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CHARACTERIZATION OF POLYMERIC BINDERS FOR SILICON ANODES IN
NEXT-GENERATION LITHIUM-ION BATTERIES

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Abstract

This doctoral research focuses on the development, characterization, and industrial transfer of advanced polymeric binders for silicon-based composite anodes in next-generation lithium-ion batteries (LIBs). Silicon is a highly promising alternative to graphite due to its theoretical capacity of ~ 4200 mAh/g, nearly ten times higher than that of graphite (372 mAh/g). However, its use is limited by the severe volumetric expansion upon (de)lithiation, leading to particle cracking, unstable SEI formation, and rapid capacity fading.

The scientific framework supporting these challenges is discussed in Chapter 1, which introduces lithium-ion battery fundamentals and performance requirements, followed by a detailed description of cell components, including electrolytes, cathode materials, and graphite-based anodes (Sections 1.2.1–1.2.3). The chapter then focuses on silicon-based anode materials (Section 1.3), analysing their advantages and intrinsic limitations. The transition from Si/C to SiO_x -based composites (Sections 1.3.1–1.3.3) is emphasized, highlighting how the oxide matrix and carbon coating buffer mechanical stress, stabilize the SEI, and enhance processability. Among them, Li-doped and Mg-doped SiO_x @C composites emerge as promising scalable materials combining high capacity with mechanical resilience.

Recognizing that the active material alone cannot guarantee electrode stability, Section 1.4 explores the key role of polymeric binders in ensuring cohesion, adhesion, and interfacial integrity within the electrode. The binder influences the overall rheology, mechanical strength, and electrochemical compatibility of the anode. Within this context, a family of poly(acrylic acid) (PAA)-based linear terpolymer binders developed by *Syensqo Specialty Polymers S.p.A.* was investigated to achieve optimized processability and cycling stability. The research strategy (Section 1.5) integrates laboratory-scale studies with pilot-scale validation to correlate binder chemistry, slurry rheology, adhesion, and electrochemical performance.

Chapter 2 presents the materials and experimental methods used at both scales. It first describes the chemical structure and functional features of the binders, then the active materials, Li– SiO_x @C and Si/C at laboratory scale, Mg– SiO_x @C at pilot scale, and the carbon conductive agents ensuring electronic percolation. The cell configuration adopted for electrochemical testing is also detailed, specifying the NCM-based cathode, separator,

and electrolyte formulation. Section 2.1 outlines lab-scale electrode preparation, from slurry formulation to coating, drying, and characterization. The rheological, mechanical, and electrochemical properties were analysed to assess binder compatibility.

Section 2.2 covers pilot-scale processing, including slurry mixing (2.2.1), roll-to-roll coating (2.2.2), and final electrode preparation (2.2.3), followed by TEM microstructural characterization (2.2.4) and 1 Ah pouch cell assembly and testing (2.2.5), linking laboratory optimization to industrial validation. Chapter 3 presents the experimental results.

Section 3.1 focuses on laboratory-scale investigations, encompassing slurry rheology, coating quality, adhesion, and half-cell cycling. Four binder generations, SBR/CMC, Generation 1, Generation 3, and Generation 3 acidic, were compared, differing in molecular weight, pH, and branching degree. Each was evaluated with Li-SiO_x@C and Si/C to assess binder-particle interactions and surface affinity. All slurries exhibited shear-thinning behaviour and high homogeneity, confirming good dispersion. The Syensqo terpolymer binders provided stable viscosity profiles within the industrial process window.

Peel tests showed that Generation 3, especially the acidic variant, achieved the highest adhesion strength, surpassing both SBR/CMC (industrial benchmark) and Generation 1. This improvement derives from the optimized balance of acid-base groups and molecular interactions with copper and active particles. Hence, Generation 3 and Generation 3 acidic were identified as the most suitable candidates for scale-up.

Comparing the two active materials (Section 3.2), Li-SiO_x@C displayed superior dispersion and uniform coating due to its carbon-coated oxide matrix and partial prelithiation, which stabilize the SEI and minimize irreversible capacity loss. In contrast, Si/C slurries exhibited higher viscosity variability and lower adhesion uniformity, consistent with a more heterogeneous surface chemistry. Electrochemically, Li-SiO_x@C electrodes retained higher stability and lower impedance growth, while Si/C suffered from accelerated degradation. Based on these results, Li-SiO_x@C was selected for pilot-scale validation, using Generation 1 and Generation 3 as binders.

Section 3.3 details the pilot-scale production, encompassing planetary mixing, reverse comma-roll coating, drying, and calendaring. During early trials, gas evolution was observed due to Li₂O/Li₄SiO₄ reacting with water or binder acidity, causing coating inhomogeneities. Replacing the active material with Mg-doped SiO_x@C resolved the issue by eliminating gas formation, while maintaining comparable electrochemical properties.

The Mg–SiO_x@C-based slurries yielded defect-free coatings and stable film morphology, confirming their industrial suitability.

Section 3.3.1 presents microstructural analyses performed via TEM and EDS. Results revealed a continuous polymer film bridging graphite and Mg–SiO_x@C particles, ensuring strong mechanical integrity. Elemental mapping confirmed the homogeneous distribution of magnesium and binder-derived oxygen and carbon, validating effective doping and interfacial bonding.

Electrochemical results from 1 Ah pouch cells (Sections 3.3.2–3.3.5) demonstrated that electrodes containing Generation 3 binder showed superior cycling stability, lower resistance growth, and better thermal dimensional stability than those with Generation 1 or SBR/CMC. At 60 °C storage, the swelling ratio remained stable, reflecting excellent mechanical cohesion and minimal gas generation. These findings confirm that the Generation 3 binder offers an optimal balance between mechanical flexibility and electrochemical robustness, sustaining electrical contact without delamination.

