEC), cathode protection agents, overcharge protection agents (redox shuttle additives), wetting and flame retardant agents. For instance, VC is highly beneficial

for carbonaceous based electrodes. It helps to protect both the anode and the cathode surfaces. Its presence is highly beneficial and usually associated with stable cycling and a reduction of the irreversible capacity.

Polymer electrolyte. On the one hand, we have gel-polymer electrolytes that are defined as ternary systems comprising a Li salt and an organic liquid trapped in a polymeric matrix. This type of electrolyte has no risk of leakage and the separator is not required. Some commonly used polymers include polyvinylidene fluoride (PVDF), poly(methyl methacrylate) (PMMA), and polyaniline (PANI). On the other hand, solid polymer electrolytes are freestanding solid gels that include only salt and a polymer. Since it has no liquid solvent, the interface properties are different than those for the liquid electrolyte. High-temperatures are required for a decent ion conductivity. Similar to gel electrolytes, there is no leakage risk and the separator can be omitted. Some typical polymers are PEO and poly(phenylene oxide) (PPO). The Li ion conduction mechanism in a solid polymer electrolyte is fulfilled either by ion hopping (Li^+) or ion transport assisted by polymer chains motion (Li^+ and anions).

Ionic liquids. Ionic liquids (ILs) are salts that are liquid at room temperature. The scientific community was attracted by their safety features: non-volatile and non-flammable. They are miscible with liquid organic solvents and present a larger electrolyte stability window (up to 5 V vs Li/Li^+). The IL-electrolyte system consists of two big asymmetric ions (anion and cation) and a Li salt. The physicochemical properties such as conductivity, viscosity, and density of the electrolyte depend greatly on the selection of the anion and the cation. Typical ion conductivities are in the range of 1-5 mS/cm, higher than the solid electrolytes but lower than liquid electrolytes. Mixed IL-organic electrolytes have been investigated to improve the safety or the functioning temperature range of the liquid organic electrolytes.

Solid electrolytes. Solid electrolytes have attracted a lot of interest since they are non-flammable, display broad electrochemical stable window and no leakage risk. Furthermore, higher energy and energy densities are expected. The solid-solid interface, however, presents more challenges, for instance, to avoid the increase of Li ion concentration at

the interface.

1.5 Redox passive materials

The most appealing feature of LIBs is that they can respond to any size and shape demand imposed by the portable application. For this reason, the objective of an energy storage unit is to pack all the battery components in a limited volume while maximizing the energy storage capability and sustaining long cycling life. Hence, any component other than the active material should be reduced as much as possible. This includes binders, conductive additives as well as separators. While it is generally desired their usage to be limited to a few percentages of active materials, their importance should not be minimized as they enable high battery performance and simplify manufacturing processes.

1.5.1 Binders

Conventional electrode architecture relies on casting slurries comprising active materials and conductive additives bound together by a polymeric binder onto a metal current collector. As such, the binder is responsible for the cohesion of active material layers and the adhesion of these layers onto the current collector. Ideally, a binder should be transparent to Li ions, chemical and electrochemical stable over a wide potential range to include the anodic and cathodic environments. For manufacturing purposes, the binder needs to render stable slurries without separation of components and a constant viscosity to facilitate the casting of the slurry on the metal current collector. It should also facilitate electrode slitting and avoid any short circuit occurring. As discussed above, a binder should satisfy as much of the requirements to justify its incorporation in the electrode slurry formulation thus, sacrificing active material. Traditionally, PVDF is the preferred polymeric binder due to its binding capabilities and the electrochemical stability that allowed its usage at both anodic and cathodic sites. The mechanical stability of the electrode relies on adding a few percentages of binder to the electrode formulation. Generally speaking, adhesion properties and the molecular

weight of the polymer are strongly correlated. As a matter of fact, it is believed that graphite particles are trapped into the polymeric matrix, thus, longer chains are associated with better particles' interconnectivity. In addition, high molecular weight PVDF requires less volume thus allows an increase of active material. However, the slurry properties are also affected by a high molecular weight binder and ultimately influence the mixing, coating and casting abilities. Styrene butadiene rubber (SBR) has gradually replaced PVDF on the anode side due to the fact that it provides better properties and leads the electrode fabrication towards an environmental friendlier route by adopting an aqueous processing rather than the N-Methyl-2-pyrrolidone (NMP)-based processing required for PVDF-binder electrodes. SBR provides better adhesion and more flexible electrodes for less mass loading percentage. Also, replacing PVDF with SBR has a positive effect on the graphite anodes in terms of capacity and cycling life. This stems from the different binding properties which were assigned to the difference in the structure, long-chain for PVDF vs fine particles for SBR. This was further confirmed by the detrimental association of PVDF with high capacity materials such as Si that suffers from high stresses generated during the electrochemical reactions that affect the mechanical stability of the electrode. Van der Waals interactions between PVDF chains and Si nanoparticles are not enough to prevent components re-organization that disrupts the particle-binder interaction, thus resulting in poor cycling ability. In this direction, for high capacity materials, polymers with rich carboxylic groups have shown some promising results thanks to their enhanced binding capabilities to active particles and current collectors. This topic will be developed further in Chapter 2.

1.5.2 Conductive additives

Carbon conductive additives materials such as carbon blacks, fine graphites or nanostructured carbon are used, at a low content, in the electrode formulation, on both sides, to reduce the internal electrical resistance. Thus, assuring an active connection between active material particles and the layers of active material and current collector relies on

employing a conductive additive. The type of carbon directly regulates the electrode density, the electronic and ionic conduction via porosity. A porous electrode can be an efficient electrolyte reservoir and can facilitate ionic transport. This, however, reduces the electrode density, thus packing less active material as well as generating a higher internal resistance. Thus, the optimized configuration for high capacity retention at high rates relies on finding the gold number for electrode density as well as a C-additive that absorbs easily the electrolyte and has a good dispersibility within the electrode framework. On the cathode side, Figure 1.9a shows the electrical volume resistivity as a function of electrode density for a LiCoO_2 with 3% wt of the listed conductive additives. They are all part of the carbon blacks family with a different specific surface area as evaluated with BET³ theory and listed in the legend for each type of additives. Generally, the electrical resistivity decreases when the packing increases, no matter what type of C-additive is used.

Due to the similar carbon structure, the performance of Super P and C-ENERGYTM65 are similar, while C-ENERGYTM45 has the best compaction behavior. Figure 1.9b shows the electrical volume resistivity as a function of electrode density for a LiCoO_2 with 5% wt fine graphite particles, KS6 and KS6L, for the same types of particles. Fine graphite particles have a higher particle size and a lower specific surface [18]. It is clear that the fine graphite limits the electrode porosity and allows a greater density of active material but requires a greater load than the additives in the carbon black family. It is generally believed that the additives families are complementary. Carbon black connects the active material particles while fine graphite ensures the connection throughout the electrode. This synergistic behavior is also presented in Figure 1.9b. Despite the fact the anode is also carbonaceous, it also requires conductive C-additives. The graphite used in the anode has different surface morphology and a low specific surface (1 to 2 m^2g^{-1}), thus it typically shows low intrinsic conductivity and high contact resistance between particles.

³Brunauer-Emmett-Teller (BET) theory.

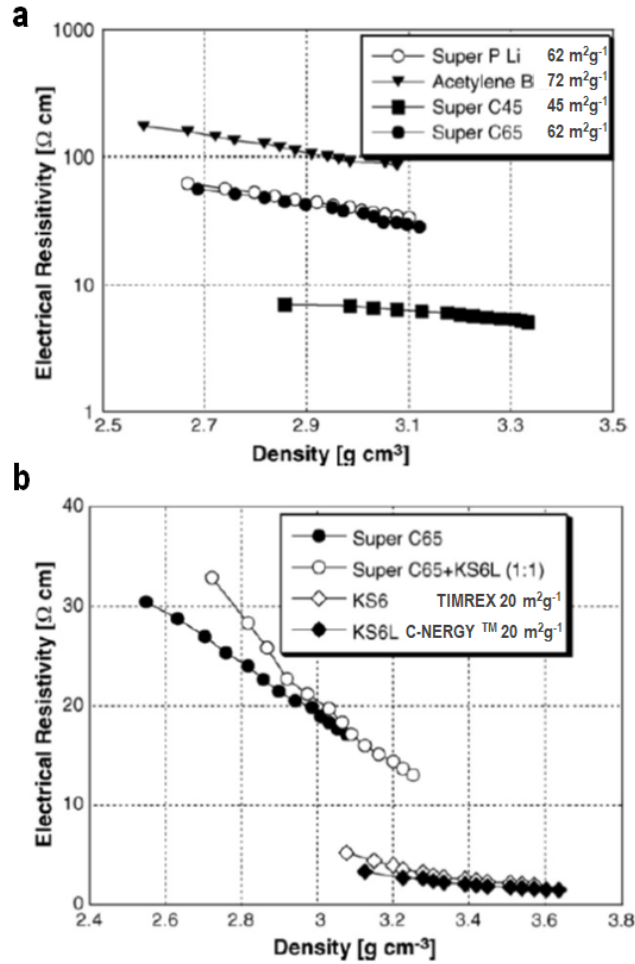


Figure 1.9: Carbon conductive additives. (a) Electrical resistivity as a function of density of LiCoO_2 powders including 3% of the C-based additives from the legend. (b) Electrical resistivity as a function of density of LiCoO_2 powders including 5% of the C-based additives from the legend. Adapted from [18].

While binders and conductive additives are addressed in a different section, in real-life applications both are considered simultaneously since they both can alter performance, electrode manufacturing processes or cost.

1.6 Nanotechnology for lithium-ion batteries

The man that was actively involved in Manhattan project⁴, Richard Feynman, also inspired the world with his visionary 1959 talk entitled *There's plenty of room at the bottom* that outlines a technological world able to replicate itself and manipulate matter at an atomic scale. His philosophy was further propagated in the 80s by some nanotechnology advocates that witness the promise of nanotechnology [19,20]. The bloom started in early 2000 when some nanomaterials have been adopted in commercial applications, quite far from the technological miniaturized universe envisioned by Feynman. Nanomaterials have found a plethora of applications in diverse fields ranging from construction to biology but they revolutionized the field of electronics. In this context, the adoption of nanomaterials and the concepts of nanotechnology in the electrochemical energy storage has seen an early adoption and was expected to revolutionize the field. As a matter of fact, the field was already aware of certain beneficial aspects of the *nano*, in particular for applications where a large surface area is required for catalysis, for example, in fuel-cells. In addition, chemists have been interacting with nanomaterials such as colloids for a very long time but only when advanced characterization techniques become available it was possible to correctly identify the materials. Finally, the functioning of the electrochemical cells relies on nanoscale interfaces where the electronic and ionic exchange takes place. With this in mind, this section aims to provide an overview of the benefits of nanostructuring in battery technology.

The good. The ideal electrode material has to be transparent to Li-ions, to allow their reversible intercalation, alloying or conversion reactions at the negative electrode and their reversible intercalation at the positive side. In other words, the functioning of the battery relies on the reversible Li transport across the interfaces. Using nano-materials will have a great impact on the reaction kinetics since shorter pathways for ionic and electronic transfer are expected. Also, the electrode porosity will increase, thus, a better electrode-electrolyte contact is expected since the electrolyte will penetrate in all the pores and facilitate the Li-

⁴The one that produced the world first atomic weapon.

ion transport. In real-life applications, this should provide faster charging and discharging rates. Some thermodynamics effects have also been reported through nanostructuring. For instance, some materials such as LiF are inactive to lithium in their bulk form, but, through nanostructuring become active [21]. Redox potential values can also be substantially modified through nanostructuring [22]. Nanostructures also show improved mechanical robustness. This is particularly beneficial for electrodes that undergo large volume variations during lithium storage. Nanostructures can accommodate these variations due to faster stress relaxation time, showing a good cycling life. Si and LiFePO₄ are generally regarded as the best examples of the positive effect of nanostructuring. LiFePO₄ was rendered commercial simply by coating a nanoscale thin coating of C layer to facilitate electron transport. For Si, only nano-Si has allowed stable cycling. The performance of nano-Si-based electrodes is exhaustively discussed in Chapter 2. Finally, alternative technologies such as Li-air and Li-S have also harvested benefits from nano. For the Li-S case, the strategy involves polysulphides confinement in a carbon matrix while Li-air benefited from the maximized porosity of the air electrode. Both of them are discussed in Perspectives.

The bad. The biggest drawback of nanomaterials is related to their increased active surface. While a high electrode/electrolyte interface is desirable for fast charge exchange, it leads to more parasitic reactions with the electrolyte. This is the critical case of low-voltage alloying anode materials that go below the electrolyte stability window and will suffer from the excessive solid-electrolyte-interphase (SEI) formation. Unfortunately, due to volume variations, the SEI is not stable and is continuously generated consuming the electrolyte and, eventually, causing cell death. Also, increased porosity means lower active material mass load, thus the volumetric energy density is greatly affected. This is quite a drawback since for electric vehicles, for instance, mass is important but volume is critical. We would like to store as much energy as possible for the available volume.

The ugly. Next, the battery community has focused efforts on reducing or eliminating the drawbacks described above. Engineered nanostructures with increased manufacturing complexity and low scalability

that sacrificed active material load for a couple of extra cycles have been intensively investigated. This is mostly the case for nano-Si as exposed in Chapter 2. This type of processing comes with huge costs which do not mirror the battery industry standards. Finally, as with any new technology, there is a potential hazard to humans and the environment, requiring further studies to assess the levels of dangers. For the moment, nanostructured materials are only used under strict working conditions to avoid any inconveniences.

Nanotechnology has certainly had a profound effect on the battery field and allowed access to new chemistries and material properties and enabled fast charge-discharge rates. The field is in infancy and more is expected to come in the following years.

1.7 Trends in lithium-ion batteries

The energy demand is projected to grow substantially during this century to accommodate the growing population as well as increased living standards [23]. People do not need energy per se but rather they rely on infrastructures, the physical context, and the services powered by this energy for their activities. Meantime, we need to lower the green-house emissions to limit the devastating effects of global warming while projecting in a future that requires the development and implementation of near-zero-emissions energy ecosystems [6]. Batteries are certainly fundamental building blocks for this future since they will allow decarbonizing transportation and basic residential requirements when used in conjunction with various renewable energy sources such as solar and wind. In this sense, a circular approach is required for the entire system life-cycle, from materials to performance and waste management and valorization. An eco-social-technological responsible system that targets near-zero-emission has to follow the diagram sketched in Figure 1.10. Following this, we discuss the trends in LIBs from a technological standpoint and a sustainability perspective. We particularly address: unconventional battery designs and sustainable⁵ choices for LIBs technology.

⁵The term *sustainable* is used throughout this work with the meaning given by the United Nations in the Report of the World Commission on Environment and



The representative commercial high-energy cell configurations, shown in Figure 1.11, are cylindrical, prismatic and pouch cells. A certain number of these cells are connected into modules or battery packs to satisfy the application requirements, in terms of power, dimensions as well as safety. For instance, Tesla, Inc. adopted a battery pack with Panasonic

Development: “sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”

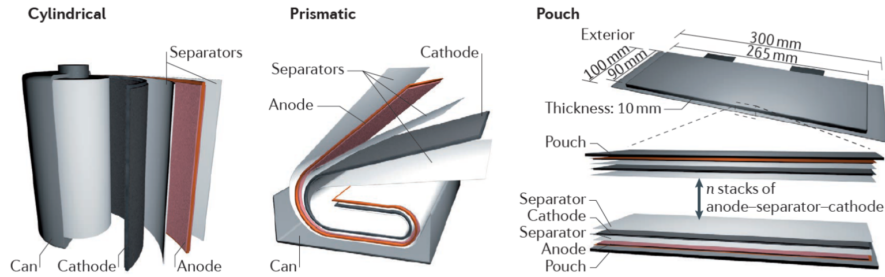


Figure 1.11: Representative commercial Li-ion cell structures.

18650 cylindrical cells that can hold up to 20% more energy density than their prismatic or pouch cell versions [24]. Prismatic and pouch cells are usually preferred for applications where a higher degree of design freedom is required since their dimensions are easily adaptable. The battery community has continuously explored possibilities to enhance their energy and power characteristics via nanostructuring of active or passive components. In the absence of alternative high-energy electrode materials, calibration of the dead battery load such as current collectors, binders, conductive additives or battery case has made possible further improvements. Since the active materials, as well as their assembling processes, were generally the same over the last decade, the evaluation of new electrode materials was also constrained into this assembly framework. We now know that alloy- and conversion- types of electrodes that suffer from volume variations, perform better into a porous framework. Thus, new Li-ion chemistries have to be complemented by a suitable electrode and cell design.

On another level, the battery technology slowed-down, to a certain extent, the advancement of the electronics industry in the context of Internet-of-Things (IoT). IoT is simply about the seamless integration of technology into human-environment. In this sense, on the electronics part, we have seen an explosion of flexible, transparent and light-weight sensing devices capable of a smooth interaction with humans and their environment. The battery part lags the electronics but the battery community is aware of the current requirements and started

exploring unconventional electrochemical designs to accommodate the demands. For instance, a transparent battery design encapsulated into a bio-compatible polymer is shown in Figure 1.12a. Also, transient batteries coupled with transient electronics can revolutionize the industry of disposable devices [25]. More unconventional electrode designs are explored in Chapter 2 for nanostructured Si. Other slurry dispensing approaches rely on 3D, as shown in Figure 1.12b, or inkjet printing. In this sense, inkjet printing is extremely advantageous due to its compatibility with paper electronics. Nowadays, the use of paper has gone beyond printed information towards electronic devices. While paper electronics is challenging due to paper's highly porous framework and surface roughness, energy storage devices can benefit from these features. Furthermore, paper can enable lightweight and environmentally friendly Li-ion batteries, as discussed later on in Perspectives.

1.7.2 Exploring sustainability

A sustainable LIB technology requires the selection of chemistry with a minimum C-footprint that facilitates the recycling processes and can integrate seamlessly into a circular technological approach as sketched in Figure 1.10. Life-cycle-assessment (LCA) models have revealed that the well-established LIB chemistries are not so friendly as initially hypothesized. The predictions of these models are quite rough since it's difficult to quantify the greatness and richness of LIBs technology, spread across multiple, independent players across the continents. They estimate, averaged over all LIB chemistry, that for a 1 kWh of energy storage, 328 kWh of energy is required coupled with 110 kg CO_2 [28]. Note that 80% of this energy requirements are consumed during the material fabrication step [29]. The LFP-LCO couple is generally considered the most sustainable among the current LIB chemistries due to their long cycling life, a key performance indicator for a good environmental performance. Consequently, material availability and material synthesis are the main rationales behind a greener and more sustainable LIB technology. Generally speaking, the main element constituents of biomass, *i.e.* H, O, S, P, Na, K, Ca, Mg, Fe and Ti, are also the most sustainable choice

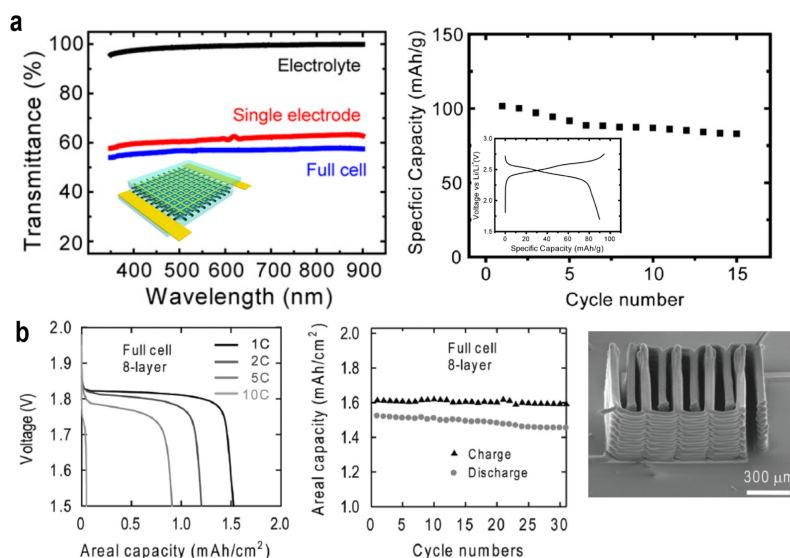


Figure 1.12: Unconventional battery designs. (a) Transparent battery. Transmittance spectrum by UV-VIS spectroscopy for the electrolyte -1M LiClO_4 in EC:DEC and PVDF, single electrode and full cell - $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ (left). Cycling life of a 60% transparent battery. Inset shows the voltage profile (right). Adapted from [26]. (b) 3D printed battery. Full-cell performance of $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$. Adapted from [27].

for the eco-social-technological responsible LIB technology [29–31]. The abundance of currently used LIB elements together with more sustainable elements choice are presented in Figure 1.13. In this sense, it is not surprising that biological waste has been valorized to extract active materials for LIBs: Si was extracted from rice husks [32], reed leaves [33] or banana-peels [34]. LFP is generally considered the most sustainable since it is composed of sustainable materials if the presence of Li is ignored. Nonetheless, its synthesis has a high energetic score making it comparable with other less friendly Co or Ni-based cathode alternatives. On the anode side, due to a lack of stable alternatives, carbonaceous materials are still the most sustainable due to their high cycling life and low working voltage. Li-ion technology based on abundant materials such as Si or S are promising but, for now, are stalled by the underlying

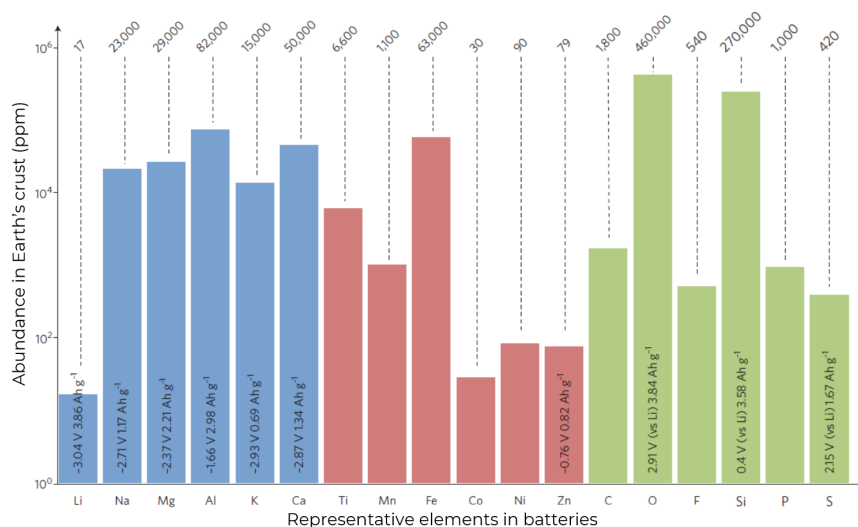


Figure 1.13: The abundance of elements currently used in the battery technology. From [29].

chemistries issues that lower their cyclability. We invite the reader to refer to the Perspectives part of this work for an overview of Li-S technology. Nano-Si has seen some incremental improvements but it is usually associated with complex and limited-efficiency synthesis with high cost and expensive equipment. A detailed analysis of the current state of nano-Si anodes is discussed in the next Chapter.

Finally, the problem of Li availability is still pending, being the subject of studies with conflicting results since the reserve and resource estimates of lithium are far from precise [35,36]. Furthermore, some battery scientists argue that similar pessimistic claims have been made with oil but that has yet to happen [37]. While exploitation and mining have seen their own revolution, the long last social and environmental effects of such activities are difficult to overlook. Thus, a further incentive is given to battery recycling and waste valorization.

Sustainability beyond Li-ion systems. Li scarcity has lead the scientific community in exploring other battery technology such as Ca-, Mg- or Na-ion. Na-ion is by far the most developed and is projected to

be more sustainable and cheaper than its Li-ion counterpart since Cu, for instance, can be replaced with the more-abundant Al as a current collector. The Na-ion is not expected to outperform the Li-ion technology, it is expected to take control of short-life, disposable electronics and, to some extent, relax the Li-ion demand for some applications. Divalent ion technology such as Ca- or Mg- ion are still in infancy with the advantages being eclipsed by the difficulties of the intrinsic chemistry.

Recycling. Urban sustainability is not possible without transport electrification thus, the automotive fleet is expected to be rapidly dominated by electric vehicles (EVs) [38]. The Li content in a generic EV battery pack is around 4 kg [39]. Currently, only 1% of spent Li is recycled in favor of more profitable materials such as Co or Ni [40]. The chemistry of recycling will become critical in the next decade due to the significant amount of spent Li associated with e-waste from EVs. Related to this, recycling specialists call for a homogenized mechanism in manufacturing, classification, collection, and recycling between the players to enhance the efficiency of the recycling processes. It will also allow a precise LCA of the battery technology and to precisely quantify the economic and environmental risks associated with LIBs.

This chapter defined the current LIB technology and presented the most relevant materials from the vast LIB library. We discussed the nanotechnology's footprint on the LIB technology together with unconventional battery designs to achieve flexibility, transparency and dimension reductions. All this has to be put in the context of sustainability to redirect the field into a greener and safer path. Next, we will refer to the nano-Si electrode, and discuss the efforts being made to cope with the difficult Li-Si chemistry.

Towards high-energy Si anodes

The only true wisdom is in knowing you know nothing.

Socrates

Silicon has been in the spotlight as the next generation anode material due to its distinctive Li-related features such as the ability to form Li-rich compounds corresponding to an exceptional capacity of 3579 mAh/g at low working voltages. Adopting Si electrodes can lead to lighter, safer and higher-performance batteries. For the moment, some of these advantages are overshadowed by the extraordinary volume expansion that Si electrodes suffer during Li ions insertion, responsible for lithiation-induced stresses that can generate material degradation and solid electrolyte interface damage. Herein, we explore the rich Si-Li electrochemistry and discuss the progress in understanding the degradation mechanisms in Si electrodes. Ultimately, we review the strategies and the recent developments for extending the cycling life of Si anodes and discuss their feasibility and limitation for real-life applications. The Chapter continues with some relevant methods for the nanostructuring of Si. We briefly discuss the most common nanowires synthesis methods, highlighting the merits and drawbacks of each. We particularly stress the advantages of top-down metal-assisted chemical etching for the controlled fabrication of Si nanowires.

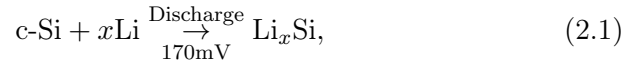
Due to its ubiquity in the electronics industry, Si has been intensively studied and relies on a matured processing infrastructure. Additionally, the high Li accommodation capacity and natural abundance have convinced the scientific community about the disruptive role that Si can play for the future's lighter, safer, best-performing batteries. The behavior of Si during Li insertion is extremely rich and controlled by a variety of parameters such as Si crystallinity, orientation, morphology or cycling rate. As a matter of fact, Si's ability to form Li-rich alloys is what renders Si such a desirable anode. However, related to its high Li storage capacity, major challenges limit the cycling life of Si-based electrodes.

2.1 Si electrochemistry

The electrochemical alloying reaction of Li with Si at room temperature is complex and depends on the initial Si structure as well as voltage limits as it will be discussed next. Figure 2.1 shows the voltage profiles characteristic to the electrochemical conversion that Si can undergo, notably, the crystalline to amorphous transition via a solid state amorphisation reaction with Li.

2.1.1 Lithiation of crystalline Si

The initial lithiation of crystalline Si (c-Si) at room temperature follows:



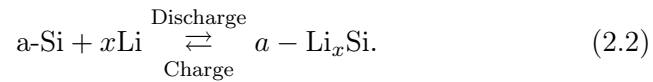
with $x=3.75$ corresponding to the crystalline $\text{c-Li}_{15}\text{Si}_4$. The voltage profile of the electrochemical conversion of the crystalline Si to amorphous $\text{a-Li}_x\text{Si}$ is shown in Figure 2.1, Region I corresponding to a two-phase region where c-Si and $\text{a-Li}_x\text{Si}$ coexist. At this stage, the front of $\text{a-Li}_x\text{Si}$ consumes the Si core. The reaction front was found to be atomically sharp, 1 nm thick, and remains constant during the electrochemical conversion [41]. Furthermore, the interface mobility is orientation-dependent which results in an anisotropic growth of the lithiated phase, with $\langle 100 \rangle$ being the fastest [42]. When the reaction front reaches the

Si core, all c-Si was converted to a-Li_xSi. The gravimetric capacity associated with these metastable Li_xSi phases was shown to be around 3250 mAh/g at a potential of around 100 mV vs Li/Li⁺ [43].

Continuing the lithiation at this stage, thus going to lower potentials of around 50 mV vs Li/Li⁺, we can access the crystalline Li₁₅Si₄ at room temperature, and Li₂₂Si₅ which corresponds to the maximum insertion capacity of 4200 mAh/g. The voltage profiles associated with these transitions are shown in Figure 2.1, Region II. The highest lithiated phase, i.e. Li₁₅Si₄ at room temperature corresponds to a gravimetric capacity of 3579 mAh/g. Related to this, it was shown that a volume expansion of 280% is expected when a Si atom accommodates 3.75 Li atoms (i.e. Li₁₅Si₄ forms). The detrimental effects of volume expansion and the stresses and strains associated will be discussed further in this Chapter. Many papers have assumed Li₂₁Si₅ (corresponding to 4008 mAh/g) or Li₂₂Si₅ (4200 mAh/g) as the fully lithiated phase based on the expectations that the Li-rich phases from the Li-Si phase diagram can be achieved. Nonetheless, at room temperature, Li₁₅Si₄ remains the highest lithiated state that can be achieved. Delithiation of the Li₁₅Si₄ is expected to occur similarly via a two-phase reaction. First, the crystalline Li₁₅Si₄ is converted to a-Li_xSi that is further uniformly delithiated to a-Si. Figure 2.1, Region III marks the voltage profiles for the delithiation of the crystalline Li₁₅Si₄, that corresponds to a large voltage plateau around 0.45 V vs Li/Li⁺.

2.1.2 Lithiation and delithiation of amorphous Si

The lithiation and delithiation of a-Si follows:



The lithiation of amorphous Si follows the voltage curves from Figure 2.1, Region IV presenting two quasi-plateaus. The low voltage plateau is indicative of Li entering into a Li-rich environment. If the lithiation of a-Si is interrupted before the potential reaches 70 mV vs Li/Li⁺, Li₁₅Si₄ will be avoided and the delithiation of a-Li_xSi will proceed following the

reverse reaction from 2.1, Region V from Figure 2.1a. Otherwise, continuing the lithiation of a-Si will result in the formation of $\text{Li}_{15}\text{Si}_4$ (Region III from Figure 2.1a). Thus, delithiation from here follows the description from Region IV, Figure 2.1 where $\text{Li}_{15}\text{Si}_4$ is transformed to Li_xSi and further to a-Si. For the amorphous case, a-Si undergoes isotropic expansion since there is no intrinsic crystallography to alter the process.

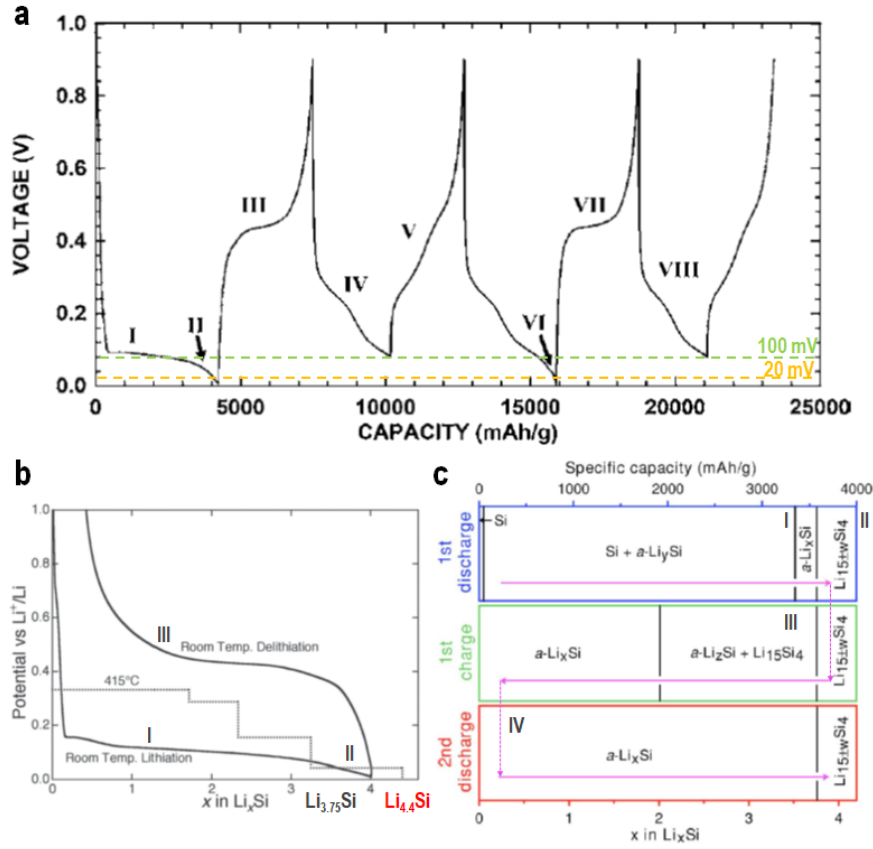


Figure 2.1: Silicon electrochemistry. (a) Voltage curve of crystalline Si cycled to highlight the phase transformation of the electrode. Adapted from [43]. (b) The gradual slope of the galvanostatic discharge curve of the Li-Si system at room temperature versus the stepped Coulombic titration curve at 415°C (dotted line). Adapted from [44]. (c) Simplified phase diagram corresponding to the transformation of crystalline Si electrode during the charge and discharge between 0.005 and 0.9 V. Adapted from [45].

The behavior described above applies to all types of Si, whether bulk or nano-Si as well as thin film. However, nanosizing, as discussed in Chapter 1, has important consequences on the $\text{Li}_{15}\text{Si}_4$ formation, solid electrolyte interphase (SEI) evolution, and particle fracture. Finally, it is generally accepted that the two-phase regions should be avoided since they are usually associated with capacity fade [46]. Both experimental and theoretical studies confirm the accentuated damage due to inhomogeneous volume variations related to the two-phase lithiation. The absence of a two-phase reaction, for instance during the cycling of a-Si generally minimizes the electrode damage as long as a potential above 170 mV vs Li/Li^+ is maintained and the formation of $\text{Li}_{15}\text{Si}_4$ is avoided. This was also highlighted by various studies that show that the conversion of c-Si into a-Si during the initial lithiation triggers more fracture events than the following cycles. Thus, it is clear that understanding the behavior of crystalline Si during the Li-alloying reaction is essential for high-performance Si cycling.

2.2 Volume expansion in crystalline Si

Crystalline Si can undergo a volume expansion of 280% corresponding to $\text{Li}_{15}\text{Si}_4$ formation [49]. This volume expansion has harmful consequences on multiple levels. First, subsequent volume variations can lead to material reorganization and an eventual loss of electrical contact and finally electrode delamination and pulverization resulting in electrochemical cell death. Secondly, at the particle level, subsequent volume variations damage the fragile SEI and promote the conditions of continuous SEI formation, leading to electrode and electrolyte consumption and eventually to capacity fading. Finally, stresses that develop during volume expansion lead to fractures that result in limited cycling. Thus, in the following, we discuss the Si behavior during lithiation and the related destructive stresses.

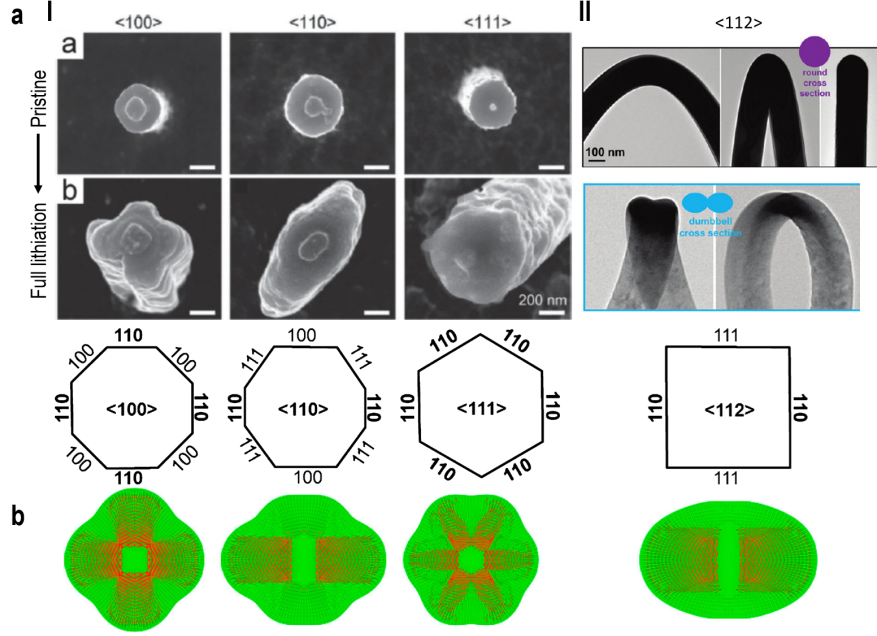


Figure 2.2: Anisotropic lithiation and swelling of Si electrodes. (a) I. Ex-situ SEM images showing the anisotropic lateral swelling for three different Si orientations: $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$. Adapted from [47] II. In-situ TEM images of anisotropic expansion of a $\langle 112 \rangle$ -oriented wire. Adapted from [48]. The crystallographic characteristics of each studied orientation are shown below [42]. (b) Lithium flux profiles corresponding to each of the evaluated Si orientation. Adapted from [42].

2.2.1 Anisotropic Li_xSi growth

Using *in-situ* and *ex-situ* methods, several studies report on the anisotropic transformation of c-Si during Li insertion. For instance, one ex-situ study reports on the lithiation induced shape-shifting of crystalline nanopillars with different crystallographic orientations [47]. Figure 2.2a shows the full lithiation morphologies of three different Si orientations, $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ in panel I and $\langle 112 \rangle$ in the panel II. The initial circular cross-section of the nanopillar dramatically is altered into a cross, ellipse and a hexagon depending on the crystallographic orientation of the c-Si. These shapes result from the preferential vol-

ume expansion of the $\{110\}$ surfaces. For instance, $\langle 100 \rangle$ orientation SiNWs have 4 $\{110\}$ surfaces as shown in Figure 2.2a. The preferential expansion of these facets leads to the cross-like morphology. Direct observation of this anisotropic growth was possible by *in-situ* experiments as shown in Figure 2.2 panel II [48]. Taken together, these studies found that it is kinetically easier for Li to insert and break the Si lattice along $\langle 110 \rangle$. Eventually, it was shown that the interfacial mobility of the reaction front is dependent on the crystallographic orientation. This was further confirmed by finite element modeling that assigned different front velocities to different crystallographic surfaces that reproduced the experimentally observed shapes of lithiated nano-pillars [42]. Figure 2.2b shows the numerical Li flux profiles with the dominant flux in the $\langle 110 \rangle$ directions resulting from the high mobility of the $\{110\}$ interface. As a matter of fact, numerical simulations have also shed light on the experimentally observed fracture patterns.

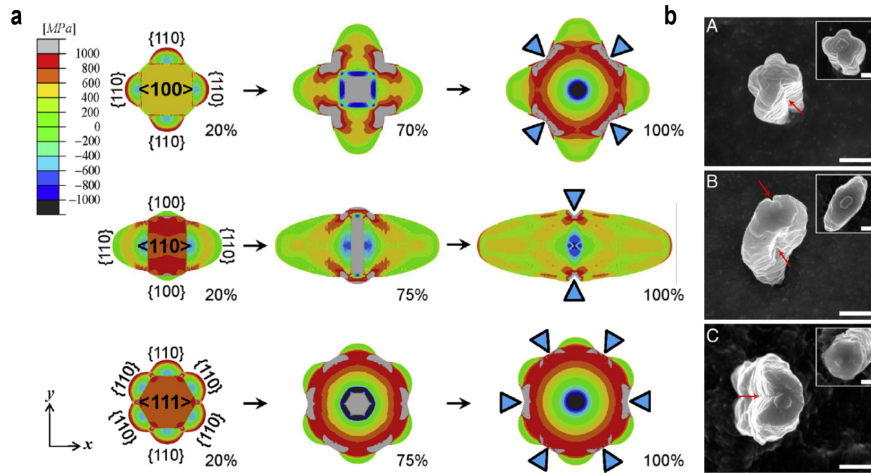


Figure 2.3: Stresses and fractures in Si nanopillars. (a) Stress evolution due to anisotropic growth of Li_xSi for Si with different crystallographic orientations. Blue triangles indicate the preferred fracture location. Adapted from [50]. (b) SEM images with cracked Si nanopillars. The arrows point to cracks. Adapted from [51].

2.2.2 Stresses and fractures

Due to anisotropic Li_xSi growth as governed by the orientation-dependent reaction front, a preferential strain and stress concentration exists leading to cracks and eventually fractures. Fractures nucleate at the surface of a- Li_xSi shell and further propagate along the axis at the surface of the nano-pillars. Figure 2.3 emphasizes the correlation of anisotropic expansion and fractures. For instance, cracks in $\langle 100 \rangle$ Si nanopillars occur along $\{100\}$ surfaces, between neighboring $\{110\}$ surfaces. Chemomechanical models have been developed to shed some light on the stress and strain evolution related to the lithium accommodation [50]. Finally, fractures can be controlled or avoided due to nanosizing. *In-situ* experiments have established a critical fracture size between 300 to 150 nm, correlated to the reduced anisotropy typically observed in these nanostructures [51–53].

To resume, detrimental strains and stresses originate in the anisotropic volume expansion due to the conversion of c-Si to a- Li_xSi negatively impact the mechanical integrity of the Si electrode. Since the inherently damaging volume expansion is concurrent with Li_xSi formation, much of the research has been focused on the alleviation of these effects while preserving the Li storage capacity.

2.3 Degradation mechanisms of Si anodes

The main degradation mechanisms of Si electrodes fall within the spectra dictated by the anisotropic volume expansion, as resumed in Figure 2.4. First, the mechanical integrity of the electrode is vulnerable due to delamination and material reorganization. Related to this, particle isolation can also impede electron transport, thus Li ions shuttling. Secondly, the mechanical stability of the particle is also in danger due to the large stresses developed during expansion and the subsequent contraction. Finally, the SEI formed on Si also suffers from the volume variations corresponding to Li insertion and removal from the Si lattice, resulting in the continuous formation of the SEI. Progress in these areas has been possible, to a certain point, by nanotechnology that helps avoid

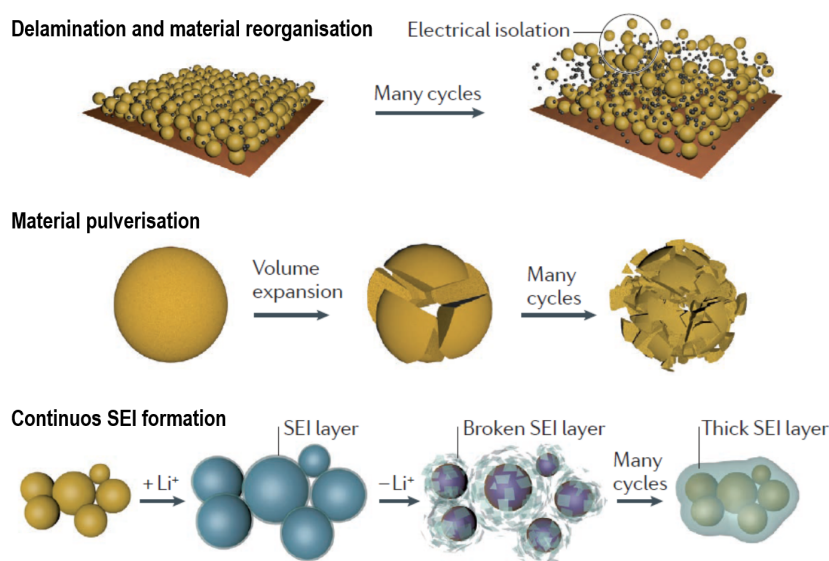


Figure 2.4: Main degradation mechanisms in Si anodes.

fractures. However, such approaches amplify the SEI-related issues due to the higher specific surface area, as discussed in Chapter 1. In other words, to move towards widespread industrial adoption of Si electrodes, progress has to be made in the following core areas: (i) mechanical integrity of the electrode and the active materials, (ii) enhanced electronic and ionic transport and (iii) stability of the electrode-electrolyte interface. In the following section, we will discuss the recent developments in Si anodes that picture a bright prospect for the future of Si-based electrodes.

2.4 Recent developments in nano-Si anodes

Engineered materials and electrodes to promote mechanical stress relief took priority over any other matter in order to significantly extend the cycle life of the Si electrode. Nanostructuration allowed the exploration of many stress relief strategies that promote strain relaxation and avoid fractures via nanowires, nanotubes or engineered hollow Si-C composite structures. However, Si nanostructuring creates other complications

such as amplified interfacial issues, low electronic conductivity, and low volumetric energy density. Thus, multi-functional binders and conductive additives, as well as a judicious selection of electrolyte systems, are required to address these issues.

Table 2.1 lists some of the recent developments regarding material sources and synthesis, electrode engineering as well as electrolyte systems in order to address the challenges of Si anodes. The entries include the most relevant cycling parameters: (i) active materials load, that can include only the Si contribution or Si and C and can be expressed either as a load (in mg) or an areal load (mg/cm^2); (ii) the parameters for the 1st cycle, or the formation cycle where crystalline Si is converted into amorphous Si; (iii) the Li storage capacity after n cycles at a specific cycling rate (C rate). Unfortunately, a fair comparison between entries is quite difficult, however, we can distinguish general trends. For instance, a low Si load is usually associated with high rates and high cycling life, nonetheless, the overall electrode capacity will suffer and, as such, using Si is no longer justified. Ionic liquids-based electrolyte systems are quite promising with Si anodes in terms of performance and safety. Coulombic efficiency for the first cycle is generally low thus, the irreversible capacity is high, compared with commercial graphite electrodes signaling the importance of harvesting a good SEI on Si. A vast collection of nanostructures or complex hierarchical structures were designed to respond to the requirements imposed by the volume expansion during Li insertion. Last, but not least, some of the cycling parameters were not readily available thus, they were either calculated or visually estimated and they are accompanied by the $\approx$ sign. These reports are further discussed below to highlight the progress as well as the limitations of certain approaches.

Taking everything into consideration, the enhancement in the Si electrode performance results from synergistic developments in material and electrode engineering, multi-functional binders and conductive additives as well as advanced electrolyte systems. As such, it is difficult to dissociate between each area since their functionalities overlap most of the time since they are all trying to limit the effects of volume variations during the reaction with Li. For instance, advance electrode architectures were designed to isolate Si from the electrolyte and promote a stable SEI. An

Anode composition	Synthesis method	Electrolyte	Cycling parameters				Ref.
			Si load	Parameters 1 st cycle CE (%)	C rate (mA/g)	Discharge Capacity (mAh/g)	
SiNPs 'yolk' with a C 'shell' Si@void@C (71% Si) with NaAlg & Carbon black 65:20:15% wt	Sol-gel methods Pyrolysis	1M LiPF ₆ in 1:1 wt/wt EC/DC with 3% vol VC	n.a.	2833 mAh/g _{Si@void@C} @ C/10 (1C = 4200 mAh/g) 96% CE	1C	1110 (74% retention)	[54]
Nano-Si with a cyclized PAN shell nSi-cPAN 3:7 wt	Solution coating DMF Thermal treatment	1.2M LiTFSI in PYR ₁₃ FSI	1.1-1.3 mg/electrode	≈ 2200 mAh/g _{Electrode} @ C/20 (C/10 ≈ 353.6 μA/cm ²) ≈ 81% CE	C/10	≈ 1600 (76.7% retention)	[55]
SiNPs with PEDOT:PSS (FA dopant) 80:20% wt	Classic slurry manufacturing	1M LiPF ₆ in 3:6:1 v/v/v EC/DC/FEC	1.1 mg/cm ²	2854 mAh/g _{Electrode} @ 1 A/g 77% CE	1 A/g	1927 (75% retention)	[56]
SiNWs with a cyclized PAN shell SiNWs-cPAN 3:7 wt	Solution coating DMF Thermal treatment	1.2M LiTFSI in PYR ₁₃ FSI	0.5-0.7 mg/electrode	≈ 3600 mAh/g _{Electrode} @ C/20 (C/10 ≈ 157.5 μA/cm ²) ≈ 85.03% CE	C/10	≈ 1700 (≈ 80% retention)	[57]
SiNPs encapsulated in C'Ts SiNWs@CT 47% wt Si	Sol-gel methods Electrospinning Carbonization	1M LiPF ₆ in 1:1 v/v EC/DEC	0.1 mg/cm ²	969 mAh/g _{Electrode} @ 1 A/g (1C = 1A/g) ≈ 71% CE	C/10	≈ 900 (≈ 90% retention)	[58]
SiNWs core with Cu shell encapsulated in PVdF 47% wt Si	MACE Polymer infiltration	1M LiPF ₆ in 1:1 v/v EC/DMC	n.a.	≈ 3900 mAh/g _{Si} @ C/20 (1C = 4200 mA/g) ≈ 92% CE	C/20	≈ 2000 (≈ 80% retention)	[59]
Pomegranate design clusters of SiNPs (77% Si) 'yolk' with a C 'shell' PVDF and Carbon black (8:1:1 wt)	Sol-gel methods Pyrolysis	1.0 M LiPF ₆ in 1:1 wt/wt EC/DC with 3% vol VC	0.2 mg/cm ² (Si and C)	2350 mAh/g _{Electrode} @ C/20 (1C = 4200 mAh/g) 77% CE	C/2	1160 (97% retention)	[60]
Double walled Si nanotubes DWSiNTs (SiO ₂ outer wall) (60% Si)	Electrospinning Carbonization CVD	1.0 M LiPF ₆ in 1:1 v/v EC/DC	0.02 - 0.1 mg/cm ²	1780 mAh/g _{Electrode} @ C/5 (C/5 = 0.4 A/g) 76% CE	C/5	≈ 1400 (76% retention)	[61]
Si particles with C & Self healing polymer (SHP) 2:1 wt	Classic slurry manufacturing	1.0 M LiPF ₆ in 1:1:0.005:0.05 v/v/v/v EC/DC/VC/FEC	0.5 - 0.6 mg _{Si} /cm ²	2600 mAh/g _{Electrode} @ C/5 (1C = 4200 mAh/g) 86% CE	C/5	≈ 2000 (80% retention)	[62]

Anode composition	Synthesis method	Electrolyte	Cycling parameters					Ref.
			Si load (mg)	Parameters 1 st cycle CE (%)	C rate (mA/g)	Discharge Capacity (mAh/g)	After <i>n</i> cycles	
Watermelon inspired Si-graphene microspheres (15% wt Si) Super P, CMC & SBR 90:5:2.5:2.5	Solution processing Ball milling Calcination	1M LiPF ₆ in 1:1:1 v/v/v EC/DMEC/DC	4.1 mg _{Si/C} /cm ²	620 mAh/g _{Si/C} @ 0.1C (1C = 600 mAh/g) 89.2% CE	0.1C	≈ 500 (80% retention)	250 @ 50°	[63]
Si/Graphene/C Flexible Si/CNF 47% wt Si	ALD Electrospinning Calcination	1M LiPF ₆ in 1:1 wt/wt EC/DC	n.a.	2143 mAh/g _{electrode} @ 700 mA/g (1C = 4200 mAh/g) 78.6% CE	700 mA/g	2002 (≈ 97% retention)	1050	[64]
C-coated SiNPs from low grade Si sources Ferrosilicon (83.48% Si) ACB & CMC 3:1:1	Ball milling Heat treatment	1M LiPF ₆ in 1:1 wt/wt EC/DC with 2% vol VC	0.5 mg _{Si/C} /cm ²	1250 mAh/g _{electrode} @ 0.4 A/g (1C = 4200 mAh/g) ≈ 70% CE	0.4 A/g	1205 (97% retention)	100	[65]
SiNPs with Carbon black 3:1 wt with 15% wt NaAlg	Commercial materials	1M LiPF ₆ in a mixture of carbonates	n.a.	3000 mAh/g _{Si} @ 140 mA/g (1C = 4200 mAh/g) ≈ 97% CE	4200 mAh/g	≈ 1800 (97% retention)	300	[66]
Silicon microparticles with SHP 1:1 wt	SHP Condensation reaction	1M LiPF ₆ in 1:1:0.04 v/v/v EC/DC/FEC	0.5-0.7 mg _{Si} /cm ²	2617 mAh/g _{Si} @ 0.4 A/g (1C = 3600 mAh/g) ≈ 72% CE	0.4 A/g	≈ 2350 (80% retention)	100	[67]
SiNPs clusters@Si@G 92% Si with PVDF 9:1 wt (NMP)	Microemulsion CVD Carbonization	1M LiPF ₆ in 1:1 v/v/v EC/DC with 10% FEC and 1% VC	0.6 mg _{Si/C} /cm ²	3096 mAh/g _{electrode} @ C/20 (1C = 4.2 A/g) 90.4% CE	C/2	≈ 1388 (≈ 90% retention)	300	[68]
Nanoporous Si from rice husks 60% wt Si with 20% wt Super P & 20% wt (NMP)	Thermal treatment Carbonization	1M LiPF ₆ in 1:1 v/v/v EC/DDEC with 5% vol FEC	0.3 mg _{Si} /cm ²	1615 mAh/g _{Si} @ 0.2 A/g (1C = 2000 mA/g) 84.2% CE	0.2 A/g	1554 (100% retention)	200	[32]

Table 2.1: Developments in nanostructured Si anodes

appropriate binder can also reinforce the separation Si-electrolyte via a passivation effect, thus going beyond the conventional binder functionalities. Additionally, if the binder conducts electrical charges, it can also be, to a certain extent, a conductive additive. Generally speaking, the binders that encourage reasonable performance with Si are all multifunctional since they go beyond the functions of conventional binders used in the carbonaceous systems. Following the same rationale, Si surface passivation is one of the most explored research direction and can be achieved via material engineering, functional coatings as well as advanced electrolyte systems, as discussed in the following sections.

2.4.1 Material and electrode engineering

As mention earlier, there are several advantages of using nanotechnology for LIBs, in particular, nanostructured Si over bulk Si. Among the first in exploring these advantages was a study by Cui and coworkers that showed that pulverization, critical in bulk Si, can be circumvented with silicon nanowires (SiNWs) [69]. These nanowires were directly grown via a vapor-liquid-solid (VLS) mechanism (as discussed later in this Chapter) onto the metallic current collector. This considerably improved the charge collection and allowed cycling at higher rates. However, other issues emerged mostly related to the largely electrolyte exposed surface of nano-Si that would continuously form SEI and consume the electrolyte. Thus, other strategies were required to mitigate these disadvantages. Cui's group at Stanford was particularly active in this field developing and engineering complex, hierarchical structures to enhance the life of Si anodes. For instance, hollow nanostructures with engineered empty space where nano-Si protected by a C shell. Among the first reports in this direction describes the inoculation of silicon nanoparticles in a carbon tube [58]. This design isolates nano-Si from the electrolyte and provides sufficient voids to accommodate the volume variations. Finally, it also enables the generation of a robust SEI on the surface of C. The next step consisted in the inoculation of a SiNPs in a C bubble or a Si@void@C nanostructure, that follows the same design reasoning [54].

As such, the Coulombic efficiency for the first cycle is quite impressive, reaching 96%. From a practical standpoint, however, the capacity is reported only with respect to Si ($1100 \text{ mAh/g}_{\text{Si}}$ @ 1C after 1000 cycles, Figure 2.5b). If we consider the entire electrode mass, the capacity will be reduced by half, thus comparable to commercial carbonaceous anodes which cannot justify the usage of such structures, that involve multi-step synthesis, for real-life applications. This was partially resolved in a subsequent study that concentrated clusters of SiNPs in a C-based shell, the so-called 'pomegranate' design rather than individual SiNPs [60]. This allowed, to a certain extent, to increase the Si load of the electrode as well as to limit the C-surface in contact with the electrolyte. Figure 2.5c shows the specific SEI area (defined as the surface area in contact with the electrolyte divided by the Si mass) in contact with the electrolyte as a function of SiNPs cluster diameter and the number of SiNPs a cluster can include. This is clear that the active material surface in contact with the electrolyte can be reduced to a great extent when the SiNPs cluster size is increased, grouping more SiNPs. This leads to a different research avenue, going towards micro-Si and developing other tools to avoid fractures rather than excessive SEI, as it will be discussed in the next section. This type of electrode shows a capacity of $1160 \text{ mAh/g}_{\text{electrode}}$ @ C/2 after 1000 cycles as shown in Table 2.1. However, while there is an improvement in terms of Li storage capacity per gram of electrode, the active material load per area is extremely small, only 0.2 mg/cm^2 , which results in an theoretical areal capacity of only 0.5 mAh/cm^2 , four times lower than the recommended value for commercial applications. Thus, in Figure 2.5d is shown the promising performance of such nanostructures at higher area loading. Such structures are indeed interesting in terms of performance but the complexity of the synthesis cast a shadow on their industrial adoption. Also, fruit-related, a watermelon inspired Si-C microspheres bundles packed in a sea of flake graphite, all surrounded by a C-shell has also been evaluated as anode [63]. While the Si load is quite small (only 15% wt of the electrode), more of a *graphite 2.0 electrode* and not really a Si-based anode, however, it does show that the current graphite electrode can benefit from reduced Si loads without any Si-related detrimental effects.

In another effort, double walled Si nanotubes in which the inner wall is silicon and the outer wall is SiO_x were evaluated. Since the outer wall is mechanically rigid, Si expansion is expected to occur towards the tube interior where is isolated from the electrolyte [61]. This design responds, in theory, to all the requirements of Si anodes and it is an impressive demonstration of what material engineers can do, however, the reported electrochemical performance is limited to an extremely low Si load (0.02 to 0.1 mg/cm^2 of active material of which only 60% wt Si), which does not respond to real-life applications.

Some of the drawbacks of Si were also addressed by new electrode architectures designed to accommodate the volume expansion and to mold to some application requirements such as flexibility or maximizing the performance as discussed in the previous Chapter. In this sense, a self-standing C-coated SiNWs-based fabric fabricated by a simple filtration showed some promising performance. The resulting materials have enough void spaces to accommodate the expansion and preserve mechanical integrity without any passive elements such as binders as presented in Figure 2.5f [70]. Another notorious example of unconventional electrode design, shown in Figure 2.5e, is a flexible SiNWs-based electrode embedded in a polyvinylidene fluoride (PVDF) matrix [59]. This report is also among the first that presents an adapted synthesis for large-scale, room temperature fabrication SiNWs. In addition, it shows that recycled Si, in particular from electronics, can be given another life as LIB anodes. As such, other Si sources were explored in order to provide the simplest, fastest, price-efficient way of producing nano-Si. For instance, rice husks can be a massive resource for LIB technology if we exploit the inherently interconnected nanoporous structures [32]. The key steps of the synthesis are shown in Figure 2.5g. In other words, the rice husks stockpile is not only a good Si source but it also provides a unique 3D porous structure beneficial for Si anodes. Other low-grade silicon sources, such as metallurgical Si and ferrosilicon were also evaluated for producing low-cost nano-Si via ball milling [65]. Both types show stable cycling up to 100 cycles with 97% capacity retention, excluding the formation cycle.

To conclude, the challenge resides in developing simple, cost-effective, scalable synthesis methods with minimal required resources, either for

production (such as high priced equipment or high temperatures) or for consumption (for instance where a polymeric matrix is required for the production of a C shell) for nanostructures and architectures that are beneficial to Si anodes.

2.4.2 Multi-functional binders, conductive additives and surface coatings

The conventional passive components, as inherited from the carbonaceous systems, can not fulfill the requirements for improving the cycling life of Si electrodes. In the case of binders, for instance, their main function is to ensure the binding between active particles layers as well as their adhesion to the current collector. It must be transparent to Li ions. However, when it comes to Si-based anodes, the stress and strain evolution during electrochemical reactions disrupt the mechanical integrity of the electrode fortified by conventional binder systems, resulting in early cell death. The binders are essential for the long-term cycling of Si anodes. The extensive binder research has provided some generally accepted guidelines for what it should be a stable binder system for high-capacity alloying materials such as Si. First, it has to provide good adhesion between the alloy particles as well as between active material and current collector. The weak van der Waals interactions between PVDF and active particles are not enough to withstand the volumetric expansion of Si during Li insertion. Along this line, carboxylic groups rich binders such as carboxy methyl cellulose (CMC), polyacrylic acid (PAA) or sodium alginate (NaAlg) use hydrogen bonds to attach to the Si surface. Although these types of bonds are fairly weak, they are presumed to have self-healing abilities, *i.e.* if the bond breaks, it can easily be restored [71]. Generally, their performance was found depending on the concentration and distribution of carboxylic groups [66, 72]. Furthermore, the self-healing chemistry has enabled the synthesis of binders design to spontaneously rearrange thus repairing disruptions in the mechanical integrity [67]. Secondly, the ability to uniformly cover the surface of the active particles to isolate the Si from the electrolyte. Thus, a limited binder-electrolyte interaction is desirable to avoid the SEI dam-

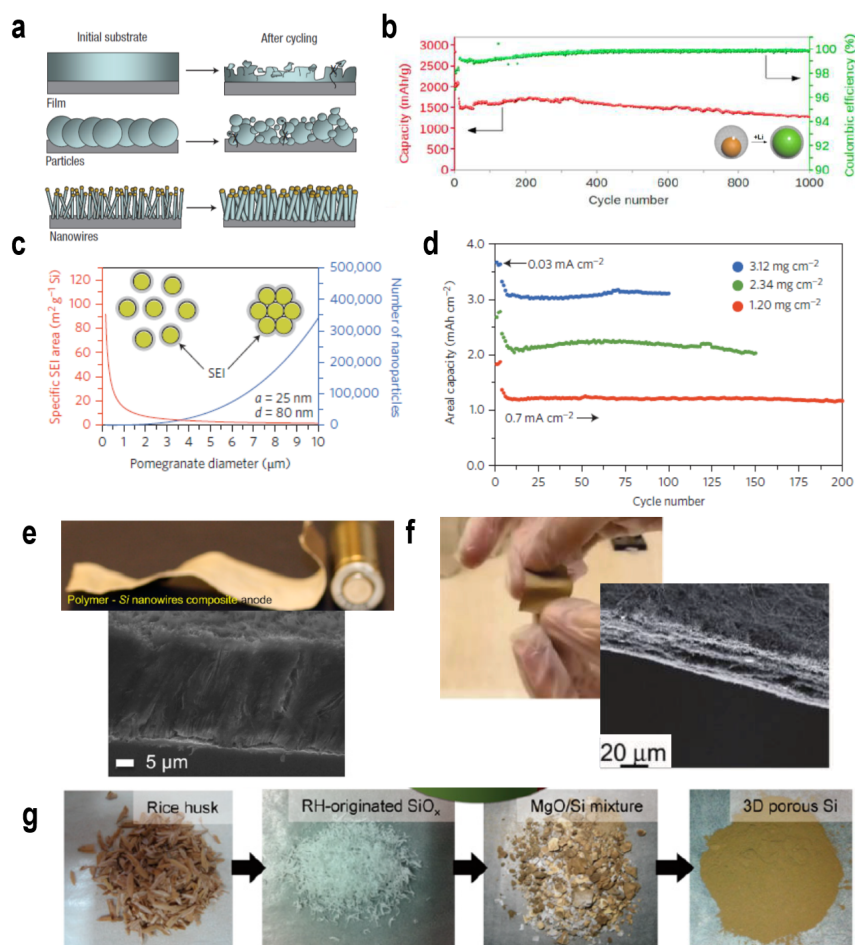


Figure 2.5: High-performance Si electrodes. (a) Si morphological transformations during Li insertion. Nano-Si can circumvent the common issues with bulk Si. Adapted from [69]. (b) Extended cycling life for hollow nanostructures with engineered empty space where nano-Si is protected by a carbon shell. Adapted from [54]. (c) and (d) Si anode with a 'pomegranate' design to reduce the electrolyte exposed Si surface. Adapted from [60]. (e) Flexible SiNWs-based electrode embedded in a PVDF matrix. Adapted from [59]. (f) A self-standing carbon-coated SiNWs-based fabric as anode material. Adapted from [70]. (g) The synthesis chain to recycle nanostructured Si from rice husks. Adapted from [32].

ages. Since PVDF forms a network of fine polymer treads, much of the Si surface is exposed to the electrolyte. The binders that present no swelling in the electrolyte have generally a positive impact on the Si cycling life. Third, the binder should accompany the volume expansion via stretching or self-healing thus, the Si surface is continuously isolated from the electrolyte [57, 67]. Additionally, the binder can also perform as a conductive additive to a certain extent [56].

To sum up, the utopian binder for Si would assist both electron and ion conduction, ensure good adhesion between active material particles and the current collector, can tolerate volume expansion by stretching or have the ability to self-heal, provide some sort of compatibility with the electrolyte to facilitate the formation of a permanent SEI, facilitates electrode production processes, is easy to produce and has a low environmental impact. Actually, the binder can redirect the manufacturing processes towards a cleaner direction by using friendlier solvents such as ethanol or water and eliminate the current carbonaceous NMP-based slurries and the risk associated with them [56, 72].

The binder alone cannot provide efficient electron transport at low binder content, thus conducting additives are required if the electrode performance at high rates is important. Conventional C-conductive additives are still ubiquitous in the electrode composition due to their specific properties as discussed in Chapter 1. Looking at Table 2.1, conductive additives from the carbon black family are typically added to assure the electrical connection between big active particles or cluster of active particles [54, 60, 63, 67]. Finally, let's not forget that the entire Si anodes technologies were built on the carbonaceous one, thus, compatible manufacturing to ensure a smooth transition between technology was something that the entire scientific community agreed on. Therefore, most of the developed Si nanostructures were first evaluated in an electrode configuration following graphite knowledge, with traditional binders and C-additives [32, 68].

Another design strategy to enhance electron transport is with conductive surface coatings. The functional C-based or metallic coatings such as Cu, Ni, Ag have been found to have a great impact on the cycling performance of nano-Si electrodes. First, surface coatings iso-

late Si from the electrolyte, thus the formation of a more stable SEI is expected. Secondly, they lower the inner electrode resistance, thus facilitate a better redox kinetics at the electrode. Surface coatings can impose some mechanical constraints on the Si expansion preventing electrode pulverization [73]. Finally, conformal metallic coatings on nano-Si were also exploited as current collectors in non-conventional nano-Si architectures [74]. Surface passivation via binders and surface coatings has a profound effect on the cycling life of Si electrodes. Chapter 3 offers further insights into the mechanisms responsible for the observed performance.

2.4.3 Electrolyte systems and additives

The electrochemical performance of Si anodes is intimately connected to the choice of the electrolyte, solvent, salt, and additives. In general, it is difficult to generate a good SEI on Si since the consecutive stressful volume variations affect the passivating SEI film. Furthermore, fracture of Si would expose fresh Si surface to the electrolyte which leads to additional SEI forming. Particle isolation and Li trapping can also occur if the anodes are affected by pulverization. The SEI is an endless issue with Si anodes, consuming Li ions and the electrolyte, thus, controlling the parasitic SEI chemistry and morphology is crucial for the long-cycling life of Si anodes. The chemistry of the SEI is rich and depends on the salt, solvent or additives. In electrolyte with LiPF_6 salt, the SEI is composed of terminated species that are formed from the reduction of LiPF_6 such as LiF or LiP_xF_y in addition of the solvent decomposition products, alkyl carbonates [75]. The products form a porous SEI, not suitable for the Si anode that requires effective passivation. The addition of fluoroethylene carbonate (FEC) or vinylene carbonate (VC) helps form a more stable, thinner with elastomeric properties SEI [76]. This is clearly visible in the stable cycling of the Si electrode in these electrolytes.

Ionic liquids (IL) have also proven their compatibility with Si electrodes. Anion choice is dominated by bis (fluorosulfonyl)imide (FSI^-) and bis (trifluoromethanesulfonyl)imide (TFSI^-) combined with a pyrrolidinium (PYR_{1n}^+) or 1-ethyl-3-methyl-imidazolium (EMIM^+) cations.

LiTFSI or LiFSI is the Li salt commonly associated with ILs. The best performance of the nano-Si is with $\text{PYR}_{13}\text{FSI}$ system and is attributed to the formation of a stable SEI resulted via the decomposition is the FSI^- . FSI^- rapidly releases F^- , most likely forming LiF , similar with FEC decomposition [55]. Figure 2.6 shows the electrochemical performance of a nano-Si electrode in two electrolyte systems, conventional organic electrolyte, and IL-based electrolyte. The nano-Si cycled in IL-based electrolyte present extended cycling stability. The capacity stabilizes after the first cycles and retains 76.7% of the initial capacity after 100 cycles. These results validate the benefits that IL-based electrolyte can have on the cycling stability of nano-Si electrodes.

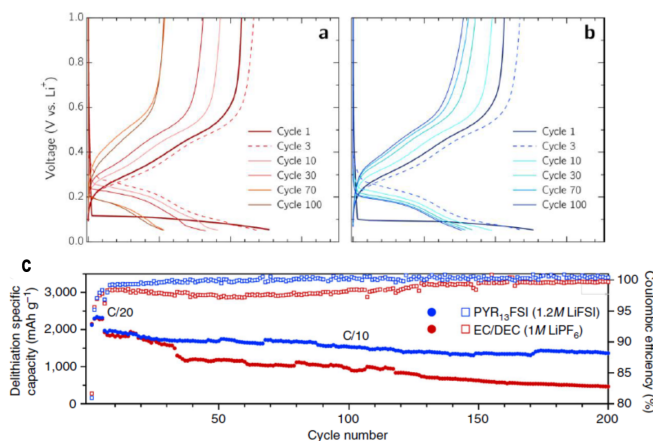


Figure 2.6: Galvanostatic performance of nano-Si electrodes with different electrolyte systems. Adapted from [55]. Charge-discharge curves corresponding to (a) an organic electrolyte comprising 1M LiPF_6 in EC/DEC and (b) an ionic liquid with 1.2M LiFSI in $\text{PYR}_{13}\text{FSI}$. (c) Specific capacity and Coulombic efficiency for the two electrolyte systems.

2.5 Silicon nanostructuring strategies

2.5.1 The beginnings

Nanostructuring unfolds exciting avenues for the well-established Si-based semiconductor industry enabling the generation of exceptional

electrical and mechanical properties, surface customization and functionalization and bio-compatibility. Consequentially, functional Si nanomaterials are the core of modern high performance devices in the fields of electronics, photonics, energy conversion and storage as well as biotechnology [69, 77–82]. However, the synergy between these properties and their target application requires precise tuning of the characteristic parameters of the nanostructures such as morphology, size or crystallographic orientation. Controlled fabrication of Si nanostructures is thus a prerequisite in order to explore their potential in various applications [83]. For instance, silicon nanowires (SiNWs) have been extensively studied for their remarkable properties, in part because of the plethora of methods proposed for the reliable fabrication of these nanostructures [84–87].

The story of SiNWs begins in 1960s when Wagner and Ellis from Bell Labs published their work on the vapor-liquid-solid (VLS) mechanism of single crystal growth of $\langle 111 \rangle$ silicon *nanowiskers* [88]. Their method was revived in the 90s when the advances in microtechnology triggered the interest in exploring and understanding the fundamental aspects of dimensionality and size. The research surrounding SiNWs and their applications really started to gain momentum due to the various developed synthesis techniques, catalyzed in particular by the development of accessible synthesis methods that allowed many research facilities to explore their properties. Generally speaking, the structuring mechanisms for SiNWs are classified as top-down (etching) and bottom-up (growth) approaches. Indeed, the properties of the nanowires vary greatly with their synthesis, thus, depending on the application the synthesis might change. Nonetheless, cost, availability and throughput are also major criteria. The most notable bottom-up mechanism is the VLS, with small variations in particular for the catalyst definition/structuration from the method described by Wagner and Ellis [88]. On the top-down side, we can distinguish between wet and dry etching. Top-down approaches rely on the patterning of a silicon substrate according to a predefined template. However, most of these methods require specialized equipment and involve highly sensitive procedures for mass production. In contrast,

metal-assisted chemical etching (MACE) profits from the simplicity of the process while allowing for the control of various parameters such as morphology (solid or porous), diameter, length and to a certain extent, crystallographic orientation [83, 86, 89, 90].

2.5.2 SiNWs via vapor-liquid-solid mechanism

The VLS mechanism, as described by Wagner, relies on two observations. First, an impurity is required for the growth. Second, small impurity globules were located at the top of the nanowire. From this, it was deduced that the role of the impurity is to mediate the growth of the nanowires. Thus, when a small Au particle is placed on a Si substrate and heated above the Au-Si eutectic point, a liquid droplet of Au-Si alloy will form. Next, when the droplet is exposed to a gaseous Si precursor such as silane, SiH_4 , or silicon tetrachloride SiCl_4 , the droplet will supersaturate with Si supplied by the gas phase and will freeze out at the droplet/Si interface. Therefore, the VLS stems from the Si phase transitions, which is inserted in the vapor phase, then goes through the Au-Si supersaturated liquid to finally precipitate at the Si/droplet interface. The mechanism requires a nanoparticle catalyst that dictates the position and the diameter of the nanowire since the growth is confined to the liquid Au-Si droplet as shown in Figure 2.7. As a matter of fact, the growth direction depends on the diameter of the impurity as well. In this context, much effort has been concentrated on the nanostructuring of the metal catalyst for a controlled fabrication. Indeed, a continuous nanoscale film metal catalyst will convert to randomly distributed nanodroplets at high temperatures due to surface tension effects. This was one of the preferred technique, however, it is useful to combine catalyst deposition and nanowire growth in the same system in order to avoid the unwanted parasitic reactions, activated by oxygen exposure for instance. Since the VLS growth requires high temperatures and controlled pressure it is usually associated with a chemical vapor deposition (CVD) facility where a Si gaseous precursor is dissociated. Laser ablation (LA)

and molecular beam epitaxy (MBE) use solid Si targets. Nanostructuring of the catalyst by laser ablation allowed the growth of nanowires with 6 nm diameter but requires higher temperatures since it employs a Si-Fe alloy to modify the interface energy and activate the formation of nanowires [91].

VLS growth allows for the synthesis of truly nanometric nanowires with diameters as low as 6 nm and offers the possibility of controlled doping. The major downside is the variability in the growth direction, in particular for small diameters. The growth direction of the nanowires changes for $\langle 111 \rangle$ to $\langle 110 \rangle$ with decreasing the diameter. Related to this, $\langle 100 \rangle$ SiNWs are not possible per se via VLS and require advanced nano-lithographic techniques such as anodic alumina oxide (AAO) templates to confine the growth and to generate ordered SiNWs arrays with controlled diameter. Finally, while Au is the preferred catalyst due to Au-Si alloy formation at relatively low temperature, Au contamination is a great concern, thus, other catalysts have been explored such as Ni or Fe but with negative impact from an energy standpoint.

2.5.3 SiNWs via metal-assisted chemical etching

Metal-assisted chemical etching is a versatile, inexpensive tool for the large-scale synthesis of vertically-aligned arrays of SiNWs allowing for precise tuning of diameter and length. MACE presents several advantages over its VLS counterpart. First, it is simple to experimentally implement since all the processing can be done in a chemical laboratory at room temperature. Secondly, it facilitates the control of several critical parameters such as shape, diameter, length, doping and, to some level, the crystallographic orientation. MACE is not only limited to the synthesis of SiNWs. In addition, the etched nanostructures inherit the crystallographic orientation of the initial Si source. Similar to VLS, a nanostructured catalyst is required to lead the way to the fabrication of vertically-aligned SiNWs arrays. These SiNWs-defined metasurfaces have shown exceptional photonic, phononic and electrical properties that have been intensively studied in their early exploration days.

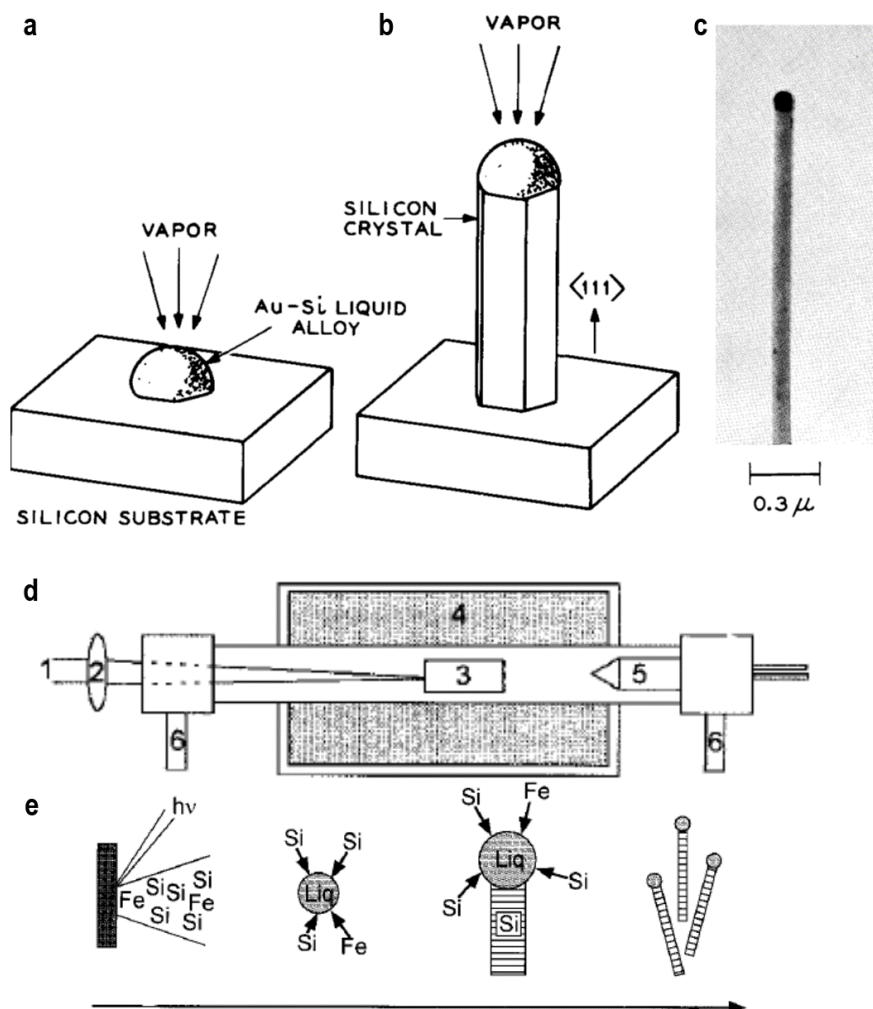


Figure 2.7: Si crystal growth by VLS. (a) Schematic illustration of the growth of a Si crystal during initial condition and (b) at later stages of growing. (c) TEM with the silicon crystal showing the gold-silicon alloy at the tip. Adapted from [88]. (d) Schematic of the VLS growth apparatus using laser ablation to generate the gold clusters. (e) The proposed nanowire growth model [91].

Methods and mechanism. Metal-assisted chemical etching resides on a noble metal catalyst to accelerate the dissolution of Si into an HF and an oxidizing agent-based electrolyte by generating electrical currents flowing between cathodic sites where holes are generated and, the anodic

sites where Si is oxidized and further dissolved. The noble metal is usually deposited via physical deposition in vacuum such as thermal evaporation, e-beam evaporation or sputtering, electroless methods and spin coating of the catalytic nanoparticles. The specialized literature mostly details on the electroless plating since it is a MACE process itself. Simply put, the most common method relies on a galvanic displacement reaction via an HF/AgNO₃ electrolyte with Ag nuclei forming and growing on the Si surface by taking electrons from Si, thus the latter is oxidized and further dissolved in HF [92]. In this situation, the Ag particle is sinking in the Si substrate forming tunnels. In this sense, this procedure allows the fabrication of SiNWs or pores with a broad spectrum of diameters and no particular spacial ordering. Thus, template-based nanostructuring of the catalyst was introduced to control the geometrical parameters of the SiNWs and their arrays, as discussed next. Under the current understanding, the etching proceeds with the catalytic decomposition of the H₂O₂ providing the holes (h⁺) that are further required for Si oxidation, facilitating its dissolution. The etching is an uninterrupted process as the catalyst protected Si is continuously etched leaving the SiNWs as residues on the Si substrate. Thus, MACE is associated with the movement of the catalyst that needs to preserve an intimate contact with the Si substrate.

Template-based metal-assisted chemical etching. The fabrication of highly ordered SiNWs arrays was only possible by the development of template-based MACE. Spacial ordering and diameter control of the SiNWs have expanded their applications. For instance, properties required for anti-reflective coating, superhydrophobic surfaces, biologic sensing or photovoltaics were only accessible after the development of template-based MACE. A key step in the fabrication of such structures is the nanostructuring of the catalyst mask on the Si surface. Literature details on several approaches to pattern this noble metal layer such as nanosphere lithography, porous anodic alumina membrane or interference lithography [86, 93, 94]. Among them, nanosphere lithography is preferred since it can be easily modified to produce a wide range of diameters and array densities. It relies on the self-assembly of a closed-pack monolayer of colloids such as polystyrene (PS) [94] or SiO₂ [93]

spheres. Next, the closed-packed monolayer is transformed into a non-closed-packed via colloidal etching, via reactive ion etching (RIE) for the PS particles or HF for the SiO₂ beads. The last step consists in the deposition of the noble metal. This process defines a mask with the pore position and openings as dictated by the etched colloidal particles. The nanosphere lithography of the catalyst mask allows for the etching of high aspect ratio wires with diameters ranging from nanometer to micrometers size [83].

Vertically aligned silicon nanowires. Figure 2.8 presents the key steps for the metal-assisted chemical etching with the catalyst mask defined by nanosphere lithography. Silicon substrates (*p*-type, <100>, resistivity 10-25 Ωcm) have been used after 10 minutes ultrasonic treatment in methanol. Next, a short oxygen plasma treatment was performed to render their surface hydrophilic for the colloidal processing. A monolayer of 260 nm nominal diameter polystyrene (PS) spheres (Microparticles GmbH) was assembled on the pre-treated Si substrate.

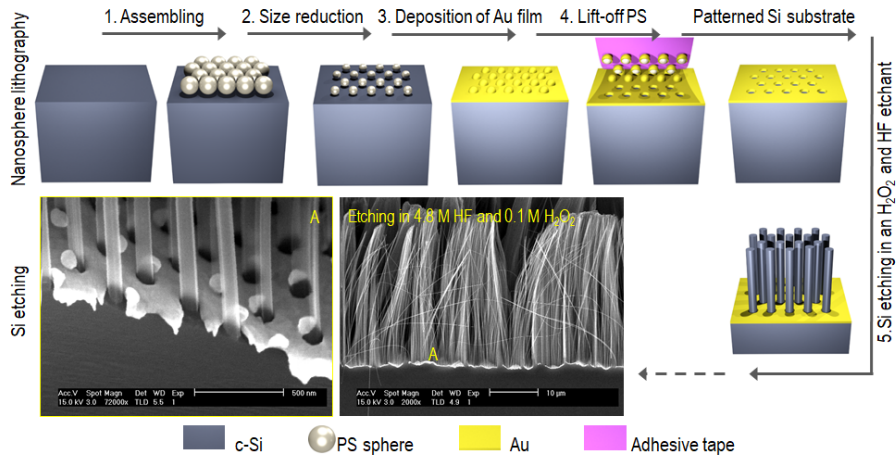


Figure 2.8: Metal assisted chemical etching for the controlled synthesis of high aspect ratio vertically aligned SiNWs.

In the next step, reactive ion etching was used to reduce the PS sphere diameter while retaining the initial close-packed hexagonal ordering. A 15 nm Au layer is subsequently deposited on the PS-decorated

Si substrate by physical vapor deposition. Adhesive tape followed by an overnight stay in dichloromethane was employed for the lift-off of the PS spheres. Typically, 50 μm straight SiNWs were produced by metal-assisted chemical etching in a solution containing 4.8M HF and 0.1M H_2O_2 for a total etching time of 2 hours. The complete process is listed in Appendix A. As we mentioned before, in template-based metal-assisted chemical etching, the diameter is dictated by the nano-pattern of the mask catalyst, while the length and the morphology of the nanowires depend on the etchant concentration. In Figure 2.8, results are shown for a 30 nm thick catalyst mask with 100 nm diameter SiNWs. The etching conditions are favorable for the etching of arrays of solid SiNWs [89]. Indeed MACE can be an attractive Si nanostructuring strategy due to its advantages related to the controlled etched geometry, inherent simplicity of the procedure without specialized equipment and, with that, reduced cost. However, optimization is still required to enable large-scale synthesis and a possible adoption in LIB technology as discussed in the Chapter 4.

While we have witnessed tremendous progress in understanding the lithiation behavior of Si electrodes and in developing complex structures and architectures to alienate some of the detrimental effects of Li insertion, a viable Si anode that also satisfies the industry requirements is still missing. We have seen that a variety of methods have been developed for nanostructuring of silicon. Most of them have a high cost requiring high-temperature and specialized equipment with a low output. Metal-assisted chemical etching certainly stands out due to its simplicity and equipment requirements as highlighted in the following Chapters. Nowadays, industrial adoption of Si-based electrodes relies not only on the electrochemical performance but also on the complexity of the synthesis and the efficiency of the process as well as recycling capabilities or end-of-life possibilities.

Surface passivation effects on nano-Si electrodes during Li insertion

At 94, you no longer worry about keeping your job.

John Goodenough on Intellectual Freedom

Surface passivation has certainly a positive impact on the cycling stability of Si-electrodes. However, the mechanism responsible for this is not clear since we do not know what happens to the coating, or for that matter, coated nano-Si electrodes during Li insertion. Here, we show that the Ni surface coating mediates the swelling and fracture of crystalline Si nanowires during lithiation. Furthermore, we discriminate between different swelling and fracture regimes depending on the thickness of the coating and the radius of the nanowire. Based on these findings, we identify the most favorable configuration for better performing Si electrodes.

We have seen previously, in Chapter 2, that functional surface coatings comprising metals, carbon or oxides can positively impact the cycling stability of Si anodes [59,61,73,95–103]. These improvements have been attributed to several factors. First, a surface coating prevents direct contact with the electrolyte and, thus, controls the SEI formation. Second, the surface coating can act as a mechanical constraining layer by buffering the volume change, preventing electrode pulverization. Furthermore, electronically conducting coatings (such as metal and carbon) improve the current collection efficiency thus enhancing the redox reaction kinetics at the electrode. Finally, a surface coating can also prevent detrimental electrochemical welding between active material particles [104–106].

A key feature of Si-coated structures is their mechanical stability when deformed by action of the anisotropic Li_xSi growth. If the coating layer cracks, much of the expected benefits are simply lost. The electrical conductivity can be severely affected by the generated discontinuities, whereas the direct exposure of fresh silicon surface to the electrolyte inevitably results in new SEI formation. Eventually, cracks initiated in the surface layer may propagate into the lithiated silicon, further amplifying the degradation. Despite the general consideration that surface coating enables sustained cycling, single particle *in-situ* studies have actually revealed irreversible and dramatic damages to the coating, not fully corroborating the larger-scale electrochemical cycling experiments [100,102,103]. Furthermore, while carbon coatings have been generally considered as beneficial for cycling stability and charge collection efficiency, carbon becomes brittle when lithiated [107], delaminates [108], and undergoes dramatic irreversible damage [101]. Finally, cracking of metallic coatings during lithiation was also reported [100]. Whereas hollow nanostructures have been shown to maintain structural integrity by directing the volume expansion towards the interior [61,73,108,109], scalability of the fabrication processes, low mass loading as well as progressive SEI accumulation in the internal void spaces limits their widespread implementation. Understanding and controlling the lithiation dynamics as well as the swelling and fracture behavior in coated Si structures are thus of primary interest towards real-life battery applications. Ni

coated silicon nanopillars are selected as a model system for analyzing the swelling and fracture behavior during initial lithiation.

We selected Ni to investigate the effect of surface passivation on the electrochemical performance of the kinked silicon nanowires (k-SiNWs)-based assembly. Ni was selected because of its high electron conductivity and good adherence to silicon. Furthermore, Ni hinders excessive SEI formation, has a low reactivity with lithium yet allows a lithium flux [47, 69, 73, 97, 110–112]. In addition, conformal Ni coatings can be considered an integrated current collector intimately coupled to Si, providing direct electrical pathways as well as effective Si electrode passivation.

3.1 Core-shell SiNPs design and testing protocol

The crystalline silicon nanopillars of $\langle 100 \rangle$ axial crystal orientation have been fabricated using combined nanosphere lithography and metal-assisted chemical etching protocols as described in Chapter 2 and Appendix A, enabling precise crystallographic orientation mapping and visualization.

The Ni electroless deposition procedure was used for the conformal coating of the nanopillars with Ni. This procedure allows the growth of a Ni layer with a uniform thickness along the radial and axial directions (Figures 3.1a and 3.1b) and a precise morphology control. In order to investigate the impact of the structure dimensions, Si nanopillars with different nominal diameters (170, 330 and 480 nm) and varying coating thicknesses (40, 80 and 120 nm) are considered. For simplicity, the composite structures are referred to as $\text{Si}_{2A}@\text{Ni}_h$, where subscripts A and h stand for the Si core radius and Ni shell thickness, respectively. The composite structure is considered isotropic and at equilibrium before lithiation. The lithiation of coated Si nanopillars follows a documented *ex-situ* experimental protocol as described in Appendix B [47, 51]. In short, the set-up consists in a half-cell with the composite nanopillars supported by the Si substrate as working electrode and a Li-metal foil as reference and counter electrode (Figure 3.1c).

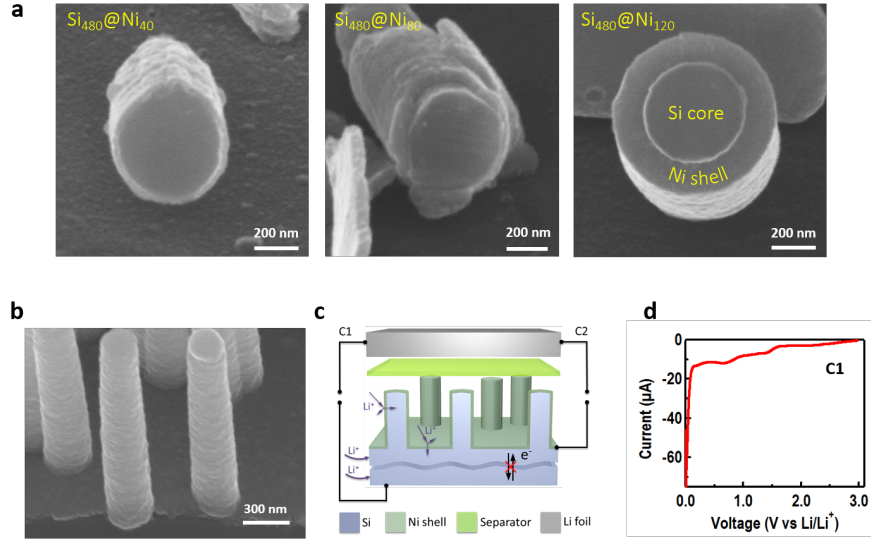


Figure 3.1: Experimental design. (a) Cross-section SEM views of the conformal Ni shell with different thicknesses deposited around the circular silicon core nanopillar. (b) SEM side view of conformally Ni wrapped silicon nanopillars. (c) Schematic of the lithiation set-up. Two circuit configurations have been used depending on the metal shell thickness: C1 for uncoated Si or thin Ni deposits and C2 for thick Ni coatings. (d) Typical current vs. voltage profile during electrochemical lithiation experiments.

The cell voltage was slowly ramped down to 10 mV vs. Li/Li⁺ and held at this potential for at least 6 hours to ensure deep lithiation (Figure 3.1d). Thick Ni coated samples were found to severely slow-down the initial lithiation of the nanopillars (see hereafter), requiring longer lithiation period (more than 12 hours). Eventually, this led to fracture and pulverization of the underlying silicon substrate resulting in the loss of electrical contact with the bottom current collector (circuit C1 in Figure 3.1c). To avoid this and to ensure reliable lithiation conditions, the electrical contact was established through the Ni layer covering the substrate top surface and the Si nanopillars (circuit C2 in Figure 3.1c).

3.2 Lithiation behavior

Figure 3.2 shows representative morphologies of $\text{Si}_{480}\text{@Ni}_0$ after lithiation. Note that the pristine Si nanopillars already have a surface coating made of native SiO_2 , of approximately 2 nm thickness.

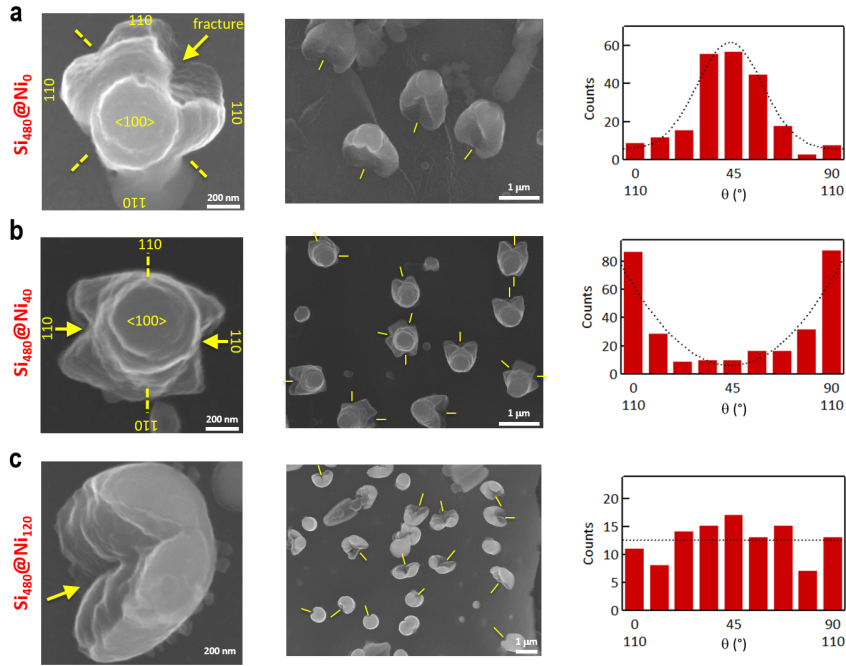


Figure 3.2: Ni-coating mediated swelling and fracture for Si nanopillars with $2A = 480$ nm. High and low magnification SEM micrographs of lithiated silicon pillars as well as statistical analysis of the cracking sites for pristine (row a), 40 nm (row b) and 120 nm (row c) thick Ni coated silicon nanopillars. The angular location of cracking sites (θ) is measured with respect to one quadrant delimited by the $\langle 110 \rangle$ directions. The yellow lines indicate the preferred location of the cracks, while the arrows point to developed cracks. The swelling and the cracking behaviors of core-shell structures markedly vary with the coating thickness.

Consistent with previous reports, bare silicon nanopillars display anisotropic swelling with preferentially faster expansion on the $\{110\}$ planes. The anisotropic swelling of crystalline Si during solid-state amor-

phization results from the different reaction kinetics on the $\{110\}$, $\{100\}$ and $\{111\}$ crystallographic planes [42, 113]. The lithiated nanopillars typically display one or two axial cracks on the surface of $\{100\}$ lateral planes, consistently with previous reports (Figure 3.2a, fracture site statistics). Coated nanopillars exhibit a markedly different behavior. Distinct swelling behavior and accompanying fracture regimes have been identified in nanopillars, respectively *thin* ($\text{Si}_{480}\text{@Ni}_{40}$ and $\text{Si}_{480}\text{@Ni}_{80}$ display similar patterns and *thick* ($\text{Si}_{480}\text{@Ni}_{120}$) coatings. For thin coatings, the lithiation-induced cracks are now located on the surface of $\{110\}$ lateral planes as evidenced by SEM images and the statistical analysis presented in Figure 3.2. Cracks nucleate in the Ni shell and propagate into the Li_xSi as the lithiation proceeds. Several cracks can be accommodated within the same structure. Nanopillars with up to three cracks have been observed, while mainly a single crack per nanopillar was usually identified in the uncoated structures. Whereas the lithiation induced swelling anisotropy for $\text{Si}_{480}\text{@Ni}_{40}$ and $\text{Si}_{480}\text{@Ni}_{80}$ configurations is less obvious than in the $\text{Si}_{480}\text{@Ni}_0$ case, the existence of clear preferential fracture sites unambiguously suggests that the underlying morphology evolution retains its anisotropic swelling character. Furthermore, cracked nanopillars exhibit asymmetric morphology evolution, indicative of preferential lithiation through the cracks. In contrast, the remained undamaged $\{110\}$ planes do not exhibit large deformation, indicating a lower degree of lithiation.

Further increase of the coating thickness induces yet another swelling and fracture regime (Figure 3.2c). The lithiated $\text{Si}_{480}\text{@Ni}_{120}$ nanopillars display only one fracture site per nanopillar and, remarkably, the crack shows no preferential crystallographic orientation (Figure 3.2c, fracture site statistics). The crack propagates radially through the nanopillar section, and may ultimately split the latter into two roughly symmetric half-cylinders. Noticeably, the lithiated silicon half-core is protruding from inside whereas the Ni half-shells roughly maintain their original shape.

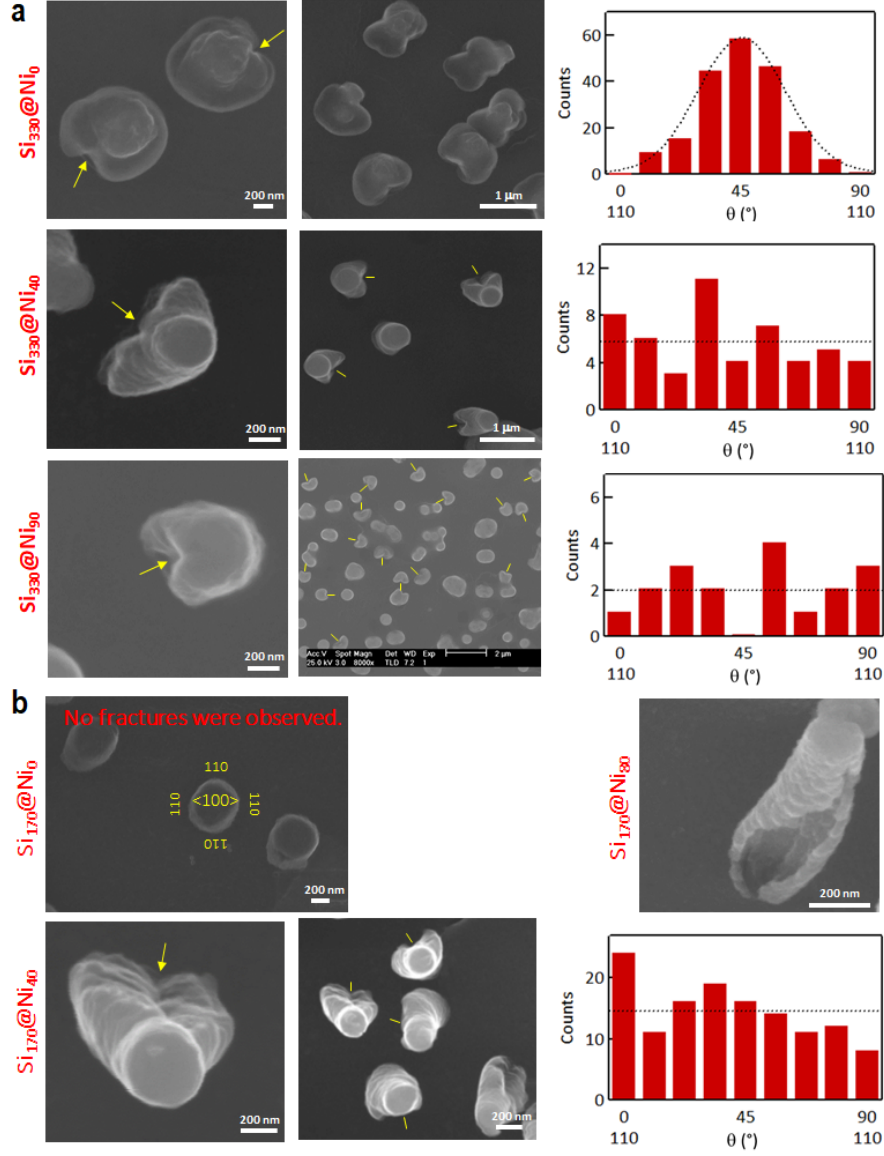


Figure 3.3: Ni-coating mediated swelling and fracture for Si nanopillars with $2A = 330$ nm and $2A = 170$ nm. (a) High and low magnification SEM micrographs of lithiated silicon pillars as well as statistical analysis of the cracking sites for pristine, 40 nm and 90 nm thick Ni coated silicon nanopillars with $2A = 330$ nm. (b) High and low magnification SEM micrographs of lithiated silicon pillars as well as statistical analysis of the cracking sites for pristine, 40 nm and 80 nm thick Ni coated silicon nanopillars with $2A = 170$ nm. The angular location of cracking sites (θ) is measured with respect to one quadrant delimited by the $\langle 110 \rangle$ directions. The arrows point to developed cracks.

However, the extent of lithiation varies for different nanopillars (Figure 3.2c, middle panel). Despite the fact that these experiments were performed for 24 hours or more using the circuit configuration C2 (to ensure reliable electrical contact, Figure 3.1c), some nanopillars seem lithiated to a high extent whereas others appear not to be affected at all. Intermediate configurations with various degrees of radial crack advancement can be visualized as well. This suggests that lithiation may be slowed down even after the onset of fracture of the Ni shell. Finally, no transverse cracks were detected in any of the studied configurations. We have performed a similar analysis on nanopillars with a smaller initial Si diameter as shown in Figure 3.3.

As expected, the $\text{Si}_{330}@\text{Ni}_0$ and $\text{Si}_{170}@\text{Ni}_0$ configurations display the preferential swelling anisotropy normal to the $\{110\}$ planes. However, the anisotropic deformation of small diameter nanopillars is less pronounced, as previously reported. For instance, whereas cross-shaped morphologies can be clearly visualized for the pristine diameters larger than 350 nm, rectangular shapes are barely distinguished for diameters below 170 nm (Figure 3.3b). On the other hand, coated $\text{Si}_{330}@\text{Ni}_{40}$, $\text{Si}_{330}@\text{Ni}_{90}$ and $\text{Si}_{170}@\text{Ni}_{40}$ nanopillars overall display isotropic cracking and swelling patterns. Only one fracture site with no apparent preferred orientation is observed, similar to the previously detailed $\text{Si}_{480}@\text{Ni}_{120}$ configuration. However, in contrast to the $\text{Si}_{480}@\text{Ni}_{120}$ case, a larger fraction of small diameter nanopillars were found lithiated and cracked.

3.3 Modeling and analysis

The broad spectrum in the swelling and fracture behavior suggests a complex interplay between various chemo-mechanical processes, depending on the characteristic dimensions of the system under interest. The initial lithiation of crystalline silicon at room temperature results in the formation of an amorphous Li_xSi phase ($x \approx 3.75$) [114] which progresses towards the interior of the nanopillars [41, 115]. Anisotropic growth of the lithiated phase is explained by the orientation-dependent mobility of the reaction front [41, 42, 113, 116]. Lithiation also requires the transport of Li through the Ni coating and the lithiated phase, up to the reaction

front. As lithiation proceeds, mechanical stresses are generated as a result of the heterogeneous swelling and constraining action of the Ni layer. Mechanical stresses may in turn significantly impact the various chemical processes. In the following, we rely on a chemo-mechanical analysis to gain more insight into the relevant factors governing the observed swelling and fracture regimes. We particularly discuss (i) Li transport through the Ni coating, (ii) the buffering effect of the Ni layer and (iii) the impact of mechanical stress on the lithiation kinetics. Diffusion of Li through Ni metal films is often considered as improbable because no Li-Ni alloys are known at room temperature. However, some analyses have shown that Li can freely move through inert metallic films (Cu or Ni) which are efficiently used as an ion-selection membrane or for surface passivation [73,97,110]. Taking Cu, the Li diffusivity was initially estimated to fall in the range of $10^{-7} - 10^{-6}$ cm²/s [117], with a recent report estimating the room temperature Li diffusion for poly-crystalline Cu as low as $10^{-15} - 10^{-17}$ cm²/s [118]. Thus, the least favorable estimation would put Li diffusivity through Cu concurrent with Li diffusion through Li_xSi, estimated at around $10^{-12} - 10^{-14}$ cm²/s. In turn, diffusion of Li through lithiated silicon is very fast compared to the lithiation reaction kinetics [113]. Although, the Li diffusion in Ni is not readily available, it is expected to share similarities with Cu, thus, from the above observations, the entire process is expected to be reaction-limited, rather than diffusion-limited. Experimentally, these conclusions are also valid. Based on these considerations, Li diffusion through Ni is thus considered as having a negligible impact on the observed swelling and fracture patterns.

To investigate the effect of the Ni layer on the morphological evolution and mechanical stress development during lithiation, we implemented a 2D continuum chemo-mechanical model into the Finite Elements software Abaqus (see Reference [119] for a complete description of the model). Simulation of the lithiation of uncoated nanopillars (Figure 3.4a) predicts a cross-shaped morphology in good agreement with experimental observations (Figure 3.2a), as well as high tensile stresses on the surface of {100} lateral planes which are situated at 45° angles from the preferentially expanded {110} planes, explaining crack initiation at

these locations.

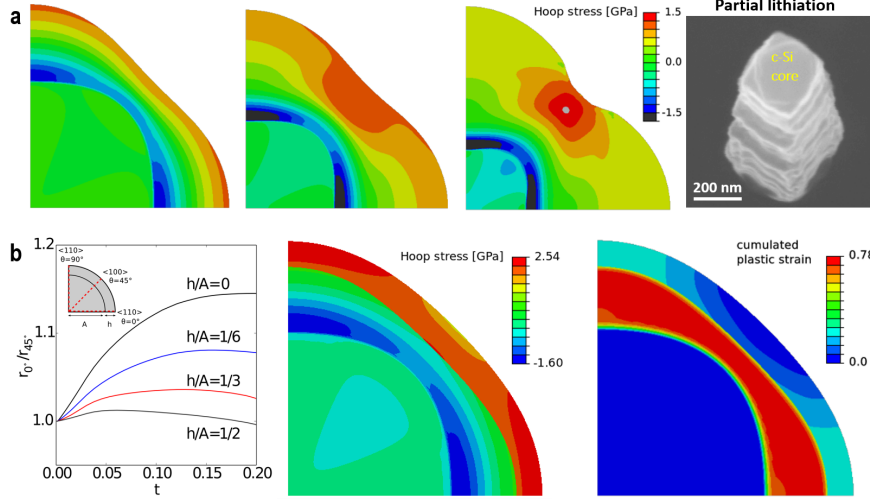


Figure 3.4: Numerical hoop-stress distribution. (a) Contour plots of hoop stress in uncoated nanopillars. Profiles are shown for normalized lithiation times $t = 0.15, 0.3$ and 0.45 . The SEM images shows the rectangular c-Si core after removal of the lithiated Si in methanol, coherent with the simulated profiles. (b) Numerical simulations indicate that the coating reduces the overall anisotropic expansion of the nanostructure by buffering the swelling strain. The anisotropy is measured by the predicted ratio of current outer radii at 0° and 45° (r_0/r_0^{45}) for normalized lithiation time ($0 \leq t \leq 0.2$). Contours of hoop stress and cumulated plastic strain for $h/A = 1/6$ (representative of $\text{Si}_{480}@\text{Ni}_{40}$). The highest tensile hoop stresses in the Ni shell are found along the $\langle 110 \rangle$ directions. Qualitatively similar contour plots are obtained in the simulations with $h/A = 1/4, 1/3$ and $1/2$.

We simulated the morphological evolution of coated nanopillars with various coating h and A parameters. A remarkable effect of the coating is to buffer the volume expansion through non-uniform deformation of the coating, effectively reducing the overall anisotropy of the structure (Figure 3.4b). The buffering effect increases with the relative coating thickness. The model also predicts the largest hoop stress levels and plastic strain accumulation on the coating surface along the $\langle 110 \rangle$ directions (Figure 3.4 for the case $h/A = 1/6$), as a result of the faster

front velocity. Qualitatively similar trends are found for $h/A = 1/6$, $1/4$ and $1/2$. These trends are consistent with the reduced anisotropy observed experimentally when the coating thickness increases. It also explains the initiation of cracking on the surface of $\{110\}$ lateral planes in structures with relatively thin coating ($\text{Si}_{480}\text{@Ni}_{40}$ or $h/A = 1/6$, Figure 3.4b). However, these predictions are not sufficient to explain the random location of cracks for relatively thick coatings, namely the cases $\text{Si}_{480}\text{@Ni}_{120}$ ($h/A = 1/2$), $\text{Si}_{330}\text{@Ni}_{90}$ ($h/A \approx 1/2$), $\text{Si}_{330}\text{@Ni}_{40}$ ($h/A \approx 1/4$) and $\text{Si}_{170}\text{@Ni}_{40}$ ($h/A \approx 1/2$) (see Figure 3.2c and 3.3a). As a matter of fact, the mechanical constraint induced by the Ni coating is expected to have an impact on the reaction kinetics, as discussed below. Another important argument that could explain the transition from anisotropic to isotropic swelling and fracture behavior is based on kinetic considerations. It has been shown in several studies that the high compressive stresses that develop at the lithiation front could slow down the chemical reaction [116, 120, 121]. In a recent study, Zhao *et al.* identified the driving force for reaction as depended on the mechanical stresses developed across the reaction front can contribute positively or negatively to the reaction kinetics [116].

Numerically predicted hydrostatic stress profiles are shown in Figure 3.5a for different h/A ratios together with the corresponding normalized concentration profile, in the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. Figure 3.5a clearly shows that the h/A ratio significantly impacts on the hydrostatic stress levels near the front, and delays the reaction in $\langle 110 \rangle$ directions. In contrast, Figure 3.5b indicates that the delayed contribution of the stress has a lower impact for the directions $\langle 100 \rangle$. This effect plays a role in all configurations, but is less important for small h/A ratio. Overall, the numerical results suggest that the presence of the coating increases the hydrostatic pressure at the front, which presumably slows down the lithiation kinetics as a whole, and, furthermore, reduces the swelling anisotropy. Based on these considerations, it is likely that the mechanical constraint induced by the thick coating ($\text{Si}_{480}\text{@Ni}_{120}$, $h/A = 1/2$) strongly limits the extent of lithiation, as well as the swelling anisotropy, leading to more isotropic stress distribution and a single randomly located fracture site.

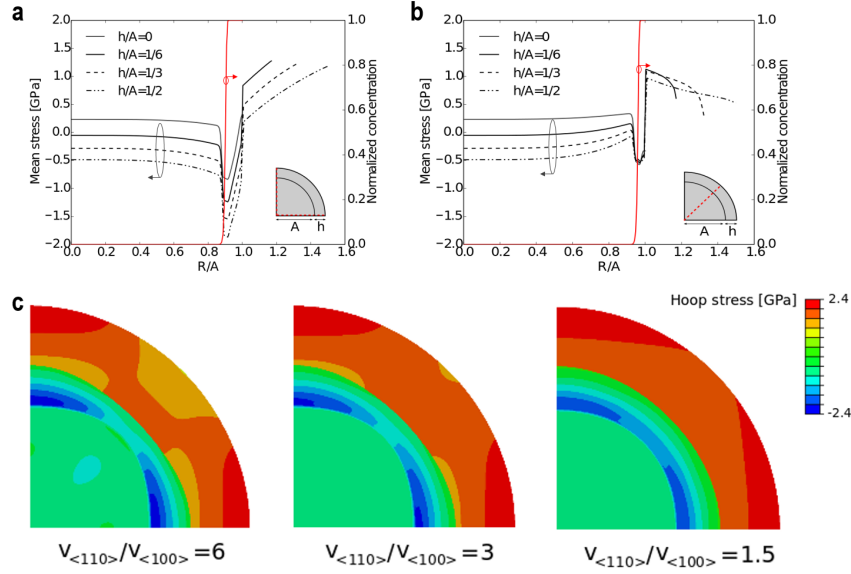


Figure 3.5: The mean stress profiles along (a) $\langle 110 \rangle$ and (b) $\langle 100 \rangle$ directions for different h/A ratios at the beginning of lithiation. Here R is the radial coordinate in the undeformed configuration. The corresponding normalized concentration profile is also represented on the right-hand side ordinate-axis. (c) Contours of hoop stress in the Ni shell for different ratios of the front velocities in the $\langle 110 \rangle$ ($v_{\langle 110 \rangle}$) and $\langle 100 \rangle$ ($v_{\langle 100 \rangle}$) directions. When this ratio is close to 1 (for instance, due to the mechanical stress effect on the lithiation kinetics), the tensile hoop stress is more homogeneous. Such scenario explains the random fracture pattern experimentally observed in nanopillars with a thick coating.

As can be seen in Figure 3.5, when the ratio of the front velocities along the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions is close to one, the hoop stress distribution in the Ni shell is almost uniform. Fracture is then dominated by defects existing in the thick shell (i.e. roughness and grain boundary grooving), rather than by mechanical stress or plastic strain concentration. The mechanical constraint of the thick shell acts even after the initiation of a crack. Indeed, the $\text{Si}_{480}@\text{Ni}_{120}$ nanopillars display different swelling (and hence lithiation) degrees, as well as different crack extensions (Figure 3.2) despite forced lithiation during prolonged times (by holding the voltage at 10 mV vs. Li/Li^+ for more than 24

hours). Even after the onset of fracture, lithiation is sometimes unable to proceed. This is surprising as one would expect that the unzipping of the core-shell structure would relax the mechanical stress. This indicates that the undamaged portion of the Ni layer is able to maintain its strong mechanical constraint, preventing further lithiation (or core expansion). Finally, some of the nanopillars in the $\text{Si}_{480}@\text{Ni}_{120}$ configuration did not experience any swelling or fracture, indicating that the coating may completely impede the reaction in some cases.

3.4 Discussion

The adopted model provides insight into the experimental trends, although we could not determine the actual ratio of the reaction front velocities in the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions in the considered configurations. This ratio is affected by the local stress and thus evolves in time; *in-situ* monitoring could reveal additional features of lithiation kinetics in coated structures [41]. According to our model, the same trends are expected for a given h/A ratio, independently of the radius A . However, some discrepancies are found when comparing the behavior of small diameter nanowires ($2A = 330$ nm) and larger diameter ($2A = 480$ nm). Relying solely on the h/A ratio, anisotropic swelling and fracture pattern would be expected for the $\text{Si}_{330}@\text{Ni}_{40}$ nanopillars ($h/A = 1/4$), as both the $\text{Si}_{480}@\text{Ni}_{40}$ ($h/A = 1/6$) and $\text{Si}_{480}@\text{Ni}_{80}$ ($h/A = 1/3$) display anisotropic behavior. In contrast, a preferentially isotropic behavior was observed (although specificity along $\{110\}$ planes could be detected as well). Additional size-dependent effects play a subtle role. Here, the isotropic behavior of the $\text{Si}_{330}@\text{Ni}_{40}$ nanopillars is reminiscent of the reduced anisotropy observed in uncoated pillars of small diameters also reported by other groups. Experimental observations showed that below a critical size of approximately 300 nm, the anisotropic expansion is less pronounced and fracture can be avoided [50, 51]. Hence, the radius of the Si core (i.e., its curvature) affects the lithiation kinetics, irrespective of the presence of a coating layer. To the best of our knowledge, the physical origin of this size effect has not been elucidated yet. Note finally that the size effect can also result from the complex

thickness dependence of strength and ductility of the Ni film. For h/A values close to $1/3$, the lithiated structures display a peculiar cracking pattern. The volume expansion of the core leads to the unzipping of the shell, and the cracking (and the lithiation) further progresses in the radial direction with significant shell deformation, finally leading to a fully open frame (Figure 3.2c). The main difference observed for the $\text{Si}_{480}@\text{Ni}_{120}$ configuration is that the Ni shell deforms less, preserving the initial circular shape. This hints at a larger structural stiffness of the thicker Ni coatings. Axial-unzipping pattern could be exploited for the design of alternative nanostructures. Indeed, it leads to a configuration resembling the Si thin-film on a Ni substrate (Figure 3.2c), known to sustain repeatable cycling due to the unconstrained volume expansion and retraction during lithiation [49, 122]. Such configuration would also minimize the exposed silicon surface in contact with the electrolyte. Thus, coatings thick enough to drive isotropic swelling and cracking are expected to provide better cycling performances. Although the initial lithiation is clearly impeded by the coating, engineered structures with defects introduced on purpose could be used to accelerate the initial lithiation.

As a summary, we studied the lithiation behavior Ni coated nano-Si that display markedly different swelling and fracture patterns depending on the coating thickness and the silicon nanopillar diameter. Nanopillars with relatively thin coating display anisotropic swelling similar to that observed in the case of pristine nanopillars, but with different preferred fracture sites. As the coating thickness increases, swelling and fracture patterns undergo an anisotropic to isotropic transition, with a single randomly oriented longitudinal crack. A numerical chemo-mechanical analysis suggests that the transition from anisotropic to isotropic behavior follows from the mechanically altered lithiation kinetics. While fracture in plain, coated silicon nanostructures seems inevitable, our results suggest that the fracture pattern could be tailored through an appropriate choice of the coating thickness and morphology. These findings will be experimentally validated in Chapter 6 for the custom nano-Si developed next.

This chapter showed how the surface coating will impact the swelling and fracture behavior during the initial lithiation. Two regimes are identified based on the ratio thickness of the Ni coating and the diameter of nanopillars. The most favorable configuration is associated with thicker coatings where the detrimental swelling anisotropy is reduced. The knowledge provided here will be experimentally applied in Chapter 6 for the nanostructures developed in the next Chapter.

Nanostructured silicon

C'est véritablement utile puisque c'est joli.

Antoine de Saint-Exupéry via The Little Prince

Battery technology can greatly benefit from simple synthesis processes that allow mass production. Herein, we extend on metal-assisted chemical etching of Si to increase the efficiency by re-using the substrate for consecutive etchings. We then report on a generic process based on metal assisted chemical etching of Si for the synthesis of high aspect-ratio, hybrid orientation kinked Si nanowires. This approach enables the control of the number of kinks, their location and, to a certain extent, their angle via successive etch-quench sequences. We coupled relevant Au catalyst parameters to systematically assess the impact on the etched morphologies.

We have seen in Chapter 2 that the industrial adoption of a Si-based electrode does not only require a working configuration but also simple, low-cost, and efficient synthesis since, for batteries, nano-Si quantity is critical. In addition, for some applications, the Si substrate can have a detrimental effect, as such, to fully exploit the properties of the SiNWs, collecting the SiNWs is required. However, top-down processing requires complementary procedures to separate the SiNWs from their parent Si substrate and to allow full exploitation of their properties. Such approaches rely either on mechanical peeling or require subsequent processing such as polymer embedding or metal contact definition in the case of electro-assisted methods [94, 123, 124]. While each method has its particular merit depending on the application, a universal solution that assists the extraction of etched SiNWs is still lacking.

4.1 Continuous SiNWs synthesis enabled by chemical peeling

Here, we exploit the porous morphology that can be accessed by altering the concentration of oxidizing agent to etch mechanically weaker segments in the NWs. For the chemical peeling, the etching in a solution containing 4.8M HF and 1M H₂O₂ favors the etching of a highly porous segment. This sacrificial porous segment facilitates the separation of the SiNWs from the Si substrate with a short ultrasonic treatment in methanol. While other reported techniques pivot around the porosity-mediated separation, the proposed procedure enables fast SiNWs extraction as an integrated step in metal assisted chemical etching of Si. Furthermore, mask-induced processing defects present on the Si substrate will resist the ultrasonic treatment as the high oxidant concentration is expected to affect only SiNWs. This extraction selectivity is a great advantage over other methods such as mechanical peeling that cannot discriminate between the etched nanostructures and defects. After this step, the metal mask remains intact and can be reused for a new etching sequence. The thickness of the Si substrate is the only limitation for this continuous etching scheme. Figure 4.1 shows the re-use of an

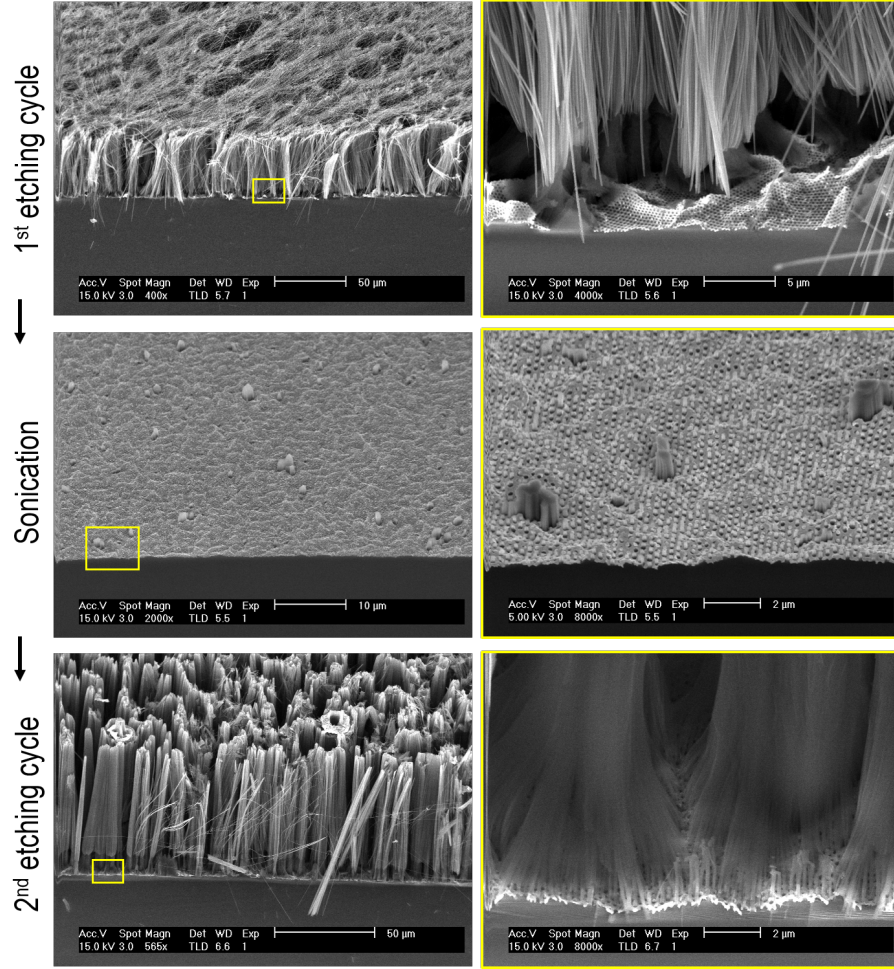


Figure 4.1: Continuous SiNWs synthesis enabled by chemical peeling.

Au-patterned Si substrate enabled by chemical peeling.

Extensive theoretical studies demonstrated that kinked SiNWs (k-SiNWs) display superior mechanical, electrical and thermal properties compared to their vertical counterparts. Yet, on the experimental front, a simple, accessible and controlled fabrication method to explore and exploit these theoretical predictions was not readily available. Next, we will adapt the classical metal-assisted etching scheme for the controlled fabrication of k-SiNWs.

4.2 Kinked silicon nanowires

While the general understanding of MACE emphasizes on the isotropic $\langle 100 \rangle$ etching predisposition as prescribed by the back-bone theory, non- $\langle 100 \rangle$ SiNWs have been demonstrated, regardless of the initial Si wafer orientation. In particular, hybrid orientation SiNWs or kinked SiNWs (k-SiNWs) are extremely interesting for both theoretical and experimental research considering their associated spring morphology that has a positive impact on the photon absorption, elastic properties as well as thermal insulation [90, 125, 126]. In this context, the development of simple approaches that allow for the large area controlled fabrication of k-SiNWs is essential for exploring their physical properties in fundamental studies and enable their use as building blocks for advanced applications. Along this direction, several reports explored advanced etching schemes to control the etching direction and engineer custom crystallographic nanostructures [127–130]. These studies suggest that the local depletion of etchants create concentration gradients which should impact the anodic current. Furthermore, the addition of high surface tension additives such as glycerol can greatly alter the etchants availability through limited diffusion of etchants [127]. Indeed, the miscibility of the etchants is a critical parameter with metal-assisted chemical etching in particular for etching conditions without mechanical agitation. As a matter of fact, the kinks are almost exclusively associated with static etching conditions without mechanical agitations while stirring typically renders $\langle 100 \rangle$ SiNWs since the etchants are continuously replenished. However, such procedures cannot account for reliable large scale fabrication of high aspect ratio k-SiNWs since the induced perturbations are local and require particular conditions which are difficult to control. Undeniably, metal-assisted chemical etching of Si is a dynamic process with parameters changing as the etching advances. Therefore, controlling the etching patterns to produce k-SiNWs, such as deviating the catalyst motion and turning on and off crystallographic dependencies are particularly challenging. Here we detail on a straightforward k-SiNWs etching scheme that facilitates the fabrication of high aspect-ratio, hybrid orientation Si superstructures. This etching mechanism relies on

repetitive etch-quench sequences to induce the kinks using low surface tension ethanol co-solvent. The length of the etched segments in the Si superstructures simply depends on the etching time. Multiple etching baths are no longer required as the etchant availability is modulated via the methanol quencher, and risks related to the etchants bath imbalance at advanced etching stages are reduced. This one-pot-type synthesis facilitates the etching of mechanically stable, high aspect ratio (AR¹) superstructures at high etching rates. The systematic assessment of the main MACE parameters, namely Au catalyst mask thickness coupled with opening diameter, has allowed the etching of a wide spectrum of nanostructures as we will see next.

4.2.1 Materials and methods

After the colloidal lithography, MACE was performed at ambient conditions with no agitation using ethanol as co-solvent. The etching of k-SiNWs required two consecutive steps. First, the Au-patterned Si substrate was etched in a solution comprising 9.3M HF and 1.6M H₂O₂ ($\epsilon = [\text{HF}]/[\text{H}_2\text{O}_2] = 5.8$) for 5 minutes. The reaction is quenched in methanol for less than 1 minute. The second etching step employed for the k-SiNWs fabrication relied on a series of etch-quench sequences with 5 minutes etching in an etchant with 14M HF and 1.3M H₂O₂ followed by a 1-minute quench in methanol. The complete MACE process lasts a total time of 41 minutes. The k-SiNWs formed during this time typically had 6 kinks and 40 μm in length. The sequential, top-down etching approach used in the fabrication of the k-SiNWs allows for the creation of a final porous nanowire segment. For this purpose, the etching was performed in a solution containing 4.6M HF and 8.3M H₂O₂ for 3 minutes (Figure 4.2). The k-SiNWs were subsequently collected in methanol with a 10 seconds ultrasonic treatment.

Summarizing, etching in a solution with $\epsilon_1 = 5.8$ results in the formation of porous SiNWs, while the etching in a solution with $\epsilon_2 = 10.7$ follows non- $\langle 100 \rangle$ directions. The measured angle (Figure 4.2) indi-

¹Computed here as the ratio of the opening diameter s and the etching depth of the Si wafer.

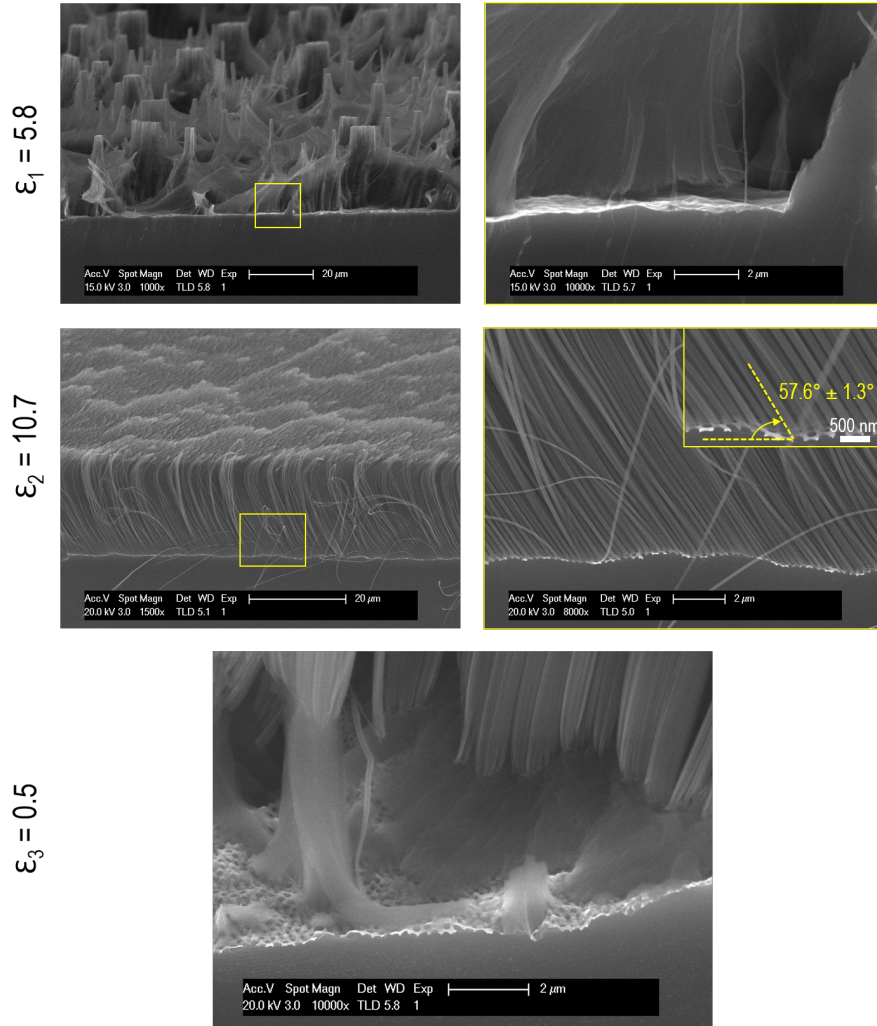


Figure 4.2: Silicon etching under different conditions of etchant concentrations.

cates $\langle 111 \rangle$ -oriented SiNWs. The etching time for both solutions was 20 minutes. For the high oxidant concentration, $\epsilon_3 = 0.5$, highly porous SiNWs are formed.

Figure 4.3 presents a schematic route for the controlled fabrication of superstructures of k-SiNWs with high aspect ratio, and regular geometry and morphology, enabled by a simple MACE scheme. The first step is the patterning of the catalyst Au mask via colloidal lithography. This oper-

ation requires the closed-packed self-assembly of PS spheres of 260 nm in diameter on the starting Si substrate. The PS spheres are size reduced with reactive ion etching to the desired breath representing the final diameter of the etched SiNWs. Subsequently, the Au catalyst is deposited on the PS-decorated Si substrate. The nanohole Au mask is obtained by the lift-off of the PS spheres with adhesive tape. The next step is the Si etching in a solution of HF and H₂O₂, with ethanol as co-solvent, under static conditions. To form the kinks at the desired location, Si etching is interrupted at the specific times by submerging the sample in methanol. Varying these etch-quench sequences at specific times renders superstructures of k-SiNWs. Here, E_p is used for designating the etching time (in minutes), p, and Q_q for the quenching time (in minutes), q. The number of kinks n is simply controlled by the performing $(n + 1)$ [E – Q] sequences.

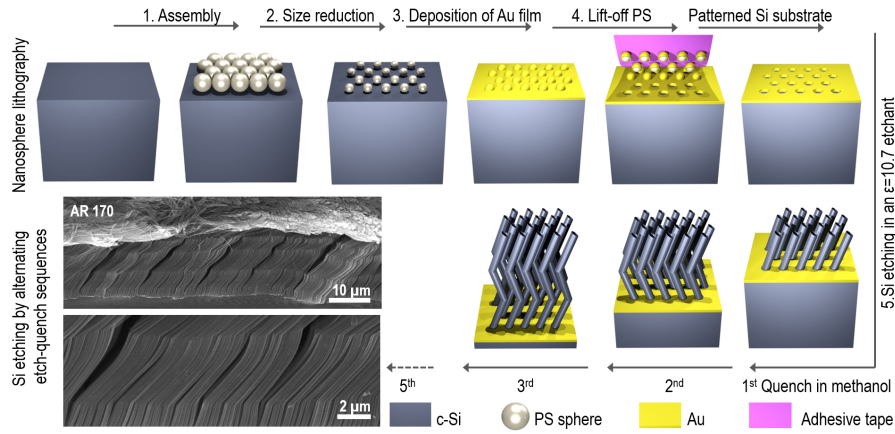


Figure 4.3: MACE-based synthesis of superstructures of k-SiNWs.

The cross-section scanning electron microscopy (SEM) pictures from Figure 4.3 show highly ordered k-SiNWs fabricated by 5 sequences $E_5 - Q_1$. On the one hand, by altering the etching time we can control the length of the etched segment and related to this, the location of the kink. On the other hand, the geometrical parameters of the gold catalyst mask are extremely important. They will influence the porous or solid nature

of the etched Si nanostructures, the etching rate as well as the mechanical stability of the Au mask during the downward movement and the gas evolution associated with Si etching. As a matter of fact, catalysts greatly impact the mass transport of active species and reaction products. For instance, as the thickness decreases, the transport of reactants and by-products is expected to occur via small pores (grain boundaries) in the catalyst. In addition, collision and coalescence of gas bubbles can alter the Si-Au contact resulting in hazardous etching and, ultimately, in Au delamination.

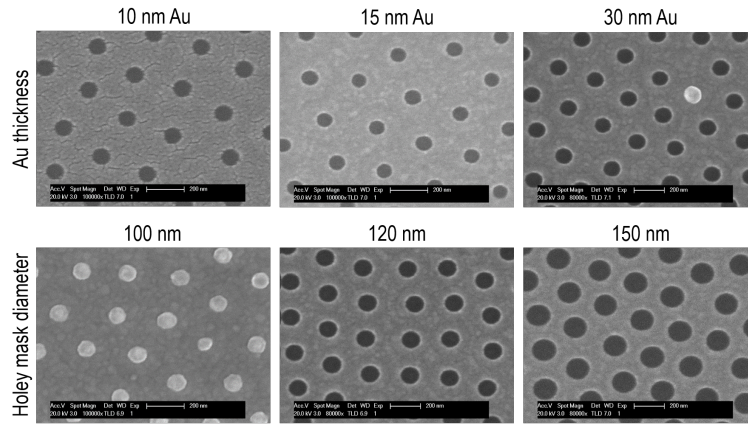


Figure 4.4: Physical parameters of the processed Au masks (SEM images). This study includes three thicknesses, t_h : 10, 15 and 30 nm, as well as three opening diameters s : 100, 120 and 150 nm. For the thickest mask, a 1 nm Ti adhesion layer was included to allow for the lift-off of the polystyrene spheres and to avoid any Au delamination. As evaporated, the 10 nm-thick Au mask is not continuous; thicker films are required for a uniform catalyst layer.

Nonetheless, etching proceeds with thick Au catalysts and does not require a porous catalyst film. To get insight into this behavior and to explore the etching possibilities under these conditions, we evaluated different catalyst thicknesses t_h (10 nm, 15 nm, 30 nm), associated with different opening diameters, s (100 nm, 120 nm, 150 nm). Details of the deposited Au mask morphology are shown in Figure 4.4.

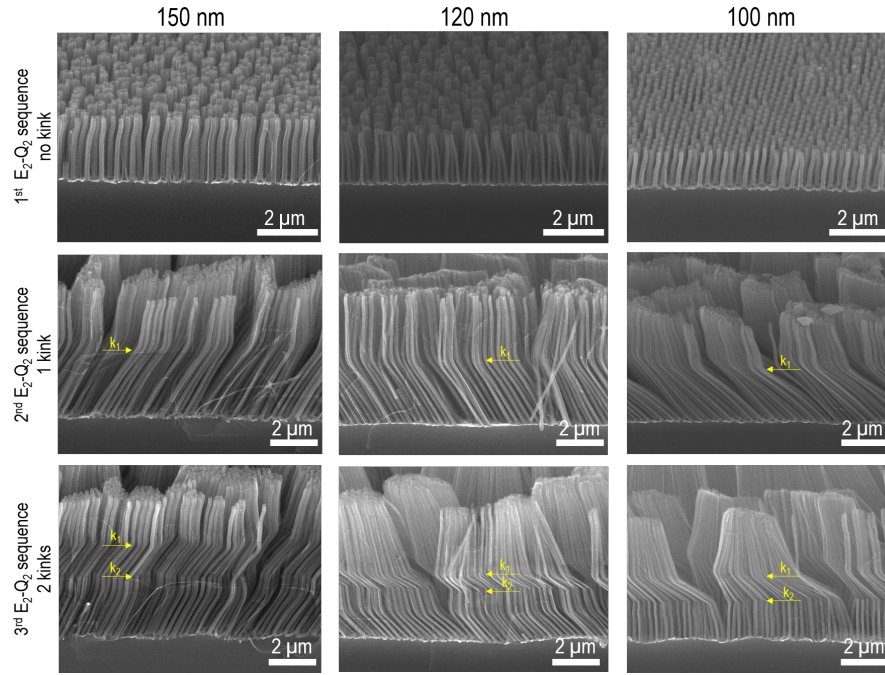


Figure 4.5: Kinks generation in SiNWs for 10 nm-thick Au masks with different diameters of openings, 150, 120, and 100 nm (SEM images). From top to bottom, images for 1st, 2nd, and 3rd $E_2 - Q_2$ sequences are displayed for single (k_1) and double (k_1, k_2) kinks.

4.2.2 Kink physical parameters

Figure 4.5 shows the kink formation according to the number of times the reaction was quenched for a 10 nm-thick Au mask and three different nanowire diameters. For the first E_2 segment, vertically aligned nanowires are obtained. The nature of this segment is particularly interesting since vertical nanowires are obtained only for thin Au mask, while for thicker Au masks the etching proceeds in a non- $\langle 100 \rangle$ direction, as shown in Figure 4.6.

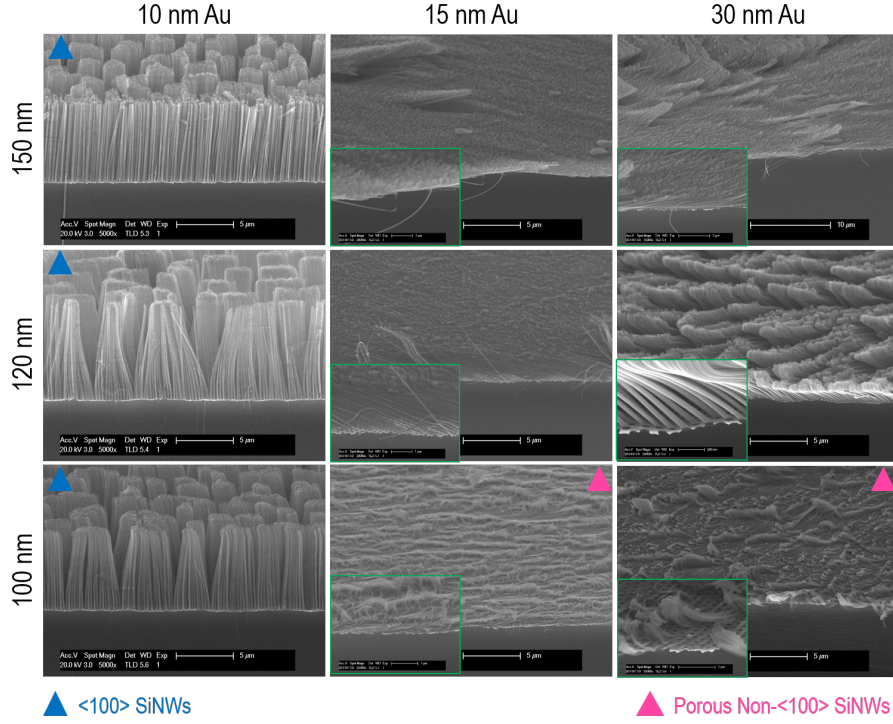


Figure 4.6: The first etched segment (5 minutes etching time) for all the investigated Au catalyst masks (SEM images). The diameter of the openings greatly influences the porosity of the etched nanostructures.

After a 2 minutes quenching time, the etching will proceed in a non- $\langle 100 \rangle$ direction, leading to the first kink formation. Repeating this E_2 - Q_2 sequence allows for the creation of the second kink. Therefore, to form n kinks, $(n+1)$ E_p - Q_q sequences are required. For this work, a kink represents the intersection of two adjacent etched segments and may include inflexion points. To characterize the kink, its arms' length and angle have to be considered in relation to the Au mask geometrical parameters. For this study, to control the kink arm length, we used etching times, p , ranging from 2 to 5 minutes. The k-SiNWs fabricated by 9 repetitive $E_2 - Q_1$ and $E_5 - Q_1$ sequences are shown in Figure 4.7 for a $t_h = 15$ nm, $s = 120$ nm Au mask.

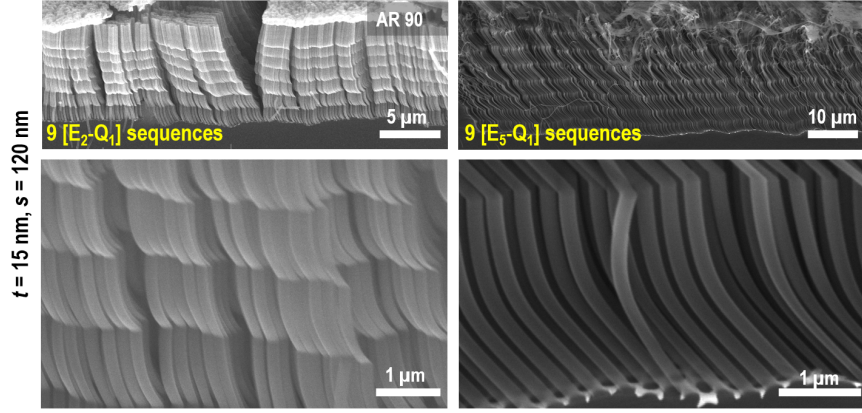


Figure 4.7: High-aspect ratio k-SiNWs fabricated by $9[E_2 - Q_1]$ (left) and $9[E_5 - Q_1]$ (right) sequences for a $t_h = 15$ nm, $s = 120$ nm Au mask.

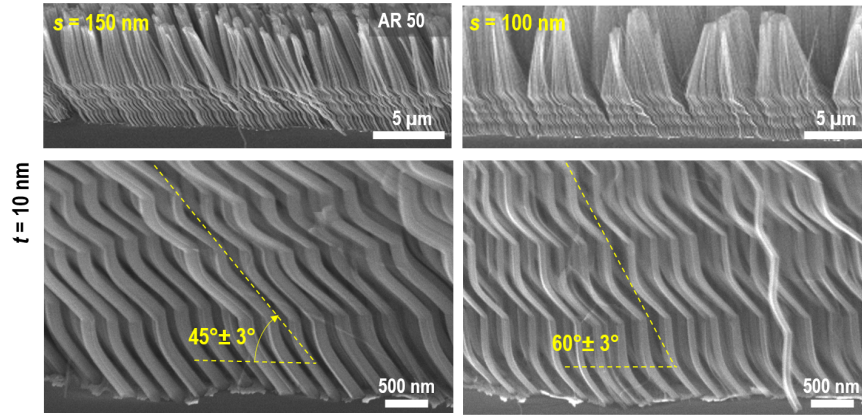


Figure 4.8: Dependence of the longitudinal axis of the k-SiNWs upon Au mask parameters. The longitudinal axis of the k-SiNWs deviates by 45° or 60° with respect to the Si substrate, depending on the diameter of the Au mask openings (150 or 100 nm). The Au mask is 10 nm thick.

Figure 4.8 shows the k-SiNWs fabricated with a 10 nm thick Au mask with s equal to 150 nm and 100 nm and reveals the titled nature of the k-SiNWs, dictated by s .

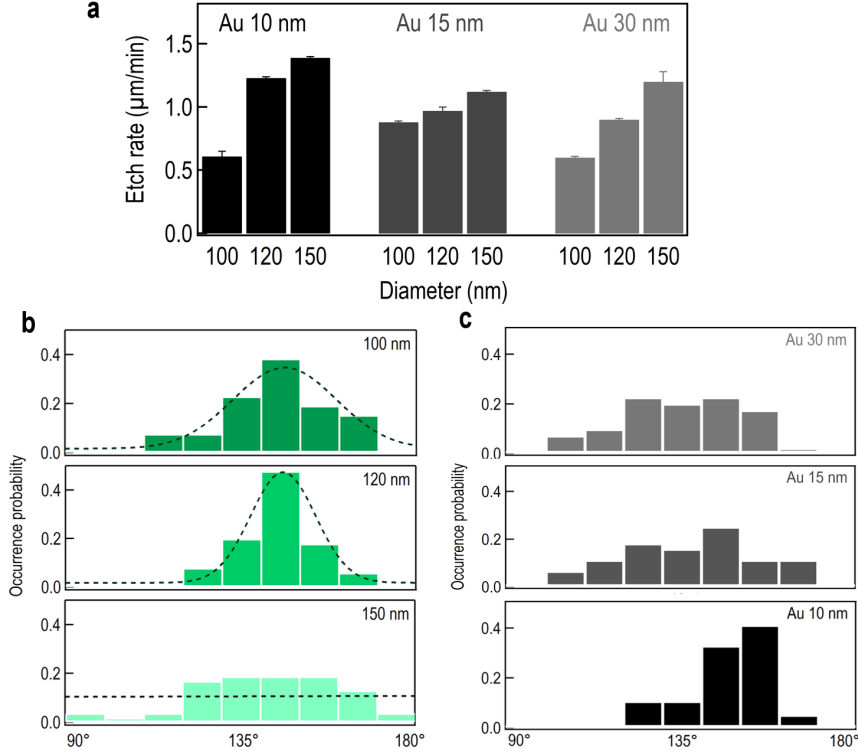


Figure 4.9: Influence of the geometrical parameters of the Au masks on k-SiNWs. (a) Etching rates associated with the geometrical parameters of the Au masks. (b) Occurrence probability for the observed kink angles as a function of s . (c) Kink angles occurrence probability as evaluated according to the catalyst thickness.

The opening diameter of the catalyst mask plays a significant role in the kink formation. First, as expected, it impacts the SiNWs etching rate. The length of the etched segment decreases as the opening diameter narrows since more Si has to be removed in order to generate thin k-SiNWs. A compilation of the etched rates obtained for studied parameters is displayed in Figure 4.9a. The etching rates were also estimated by the etching depth of the Si wafer. Interestingly, the highest etching rates are obtained for thin catalysts, while the etching rate generally increases as s increases. Specifically, the highest etching rate reaches $1.4 \mu\text{m}$ per minute for $t_h = 10 \text{ nm}$, $s = 150 \text{ nm}$ Au masks. Secondly, the

opening diameter clearly impacts the kink's angle; sharper angles are more characteristic to thin k-SiNWs or low s , as it can be observed from the statistical analysis of Figure 4.9b. Metal mask thickness does not appear to influence the kink angles, as shown in the distribution of angles in Figure 4.9c. Overall, the turning angle, α , becomes larger as the etching proceeds. In our experiments, α is found to take a broad spectrum of values as shown in the occurrence probability distribution from Figure 4.10. Due to the k-SiNWs peculiar morphology, the experimental values of α are dependent on the observation angle. For the statistical analysis of α , the kink angle formed by adjacent segments, k-SiNWs were imaged by SEM. Details of such joints can be observed in the top panels 1 - 6 from Figure 4.10. Fitting the experimental data with a least squares model helps to identify the most probable crystallographic etching directions. We found that the most probable pairs of etching directions are: $\langle 111 \rangle - \langle 100 \rangle$ ($\alpha = 125.26^\circ$) and $\langle 111 \rangle - \langle 210 \rangle$ ($\alpha = 145.77^\circ$) as shown in Figure 4.10. While there are other reports related to k-SiNWs [127, 128], here we emphasize on the opportunity of multiple crystallographic orientations etching. Experimental findings suggest that the direction of the current etching segment depends on the etching direction of the previous segment. For the first segment, the etching direction is mainly $\langle 111 \rangle$. The presence of high-viscosity ethanol co-solvent is expected to accelerate the delivery of the reactants and, associated with that, an alteration of Au-Si coupling that ultimately affects the movement of the Au mask. The geometrical parameters of the holey catalyst mask clearly influence the movement of the metallic mask since the hole generation takes place at the metal-electrolyte interface. If this interface is altered, the H_2O_2 decomposition will also be affected and, with that, the etching rate. Nonetheless, mechanical considerations are not enough to explain the current etching mechanism, that requires further investigations, since the complexity of the k-SiNWs hints at a subtle interplay between various physico-chemical processes involved in the metal-assisted chemical etching of Si. We invite the reader to refer to [131] for further insights on the kink formation and the interactive physico-chemical events at the Si-Au interface.

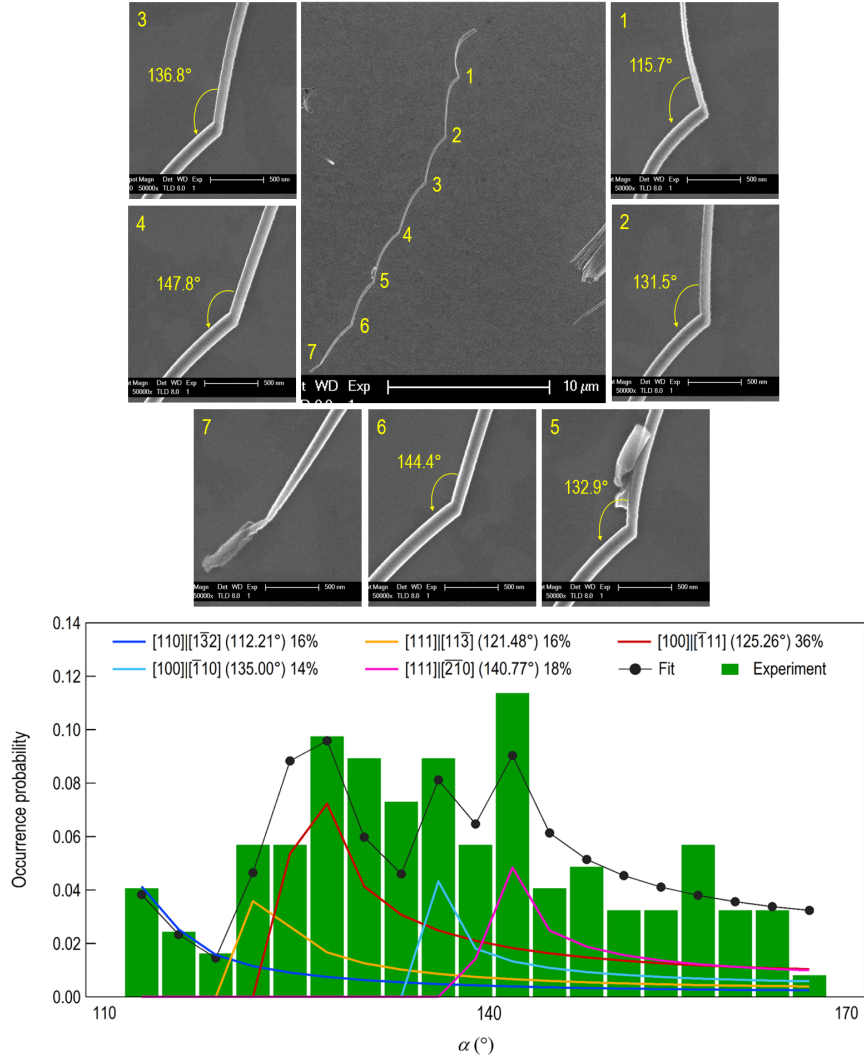


Figure 4.10: Scanning electron microscopy (SEM) characterization. For the statistical analysis of α , the kink angle formed by two adjacent segments, k-SiNWs were imaged by SEM. Details of such joints can be observed in the top panels 1 - 6. Occurrence probability distribution of the measured α in SEM along with the least squares fit. The fitted model gives the distribution of angles formed by pairs of crystallographic directions, as seen from the top. Major contributions are provided by the two most probable pairs of etching directions: $\langle 100 \rangle$ - $\langle 111 \rangle$ ($\alpha = 125.26^\circ$) and $\langle 111 \rangle$ - $\langle 210 \rangle$ ($\alpha = 145.77^\circ$).

Figure 4.11 shows the transmission electron microscopy characterization of a typical k-SiNW, including details on the kinks as well as on the sacrificial porous segment. Upon a detailed microscopic evaluation, we found that these k-SiNWs present a distinctive geometry. First, the diameter of the k-SiNWs before and after the kink considerably differs from the mask's hole diameter, s . Second, the electron tomography images reveal an elliptical geometry upon the tilting of the sample as seen in Figure 4.11b. This indicates that these k-SiNWs are the result of the downward and radial displacements of the Au mask, triggered by altering the etching kinetics through the reaction interruptions.

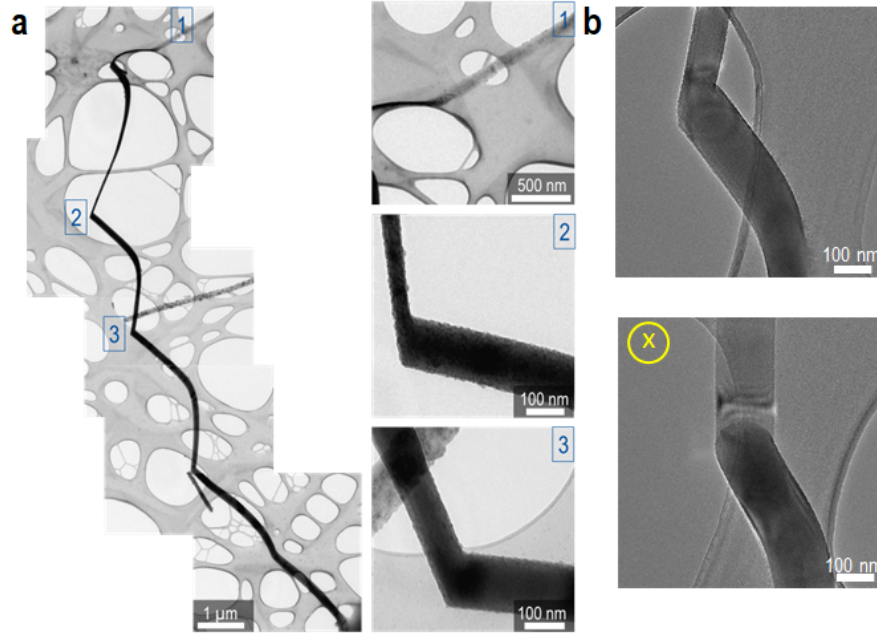


Figure 4.11: k-SiNWs characterization by TEM I. (a) TEM image for a k-SiNW obtained by metal assisted chemical etching on a $\langle 100 \rangle$ Si substrate, showing the porous segment as well as details on the kinks with different angles between adjacent segments. (b) Tomography TEM images of the kink revealing the elliptical shape upon tilting of the sample.

Furthermore, the Au catalyst oscillatory motion is clearly visible in

the kink wall close up from Figure 4.12a. In fact, this rhythmicity is obvious in the 3D reconstruction of the kink as shown in Figure 4.12b. Again, the expected cylindrical shape of the kink is altered, thus, confirming the horizontal shift of mask and not only the downward movement typically associated with Si etching. This behavior mirrors the 3 degrees of freedom motion as expected from a pinned catalyst. In addition, upon a closer examination of the kinks, as shown in Figure 4.12a and c, the surface of the kinks is also decorated with Au nanoparticles, some of them reaching ≈ 15 nm in diameter for thick Au catalyst as shown in the inset from Figure 4.12c. This must be the effect of the energetic etching conditions that can attain rates as high as ≈ 20 nm/sec, thus, high stress and strains are also expected to develop into the metal, leading Au disintegration. Finally, the elemental mapping from Figure 4.12d also confirms the Au decoration of k-SiNWs. We can further see that the Au is only limited to Si surface and is not detected deep into the Si surface. Notable are the porous trenches formed in the Si substrate, beneath the Au, at the lithographic openings of the metal. Such porous regions are known to facilitate diffusion of the electrolyte. [132] In addition, the shape of the trenches hints at an anisotropic growth or a preferential electrolyte diffusion via the lithographic openings of the Au mask. This is rather conflicting since mass transport of usually occurs via pores or cracks in thin film or discontinuous catalyst mask, therefore an isotropically expanded porous segment at the metal-Si interface is expected. [133] Also, the porous region does not extend to the foot of the nanowire as previously reported [132]. Understanding the fundamentals of MACE requires a close examination of the Au-Si-electrolyte interfaces and of the events pinned to these interfaces. Finally, the curvature of the SiNW kink arms is an intriguing phenomenon and the etching of curved SiNWs has been associated with co-solvent etchants such as methanol, ethanol or glycerol [127, 134, 135]. While experimental observations sustain the curvature dependence with the co-solvent concentration, curved segments are typically linked to large thicknesses and large diameter openings of the Au mask.

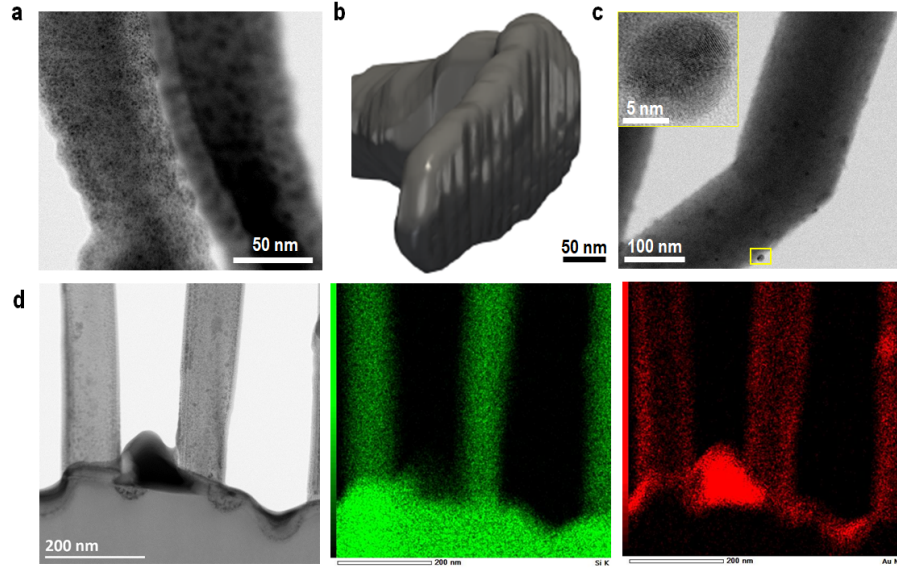


Figure 4.12: k-SiNWs characterization by TEM II. (a) Kink close up as imaged with scanning TEM (STEM) with a bright field detector for a wire with $s = 100$ nm and $t_h = 10$ nm. (b) Three-dimensional reconstruction of a SiNW kink obtained with a $t_h = 30$ nm, $s = 150$ nm Au mask. (c) Au nanoparticles decorated kink with $t_h = 30$ nm, $s = 100$ nm. (d) Elemental mapping by energy-dispersive X-ray spectroscopy of Au-Si interface via STEM.

4.2.3 Customized Si superstructures

Our etching protocol combines the simplicity and scalability of MACE to enable functionality driven design of Si nanostructures. Figure 4.13 shows the fabrication of ordered, high aspect ratio superstructures of k-SiNWs by quenching the etching at user-defined points during MACE. These results indicate that k-SiNWs with a large range of angles and user-defined arm lengths are possible by simply controlling the etching time and the catalyst parameters. However, the catalyst mask parameters are intimately coupled with the etching rates and curvature effects and will greatly influence the k-SiNWs morphology. Zigzag SiNWs are locally observed under the studied etching conditions as shown in Figure 4.14.

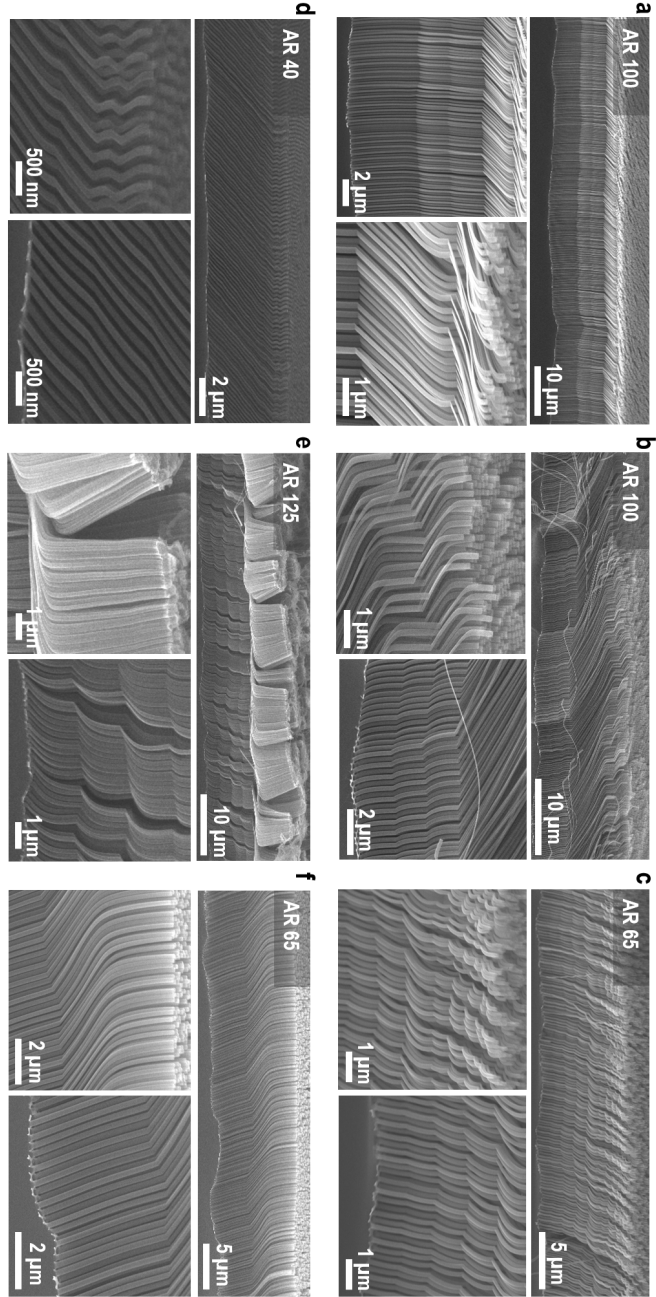


Figure 4.13: Si superstructures obtained by superposing different etching times with different catalyst shapes. a. $t_h = 30$ nm, $s = 150$ nm, $E_p - Q_1$; $p = \{5, 3, 3, 3, 5\}$. b. $t_h = 15$ nm, $s = 120$ nm, $E_p - Q_1$; $p = \{5, 7, 3, 3, 3\}$. c. $t_h = 30$ nm, $s = 120$ nm, $E_p - Q_1$; $p = \{2, 2, 2, 3, 3, 3\}$. d. $t_h = 30$ nm, $s = 120$ nm, $E_p - Q_1$; $p = \{3, 2, 2, 2, 2\}$. e. $t_h = 15$ nm, $s = 120$ nm, $E_p - Q_1$; $p = \{5, 3, 3, 3, 3\}$. f. $t_h = 30$ nm, $s = 150$ nm, $E_p - Q_1$; $p = \{5, 5\}$.

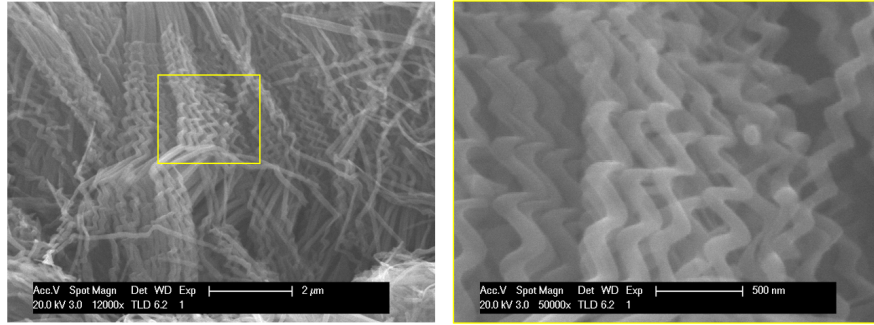


Figure 4.14: Zigzag SiNWs. Zigzag SiNWs observed locally under the studied etching conditions. Such nanostructures cannot account for reliable k-SiNWs fabrication.

4.2.4 Continuous k-SiNWs synthesis sustained by chemical peeling

Similar to the chemical peeling protocol developed for the extraction of the vertically-aligned SiNWs, a porous segment is induced at the base of the k-SiNWs to allow the separation of the k-SiNWs from their Si substrate by changing the etching conditions. The k-SiNWs can be collected with a short ultrasonic treatment. As such, the metal mask can be reused for a new etching sequence. It is important to note that after the ultrasonic treatment etching defects will remain on the substrate and the low ϵ etching conditions are expected to affect only the k-SiNWs. The etching will proceed normally in the areas with intact metal mask. This is an interesting advantage of this selective method as it facilitates the extraction of only nanowires and not of the inherent defects. Figure 4.15 indicates the steps required for the continuous synthesis of k-SiNWs sustained by chemical peeling. In addition, k-SiNWs etching with a re-used Si substrate is shown in Figure 4.16.

In order to develop this procedure, commercial Si wafers were used. Nonetheless, this metal-assisted chemical etching of Si, on which our procedure is based, has been used to etch recycled Si chips [59], thus, can easily be extended to employ leftovers from the electronic industry.

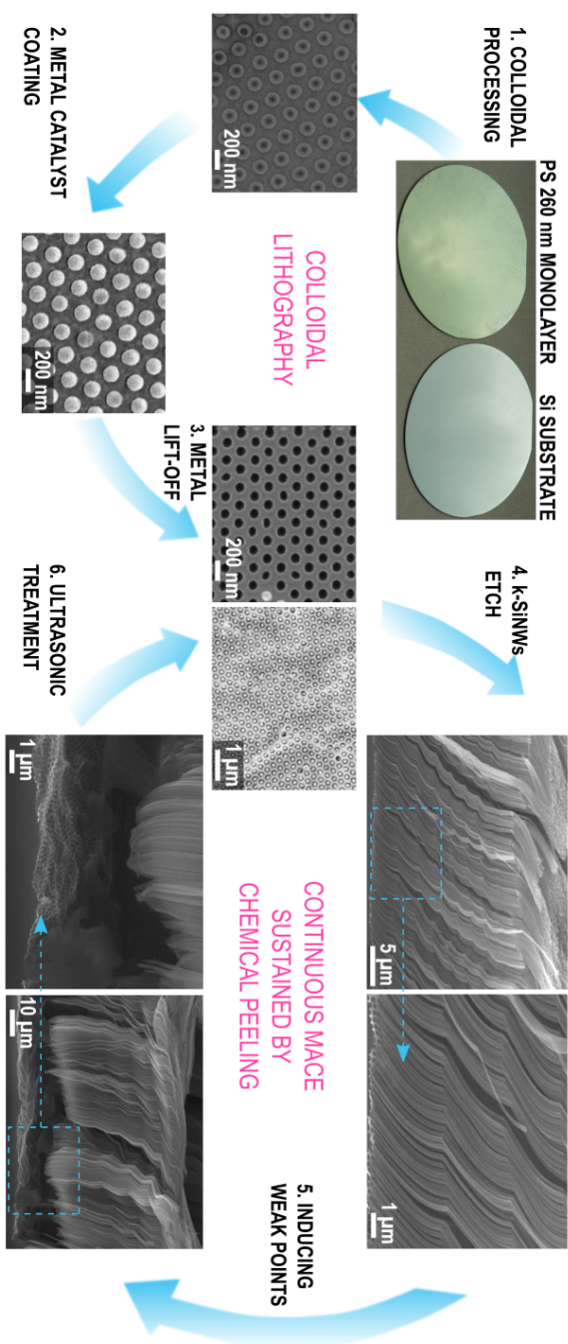


Figure 4.15: Continuous synthesis of k-SiNWs sustained by chemical peeling. The first step is the nanopatterning of the metal catalyst mask, conveniently achieved by colloidal lithography with polystyrene spheres. Their diameter can be customized by reactive ion etching (1). The holey Au mask can be obtained after the coating of the patterned Si substrate with a thin film (2) and the subsequent removal of the polystyrene spheres (3). The main fabrication step involves etching in a solution containing HF and H_2O_2 . The etching parameters are favorable for non-(100) etching directions. Interrupting the etching at certain points induces changes in the etching direction and triggers the formation of kinks between adjacent segments (4). When the desired length is achieved, the etching conditions are again modified to favor the presence of a porous segment at the base of the k-SiNWs (5). This porous segment facilitates the separation of k-SiNWs from their Si substrate with a short ultrasonic treatment, leaving the metallic mask intact and ready for a new etching sequence (6).

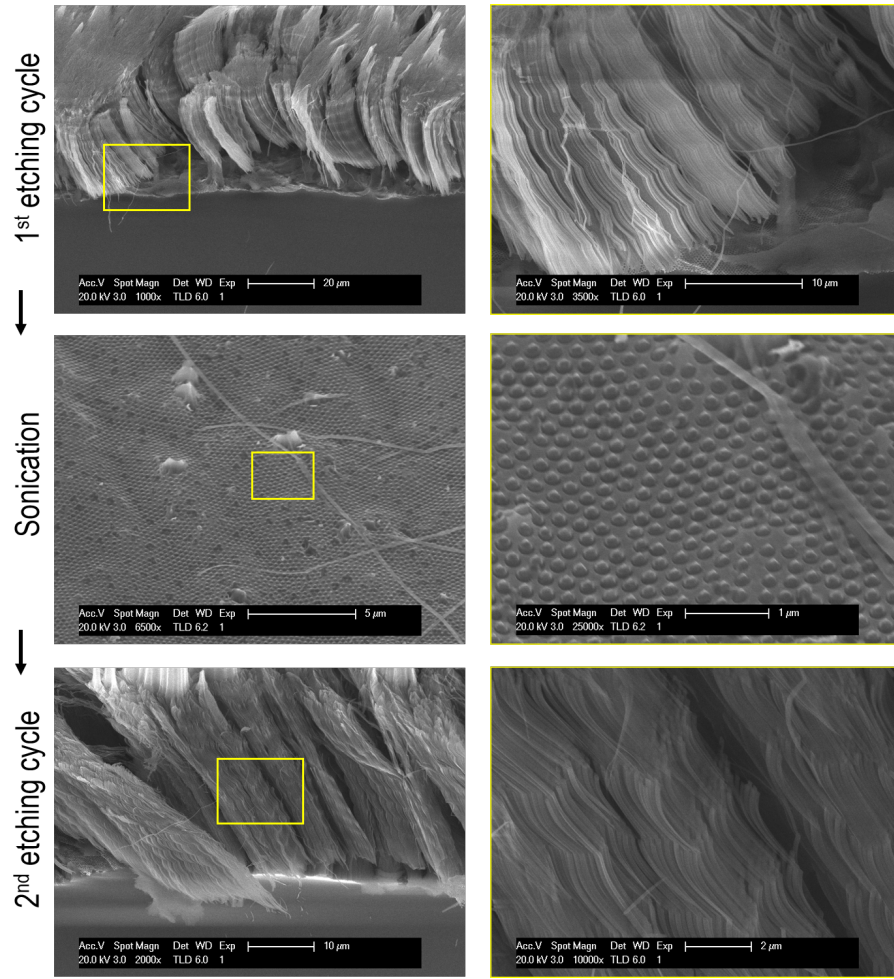


Figure 4.16: Details on the continuous synthesis of k-SiNWs sustained by chemical peeling. A porous segment is induced at the base of the k-SiNWs to allow the separation of the k-SiNWs from their Si substrate by changing the etching conditions. The k-SiNWs can be collected with a short ultrasonic treatment. The metal mask can be reused for a new etching sequence. It is important to note that after the ultrasonic treatment etching defects will remain on the substrate and the low ϵ etching conditions are expected to affect only the k-SiNWs. The etching will proceed normally in the areas with intact metal mask. This is an interesting advantage of this selective method as it facilitates the extraction of only nanowires and not of the inherent defects.

The essential benefits of our k-SiNWs synthesis follow from:

(i) the controlled k-SiNWs synthesis in a simple and efficient matter; We propose a simplified etching scheme via one-pot-type synthesis that facilitates reproducibility, reduces chemicals consumption and limits, to some extent, the exposure to hazardous processes and materials. Multiple etching baths are no longer required since the etchant availability is modulated via the methanol quencher. Thus, risks related to the etchant baths imbalance at advanced etching stages are reduced. This, ultimately facilitates the etching of high-aspect ratio superstructures.

(ii) the etching of high-aspect ratio superstructures associated with fast etch rates;

We show the etching of mechanically stable superstructures with up to 10 kinks and an aspect ratio of up to 250. This etching accuracy at such high etching rates is not common with MACE since high etching rates typically lead to hazardous etching. These types of nanostructures are essential for photovoltaic or sensing applications.

(iii) the etching of a broad spectrum of nanostructures made controllable by the systematic assessment of the MACE parameters;

Examples with the etching possibilities by following our procedure are given in Figure 4.13 with other fine etching details given throughout this Chapter. We want to highlight here the possibility of the etching of curved or porous segments, which adds another dimension to our Si superstructures.

(iv) the increased etching efficiency via the chemical peeling that facilitates the extraction of the superstructures as well as re-using of the Au patterned Si substrate. The knowledge provided here empowers other research groups to evaluate, adapt and optimize such structures according to the application.

From an experimental point-of-view, MACE of Si is beautifully simple since it only requires a catalyst and an HF-based electrolyte. However, for the etching of Si nanostructures with increased complexity, fine-tuning of all variables becomes critical, and, essentially, an art. Here, we introduced some of the high-aspect ratio super-complex Si nanostructures that are possible with MACE, etched in a safe and efficient matter. Such a simple etching procedure will empower other research groups to fully explore the properties of these superstructures. Applications where the surface-to-volume ratio is critical will undoubtedly benefit from such structures - photonics or sensing applications, to name a few. These k-SiNWs will be exploited next in an alternative Li-ion battery electrode configuration that shows some advantages over conventional graphite electrodes, as discussed in the following chapters.

Self-standing three-dimensional nano-Si electrodes

Emil Cioran

One of the greatest advantages of LIBs is that they come in many sizes and shapes, shape-shifting according to the applications. To a certain extent, traditional slurry-on-metal architecture can accomplish most of the dimensional requirements. Nonetheless, it should not be expected that such architecture is also suitable for alloy-based electrodes that suffer from extreme volume expansion. Here, we challenge the current electrode design paradigm and propose a self-standing, highly porous nano-Si-C architecture that provides the void spaces required for the electrode expansion during Li alloying and shows good mechanical stability to preserve the electrode interconnectivity.

Self-standing Si-based nanostructured architectures have already been proposed to circumvent the use of common inactive constituents in LIB electrodes like binders, C-based additives or current collectors [74, 136–138]. Eliminating such elements is desirable as it will increase the gravimetric capacity of the electrode. Interestingly, here, the resulting 100% kinked silicon nanowires (k-SiNWs) assembly is self-standing in contrast to the 100% SiNWs assembly, as discussed below. Nonetheless, Si's amorphization is complemented by the loss of the intrinsic electrical conductivity and requires an electroactive additive. In this context, multi-walled carbon nanotubes (MWCNTs) can be integrated into the Si-based anode assemblies [139]. In addition, MWCNTs integration is also expected to provide additional mechanical support considering that self-standing MWCNTs assemblies have already been proposed [140]. These are the two main hypotheses of our endeavor.

5.1 Processing

A three-dimensional inter-locking framework is assembled via vacuum-filtration with SiNWs or k-SiNWs with MWCNTs as a conductive structure. As we discussed in the previous Chapter, the Si nanostructures are collected with a short ultrasonic treatment in methanol. The separation of SiNWs from their parent Si wafer is promoted by the mechanically-weaker porous segment induced by increasing the concentration of H_2O_2 . The optical images from Figure 5.1a show the SiNWs bundles detaching from the Si substrate simply by the combined action of evaporation and surface tension forces. This is the case when methanol is used. Upon a short ultrasonic treatment, all the etch SiNWs will be collected and, as we showed in Chapter 4, the Au-patterned Si substrate can be re-used for another etching cycle. This is valid for both SiNWs and k-SiNWs etching schemes as long as the porous segment is generated. Interestingly, in methanol, the SiNWs and k-SiNWs behave differently, as shown in the optical images from Figure 5.1b. The SiNWs in methanol, under agitation, have the tendency to align and form domains similar to liquid crystals, while the k-SiNWs are prone to form bundles and rapidly sediment. The sedimentation is accompanied by k-SiNWs flocculation

as shown in Figure 5.1c. This is expected to impact the homogeneity of the constituents in the electrode, as it will be discussed in the following.

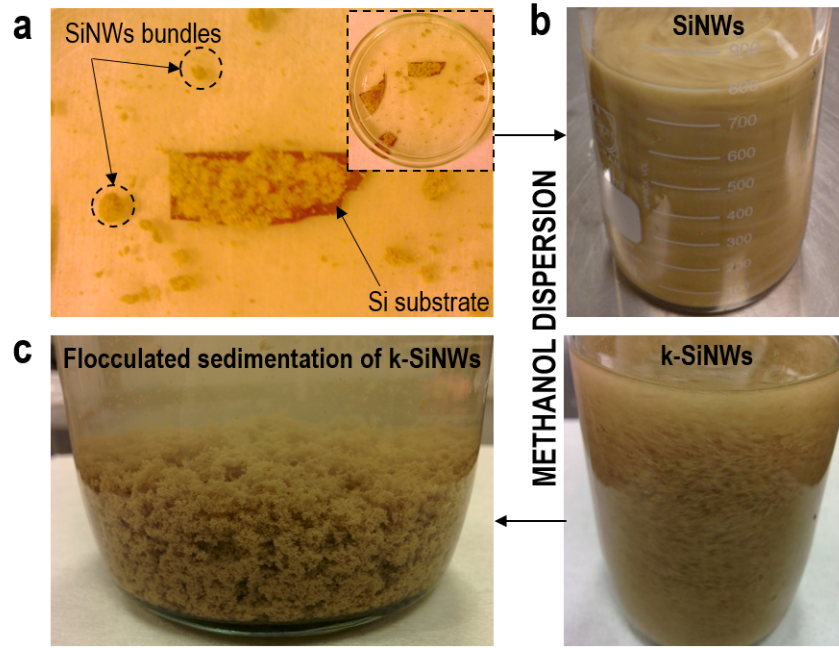


Figure 5.1: Collection and dispersion of nano-Si. (a) Optical images of the bundles of SiNWs separating from their parent Si wafer. (b) Dispersion of SiNWs vs. k-SiNWs in methanol. (c) Optical image of the flocculated sedimentation of k-SiNWs.

The collected nanostructures are then mixed with a MWCNTs prepared methanol suspension. For this work, it was difficult to estimate the quantity of nanostructures after each etching. One solution to control the Si load was to collect the Si nanostructures from multiple etching processes in one container. Thus, the MWCNTs load was kept constant at 10 mg, while the added volume of nano-Si methanol suspension was increased in order to prepare different Si-C compositions. Figure 5.2 includes optical images of all the assemblies containing k-SiNWs, SiNWs, and MWCNTs. For now on, for simplicity, the nano-Si-C composite will be identified as a function of nano-Si load expressed in weight percent-

ages (% wt). For instance, a k-SiNWs-based assembly comprising 35% wt k-SiNWs and 65% wt MWCNTs, will be simply identify as: 35% k-SiNWs assembly. By visual inspection, the k-SiNWs-based anode assembly has a uniform color, indicating the homogeneous distribution of the two constituents. On the contrary, the SiNWs-based anode assembly presents distinct regions dominated by either SiNWs or MWCNTs.

The efficient mixing of k-SiNWs with MWCNTs is also confirmed by the cross-section scanning electron microscopy images of the composite from Figure 5.3 showing its characteristic interconnected morphology with k-SiNWs randomly distributed in the electrically conducting network of MWCNTs. Such composite architectures are quite friendly for LIB anodes since the synergistic interconnectivity creates an interlocking framework, which can accommodate the volume variation during Li insertion, preserving an intimate electrical contact between the k-SiNWs and the MWCNTs. This is not expected for vertical SiNWs-based assemblies where a regrouping effect of nanostructures is observed leading to distinct SiNWs or MWCNTs-dominated regions usually separated by voids which ultimately gives the composite an unstable, layered structure as shown in Figure 5.2e and 5.3.

For a homogenous composite, the available open space is expected to counterbalance Si's volumetric expansion as the lithiation proceeds, resulting in an overall reduced electrode deformation (Figure 5.3).

5.2 Mechanical properties

In order to explore the advantages of the interweaving k-SiNWs-MWCNTs morphology, mechanical properties were evaluated via tensile tests. SEM and optical images of the evaluated assemblies are shown in Figures 5.4a.

Explicitly, the mechanical properties of the assemblies were evaluated using a Universal Mechanical Tester (UMT-3, Bruker). The load sensor has a resolution of 0.5 mN and is able to accurately measure forces between 0.1 and 10 N. The specimens were cut in 20 mm long and 5 mm wide rectangles prior to the mechanical evaluation. The loading rate was 5 $\mu\text{m/s}$. An optical image with the specimen after tensile testing

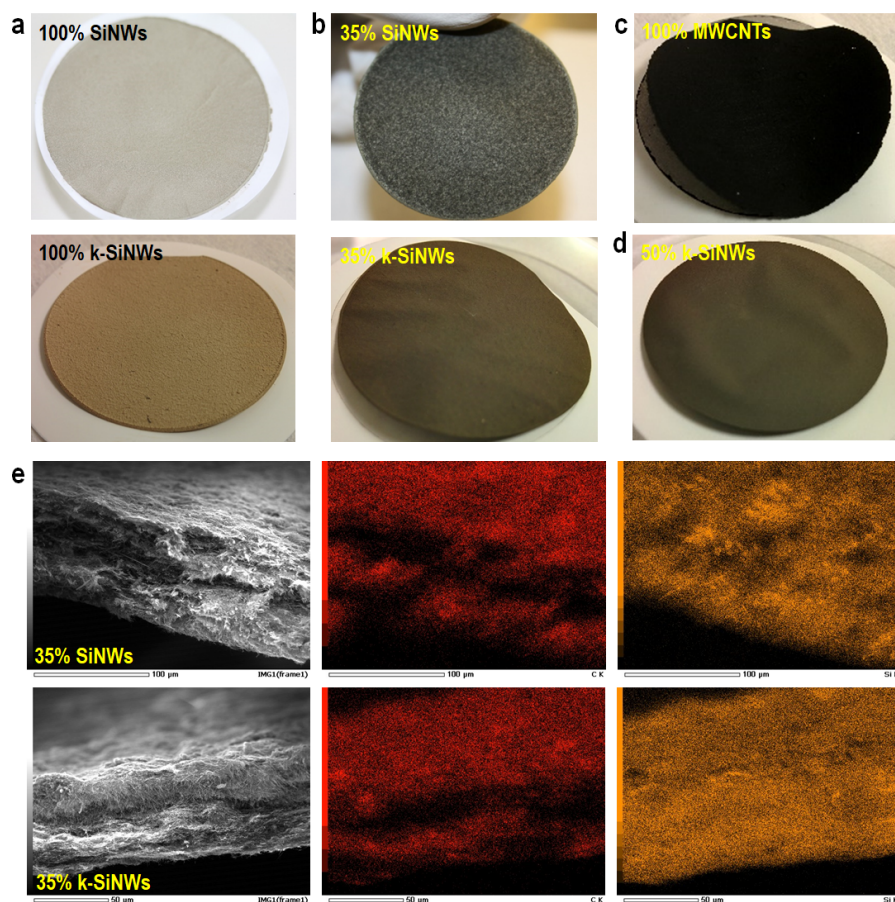


Figure 5.2: Self-standing 3D nano-Si assemblies. (a) Optical images of the assemblies containing 100% wt SiNWs vs 100% wt k-SiNWs assemblies. The 100% wt SiNWs is quite fragile and additional tools are required to separate it from the supporting nylon filter, usually resulting in damage of the material. (b) Optical images of the macroscopic assemblies with a content of 35% wt k-SiNWs and 35% wt SiNWs. The k-SiNWs assembly presents an uniform color, indicating an homogenous distribution of elements. On the other hand, with the SiNWs-based assembly, distinct regions are identifiable, dominated by either SiNWs or MWCNTs. (c) Optical images of the 100% wt MWCNTs assembly and (d) 50% wt k-SiNWs assembly. (e) Elemental mapping by energy-dispersive X-ray spectroscopy showing the distribution of the constituents in the assemblies.

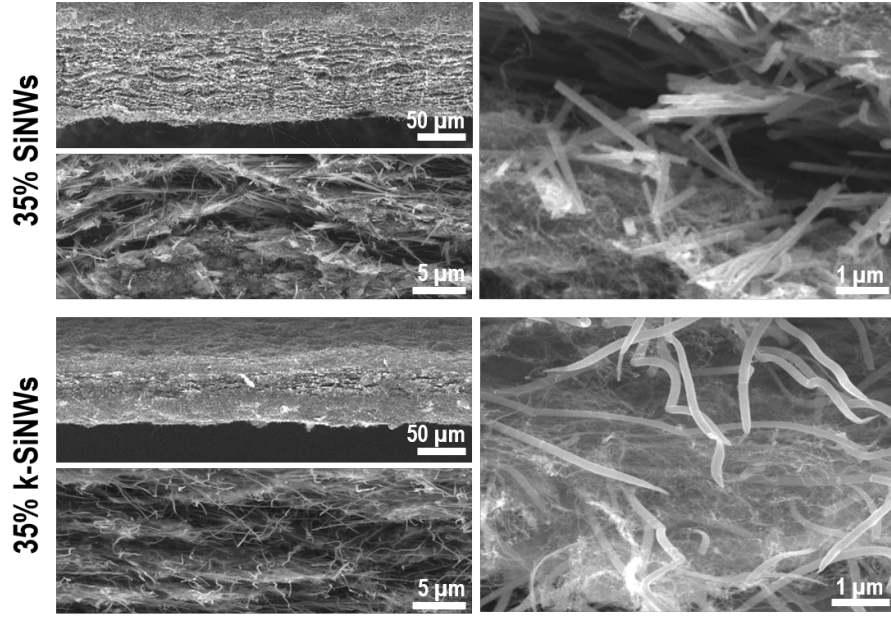


Figure 5.3: SEM images with details on the composition of the k-SiNWs and SiNWs anode assemblies.

is shown in Figure 5.4b. An average of two measurements per assembly was performed. The consistency of the results is confirmed by the low error rates, as listed in Table 5.1. Young's modulus was extracted from the linear region of the stress-strain curves corresponding to the 0.16-0.40% strain range. Results for macroscopic specimens with 100% MWCNTs, 100% k-SiNWs as well as composites comprising 35%, 50% k-SiNWs and 50% SiNWs are shown in Figure 5.4c. The tensile strength demonstrated by the 100% k-SiNWs assembly is 0.48 ± 0.01 MPa, while the 100% MWCNTs assembly displays 1.68 ± 0.06 MPa. For the k-SiNWs-based composites, the measured tensile strength is 3.10 ± 0.14 MPa for the 35% k-SiNWs assemblies and 4.00 ± 0.11 MPa for the 50% k-SiNWs assemblies (Table 5.1). The 50% SiNWs assemblies are quite fragile exhibiting a tensile strength 1.14 ± 0.08 MPa. Young's modulus is also found to be dependent on k-SiNWs load. The elastic modulus for 100% MWCNTs is 0.25 ± 0.01 GPa, while for the 35% k-SiNWs-based assembly is 0.39 ± 0.02 GPa. A further increase in the k-SiNWs load to 50% mini-

mally rises Young's modulus to 0.41 ± 0.01 GPa, compared to 0.13 ± 0.01 GPa evaluated for the corresponding SiNWs. The enhancement of these mechanical properties, even though the packing density decreases (Figure 5.4d), corroborates the three-dimensional interconnectivity provided by the interlocking joints of the k-SiNWs.

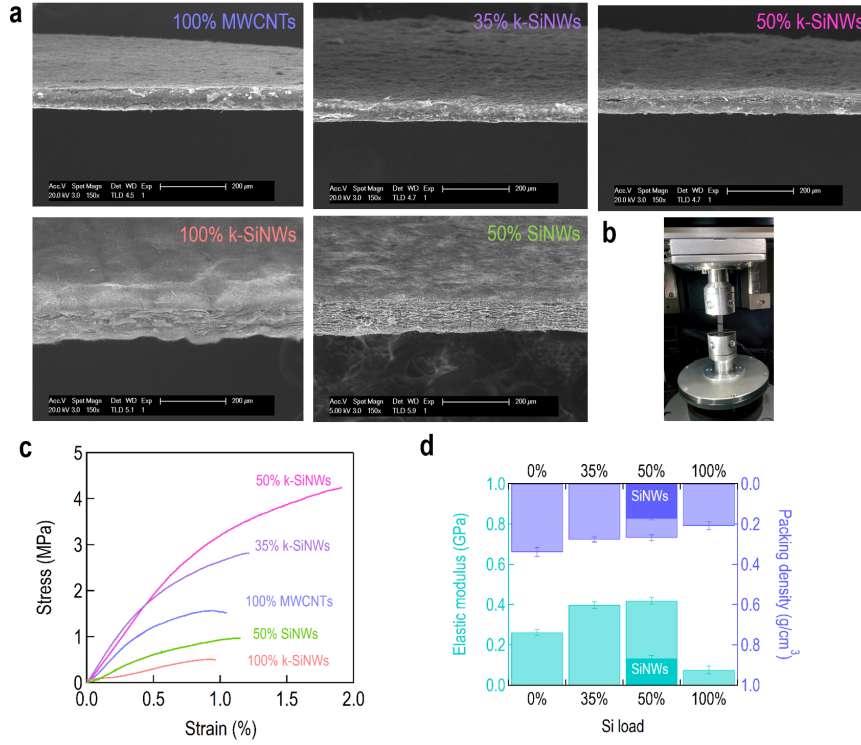


Figure 5.4: Exploring the mechanical properties of Si-based assemblies. (a) SEM images of the evaluated assemblies. (b) Optical image with the tensile testing setup. (c) Characteristic tensile stress-strain curves of the studied assemblies. (d) Adjustment of elastic modulus (left axis) and packing density (right axis) to the Si load.

In the linear regime, mainly MWCNTs stretching should account for the observed strain hardening. The presence of kinks reinforces the MWCNTs network and delays the transition to other degradation mechanisms such as slippage. In addition, these k-SiNWs are expected to be

more resilient to stress as they behave like microsprings [141]. For the 100% k-SiNWs assembly, the stretching and slippage of k-SiNWs appear to be concurrent and responsible for the observed strain hardening.

We shall note here, however, that the reported mechanical properties for the 100% MWCNTs are orders of magnitude lower than the values reported in literature [140, 142, 143]. Factors like assembly method, surface functionalization or alignment will play a critical role in determining the properties. In addition, for our vacuum filtrated assemblies, the suspension concentration, dispersion in the suspension as well as filtration velocity have to be considered. For the experiments reported here, while MWCNTs concentration was kept in the recommended range [140] (between 0.01 mg_{MWCNTs}/ml to 0.015 mg_{MWCNTs}/ml), the filtration velocity was not possible to control. In addition, the solvent, i.e. methanol, was selected based on availability and compatibility with the previous processing steps. Nonetheless, the hypothesis and observations regarding the k-SiNWs remain valid taken the properties of the 100% MWCNTs as baseline. The values for mechanical properties reported here are, however, superior to other reported LIB electrode C-based composite [144].

According to these material properties, the k-SiNWs-based assemblies have a foam-like structure. We recall that for an electrode material, porosity is desired as it accommodates volume variations and facilitates electrolyte infiltration. Following this, we evaluated the effect of k-SiNWs loading on the porosity for the studied anode assemblies. The porosity was calculated as expressed in Equation 5.1:

$$\phi = \frac{V_{\text{Void}}}{V_{\text{Total}}} = 1 - \frac{1}{V_{\text{Total}}} \left(\frac{m_{\text{Si}}}{\rho_{\text{Si, bulk}}} + \frac{m_{\text{MWCNTs}}}{\rho_{\text{C, bulk}}} \right), \quad (5.1)$$

where $\rho_{\text{Si, bulk}} = 2.33 \text{ g/cm}^3$ and $\rho_{\text{C, bulk}} = 2.26 \text{ g/cm}^3$.

Table 5.1 lists all the physical parameters of the evaluated anode assemblies. The porosity varies slightly from 0.84 ± 0.01 for the 100% MWCNTs to 0.90 ± 0.01 for the 100% k-SiNWs materials. Intermediate values were found for the 35% k-SiNWs and 50% k-SiNWs composites. A 5% reduction is observed for the 50% k-SiNWs assembly compared to the 50% SiNWs assembly. The available void volume is not enough to ac-

Specimen	Thickness (μm)	Tensile strength (MPa)	Young's Modulus (GPa)	Apparent Density (g/cm^3)	Porosity, ϕ
100% MWCNTs (20 mg)	61.55 $\pm$ 4.22	1.68 $\pm$ 0.06	0.25 $\pm$ 0.01	0.34 $\pm$ 0.02	0.84 $\pm$ 0.010
100% k-SiNWs (21.3 mg)	107.12 $\pm$ 10.47	0.48 $\pm$ 0.01	0.08 $\pm$ 0.02	0.20 $\pm$ 0.02	0.90 $\pm$ 0.009
35% k-SiNWs (13.5 mg)	52.68 $\pm$ 2.44	3.10 $\pm$ 0.14	0.39 $\pm$ 0.02	0.28 $\pm$ 0.01	0.87 $\pm$ 0.005
50% MWCNTs (15 mg)	55.18 $\pm$ 2.86	4.00 $\pm$ 0.11	0.41 $\pm$ 0.01	0.30 $\pm$ 0.01	0.86 $\pm$ 0.007
50% SiNWs (16.5 mg)	97.5 $\pm$ 5.6	1.14 $\pm$ 0.08	0.13 $\pm$ 0.01	0.17 $\pm$ 0.01	0.91 $\pm$ 0.04

Table 5.1: Physical parameters of the evaluated k-SiNWs-based electrode assemblies

commodate the expected Si swelling, and an overall electrode expansion will occur. This means that the entire electrode will undergo mechanical stresses during cycling, highlighting the importance of mechanically stable electrodes. While there is a certain incentive in lowering the porosity, thus increasing the volumetric capacity, the mechanical integrity of the electrode becomes critical with the Si-based anodes. Considering the reported porosity for the traditional slurry-on-metal architecture of Si-based anodes [56], large mechanical stresses are expected to develop during cycling that trigger electrode delamination from the Cu current collector as well as material pulverization, responsible for the limited cycling life. Integrating Si-based materials using graphite-established electrode manufacturing is thus troublesome and clearly points at novel architectures for high capacity Li storage electrodes. The porous k-SiNWs-based self-standing electrodes provide sufficient mechanical strength to sustain the dimensional changes during Si cycling as it will be discussed in the following.

5.3 Electrochemical evaluation

A cycling voltammogram of the 35% k-SiNWs-based assembly marking the main events in the Si-Li cycling is shown in Figure 5.5.

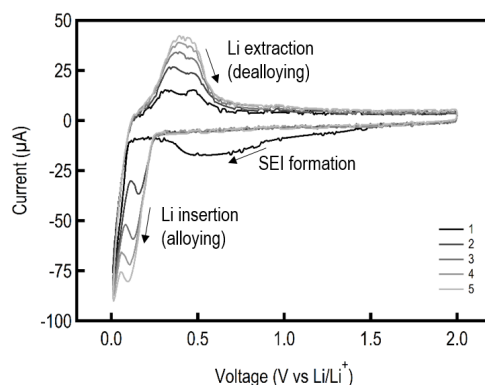


Figure 5.5: Cycling voltammetry profiles of the 35% k-SiNWs-based anode assembly. The scanning speed was 0.1 mV/s for the 5 cycles.

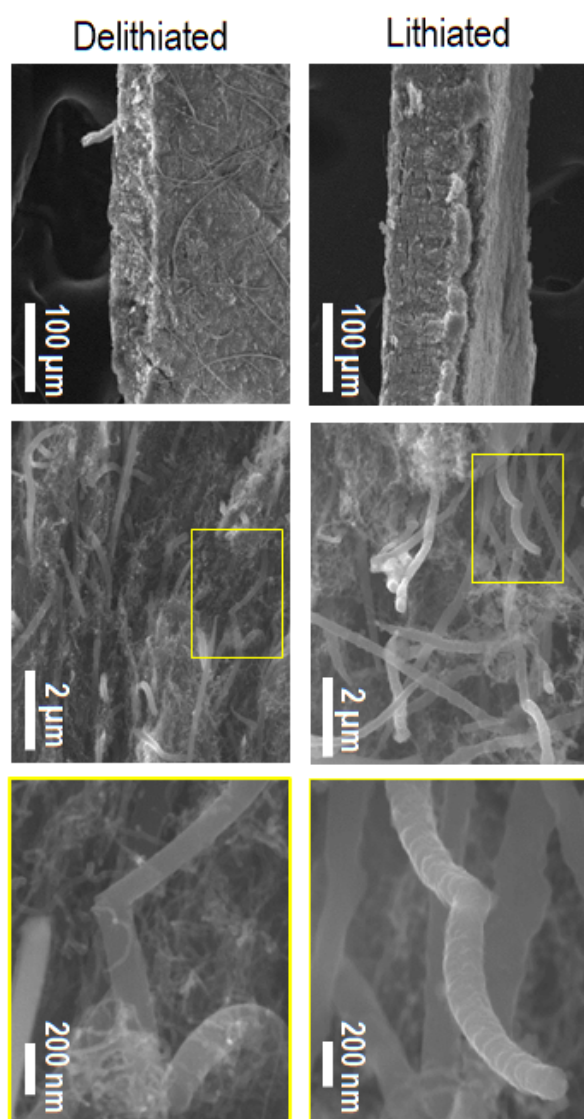
The first event relates to the electrolyte decomposition and the associated solid-electrolyte-interphase (SEI) formation. The peak disappears with subsequent cycling, a clear indication that the generated SEI is stable and prevents other parasitic reactions with the electrolyte. The peak below 0.2 V is characteristic of Si alloy formation with Li. The peak on the positive side of the current, at around 0.5 V is representative of Li extraction.

We further investigated the morphology evolution of the fabricated porous frameworks under deep lithiation conditions and the impact on the k-SiNWs volumetric expansion (Figure 5.6). The lithiation of the k-SiNWs-based electrodes is realized by linear sweep voltammetry techniques, where the voltage is ramped down from the open circuit voltage of the cell to 10 mV at a rate of 0.1 mV/sec and held at this potential for 10 hours. The cell is further disassembled in an Ar-filled glove box, followed by a wash in acetonitrile prior to the SEM investigation. The k-SiNWs appear to sustain the high Li intake. Similarly, the delithiated samples are first lithiated and then delithiated by ramping up the voltage from 10 mV up to 2 V at a rate of 0.1 mV/sec. The cell is further disassembled in the air, followed by a wash in acetonitrile prior to the SEM investigation. The k-SiNWs seem to be restored to their initial shape. Under these conditions, the maximum volumetric change is only 25% relative to the pristine state, consistent with other reported values for porous electrodes [145]. The Si extreme volume variation is accommodated by the highly porous assembly that precludes any detrimental rearrangements in the structure of the electrode. Finally, no degradation is observed at the k-SiNWs level.

Next, we evaluated the electrochemical properties of the k-SiNWs-based assemblies with various k-SiNWs content in half-cell configuration with an ionic liquid (IL) electrolyte system, 1M LiTFSi in PYR₁₃FSi, under a constant current mode. For comparison, the 50% SiNWs assembly is also included.

The obtained capacities as a function of cycle index are displayed in Figure 5.7a, while the galvanostatic charge-discharge curves are shown in Figure 5.7b. For the 100% k-SiNWs, the poor performance is attributed to the absence of conductive additive since Si's intrinsic conductivity is

Figure 5.6: Morphology evolution of the 35% k-SiNWs-based anode assemblies after full lithiation and full delithiation.



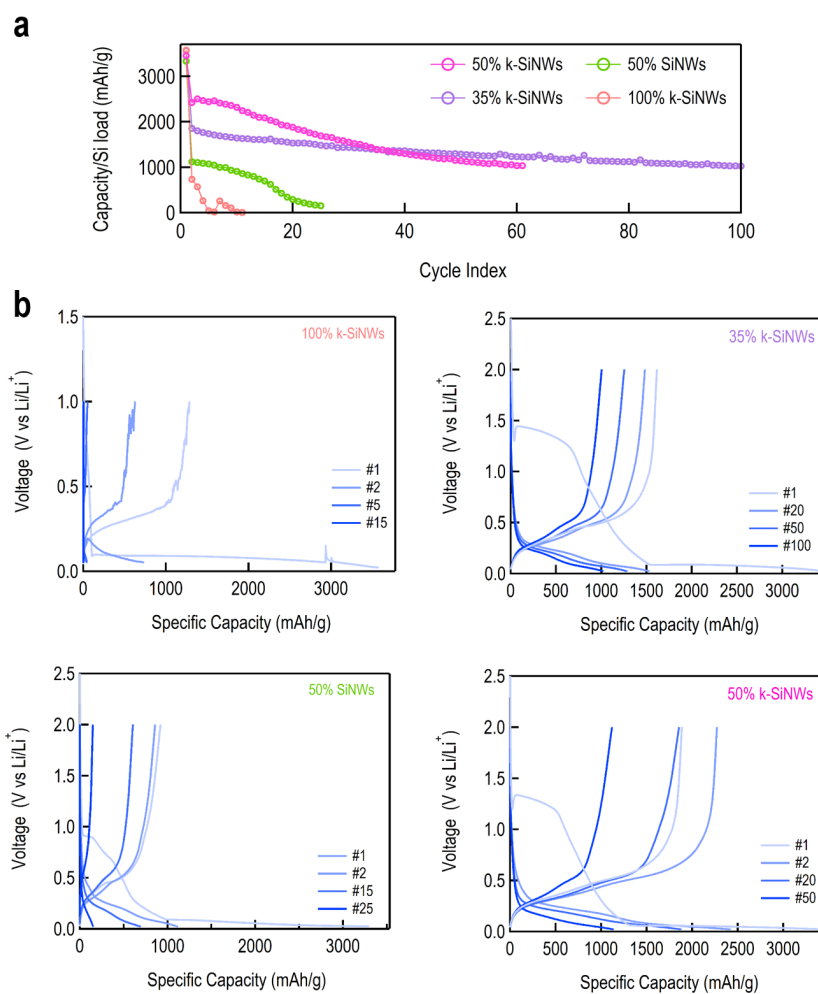


Figure 5.7: Electrochemical performance of the nano-Si-based assemblies evaluated at a rate of C/15 (1C corresponds to 3600 mA/g). (a) Capacity as a function of cycle index and (b) the corresponding galvanostatic charge-discharge curves.

sacrificed in the solid-state amorphization reaction with Li. On the other hand, the 50% SiNWs electrode suffers from the poor mixing ability of the constituents, isolating regions dominated by the SiNWs from the conductive MWCNTs as the cycling proceeds, visible in the limited cycling life. In terms of cycling stability, it is clear that the 35% k-SiNWs-based assembly stands as the best option while the 50% k-SiNWs demonstrate higher capacities that eventually fade with prolonged cycling. Such cycling stability must be related to the homogeneous mechanical properties of the k-SiNWs-based micro-geometry allowing volume variations without affecting the structural integrity of the k-SiNWs-MWCNTs network. Interestingly, while the 50% k-SiNWs also showed improved mechanical properties, the 35% k-SiNWs assembly performs better in terms of cycling performance. Specifically, the capacity of 35% assembly fades 2 times slower than the capacity of the 50% k-SiNWs. For the 35% k-SiNWs, the capacity lost for each cycle is estimated at 0.5% from the second cycle capacity. This shows that the mechanical properties of the electrode are ultimately a trade-off of active material load, mixing of the constituents, porosity and the associated packing density.

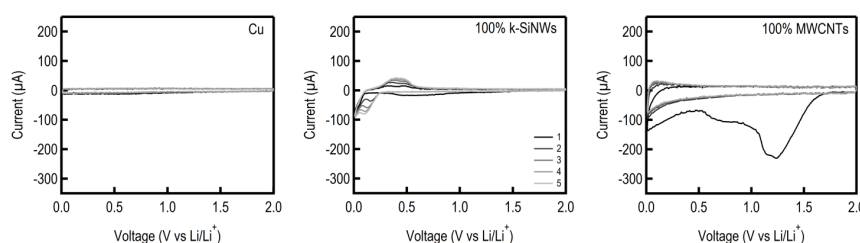


Figure 5.8: Cycling voltammetry profiles for Cu current collector, 100% k-SiNWs and 100% MWCNTs. The scanning speed was 0.1 mV/s.

To shed some light into the irreversible capacity ($\approx 30\%$ for 35% k-SiNWs-based assembly) during the first cycle, in particular the usual activity between 1 - 1.5 V vs Li/Li⁺, we evaluated via cyclic voltammetry the electrochemical activity of each component present in the assembly. In Figure 5.8, we show CV recorded for the Cu foil, the 100% k-SiNWs and the 100% MWCNTs assembly. This clearly shows that MWCNTs are

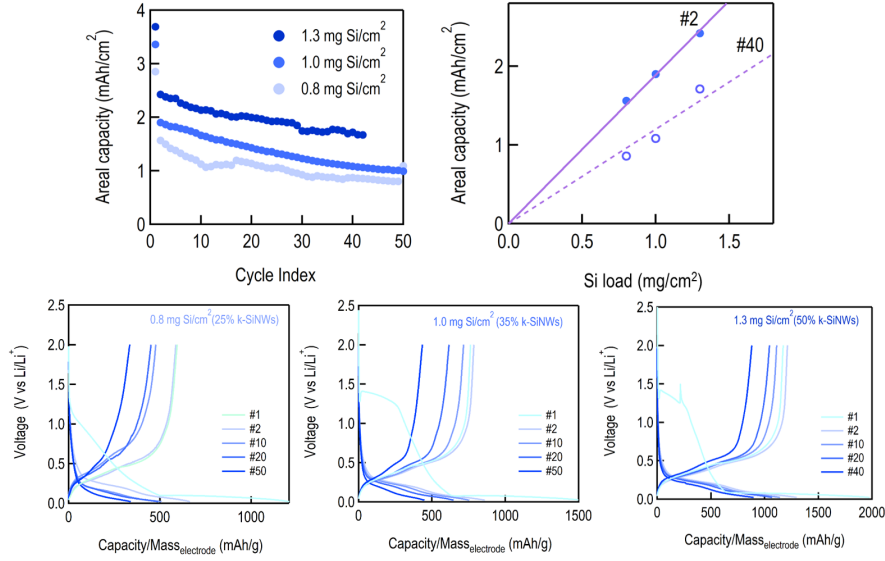


Figure 5.9: Areal capacity vs. gravimetric capacity. Electrochemical performance of k-SiNWs electrodes with different Si loadings.

responsible for this behavior. The exact reasons for this are unknown but we can speculate on the presence of impurities that undergo irreversible oxidation at this potential. This parasitic activity has an impact on the cycling life of the k-SiNWs-based electrodes since it consumes the electrolyte, traps Li ions and alters the quality of the SEI. Thankfully this event disappears after the first lithiation, thus, in the following we evaluate the k-SiNWs performance metrics starting with the second cycle.

Areal loading ($k\text{-SiNWs}_{\text{content}}/A_{\text{electrode}}$) effect on the electrochemical performance was also investigated, as shown in Figure 5.9. High areal mass loading is a requisite for adopting Si nanomaterials with the purpose of reducing the weight and the size of the anodes. The areal capacity can linearly be increased with the Si loading, achieving 2.42 mAh/cm^2 for the assembly with 1.3 mg Si/cm^2 cycled at 0.12 A/g (0.14 mA/cm^2). We also observe such dependence in the capacity fading, indicating invariability in the underlying degradation mechanisms. The corresponding galvanostatic charge-discharge curves are normalized with the total electrode mass (both Si and MWCNTs contributions). As the k-SiNWs loading is

increased from 0.8 to 1.3 mg_{Si}/cm², the electrode areal capacity linearly evolved to 2.42 mAh/cm² (1276 mAh/g_{electrode}) for the 1.3 mg_{Si}/cm². This linear behavior indicates that the two electrode components are active within the studied thickness range (Table 5.1) and establishes the homogeneous mixing of the constituents. We must emphasize here the benefits of IL cycling compared to the carbonate-based electrolyte system in terms of SEI stability (Figure 5.10). While in conventional electrolytes, Si's periodical expansion/contraction enables the continuous formation of SEI, affecting the cycling stability, for IL systems it was shown that approximately 73% of the Si-based electrode mass gain during the first cycle is preserved throughout cycling [55].

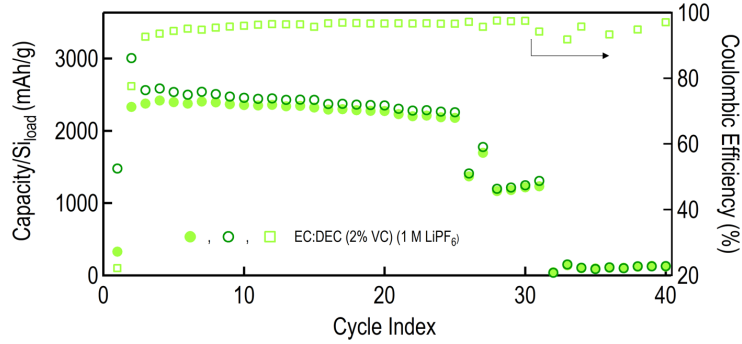


Figure 5.10: 35% k-SiNWs-based assembly cycling in conventional electrolytes at a rate of C/15. For the k-SiNWs-based anode assembly, although the first 25 cycles are relatively stable, the capacity quickly fades as the cycling proceeds. The constant SEI development during Li insertion eventually causes shedding of the pre-formed SEI, exposing the untainted Si and sustaining thus the formation of new SEI layers.

We expect the underlying degradation mechanism to be related to the charge collection efficiency that is conjectured to be rather low as the developed SEI isolates both k-SiNWs and MWCNTs, deteriorating the electrical contact, assuming that MWCNTs preserve their electrical properties after extended cycling. Nonetheless, additional experiments are required to assess the precise cause behind the degradation of these k-SiNWs assemblies. On the one hand, studies have revealed that MWC-

NTs become brittle and prone to sharp fractures after the first lithiation and upon subsequent cycling they break more easily [107]. On the other hand, we have seen in Chapters 2 and 3 that Si electrodes require passivation for stable cycling.

Here we showed that some alternative electrode construction exists and should not be limited to the conventional slurry casting. This holds true in particular for electrodes that suffer greatly from large volume variations, such as Si. Using k-SiNWs certainly enables such architectures providing inter-locking features to establish and sustain a mechanically stable, electronically active framework with a suitable porosity for a minimal electrode deformation upon Li insertion. In the following Chapter, we will investigate whether the cycling life of such electrodes can be expanded via functional surface coatings.

Surface passivation of nano-Si: Electrochemical characterization

Experience is like a lantern we carry on our back,
which only illuminates the path we have traveled.

Confucius

Surface passivation of nanostructured silicon anodes is an appealing design strategy for the development of reliable, high capacity lithium-ion batteries. For instance, functional surface coatings reduce the swelling anisotropy by buffering the volumetric expansion through a non-uniform deformation of the coating, preventing particle isolation. Associated with this, electrically active coatings can enhance the current collection efficiency eliminating the necessity for conductive additives. This chapter presents two possible routes for extending the cycling life of nano-Si electrodes. First, we explore the electrochemical performance of Ni-coated Si electrodes and discuss the mechanisms responsible for such performance. Second, a PEDOT:PSS hydrogel is investigated as a lighter, functional coating strategy for nano-Si electrodes compatible with the current graphite-established electrode processing.

We have seen in Chapter 2 and Chapter 3 that effective passivation of Si electrodes can be achieved using binders as well as functional surface coatings. In this Chapter, we'll tackle these two passivation strategies based on functional coatings for nano-Si LIBs technology.

6.1 Functional metal coatings

If we apply the insight provided in Chapter 3 for the k-SiNWs-based electrode, it is clear that the best electrochemical performance is expected for Ni coatings with $h/A = 1/2$. We recall that in this situation, the swelling anisotropy, typically responsible for material degradation, is reduced by the altered reaction kinetics induced by the Ni coating, as suggested by the numerical modeling. We showed experimentally and numerically that Ni coating will crack during initial Li insertion, regardless of the shell thickness, and some of the vehiculated benefits are altered. However, conformal Ni-coated SiNWs are still expected to provide the most advantageous configuration, presenting only one fracture per site that ultimately resembles the nanoscale version of Si thin film, which can sustain long cycling. This is the main hypothesis of our experimental strategy.

6.1.1 Electroless Ni deposition

An electroless deposition procedure was selected for the conformal coating of the nanopillars with Ni. This procedure allows the growth of a Ni layer with a uniform thickness along the radial and axial directions (Figure 6.1) and precise morphology control. Contrarily to commonly used physical vapor deposition techniques that are directional and cannot coat complex geometries and configurations, the adopted procedure is scalable and could be applied as well to other silicon morphologies including particles and powders.

For the electroless conformal Ni coating, the electroless protocol was adapted from the literature [146]. Briefly, the Ni electroless deposition bath was prepared following the instructions from Annex C. The pH was adjusted to ≈ 7 with ammonium hydroxide. The electroless deposition

of Ni was carried at room temperature under continuous agitation. The onset of the deposition was visually identified by the appearance and evolution of gas bubbles at the surface of the samples. After this point, the soaking time varied from 10 to 25 minutes depending on the target coating thickness. After the deposition, the sample was rinsed in water and methanol and let dry in air. The morphology and the thickness of the Ni shell depend on the plating time: both discontinuous, porous layers and continuous, conformal coatings can be obtained by increasing the deposition time. The Ni deposits according to the plating time are shown in Figure 6.1.

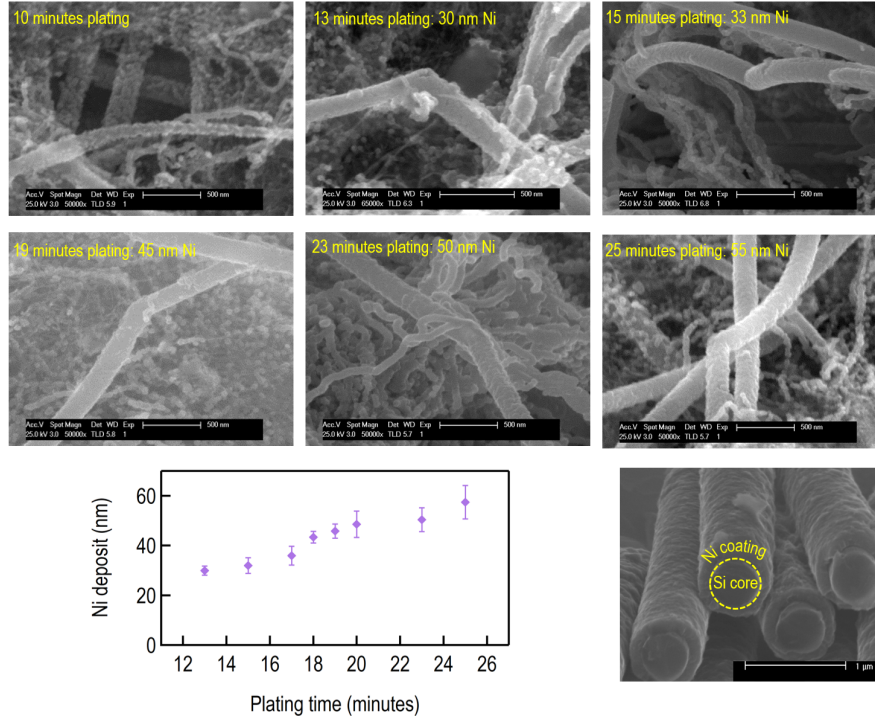


Figure 6.1: Characterization of Ni deposits. For the k-SiNWs assemblies, continuous, thin Ni layers cannot be obtained easily. After 10 minutes in the plating bath, a discontinuous, porous Ni shell decorates the k-SiNWs. Longer times are required for continuous, conformal Ni coatings. The thickness of the Ni deposit was estimated by measuring the diameter of individual Ni-coated k-SiNWs using SEM.

From the SEM inspection, we concluded that at least 13 minutes of plating time are generally required for a Ni coating that continuously conforms to the contours of the nano-Si. The estimated thickness of the Ni deposit for 13 minutes of plating is around 30 nm. Continuous thinner Ni coatings are difficult to deposit due to catalytic Ni growth. Next, to assess the electrical conductivity, electrochemical impedance spectroscopy (EIS) was performed (see Appendix B for details). The plots from Figure 6.2 show a drop in the charge transfer resistance when the Ni thicknesses increases. This will significantly affect the rate performance of the k-SiNWs-based electrodes as discussed in the following.

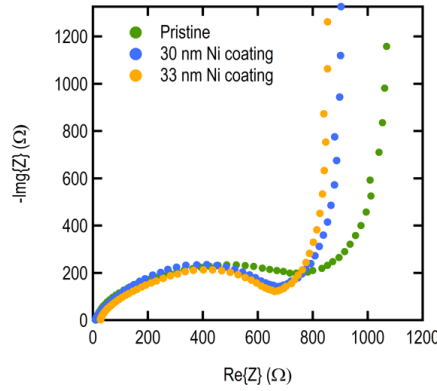


Figure 6.2: Electrochemical impedance characterization of pristine and Ni-coated 35% k-SiNWs-based anode assembly for two different Ni thicknesses.

The best electrochemical performance is, nonetheless, anticipated from Si anodes continuous and conformal coatings. This configuration is expected to provide the most effective passivation. In this sense, we focused on the fabricating Ni-coated k-SiNWs with 33 and 40 nm thick coatings.

6.1.2 Electrochemical performance

Composite anodes, fabricated as described in Chapter 4 and Appendix A, containing 120 nm diameter k-SiNWs are conformally coated with a 33 or 40 nm thick Ni layer using parameters of the aqueous electroless procedure described in the previous section and Appendix C.

Typical SEM images of Ni-coated k-SiNWs systems are shown in Figure 6.3, panels a and b. While a discontinuous, porous Ni layer would mostly improve the electrical conductivity, full structural benefits are expected from continuous, conformal coatings, in particular for thick coatings. Their resulting capacities normalized to the Si content as a function of cycle index are shown in Figure 6.3a and 6.3b, while their associated galvanostatic charge-discharge curves are shown in Figure 6.3c.

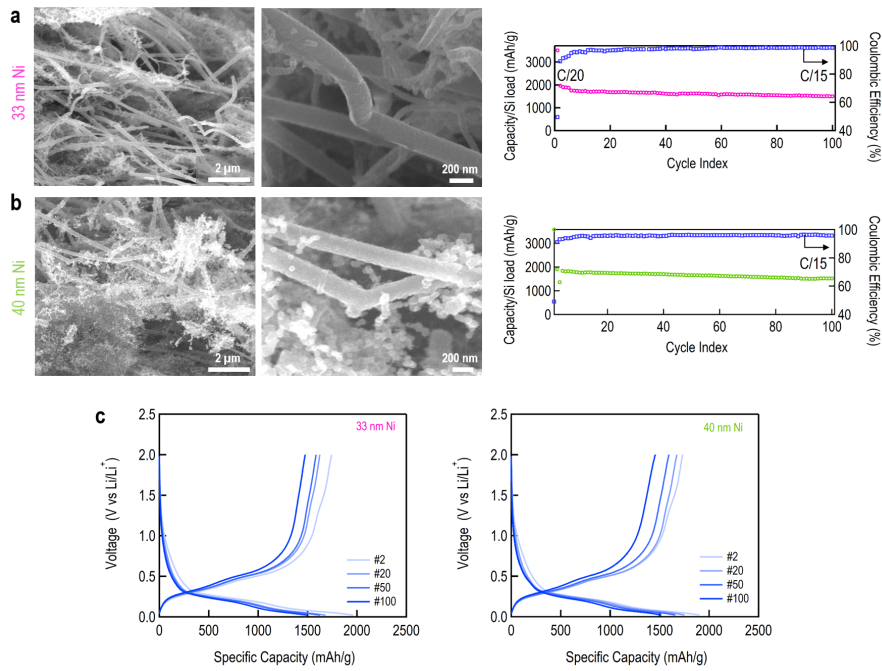


Figure 6.3: Electrochemical characteristics of 35% k-SiNWs-based electrodes coated with Ni. (a) 33 and (b) 40 nm Ni-coated assemblies and their associated electrochemical behavior and (c) their corresponding galvanostatic charge-discharge curves.

Perhaps of greater importance is the capacity normalized to the entire electrode mass, the Si and MWCNTs content, as shown in Figure 6.4. We observe a capacity of 700 mAh/g_{electrode} for the 33 nm Ni-coated assembly and 695 mAh/g_{electrode} for the 40 nm Ni-coated assembly, compared to 530 mAh/g_{electrode} for the pristine assembly after 50 cycles. This

clearly unveils that Si passivation is desirable for stable cycling.

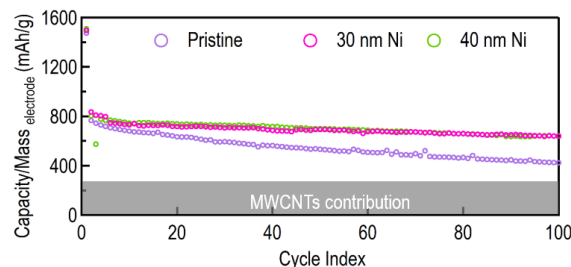


Figure 6.4: Specific capacity (lithiation) normalized to the whole k-SiNWs electrode mass (both contributions of Si and MWCNTs).

Considering the similar electrochemical performances, using the 40 nm Ni-coated k-SiNWs is not justified, since whenever possible, inactive materials should be eliminated. As previously discussed, a clear profit of the Ni coating is to provide efficient charge collection, which is expected to have a positive impact on the electrochemical rate performance.

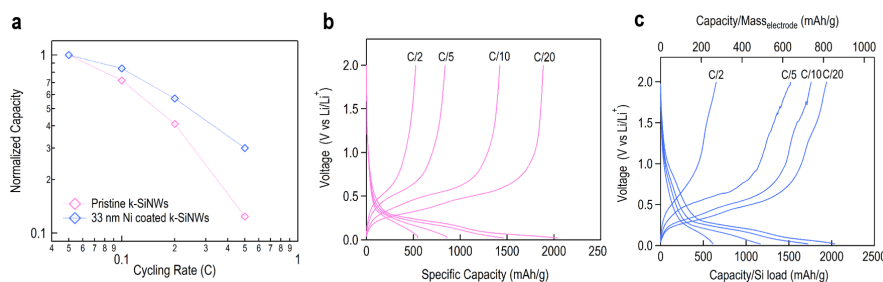


Figure 6.5: Rate performance for pristine and 33 nm Ni-coated assemblies. (a) Normalized capacity as a function of C rate for pristine and 33 nm Ni-coated assemblies with the corresponding galvanostatic charge-discharge profiles (b) and (c).

The rate capability plots from Figure 6.5 highlight the amplitude of the specific capacity at different C-rates for the as-prepared and 33 nm Ni-coated k-SiNWs anode assemblies. The magnitude of the Li uptake of the 33 nm Ni-coated k-SiNWs anode assembly is considerably greater than the as-prepared one, in particular at high rates. This response is

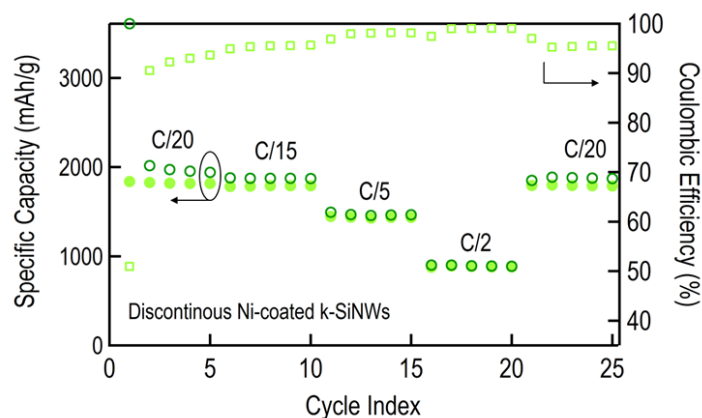


Figure 6.6: Rate capability of discontinuous, porous Ni-coated 35% k-SiNWs anode assemblies. Specific capacity (left axis) and Coulombic efficiency (right axis) vs cycle index for a discontinuous, porous Ni-coated k-SiNWs electrode. On the left axis, open circles correspond to discharging and closed circles represent charging.

the confirmation of favorable electronic pathways in the 33 nm Ni-coated k-SiNWs electrodes as shown by the EIS spectra from Figure 6.2. Nevertheless, the capacity reduces as the current density increases. This is explained by the Si sluggish lithiation concurrent with limited lithium-ion conductivity of the ionic liquid electrolyte at room temperature. The same benefits are observed for discontinuous Ni-coated k-SiNWs assemblies (Figure 6.6), confirming the importance of good charge collection in co-integrated anodes and current collectors. The Ni-coated electrodes present an areal capacity close to 2 mAh/cm² after 50 cycles, a value required for commercial usage (Figure 6.7). This behavior is primarily attributed to benefits stemming from the Ni coating, mainly the mechanical shielding and the electrical characteristics of the shell. Adopting such core-shell systems can have a powerful impact on the battery sizing, since similar capacities can be obtained using less than half of the active material packed in half of the thickness of the conventional graphite electrode.

The post mortem analysis of the k-SiNWs electrodes after 50 lithiation/delithiation cycles is presented in Figure 6.8. The structural in-

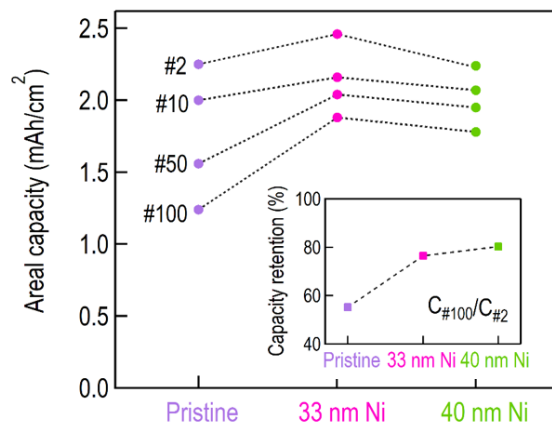


Figure 6.7: Areal capacity for the studied electrodes. At the displayed electrode load ($1 \text{ mg}_{\text{Si}}/\text{cm}^2$), an areal capacity of $2.4 \text{ mAh}/\text{cm}^2$ can be achieved. Regarding the capacity retention, both Ni-coated electrodes present similar characteristics, retaining 80% of the initial capacity (relative to cycle 2) compared to 55% for the pristine assembly.

tegrity of the as-prepared electrode appears to be preserved upon cycling. Indeed, for small diameters, under deep lithiation conditions, the swelling anisotropy of SiNWs is less pronounced [51]. The same observation is valid for k-SiNWs: they sustain the Li uptake by preserving the turning angle with no particular deformations (Figure 6.8 top). Nevertheless, after intense cycling, the kinks become indistinguishable as the k-SiNWs progressively become smoother and curved. Although elucidating the mechanism responsible for this behavior requires further investigation, an important contribution can be assigned to the unique interface between two different orientation segments and their corresponding swelling anisotropy as given by the crystallographic-dependent reaction kinetics.

The structural evolution of the Ni-coated k-SiNWs anode assembly corroborates our electrode design assumptions. The Ni coating uniformly unzips, presenting a long, longitudinal opening, typically offering the Ni-coated k-SiNWs a single fracture site as highlighted in Figures 6.8e and 6.8f. Overall, after 50 cycles, the Ni-coated k-SiNWs maintain their shape determined by the first lithiation step, due to the structural stiff-

ness induced by the Ni shell. This correlates with the observed high cycling stability of the 33 nm Ni-coated k-SiNWs anode assembly. This emphasizes the critical nature of the first lithiation cycle that is crucial for reliable cycling of silicon anodes and requires proper understanding and control, as we discussed in Chapter 3.

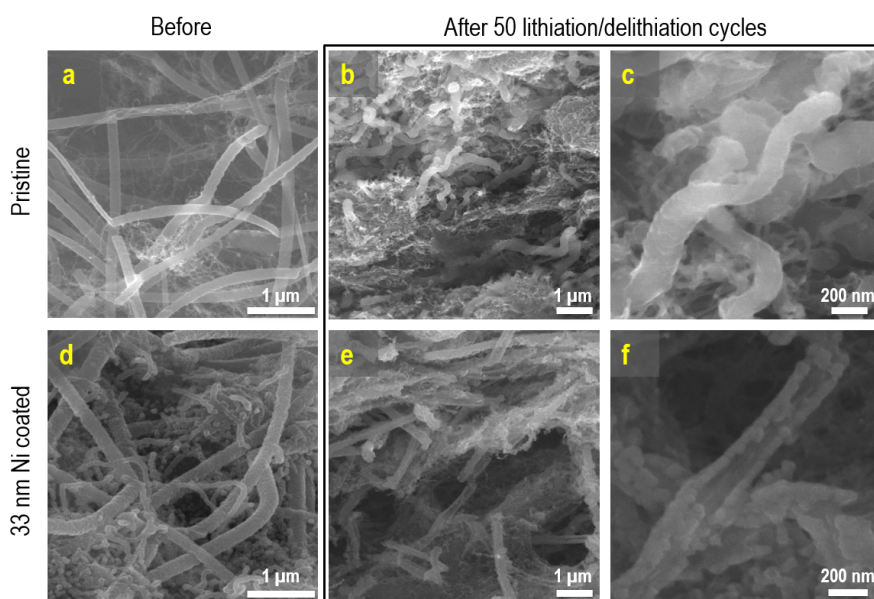


Figure 6.8: Post mortem analysis of the electrodes upon charge-discharge cycles. SEM images of pristine (a) and Ni-coated k-SiNWs assemblies (d). Morphology change after 50 lithiation-delithiation cycles: pristine (b,c) and Ni-coated (e,f) k-SiNWs assemblies. The Ni coating cracks upon Li insertion but the resulting configuration remains attractive, as it resembles the Si thin-film behavior. Si maintains an intimate contact with the electronically active Ni coating resulting in better charge efficiency, while being partially isolated from the electrolyte.

The EIS spectra were acquired before and after 20 cycles for pristine and 33 nm thick Ni-coated k-SiNWs anode assemblies. Before cycling, the surface resistance for the Ni coated electrode is lower than the pristine one, as already shown in Figure 6.2. For both electrodes, pristine and Ni coated, the impedance is lower after 20 cycles, indicative of good

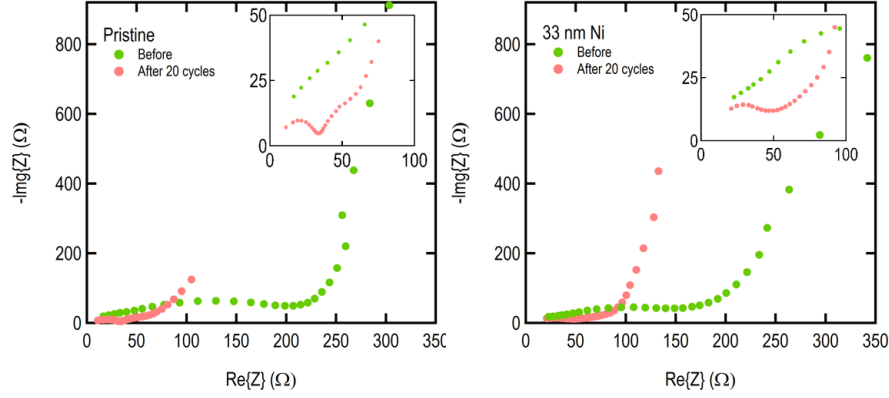


Figure 6.9: Comparison of electrochemical impedance spectra before and after 20 cycles for pristine and 33 nm thick Ni-coated k-SiNWs anode assemblies probed in half cells.

electrolyte penetration and efficient electrical pathways. Having in mind the complexity of the processes for a LIB and the fact that these spectra are very sensitive to the measurements conditions, the data shown here can only be used in a speculative manner.

This ultimately explains the electrochemical performance of the 40 nm Ni coated k-SiNW-based assemblies. While we explored the feasibility of k-SiNWs as active material for lithium ion battery electrodes and used Ni as a model system to further emphasize passivation as a requirement for stable cycling of Si-based anodes, the 33 nm-thick conformal coating of k-SiNWs is expected to increase by 20% the weight of the integrated current collector compared to the conventional Cu foil. In this sense, lighter, functional materials such as conducting polymers can successfully replace the metallic current collector and enable full exploitation of Si anodes. Next, we will discuss the benefits of adopting such functional materials for the cycling life of nano-Si electrodes [147].

6.2 Functional polymeric coatings

The conventional electrode fabrication process relies on casting slurries composed of active materials and inactive constituents such as carbon-

based conducting additives and dissolved polymer binders, onto a metal current collector [148]. Binders are generally regarded as passive elements in the battery performance, nonetheless, the cyclic stability is intimately connected to the properties of the binder [149, 150]. The binder acts as a supporting matrix, promoting the cohesion between the active material particles and the adhesion to the current collector and it has an important contribution to the stability of the SEI, in particular when working with negative electrode materials [151].

6.2.1 Aqueous conductive binders

Water-soluble binders can orient the Li-ion battery manufacturing towards an environmentally friendlier, safer and economic direction, eliminating the use of volatile and carcinogenic organic solvents associated with the conventional fluorine-based electrode assembly [152]. Fluorinated binders such as polyvinylidene difluoride (PVDF) are not suitable for conversion electrode materials, as metallic and alloy-type electroactive materials undergo large structural changes [66]. As a matter of fact, limited binder swelling by the electrolyte is desired to prevent the electrolyte decomposition that subsequently diminishes the binder-particle cohesion. In an effort to promote passivation and the mechanical integrity of the electrode, several binder concepts have been tested in recent years including conductive, self-healing and shape-memory polymers [153]. Water-based suspensions of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) have been particularly employed as conductive agent additives showing reliable cycling with some anode as well as cathode electrode materials [56, 154–156]. The physico-chemical properties of the used aqueous polymer suspensions and associated battery electrode slurries were, however, poorly detailed. In particular, the use of viscous polymer solutions will inevitably lead to inferior quality coatings since the rheological properties are expected to impact the slurry stability through particle segregation, as it will be analyzed in the following.

Water-based dispersions are difficult to stabilize, being susceptible to phase segregation when hydrophobic or dissimilar volumetric mass ma-

materials are used, requiring additives, additional processing complexity as well as texturing control agents to stabilize the slurry. Although these can be controlled to a certain extent, the ultimate challenge is to avoid particle sedimentation or aggregation upon battery electrode slurry handling as well as drying. For instance, electrically-conductive carbon additives tend to flocculate in dense electrode slurries [157, 158] leading to non-homogeneous coatings affecting the electrochemical performances. In addition, the flow behavior of the slurry closely impacts the electrode fabrication processes such as casting, pressing and slitting. Finding solutions to these drawbacks is thus required to widely adopt aqueous binder processing as a general route for lower costs and environmental processing of battery electrodes. Interestingly, the mechanochemical conversion of a regular PEDOT:PSS water-based dispersion produces a hydrogel that meets all the requirements as a binder for lithium-ion battery electrode manufacture. In the following we particularly focus on: (i) the simplicity and reproducibility of the mechanochemical conversion approach; (ii) the physico-chemical properties (adhesion, electrical conductivity); (iii) the rheological properties and suitability for electrode manufacture (viscosity and slurry stability); (iv) the improved performances of nano-Si electrodes. Additionally, given the electrically-conductive nature of the PEDOT:PSS hydrogel binder and its miscibility with other aqueous formulations, hybrid binder compositions, and carbon-free electrodes were manufactured and tested. Overall, the mechanochemically-synthesized PEDOT:PSS hydrogels, when applied as binder for lithium-ion battery electrode processing, show major advantages given the simple aqueous procedures, excellent dispersion stability, preserved electrical conductivity, enhanced structural integrity and adhesion of the prepared electrodes as well as improved power and cycling stability performances.

6.2.2 PEDOT:PSS hydrogels

The mechanochemical conversion was performed by ball milling in the presence of metallic iron. Milling emerges as a promising tool to induce chemical and physico-chemical transformations of compounds enabling the access to new materials phases and properties [159]. Commercial

PEDOT:PSS (Heraeus, Clevios PH 1000, 1.3% wt by mass) solution was used as received. Gel conversion was simply realized using ball milling in the presence of Fe sources. Typically 10 ml of stock PEDOT:PSS dispersion was poured into 50-80 ml ball milling jars. The best results (consistent and highly reproducible) were obtained by using stainless steel (316) jar and 8 to 10, 6-mm diameter balls for 1-hour processing. Using other types of jars (agate, Teflon) also results in gel conversion as long as an iron source is added (stainless steel balls, iron or stainless steel powder) are used. In the absence of an iron source (agate and/or Teflon jar and balls), no gelation was observed. The electrode slurries were prepared by adding the respective active battery materials and conductive carbon additives to the PEDOT:PSS solution followed by ball milling. No special precautions or pre-treatment have been applied. The weight of both PEDOT:PSS hydrogel and pristine forms were measured before and after water evaporation. We consistently obtained 98-99% weight loss during the drying process which is assigned to the water content.

The rheological properties are of utmost importance for electrode processing as they largely control the coating speed, current collector metal surface wetting and adhesion, ultimately affecting the defect density, electrode coating quality and electrochemical properties. The dynamic and steady-state mechanical properties of the PEDOT:PSS supramolecular hydrogels were evaluated by rotational shear rheometry. The linear viscoelastic response of the hydrogels was investigated by performing frequency sweeps under low stress control. As shown in Figure 6.10, the viscoelastic response of the material is expressed by nearly frequency-independent plateaus in moduli, which is the trademark of self-standing gels. In addition, the elastic response (storage modulus, G') is one order of magnitude higher than the viscous contribution (loss modulus, G'') in the investigated frequency range. Accordingly, the phase lag (δ) between the applied stress and the resulting strain remains close to 0° , which attests a solid-like behavior. Steady-shear experiments were also carried out by measuring the evolution of the viscosity (η) when subjected to an increasing shear rate ($d\gamma/dt^{-1}$).

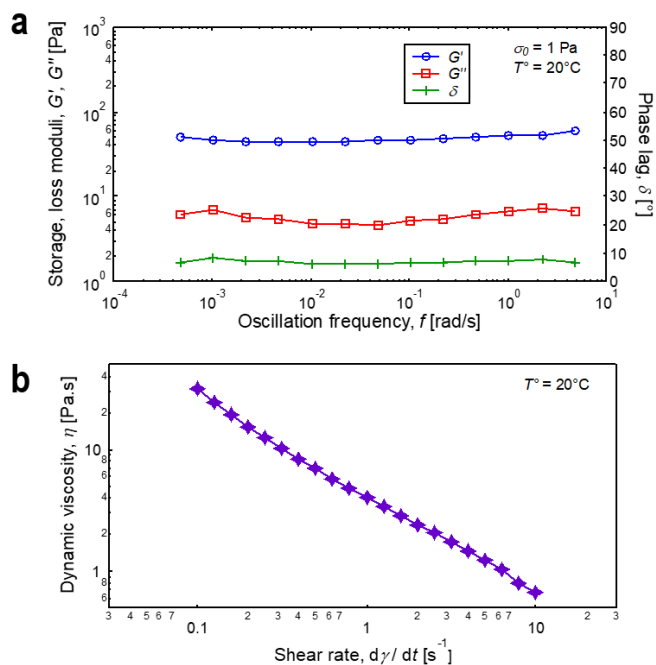


Figure 6.10: Rheological properties of PEDOT:PSS hydrogels. (a) Frequency dependence of the dynamic storage, loss moduli and stress-strain phase lag. (b) Steady-shear viscosity as a function of the shear rate for PEDOT:PSS supramolecular hydrogels.

The PEDOT:PSS supramolecular hydrogel exhibits a pronounced shear-thinning behavior usually encountered for well-dispersed suspension of interacting particles, which are forced to flow by the steady-shear stress. Precisely, the apparent shear viscosity of the material decreases by two orders of magnitude when the shear rate is varied in the range of 0.1 to 10 s $^{-1}$ (Figure 6.10b). Practically, this pseudo-plastic behavior is beneficial to the slurry casting step since it allows the films to thin and wet out the surface evenly, facilitating the formation of thin to thick coatings. Once applied, the material regains its higher viscosity due to restructuration, therefore avoiding drips and runs. Additional details on the rheological properties are available in [147].

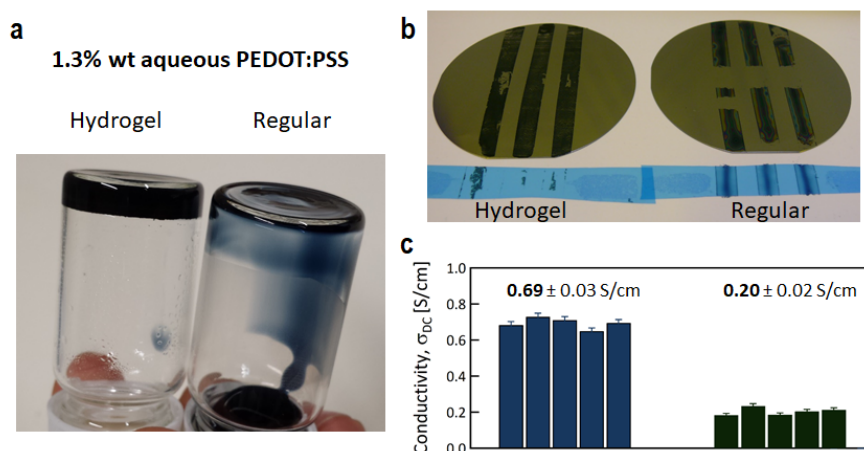


Figure 6.11: PEDOT:PSS hydrogels. (a) Photographs of the PEDOT:PSS hydrogel (left) and regular (right) formulations at 1.3% wt PEDOT:PSS content. (b) Adhesion test on silicon wafers: left - hydrogel, right - regular PEDOT:PSS coatings. (c) Electrical conductivity change upon gelation (regular - left; hydrogel - right).

The adhesive properties of the material are essential for the application as binder in the Li-ion battery electrodes. Therefore, a qualitative adhesive tape test was performed on regular and hydrogel PEDOT:PSS films cast on a silicon wafer. As it can be noticed in Figure 6.11b, the PEDOT:PSS hydrogel exhibits improved adhesion to the Si substrate in comparison to the regular one. The improved adhesion provided by the PEDOT:PSS hydrogels is further beneficial for the application as a binder in the electrodes for the Li-ion battery technology. Contrary to the currently preferred range of highly insulating polymeric binders such as PVDF with an electrical resistivity exceeding 10^{14} Ωcm , PEDOT:PSS is intrinsically conducting. Four-probe current-voltage measurements were carried out to evaluate the sheet resistance of dried films of PEDOT:PSS pristine and hydrogel. The average thickness of the dried films was evaluated to access the DC conductivity, σ_{DC} (Figure 6.11c). For pristine PEDOT:PSS films, the conductivity is 0.69 ± 0.03 S/cm without any secondary doping or post-treatment to enhance the electrical conductivity. Similarly, for dried films of PEDOT:PSS hydro-

gel the conductivity is evaluated at 0.20 ± 0.02 S/cm. This clearly shows that the charge transport is hardly affected by the mechanochemical conversion of the PEDOT:PSS, the hydrogel being a good electrical conductor. However, since the charge transfer in PEDOT:PSS occurs via a hopping mechanism between π -conjugated segments along and between the PEDOT chains, the conductivity in PEDOT:PSS films thus depends on the supramolecular organization of the PEDOT chains in the insulating PSS anionic matrix. The slight decrease in the electrical conductivity value probably stems from a reorganization of PEDOT within the PSS matrix induced by the high mechanical stress during ball milling. Other factors such as the partial reduction of PEDOT can impact negatively the intrinsic conductivity, due to the decreased number of charge carriers within the polymer structure. In any case, the material remains a good electrical conductor, a factor that further opens the possibility of building battery electrodes solely with aqueous PEDOT:PSS hydrogel binders and active battery materials.

6.2.3 Aqueous processing of nano-Si electrodes

The original aspects emphasized in this work are the simplicity, the stability, and the electrode coating uniformity when using PEDOT:PSS hydrogel binder formulations (Figure 6.12). Due to high solvent content, the physical mixing of regular PEDOT:PSS solutions with electrode active components and additives results in non-stable dispersions, with sedimentation taking place on a time-scale of few minutes (note the silicon nanoparticle sedimentation and carbon flocculation in Figure 6.12a). Since the viscosity is too low to avoid dewetting from the metal foil surfaces, coating such slurries for producing uniformly-thick films is also troublesome. The constituents further segregate during drying, resulting in electrodes with non-uniform composition and properties (Figure 6.12a). With the PEDOT:PSS hydrogel processed formulations, the slurries gain in viscosity yet remain fluid enough to be processed. These factors are essential for producing high-quality and defect-free electrodes (Figure 6.12a). Hybrid binder formulations have also been tested [160],

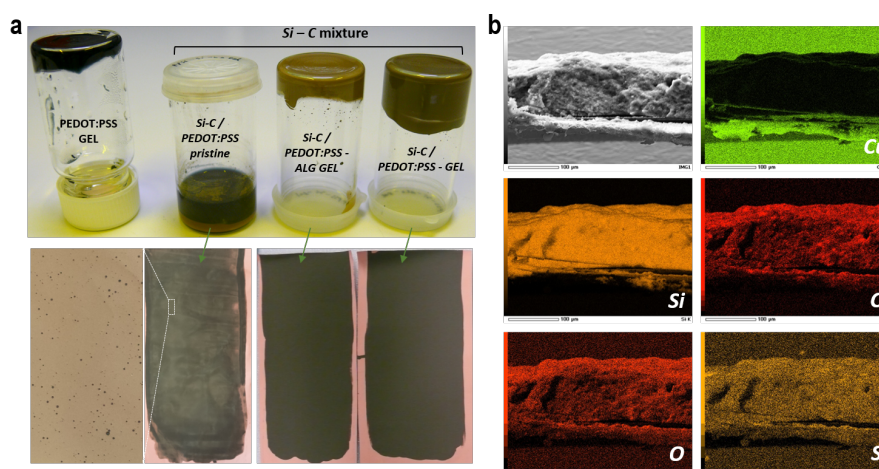


Figure 6.12: Battery electrode slurry processing. (a) Optical photographs of various PEDOT:PSS formulations used for battery electrode fabrication and the associated coatings using hydrogel and regular PEDOT:PSS formulations. (b) SEM and EDX elemental mapping of thick electrode coatings employing Si/C composite and PEDOT:PSS hydrogel binder.

with the rheology dictated by the PEDOT:PSS hydrogel phase, further highlighting the versatility of this process. These hybrid binders can be easily formulated by mixing the PEDOT:PSS solution with carboxy methyl cellulose (CMC), styrene butadiene rubber (SBR), and sodium alginate (ALG) in the aqueous phase followed by mechanochemical conversion.

The corresponding battery slurries are stable, show no phase segregation and produce highly-uniform thin ($25\ \mu\text{m}$) to very thick ($500\ \mu\text{m}$) films in a single coating step, with no material sedimentation even upon slow drying. Scanning electron microscopy and EDX mapping of the Si/C electrode cross sections from Figure 6.12 show no sign of sedimentation, phase segregation or delamination, despite the highly dissimilar volumetric presence of the constituents. Moreover, no particle breakdown is observed under these mild milling conditions. These results highlight the importance of the rheological properties of the PEDOT:PSS hydrogels and the corresponding slurry formulations suitable for aqueous

formulation of Li-ion battery electrodes.

6.2.4 Electrochemical performance

With the rheological properties and structural integrity demonstrating clear advantages over the standard aqueous binder-electrode formulations, we have next analyzed the electrochemical properties of the PEDOT:PSS hydrogels and formulated nano-Si electrodes. Si nanoparticles-based electrodes have been extensively analyzed and tested in various formulations, given the appealing properties of Si as negative electrode for Li-ion batteries (Figure 6.13). A mass loading of 1 mg/cm^2 and slow cycling conditions ($300 \text{ mA/g}_{\text{Si}}$) were applied to assess the intrinsic electrochemical properties and avoid measurement artifacts.

The PEDOT:PSS hydrogels binders were found widely compatible with many other electrolyte chemistries and additives. Overall, these electrodes have been tested with different formulations: classic carbonate-based (1M LiPF_6 in ethylene carbonate (EC):diethyl carbonate (DEC) 1:1 v:v with 10% fluoroethylene carbonate (FEC) and 2% vinylene carbonate (VC)), and ionic liquids (1.2M lithium bis(trifluoromethanesulfonyl)imide (LiTFSi) in 1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ($\text{PYR}_{13}\text{FSI}$)). No signs of solubility or degradation were observed and no swelling was detected upon extended exposure (more than 1 week), implying that highly efficient surface passivation and protection can be obtained when using PEDOT:PSS hydrogel binders. To highlight the benefic impact, extended cycle-life performance and a Coulombic efficiency of 99.8% in average were obtained for Si nanoparticles-based electrodes associating the PEDOT:PSS hydrogel binder processed electrodes with ionic liquid electrolytes (Figure 6.13a and 6.13b). Furthermore, the PEDOT:PSS hydrogel formulations clearly produce more uniform electrode coatings (Figure 6.12), which translates into better cycling stability when compared to regular PEDOT:PSS electrode processing (Figure 6.13c). In addition, the electrochemical performance of Si nanoparticles-based electrodes with relevant binder formulations including hybrid PEDOT:PSS - CMC and alginate formulations is shown in Figure 6.13d. Clearly, the surface coatings for efficient Si passiva-

tion are only obtained with PEDOT:PSS hydrogel formulation as can be observed in the top-view SEM images from Figure 6.14.

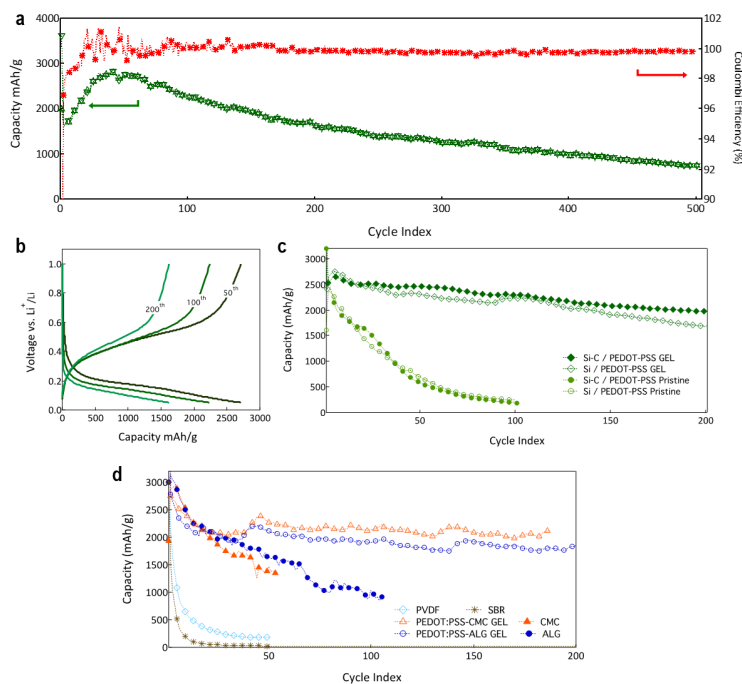


Figure 6.13: Electrochemical performances of Si nanoparticles-based electrodes. (a) Extended cycling of Si nanoparticles - PEDOT:PSS hydrogel electrodes with the ionic liquid-based electrolyte system (rate of C/6,7). (b) Associated charge-discharge profiles at different cycling extent. (c,d) Cycling stability of Si nanoparticles-based electrodes with selected binder formulations including hybrid PEDOT:PSS - CMC and alginate formulations. The cycling rate is C/12 (1C corresponds to 3500 mA/g).

Noteworthy here, is the simplicity of the selection processing compared with other functionalization strategies such as polymer grafting from/onto that requires additional steps. Indeed, with the polymer grafting, different interaction mechanisms are involved, that can avoid, for instance, any delamination issues.

There are several aspects that can be assigned to support the improvement in the observed electrochemical response. First, as described

above, the better adhesion and the deformability of the PEDOT:PSS hydrogels are beneficial for accommodating the large mechanical strain accompanying the volume changes in Li-alloying electrode materials. This preserves an intimate electrical connection with the current collector and between the particles during volume variations upon cycling. Furthermore, the non-permeability and very limited swelling of this polymer by the carbonate and other non-aqueous electrolytes effectively prevent direct contact of the electrolyte with the active materials surface (Si, Sn, graphite, etc). However, further studies are required to access the composition and stability of the SEI with the PEDOT:PSS hydrogel processed electrode. This is essential for extended cycling of high-capacity alloy materials by building a stable SEI. The fact that regular PEDOT:PSS - processed electrodes show poor capacity retention highlights the particular necessity of suitable processing conditions and physico-chemical properties of the binder. The gelled formulations prevent the migration and segregation of particles during drying, helping thus to maintain the fine particle mixing. This is primarily assigned to limited dewetting of the hydrogel formulation resulting in conformal coating of Si particles during the drying process of the electrodes, which positively differs from other non-gel formulations. While the PEDOT:PSS phase clearly affects the cycling stability, the addition of conductive carbons only slightly enhances the cycling stability (Figure 6.13c) at low cycling rate, indicating that, despite of the reduction, PEDOT:PSS hydrogel provides sufficient electric conductivity under such operational conditions. Thus, for slow cycling conditions, carbon additives have essentially no effectiveness. Consequently, carbon-free electrodes can be built and, associated to that, an increase of active material content could be considered. Since efficient charge collection is also expected to improve the electrochemical stability and, in particular, the power rate performances, we evaluated electrode formulations comprising a different content of PEDOT:PSS hydrogel without any other conductive additive. In addition, in order to maximize the energy density, it is desirable to minimize the content of inactive constituents within the electrode without altering the electrochemical performance. In this context, the polymeric binder and the conductive additive are replaced with the PEDOT:PSS hydrogel. Yet,

as discussed in the following, excess of PEDOT:PSS, although enhancing the electrical conductivity of the composite electrodes, was found to induce an adverse effect on the power performances. The PEDOT:PSS hydrogel content-dependent impermeability towards non-aqueous electrolytes has a direct consequence on the power performances.

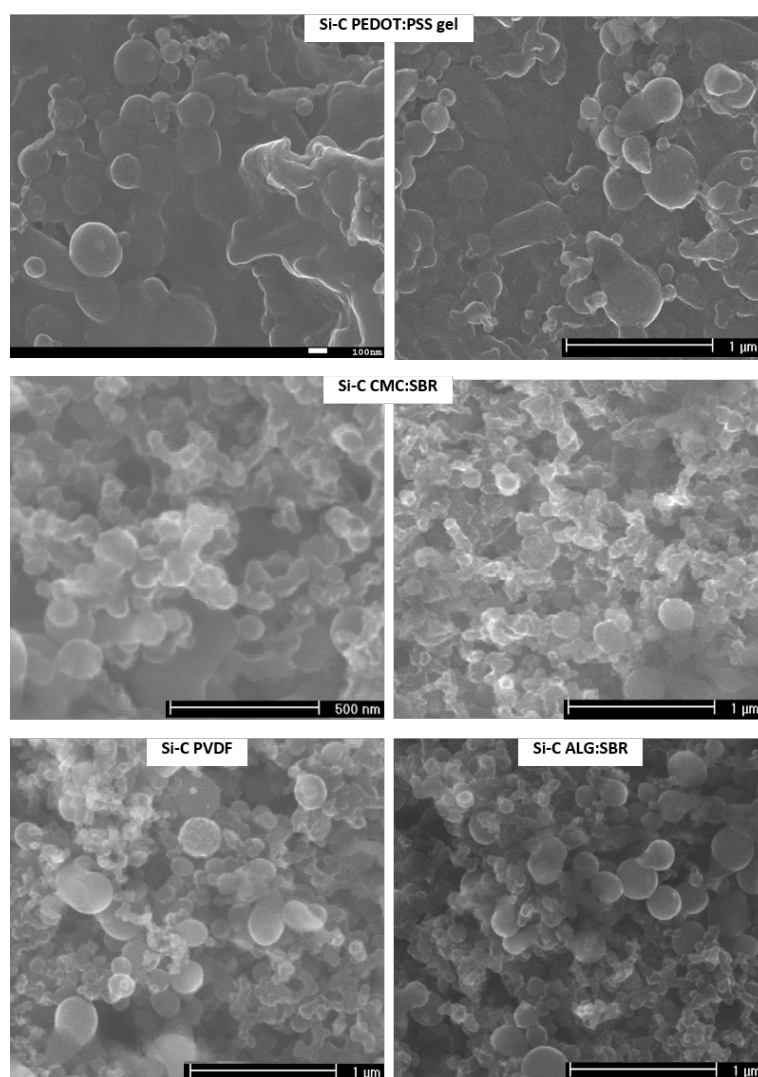


Figure 6.14: Top-view SEM images of nano-Si electrodes with different binder formulations analyzed. Uniform surface coatings for efficient passivation are obtained only for PEDOT:PSS gel formulations.

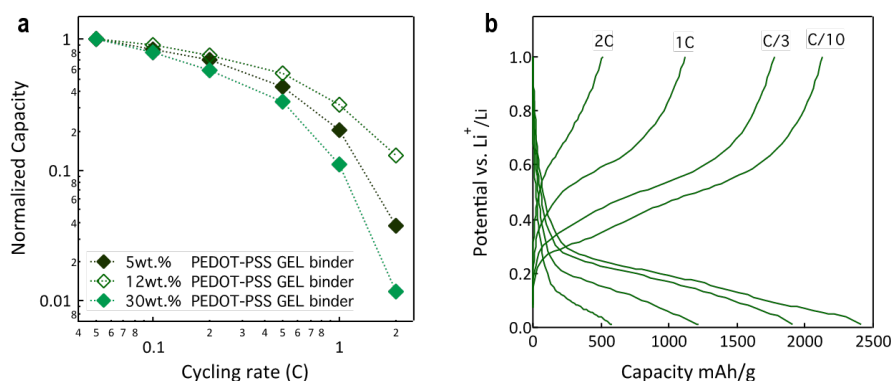


Figure 6.15: Power performances of Si nanoparticle-based electrodes as a function of the PEDOT:PSS hydrogel binder content. (a) Normalized capacity retention of Si nanoparticle-based electrodes as a function of PEDOT:PSS hydrogel binder content. (b) Potential - capacity plots at different rates for the electrodes with 12% wt PEDOT:PSS hydrogel binder.

Up to a certain (weight and volumetric) content, the power performances of the electrodes were improved, while above this threshold a detrimental effect is observed. To confirm this, electrodes with a varying amount of PEDOT:PSS hydrogel binder and only Si nanoparticles have been manufactured (with similar Si mass loading) and their power performances were analyzed (Figure 6.15). The maximum rate performances were attained for approximately 12 - 15% wt binder content. The 30% wt binder content electrode displayed poorer power capacity retention, even lower than the electrode with 5% wt PEDOT:PSS hydrogel binder, despite its higher electrical conductivity. This is explained by the lower permeability of PEDOT:PSS to carbonate electrolytes, resulting in limited Li⁺-ionic flux and conduction. Thus, for an optimized electrode formulation, the active particle morphology, the surface area and the conductivity need to be considered together with the ionic and electronic conduction properties of PEDOT:PSS hydrogel binders.

Overall, the mechanochemically-synthesized PEDOT:PSS hydrogels, when applied as binders for lithium-ion batteries, show net advantages given the simple aqueous processing, excellent dispersion stability, preserved electrical conductivity, enhanced structural integrity and adhesion

of the prepared electrodes, as well as improved power and cycling stability performances.

In this chapter, we looked at the passivation possibilities for nano-Si-based electrodes. First, we analyzed and discussed the effects of Ni-coated nano-Si strategies on the lithiation behavior, the expected morphological evolution of lithiated nano-Si and their impact on the experimentally observed electrochemical performance. Second, a multi-functional PEDOT:PSS hydrogel nano-Si passivation was explored. This avenue is compatible with current manufacturing operations producing high-quality, defect-free electrodes and can redirect LIBs technology towards a cleaner environmental path. Si electrodes clearly require passivation and these multi-functional coatings can be a solution.

Conclusions

I wouldn't compare it to sex, but it lasts longer.

Stephen Hawking on Scientific Discovery

Batteries are crucial in achieving the electrical vehicle (EV) revolution and considerably reduce the greenhouse gas emissions from fossil-fueled transportation. To achieve this, the next generation of energy storage systems has to comply with the requirements of an eco-social-technological system. In other words, we want high-performance devices that meet the social functioning requirements, such as driving range or charging time for an EV, in a safe, economical and sustainable manner. This work tries to explore the feasibility of such systems, building on the existing lithium-ion battery (LIB) technology. Indeed, the LIB technology has witness periodic performance increments but it relies on its initial electrochemistry that can not adapt nor satisfy our societal needs. The context of this thesis is dictated by the LIB technology framework as well as the current research directions towards sustainable energy systems with the help of nanotechnology as exposed in Chapter 1. Specifically, this thesis focused on a viable high-performance anode for LIBs following three main topics as follows.

(i) Sustainable materials and processing. Silicon is at the core of the electronics industry and has the potential for revolutionizing the LIB technology as well. Owing to its high Li storage capacity, nearly 10 times that of the current carbonaceous anodes, Si has been intensively studied to develop a high-performance electrode. Also, if we consider its abun-

dance as well as re-using Si from electronics waste, Si becomes a great material for the LIB anodes. However, the Li-Si alloying chemistry is quite challenging due to the electrode expansion as Li is accommodated. Nano-Si electrodes have extended the cycling life but at an important energetic cost, that limits their industrial adoption. Thus, the development of efficient, scalable, low energetic-cost synthesis procedures is essential for the implementation of next-generation energy storage. This is discussed in Chapter 2 with the recent developments of nano-Si anodes. We presented a simple, room-temperature synthesis for kinked silicon nanowires (k-SiNWs) that allows for the re-use of the Si source to continuously produce k-SiNWs. We further detail on the versatility of MACE to fabricate morphology and orientation-customized k-SiNWs based on successive etch-quench sequences. This approach enables the control of the number of kinks, their location and, to a certain extent, their angle via successive etch-quench sequences. We coupled relevant Au catalyst parameters to systematically assess the impact on the etched morphologies. On the one hand, the opening diameter impacts the etching rate and the overall kink angle distribution. On the other hand, the thickness of the Au mask has a pronounced effect on the porosity of the produced nanostructures and small catalyst thicknesses are not suitable for long etching times. This results in a wide spectrum of morphologies that can be accessed and customized as required by the application. Next, the procedure was adapted to a continuous metal-assisted chemical etching sustained by the chemical peeling method for the mass fabrication of k-SiNWs for LIB anodes. Indeed, we detailed on a chemical peeling step that facilitates the ultrasonic collection of k-SiNWs and allows for the re-use of the Si substrate. It consists of a sacrificial porous segment that facilitates the separation of the k-SiNWs from the Si substrate with a short ultrasonic treatment. After the treatment, the metal mask remains intact and can be reused for a new etching sequence. The thickness of the Si substrate is the only limitation for this continuous etching scheme. Chapter 4 detailed on this.

(ii) Suitable electrode design to promote high-cycling life. Current battery manufacturing processes can not be expected to be compatible with the Li-Si alloying chemistry, thus, here we explored a more viable

configuration for the Si electrode. We have investigated the benefits of such nanostructures as LIB anodes and proposed a self-standing electrode with k-SiNWs and MWCNTs as building blocks. In Chapter 5, we challenged the current slurry-on-metal anode paradigm by introducing a highly porous, interweaving k-SiNWs-based electrode with minimal deformation during cycling and an integrated Ni current collector for effective Si passivation and efficient electrical pathways. Such architectures seem more suitable than the conventional slurry-on-metal design to sustain long cycling of Si-based anodes. The fabricated electrodes showed k-SiNWs micro-geometry-dependent mechanical properties revealing a foam-like behavior reinforced by the kinks. The enhanced electrochemical performance of the electrodes results from the synergy between the k-SiNWs three-dimensional inter-locking features associated with the robust SEI film activated by the ionic liquid electrolytes.

(iii) Passivation strategies. Surface passivation is explored not only as a possible route for extending the cycling capabilities of Si anodes but also to redirect the LIBs towards a cleaner and friendlier environmental path. First, we used a Ni coating to investigate the effect of surface passivation on the electrochemical performance of the k-SiNWs-based assembly. Conformal Ni coatings can be considered an integrated current collector intimately coupled to Si, providing direct electrical pathways as well as effective Si electrode passivation. We saw the performance benefits of such coatings in Chapter 6 in terms of cycling stability as well as rate capabilities. Next, we looked further at the fundamental implications of the Ni coating. For this, we addressed nickel-coated $\langle 100 \rangle$ silicon nanopillars as a model system to study the deformation and fracture of core-shell nanostructured anodes during the initial Li insertion cycle. Coated structures display different swelling and cracking regimes depending primarily on the coating thickness to pillar diameter ratio. For low ratios, the swelling and cracking are anisotropic, although with different fracture sites compared to uncoated nanopillars. The swelling behavior progressively becomes isotropic when the ratio increases, which is attributed to the large stress-induced slowing down of the reaction kinetics. This effect is more pronounced in the $\langle 110 \rangle$ directions. While the absolute pillar dimension and coating thickness are likely playing a

role, the cyclic performance of the anodes intimately rely upon specific deformation and the cracking regimes during initial lithiation. Second, we showed that a hydrogel based on the mechanochemical conversion of PEDOT:PSS aqueous solutions in the presence of metallic iron can perform as a binder for LIBs. These hydrogels are found to be ideally suited for the aqueous formulation of battery electrodes given their combined exceptional rheological properties and dimensional integrity, wide-window electrochemical stability as well as compatibility with battery electrolytes and electrode materials. Overall, the mechanochemically-synthesized PEDOT:PSS hydrogels, when applied as binders for lithium-ion batteries, show net advantages given the simple aqueous processing, excellent dispersion stability, preserved electrical conductivity, enhanced structural integrity and adhesion of the prepared electrodes, as well as improved power and cycling stability performances. In addition, any ball milling related safety hazards are minimized due to the mild milling conditions in an aqueous medium.

Our society is more depended than ever before on energy storage, with an imperative demand for high energy density systems. In this direction, we have addressed materials and unconventional electrode systems that are considered more realistic and promising for the high energy density alloy-type materials. This critical evaluation included a focus on their advantages and discussed the remaining challenges concerning the governing chemistry. Si is an elegant solution from a sustainability point-of-view but, in terms of performance, we are limited to a low Si content, thus not the expected energy-dense electrode that we need. More work needs to follow on electrode stability as well as their interfaces, a classic for LIBs. A high-performance Si electrode demands creative and unconventional remedies and a willingness from industry and academia alike to explore beyond the well-established carbonaceous boundaries.

Perspectives

The truth is, everyone is going to hurt you. You just got to find the ones worth suffering for.

Bob Marley

P.1 General considerations

I would say that putting together this material allowed me to access other view-points. I would say it follows the scheme of a proof-of-concept, straight to the application, and not much into the fundamentals. It was already qualified as qualitative rather than quantitative, and to some extent, it was intended this way. Thus, I count on you, dear reader, to join me in quantifying the results. I would leave it up to you to assess the relevance and impact of each suggestion.

First, the k-SiNWs characterization will benefit from the crystallographic insight on the structure of the nanowires. It provides extra details on the etching opportunities of metal-assisted chemical etching and, with that, tuning of the physical properties. It can also reveal that the etching is actually locked to some modes due to the geometrical frustration of the system, as it is the case with the vapor-liquid-solid NWs growth [161].

Second, the k-SiNWs-C composite could benefit from an optimized fabrication. The limitations of the current experimental assemblage protocol were addressed in detail in Chapter 5. Superior mechanical proper-

ties are expected if the filtration step, for instance, allows more control. In addition, purification of MWCNTs prior to the assembly would clarify the irreversible capacity issue seen during the first lithiation. This could provide some insight on whether this passivation contributes to the cycling stability of the k-SiNWs-based electrodes. Concentrated nitric acid under reflux is usually used to decrease the metal contaminants in MWCNTs.

Third, *in-situ* experiments are required to analyze the chemical composition of SEI on the passivating layer, Ni and PEDOT:PSS. X-ray photoelectron spectroscopy or time-of-flight secondary ion mass spectrometry can be used to elucidate the interfacial chemistry. The k-SiNWs would also benefit from an *operando* monitoring to shed some light on their structural transformation during cycling (Figure 6.8).

Fourth, exploiting the k-SiNWs on other applications. Applications, where the surface-to-volume ratio is critical, will undoubtedly benefit from such structures - photonics or sensing applications, to name a few.

Lastly, I would like to expose to the reader other promising battery designs and technologies. First, the proof-of-concept of an inkjet-printed paper battery that uses paper as support as well as separator is presented. This design responds to the demands imposed by paper electronics, for instance. Then, this section continues with an overview of emerging high energy density Li technologies animated by urgency and pressure ripples from the community to develop new chemistries capable of meeting all the demands for the next-generation storage devices.

P.2 Paper battery

An alteration of the paradigm in the battery assembly can enable battery technology to seamlessly integrate into all size and shape-conditioned applications. While spray coating has been presented as a powerful tool for developing batteries on any type of surface, relying on sequential depositions of the battery constituents, the material loss during spraying as well as the equipment and facility requirements make it difficult to implement for small or limited-footprint batteries [162]. Another possible research direction for active material deposition is inkjet printing.

While this method has been less explored in battery technology, it is successfully employed in the roll-to-roll fabrication of electronic devices. The highlights of this technique include low-material waste since the deposition is local as well as low-cost given the matured technology. Thus, inkjet-printing can address the drawbacks associated with spray coating for the case of micro-batteries. In addition, inkjet-printing facilitates the use of unconventional substrates such as paper. Here, we show that a common inkjet printer can be used to dispense aqueous inks containing battery's active materials on paper. Besides, in this configuration, the paper has a dual function: a substrate to deposit the active material as well as a separator. We developed a fully-inkjet-printed paper battery that can be tuned to seamlessly integrate with any applications. Furthermore, these batteries are expected to facilitate the recycling- processes that currently rely on exhaustive metallurgical processes. While challenging, developing aqueous ink formulations for the active material will impact the battery assembling processes; eliminating the use of toxic volatile solvents as well as the end-of-life battery cycle. Adopting the inkjet-printing technique for battery assembly can respond to multiple types of applications from small scale (the common printer existing in any household) to industrial scale (roll-to-roll printers.). This method requires ink-formulations for all the battery constituents: active materials, separators, and current collectors. The current battery assembly paradigm relies on casting slurry composed of active materials onto the current collectors. The choice of active materials is done on multiple grounds such as electrochemical potential, Li storage capacity as well as safety and cost. The most common current collectors are Cu, on the negative side, and Al on the positive side.

Herein, we selected commercially available materials, focusing on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)-based anodes and LiFePO_4 (LFP)-based cathodes to exemplify the inkjet-printed paper battery concept, performances, and feasibility. On the one hand, LTO is a spinel-type of material with the insertion of Li ions at 1.5 V vs Li/Li⁺, extensively studied for its exceptional cycling stability due to the low volume variation during Li intercalation process. Despite the low capacity (175 mAh/g compared with 372 mAh/g for graphite), LTO has many advantages in terms of

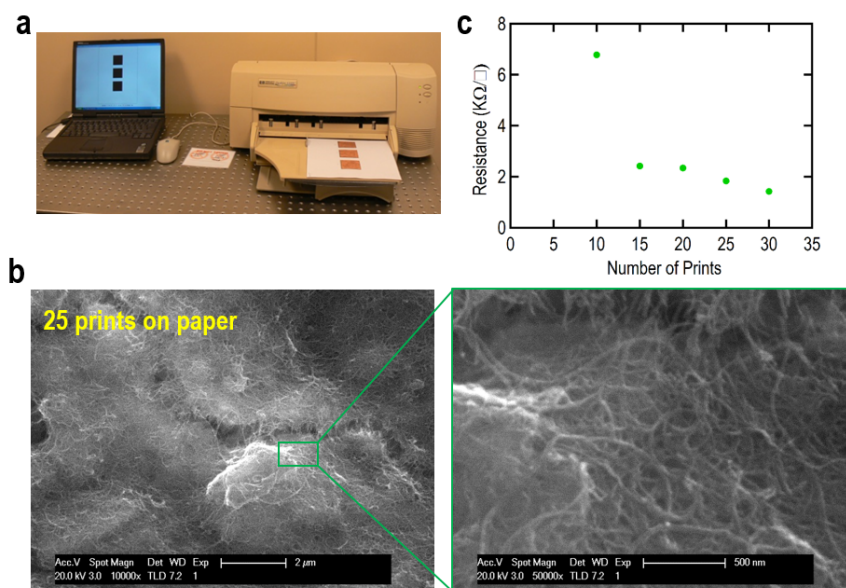


Figure P.1: Experimental setup. (a) The experimental setup used for materializing the concept. (b) Details on the structures of the printed MWCNTs current collectors after 25 prints on paper. (c) The resistance of the deposit is intimately connected with the number of prints. As a compromise between the number of consecutive prints and the value for the electrical resistance, we decided that 15 prints offers a decent value for our application.

cycling stability, which makes it ideal for the evaluation of new battery paradigms. On the other hand LFP, with the insertion potential of 3.4 V vs Li/Li⁺, is particularly attractive due to environmental and cost reasons. The LTO/LPF chemistry is well-known and commercial solutions are available for an extensive range of energy storage systems. Also, as mentioned the Chapter 1, LTO/LFP couple is also the most sustainable due to their long cycling life. For the current collector, we decided on metal-free current collectors, with a commercially available aqueous dispersion of multi-walled-carbon nanotubes. The current collector choice has an impact on the battery weight and rigidity. While Cu paints are also available, they are difficult to stabilize into low-viscosity inks re-

quired for the inkjet-printing. On the same page, Al paints represent a safety hazard and are excluded from our experiments. Figure P.1a presents our custom experimental setup used for evaluating the methods. Figure P.1b presents our results for the metal-free current collectors. While printing graphic material relies only on giving a good impression to the eye, the requirements for printed electronics are, however, different. A current collector needs to be continuous and homogenous to provide an efficient collection. Therefore, consecutive prints are required to obtain a uniform continuous deposit as can be observed in Figure P.1b. Figure P.1c sketches the dependence of the sheet resistance with the number of prints on paper. As a trade-off between the number of prints and the value of the sheet resistance, we chose 15 prints on paper.

On the anode side, we used an aqueous ink formulation with LTO as the main active material together with sodium alginate as the binder, Super P as the carbon conductive additive, and a fluorosurfactant. Although inkjet inks have low viscosity and subsequently require consecutive prints to deposit the active materials, this also allows for precise control over the mass of the deposit, i.e. the anode active material. To find the best anode configuration in terms of cycling capabilities and the number of prints, various scenarios were evaluated. The developed inks require a short ultrasonic treatment after one hour of continuous use. In Figure P.2a we can observe the LTO deposit after 10 prints on thick paper (275 g/m^2). Typically after 10 prints, we have a load of 0.8 mg/cm^2 . Swagelok-type half-cells were assembled to evaluate the electrochemical performance for the anode. The LTO-based electrode is used as working electrode and Li foil is used as the reference and counter electrode. For this situation, the paper is also used as the separator. The cyclic voltammogram from Figure P.2b shows the electrochemical activity for our printed anode. The peak at around 1.4 V on the anodic side corresponds to Li intercalation while the peak at 1.7 V on the cathodic side corresponds to Li deintercalation. Rate capability from Figure P.2c shows that the printed electrode responds to rates up to 2C. The cycling performance for the printed anode is shown in Figure P.2d and P.2e. The printed anode presents good capacity retention upon cycling with little capacity loss during the first cycles.

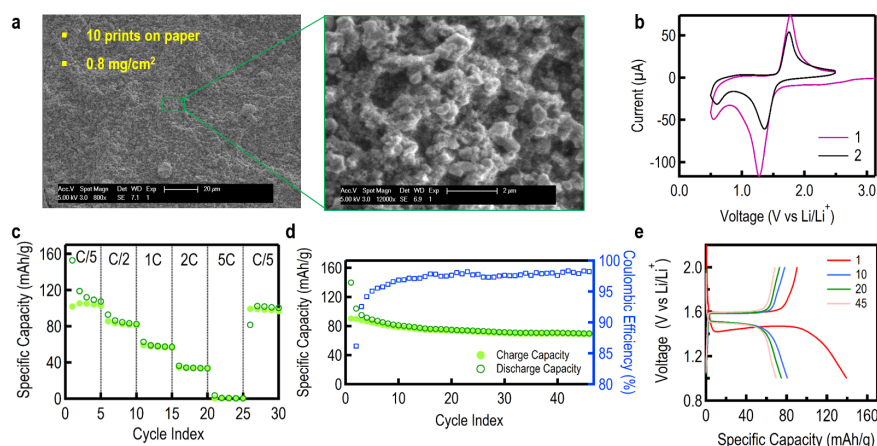


Figure P.2: LTO-based printed anode on paper. (a) SEM micrographs with the uniform LTO deposit after 10 prints. The material load after 10 prints is typically 0.8 mg/cm^2 . (b) The electrochemical activity of the LTO-based anode via cyclic voltammetry. The voltage was swept from the open circuit voltage of the cell down to 0.5 V at a rate of 0.1 mV/s . (c) The cycling behaviour at different C-rates for the LTO printed anode indicates that it responds to rates up to 2C . (d and e) Specific capacity vs. cycle numbers for the LTO/Li half-cell cycled between $2-1 \text{ V}$ vs. Li/Li^+ at a rate of $\text{C}/5$ shows stable cycling with little capacity loss during the first cycles.

LPF-based aqueous ink was produced by ultrasonic mixing of 80% wt% LFP and 20% wt% carbon black conductive additive. Figure P.3a presents details of the LFP-based deposit after 7 prints on paper. After 20 prints we have a load of 1.1 mg/cm^2 . Similar to the LTO prints, subsequent prints are required for a percolative deposit. In this case, both electrical conductivity, as well as active material load, are decisive factors for the required number of prints. Figure P.3b shows a typical cycling voltammogram for the LFP-based printed cathode. Clear cathodic and anodic peaks are present at 3.2 V and 3.7 V respectively, corresponding to Li ions insertion and removal, showing a completely irreversible process. Nevertheless, paper interferes with the electrochemical activity as shown by the high degree of polarization. Interestingly, the rate capability of the printed electrode is quite poor, responding to rates up to 1C (Figure P.3c). This must be related to poor electrical contact

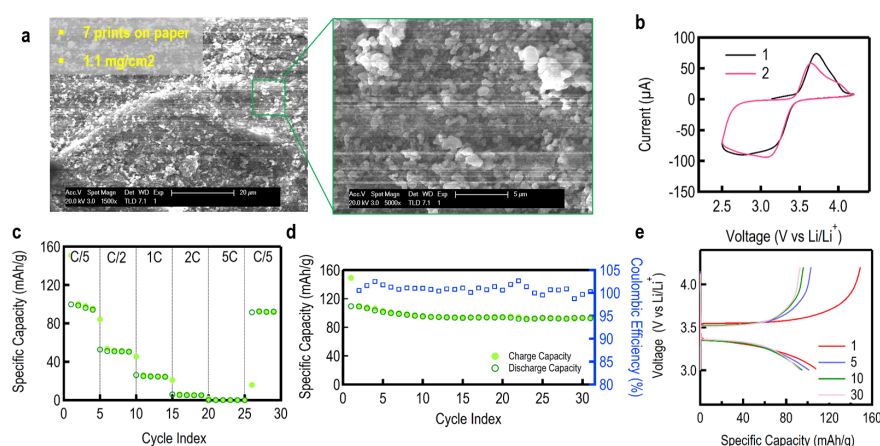


Figure P.3: LFP-based printed cathode on paper. (a) SEM micrographs with the uniform LFP deposit after 7 prints. The material load after 20 prints is typically 1.1 mg/cm^2 . (b) The electrochemical activity of the LFP-based cathode via cyclic voltammetry. The voltage was swept from the open circuit voltage of the cell up to 4.2 V at a rate of 0.1 mV/s. (c) The cycling behavior at different C-rates for the LFP printed cathode indicates that it responds to rates up to 1C. (d and e) Specific capacity vs. cycle numbers for the LFP/Li half-cell cycled between 3–4.2 V vs. Li/Li⁺ at a rate of C/5 shows stable cycling.

between the LFP particles and the conductive additive. Galvanostatic charge-discharge curves of the printed LFP-based cathode display good capacity retention upon cycling as shown in Figure P.3d and P.3e. The performance appears to be stable at a C/5 rate. Printed Li-ion full cells were fabricated by stacking together the two printed electrodes. The cycling rate was adjusted according to the cathode active material load. In this scenario, the separator is formed by the two paper layers on which the LTO-anode and LFP-cathode were printed. The full cell is cycled between 1 and 2.3 V at a rate of C/5. The cycling stability is established by the galvanostatic charging-discharging curves as presented in Figure P.4. The polarization of the curves is attributed to the thick paper separator. This results can be improved by simply printing the two electrodes on different side of the piece of paper while addressing the conductivity issues in the LFP-cathode. Inkjet printing is an attractive deposition

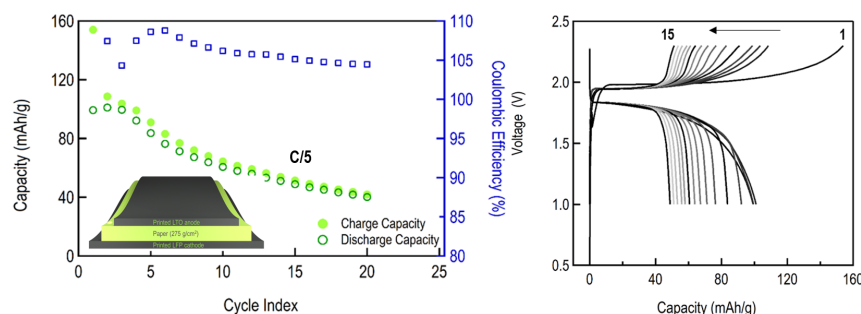


Figure P.4: Inkjet-printed paper battery.

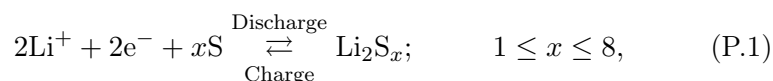
technique for battery technology. Similar to spray coating, the active material load is limited due to electrode kinetic reasons. However, this approach has several benefits. While paper seems to be the substrate of choice for inkjet printing as mentioned earlier, other types of materials can be considered, for instance, textiles. On the other hand, while inkjet printing complements spray coating for size-reduced applications, the printing capabilities cannot be neglected since a commercial, low-cost printer has A3 capabilities. We also expect an improvement in the security of use since any heating process can be avoided as heat dissipation is favorable under these conditions. Furthermore, origami-type techniques can be employed to subsequently reduce the size of the electrodes while increasing the active material load, thus the capacity of the battery. In summary, inkjet printing can be successfully used to subsequently deposit the components of a battery. The active materials can be engineered into aqueous paints, eliminating the commonly used volatile solvents like NMP and the toxicity risks associated with those. The developed inks are stable and can be used for up to 1 hour of continuous printing. A short ultrasonic treatment is required after that. The active material load is simply controlled by the number of prints. Nevertheless, multiple prints are required for a conductive network. These inkjet-printed paper batteries can meet the requirements of numerous size- and shape- sensitive applications. In addition, paper can facilitate battery recycling that currently relies on exhaustive metallurgical processes.

P.3 Li battery 2.0 technology

As discussed previously in Chapter 1, Li is one of the Group 1 metals that love to donate that one valence electron and form positive ions as well as reacting with the elements positioned at his right in the periodic system of elements. Thus, the highest energy densities theoretically possible are obtained by associating Li with the elements from further right, eliminating the noble gases, from Group 16 and 17. Of course, from Group 17, Cl, Br, I and At are not taken into consideration today due to their toxicity, cost, and availability; leaving only F that it is currently studied as lithium-metal fluoride battery as discussed in Section 1.3.1. From Group 16, only O₂ and S are considered promising electrode materials as discussed next. The Ragone plot from Figure 1.2b clearly shows the energy density promise of Li-air and Li-S technologies.

P.3.1 Li-sulfur systems

Sulfur is generally considered abundant and safe thus can drive the next-generation of batteries towards not only lower cost but also high energy density, promising a theoretical capacity of 1675 mAh/g. Of course, whether or not it will be commercially adopted as Li 2.0 depends on addressing many troubling aspects associated with conversion chemistry and S electrochemistry. In its simplified form, a Li-S cell involves a Li metal anode that will be oxidized during discharge coupled to a S cathode that is reduced to lithium polysulfides (Li₂S_x; 1 ≤ x ≤ 8) (LiPSs). Figure P.5a illustrates the basic components and functioning of Li-S cells. Li-S mechanism relies on the reversible reaction:



that leads to the formation of long-and short-chain, soluble and insoluble forms of lithium polysulfides (LiPSs) as shown in the representative charge/discharge curves for Li-S system from Figure P.5a.

On the cathode side, the first issue surrounding Li-S arises from the fact that Li₂S_x phases are insulating. Cycling of a battery requires an

electron conductive framework thus C was introduced in the electrode formulation under different configurations such as meso- and microporous carbon framework carbon fibers and nanotubes or porous hollow structures [163–166].

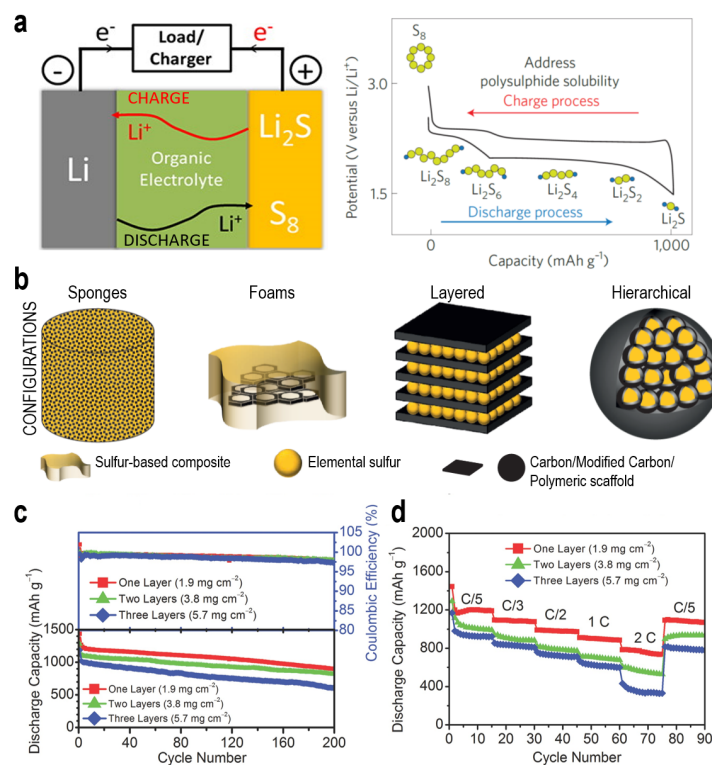


Figure P.5: Li-S battery technology. (a) Electrochemical process in a Li-S system. Adapted from [166,167]. (b) Cathode architectures for high S loading. Adapted from Ref. [168]. (c) Electrochemical and (d) rate performance for a layered S structure. Adapted from [169].

On the one hand, the LiPSs are highly soluble in the electrolyte which enables the Li-S system to function as a liquid cathode or a catholyte and allows the Li-S system to achieve very high rate capability due to the fast kinetics compared with the solid-solid redox reaction. Indeed, a high energy density Li-S system requires a flooded cell or a high electrolyte/sulfur ratio since its functioning relies on the dissolution of LiPSs

and requires sufficient electrolyte for this purpose ($> 20 \mu\text{l mg}^{-1}$) [170]. On the other hand, the dissolution of LiPSs is also regarded as a crucial matter since it gives rise to a shuttle mechanism that can damage the performance of the cell. Since, at the anode, higher oxidation states of Li_2S_x ($3 \leq x \leq 6$) are reduced to lower LiPSs which are then transported back to the cathode where they are re-oxidized and then sent back to the anode to be reduced and so on. Problems arise with the formation of the insoluble and insulating forms of Li_2S and Li_2S_2 that can passivate the Li metal anode resulting in high impedance and over polarization at first and, ultimately, cell death. The cathode architecture was modified accordingly to physically trap LiPSs and limit the shuttling-induced damages, by engineered C-based assemblies and superstructures as shown in Figure P.5b and c, 1st Configuration, that encapsulates S and limits the LiPSs shuttling. Due to low molecular interaction between C and LiPSs, LiPSs diffuse out of the cathode and ultimately reach the Li anode with ravaging effects. In this sense, recent strategies are focused on materials that chemically anchor LiPSs thus, present stronger chemical interactions with LiPSs. For instance, a polar host material can absorb the polar LiPSs and reduce the phenomena related to LiPSs shuttling. This can be obtained via N-activated carbons and graphenes, reduced graphene oxides or functional polymeric materials. Metal-organic frameworks (MOFs) interact in the form of Lewis acid-base bonding with the highest bonding energy with LiPSs but their insulating nature limited their application as host material [168, 171]. Finally, another research direction to minimize transport of LiPSs relies on organo-sulfur based polymers with S-S linkage. In other words, polymers that will polymerize to form an insoluble LiPSs form. However, the resulting polymers have poor kinetics requiring a conductive C matrix that dramatically reduced the loading of active material [172].

Li-electrolyte interface is also particularly challenging since, if left unprotected, LiPSs reach Li via the electrolyte where they are reduced and form insoluble LiPSs resulting in high surface impedance, overpolarization, and low Coulombic efficiency. In addition, during charge, partial oxidation of these species are also responsible for the shuttling effect as discussed above. As a matter of fact, this LiPSs dissolution

is also responsible for the self-discharging. Since Li_2S_x are extremely reactive and well known to get involved in reactions with most common electrolyte solvents via many reaction mechanisms such as nucleophilic, basic or radical, it appears that Li-S systems are restricted to some ethers such as dimethoxyethane (DME) or tetraethylene glycol dimethyl ether (TEGME) [167, 168, 173]. Dioxolane (DOL) is typically used as a co-solvent for its low viscosity and Li metal passivating qualities. LiTFSi is usually used as the salt. Generally speaking, the Li-S electrolyte has to partially allow the solvation of LiPSs and to generate a stable SEI on the Li metal, to have a low reactivity with Li, which limits the electrolyte decomposition. Redox mediators, in particular when Li_2S is used as active material, and room-temperature ionic liquids have also been found to facilitate the electrochemical processes [174, 175].

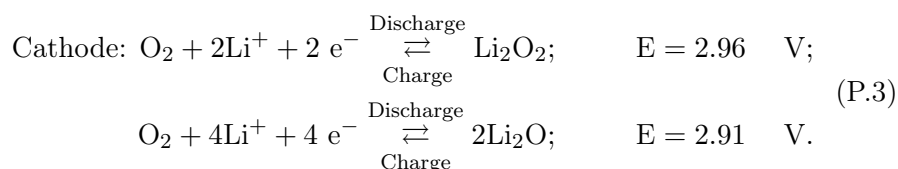
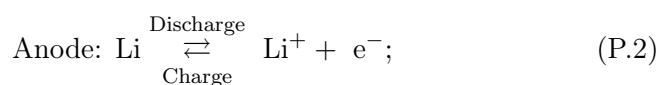
Si anodes can increase safety in the functioning of the Li-ion-sulfur system, eliminating the dendrite problem of Li metal. However, in such systems the Li reservoir is limited and the irreversible Li consumption during SEI formation requires an overcompensated Li_2S cathode or an extra Li ion source. The gap between the requirements for such systems and the current status of Li-S system was statistically analyzed and discussed in [176].

P.3.2 Li-air systems

Li-air uses O_2 as fuel at the positive electrodes having the highest theoretical specific energy. However, it relies on two challenging electrodes, Li-metal and O_2 . Since O_2 is freely available, accounting for 21% of the breathable air, the idea of taking O_2 from the air flourished, thus, the Li-air concept was born. The Li-air concept is still in infancy with many understanding gaps in the underpinning chemistry and electrochemistry. Li-air and Li- O_2 can not be used interchangeably. Most reported experimental work use O_2 rather than air to avoid any parasitic reactions triggered by water or nitrogen or any other contaminants present in the air. Thus, for an efficient Li-air system all these contaminants should be neutralized which remains a significant challenge. One research direction involves the integration of O_2 diffusion membranes to

selectively deliver the O₂ rich gasses to the cathode while retaining other gasses. LiO₂, as first proposed by Abraham, was in a non-aqueous form where the Li metal and a high specific surface carbonaceous electrodes are separated by a solid polymer electrolyte based on polyacrylonitrile (PAN) and comprising LiPF₆. On the cathode side, an O₂ permeable membrane is provided as shown in Figure P.6a. Current research directions revolve around several chemical architectures stemming from the choice of the electrolyte as shown in Figure P.6. These include a non-aqueous (aprotic) system as proposed by Abraham (Figure P.6b), an aqueous (protic) one (Figure P.6c) and a mixed system that requires an aqueous electrolyte on the cathode side and an organic electrolyte on the anode side (Figure P.6d). Solid-state Li-air concept has also been evaluated in association with ceramic-based electrolytes. Ultimately, the battery chemistry depends on the electrolyte wetting the cathode side. While each configuration has some advantages, the associated challenges are too substantial, thus, for the moment, the optimal configuration remains an open question. Above all, at the core of Li-air concept lie the oxygen reduction (ORR) and oxygen evolution reactions (OER).

Aprotic Li-O₂. As shown in Figure P.6a and b, the system comprises a Li metal, a porous O₂ absorbing cathode composed of a high specific surface carbonaceous material decorated with catalyst particles, wetted by a Li salt in an aprotic solvent. Generically speaking the principle is the same. During discharge, Li metal is oxidized with the electrons flowing through the external circuit and the resulting Li cations reduce the O₂ to form Li₂O₂ and possibly, Li₂O:



The formation of Li₂O would increase the stored energy since two times more Li reported to O is stored, however, the reaction is not readily reversible.

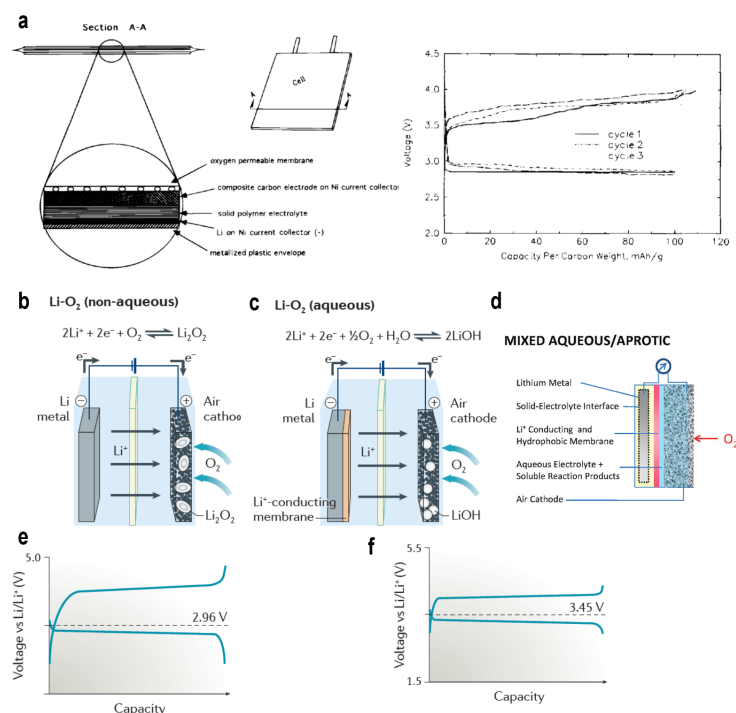
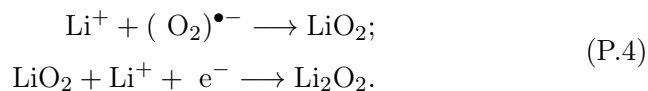


Figure P.6: Li-air battery technology. (a) Li-O₂ system proposed by Abraham. Adapted from Ref. [177]. (b) Sketch of Li-O₂ non-aqueous configuration. (c) Sketch of Li-O₂ aqueous configuration. Adapted from Ref. [24]. (d) Mixed aqueous/aprotic Li-O₂ configuration. From Ref. [178]. (e) Charge-discharge profile for Li-O₂ non-aqueous. (f) Charge-discharge profile for Li-O₂ non-aqueous. Adapted from Ref. [24].

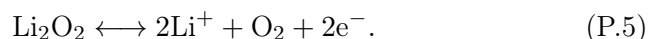
During the charge or when an external potential is applied, the peroxide is decomposed with Li plated on the anode and O₂ being generated. The solid line from Figure P.6e shows a typical charge/discharge curve of an aprotic Li-O₂ cell. The deviation from the thermodynamic potential (open circuit voltage) or the overpotentials is dictated by the cathode reactions. It was shown that the O₂ reduction mechanism that leads to the formation of Li₂O₂, at discharge, follows different formation pathways as dictated by the solvent's ability to solvate cations *i.e.* solvent donor number. First, O₂ undergoes one-electron reduction forming LiO₂ distributed either on the electrode surface, as LiO₂, or in the electrolyte

as Li^+ , O^{2-} , ion pairs or clusters as in typical aprotic solvents.

Discharge (two-step reaction):



Charge (one step reaction):

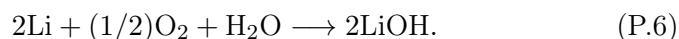


In high donor number (DN) solvents, such as dimethyl sulfoxide (DMSO) or methylimidazole (Me-Im), LiO_2 is found under the dissolved form while with low DN solvent, such as DME, on the electrode surface. From here, LiO_2 undergoes a subsequent one-electron reduction to form Li_2O_2 . Thus, in low DN solvent the insulating Li_2O_2 grows on the electrode eventually leading to the death of the cell. Specifically, a thickness of around 5 nm of Li_2O_2 can reduce or shutdown the electrochemical activity. In high DN, most Li_2O_2 grows from the solution and further precipitate in the cathode. This ultimately altered the cathode design from high specific surface materials into electrodes with large pores capable of accommodating large Li_2O_2 particles. Secondly, the charging mechanism or the Li_2O_2 oxidation to O_2 also presents its challenges since it requires the oxidation of large particles of insulating materials. Furthermore, any attempts at describing this mechanism were polluted by the parasitic reactions tied to electrolyte or electrode. Pre-loaded electrodes of the crystalline Li_2O_2 helped distance the oxidation from the side reactions highlighting the importance of the surface chemistry of the cathode to support electron transfer. To help with this, oxidation mediators or oxygen evolution catalysts have been introduced in the electrolyte formulation. These molecules are oxidized at a potential higher than the formation potential of Li_2O_2 and will further oxidize the Li_2O_2 particles. Redox mediators are also common in LIB as over-charge protection agents. Among the first in this direction were TTF and TEMPO followed by many more investigated as exhaustively listed in Reference [179]. Electrolytes comprising organic carbonates were the first choice due to their high oxidation stability and availability. Nonetheless, the O_2 reduction that leads to the formation of Li_2O_2 through a

series of intermediate reaction that include the formation of a highly reactive oxygen anion O_2^{*-} that was shown to be responsible for the electrolyte degradation via nucleophilic attacks during discharge with the formation of Li propyl carbonates, Li carbonates, CO_2 , H_2O_2 and so on [167]. Thus, the reversible cycling reported in aprotic Li-air comprising carbonates-based electrolyte studies was attributed to the cycling of the electrolyte degradation products rather than the formation of Li_2O_2 . As a matter of fact, the electrolyte stability is the most challenging part of the Li- O_2 considering the highly reactive functioning conditions. Generally speaking, polar aprotic solvents are not stable during the reduction of O_2 to Li_2O_2 due to the parallel formation of highly reactive reduced oxygen species that can undergo a plethora of side reactions with these solvents. Promising results were reported for other types of electrolytes, in particular, ethers such as DME or polymer electrolytes such as PEO. Similar challenges are on the cathode side also; C which was typically used undergoes a parasitic reaction with Li_2O_2 during cell operation at oxidative potentials, with CO_2 evolution. Passivation with Al_2O_3 coatings were also investigated to protect the C surface. Finally, TiC was also identified as more cycling reliable than carbon since it was found to form a TiO_{2-x} passivation layer which prevents further oxidation. Overall, the viability of the aprotic Li-air technology relies on solving some serious issues such as electrolyte decomposition, high overpotential for ORR (at discharge) and OER (at a charge), carbon decomposition of the air electrode and the issues associated with Li metal exposed to air.

Aqueous Li- O_2 . On the one hand, in these systems, water ingestion is no longer an issue unlike the aprotic Li- O_2 where water can induce unwanted by-products from parasitic reactions that will damage the performance of the cell. Additionally, the water also alleviates the safety concerns associated with organic electrolytes. Another benefit of this system is that the discharging product, LiOH, can be stored in the electrolyte, up to a certain limit, whereas Li_2O_2 growth leads to cathode clogging and high overpotentials. On the other hand, such type of aqueous system was possible only after the development of water isolating, Li^+ conducting membrane to protect the highly reactive Li metal anode from the aqueous electrolyte. In fact, an artificial ceramic SEI, a LISI-

CON type ($\text{LiM}_2(\text{PO}_4)_3$, $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$), typically coats the Li metal. Nevertheless, since the electrochemical mechanism of the aqueous Li- O_2 cell is different than the aprotic Li- O_2 , the cell capacity is rather small. The discharge follows:



LiOH has a solubility limit in the electrolyte at a 5.3M (12.8 g_{LiOH} in 100 g_{H₂O}) corresponding to a capacity of 170 mAh/g. Thus, the concentration of OH^- will increase with the depth of discharge and will eventually precipitate when the saturation LiOH limit is reached. Similar with Li_2O_2 growth, such precipitates can clog the air electrode and block O_2 diffusion. To overcome this saturation barrier, aqueous Li- O_2 adopted a flow cell design where the electrolyte is continuously replenished, thus, the precipitates are mechanically removed. Otherwise, to increase the capacity LiOH needs to be stored in the cell while circumventing any damage on the Li anode and the air cathode. LiOH precipitation outside the cathode was possible with the induction of an anion exchange membrane at the air-electrode/electrolyte interface that basically blocks the Li^+ from diffusing inside the air electrode avoiding the LiOH formation in the air cathode. Now, regarding the O_2 reduction to LiOH, it is based on the cleavage of the O-O bond that requires a Pt catalyst. The OER, for that matter, also requires a catalyst. It turns out that finding a bifunctional catalyst is quite difficult. Therefore, using a third electrode for O_2 evolution is an interesting solution since different catalysts can be employed for different electrodes. Finally, acidic electrolytes have also been explored for aqueous Li- O_2 , for instance based on H_2SO_4 or acetic acid, however, they will eventually become alkaline with prolonging cycling. Perhaps the biggest challenge in realizing an aqueous Li- O_2 system is to protect the Li anode. It turns out that the artificial ceramic SEI is not stable in contact with Li thus, another buffer such as PEO-LiTFSi-BaTiO₃ separates the Li metal from the ceramic-based SEI developed by Visco. Despite these efforts, Li metal corrosion could not be prevented, thus, mixed aprotic-aqueous Li- O_2 systems were developed as shown in Figure P.6d. The aprotic electrolyte is on the Li side while the aqueous part is on the air electrode so that the aqueous elec-

trolyte chemistry is preserved for the mixed systems. The two electrolyte systems are separated by a Li^+ conducting membrane.

Without a doubt, the Li-air systems require much effort and fundamental research since, from a practical standpoint, they are still in infancy and possibly offering an exciting playground for nano-Si-based anodes.

This thesis has contributed a number of nanostructuring techniques and electrode designs to the field of lithium-ion batteries and beyond.

Nano-Si by metal assisted chemical etching

For this work, we developed three types of nanostructures: silicon nanowires (SiNWs), silicon nanopillars, and kinked silicon nanowires (k-SiNWs).

Metal assisted chemical etching of Si (MACE) requires first the colloidal lithography to define the regions where Si will be etched and, second, the metal assisted chemical etching in an electrolyte comprising HF and H₂O₂.

Table [A.1](#) gives the listing of the parameters used for the etching procedure for each type of nanostructure.

Parameters				
No.	Step name	SiNWs	Si nanopillars	k-SiNWs
1	Si standard cleaning	10 min ultrasonic treatment in acetone 10 min ultrasonic treatment in propanol Blow dry N ₂		
2	PS spheres assembling	(i) 2 min 8 sec O ₂ Plasma @ 25 W, 2 mbar (ii) PS 260 nm suspension: • 15 μ l PS 260 • diluted suspensions: • 15 μ l 1% styrene in ethanol • 60 sec spin coating @ 1000 rpm & 1000 rpm/sec • 45 μ l ethanol (iii) Left to dry outside (ii) PS 260 nm suspension: • 15 μ l PS 260 • 15 μ l 1% styrene in ethanol • 45 μ l ethanol		
3	Reactive Ion Etching	3 min ^a @ 30 W, 30 sccm O ₂ & 1 sccm SF ₆ , 10 mtorr	30 sec @ 30 W, 30 sccm O ₂ & 1 sccm SF ₆ , 10 mtorr	From 2 min 45 sec to 3 min 15 sec @ 30 W, 30 sccm O ₂ & 1 sccm SF ₆ , 10 mtorr
4	E-beam noble metal deposition	1 nm Ti ^b 30 nm Au	1 nm Ti 30 nm Au	10, 15, 30 nm Au

^aSEM inspection is required
^bRequired as adhesion layer for Step 5

Parameters			
No.	Step name	SiNWs	Si nanopillars k-SiNWs
5	Lift-off PS spheres		Blue tape lift-off Overnight stay in CH ₂ Cl ₂
6	Metal Assisted Chemical Etching	0.1M H ₂ O ₂ and 4.8M HF 3 h 30 min etch time @ RT, stir @ 150 rpm	0.2M H ₂ O ₂ and 4.8M HF 5 to 15 min etch time @ RT, stir @ 150 rpm 1.3M H ₂ O ₂ and 14M HF 5, 3, 2 min etch time @ RT, 1 min quench in methanol Etch-quench sequences
7	Chemical Peeling	1M H ₂ O ₂ and 4.8M HF 10 min etch time @ RT, stir @ 150 rpm	8.3M H ₂ O ₂ and 4.6M HF 3 min etch time
8	Rinsing		10 min in DI water
9	Au removal		5 min submersion in HNO ₃ :HCl (1:3 v:v) Rinsed in deionized water
10	SEM inspection		

Table A.1: Nano-Si by metal assisted chemical etching

Electrochemistry procedures

Galvanostatic measurements. The electrochemical performances were recorded using a battery analyzer (Arbin Instruments). Coin-cells were assembled with either pristine k-SiNWs-based assembly or Ni-coated k-SiNWs-based assembly as the working electrode and Li metal foils as counter and reference electrodes. The electrolyte systems used were 1M LiTFSi in PYR₁₃FSi (Solvionic) and 1M LiPF₆ in EC:DEC (2% VC) (Solvionic). The separator was a Celgrad membrane for the organic electrolyte and a glass micro-fiber disk (Whatman GFD) for the ionic liquid electrolyte. The galvanostatic charge-discharge curves were recorded between 0.02 to 2 V vs Li/Li⁺. The half-cells were discharged (lithiated) and charged (delithiated) at different current densities as indicated throughout the main text.

Electrochemical impedance spectroscopy. The electrochemical impedance spectra were acquired using a CHI 660 B analyzer. Coin cells assembled as previously described were excited with a 5 mV AC signal with a frequency range of 100 kHz - 1 Hz was superimposed on the OCV of the cell. The cells were evaluated as assembled and after 20 cycles in the delithiated state.

Ex-situ experimental protocol for studying the morphology evolution during Li insertion and removal. Swagelok-type half-cells were assembled inside an Ar-filled glove box (MBraun) by stacking either pristine SiNPs or Ni coated SiNPs on the Si substrate, a separator (Celgrad) soaked in electrolyte (1 M LiPF₆ in EC:DEC 1:1 by volume, Novolyte) and Li foil (Sigma-Aldrich). A slow voltammetry scan (0.1

mV/s) was performed from the open circuit voltage of the cell down to 10 mV vs. Li/Li^+ . The potential was held for at least 6 hours to ensure the deep lithiation conditions. After lithiation, the cell was disassembled in the glove box and the sample rinsed in acetonitrile (Sigma-Aldrich) to remove any surface residues. The lithiated sample was then placed in an Ar-filled container to have a minimal exposure to the environmental air and then transferred for inspection by scanning electron microscopy.

Electroless Ni bath composition

Components	Supplier	Observations
2 g nickel sulfate hexahydrate	Sigma-Aldrich	Ni source
1 g sodium citrate	Sigma-Aldrich	complexant
0.5 g lactic acid	Sigma-Aldrich	Ni ions buffer
0.1 g dimethylamine borane	Acros Organics	reducing agent
50 ml deionized water	In-house production	deposition medium

Table C.1: Electroless Ni bath composition

The pH of the mixture from Table C.1 was adjusted to 7 with ammonium hydroxide. The electroless deposition of Ni was carried at room temperature under continuous agitation. The onset of the deposition was visually identified by the appearance and evolution of gas bubbles at the surface of the samples. After this point, the soaking time varied from 10 to 120 minutes depending on the target coating thickness. After the deposition, the sample was rinsed in water and methanol and let dry in air.

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