Chapter 4 synthesizes the main outcomes, establishing that binder molecular design is the decisive factor linking slurry processability to long-term electrode stability. The integration of polymer chemistry, electrode engineering, and processing control enables a unified understanding of how binder molecular architecture governs macroscopic behaviour. The Generation 3 binder, in combination with SiO_x@C composites, achieved the best compromise between rheology, adhesion, and cycling durability, demonstrating compatibility with large-scale electrode production.

Finally, this work lays the foundation for advanced investigations on the structure–property–performance relationship of binders under real operating conditions. Future studies will employ in-situ dilatometry, operando impedance spectroscopy, and surface-sensitive techniques (XPS, ToF-SIMS) to elucidate SEI evolution and mechanical degradation pathways.

In conclusion, this doctoral research provides a comprehensive framework connecting molecular-scale binder design to electrode- and cell-level performance. By bridging laboratory research and pilot-scale validation, it offers a practical route toward the industrial implementation of next-generation silicon-composite anodes for high-energy-density lithium-ion batteries.

1. Introduction

This chapter provides a brief overview of one of the most widely used energy storage systems: lithium-ion batteries. It introduces their fundamental role in modern energy applications and sets the stage for the following chapters, which will explore in detail the key components and materials used for these batteries.

1.1. Lithium-ion battery overview: an electrochemical energy storage systems

Lithium-ion batteries (LIBs) are one of the most widely used and significant energy storage technologies, powering a broad range of applications from small portable devices like smartphones and laptops to electric vehicles (EVs) and large-scale energy storage systems for renewable energy [1]. Their widespread adoption is primarily due to several key advantages, such as: *high energy density*, where LIBs offer significantly greater energy storage per unit mass and volume compared to previous chemistries; *long cycle life*, since they can undergo hundreds to thousands of charge-discharge cycles with relatively low capacity fade. [2-5] Moreover, other two key points are: *low self-discharge*, in fact LIBs retain their charge over a long time, which is particularly beneficial for mobile and standby applications and *lightweight and compactness*, essential for applications where size and weight constraints are critical. [6] Despite these advantages, lithium-ion batteries still suffer from important limitations as:

- *safety concerns*: the use of flammable organic electrolytes and high-energy materials can lead to thermal runaway, especially under particular conditions; [7]
- *limited raw materials*: the extraction and supply of specific materials (lithium, cobalt, and nickel) face environmental, geopolitical, and economic challenges; [8]
- *performance degradation*: capacity fading and resistance growth over time reduce the effective lifespan;
- *recycling complexity*: the recycling of LIBs needs development of more sustainable systems, since it remains technologically and economically challenging.

Since their commercial introduction in the early 1990s, LIBs have undergone significant technological advancements, evolving through successive generations of material and design innovations. [9] This progression has been driven by the increasing demand for high-performance energy storage systems. The evolution of LIBs can be categorized into three main technological generations (Figure 1), each characterized by advancements in materials chemistry, energy density, safety, and sustainability. [10]

	Cell generation	Cell chemistry
Post Li-ion	Generation 5	Li/O ₂ (lithium-air)
	Generation 4	All-solid state with Li metal as anode
Advanced Li-ion	Generation 3b	• Cathode: High Energy NMC, High Voltage Spinel—5 V • Anode: silicon/carbon
	Generation 3a	• Cathode: NMC622 to NMC811, LFP • Anode: carbon (graphite) + silicon composite
Li-ion	Generation 2b	• Cathode: NMC523 to NMC622 • Anode: carbon
	Generation 2a	• Cathode: NMC111 • Anode: 100% carbon
	Generation 1	• Cathode: LFP, NCA • Anode: 100% carbon

Figure 1. Several LIBs generation development over years [11]

Considering the typical architecture of a lithium-ion battery (LIB) (Figure 2) based on reversible redox reactions occurring between a positive electrode (cathode) and a negative electrode (anode), few considerations were taken into account for the development of next-generations LIB.

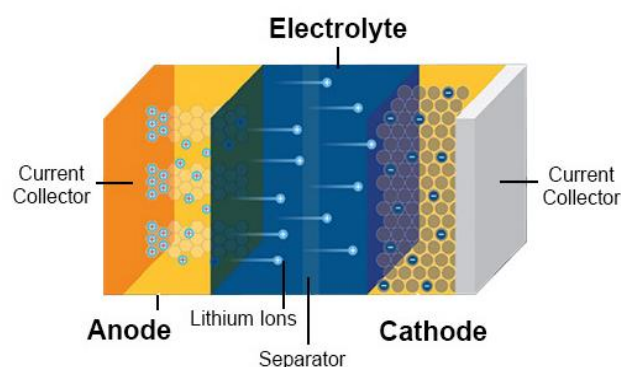


Figure 2. Schematic representation of a lithium-ion battery cell showing the anode, separator, cathode, electrolyte, current collectors, and the transport of lithium ions through the electrolyte/separator.

The *first generation* relied on cathodes such as LiCoO_2 (LCO) [12], LiFePO_4 (LFP) and LiNiCoAlO_2 (NCA) [13], paired with 100% graphite anodes. Operating typically within a voltage range of 3.0 - 4.2 V, these batteries provided stable and reversible electrochemical performance, making them ideal for portable consumer electronics. However, they also exhibited notable limitations, including safety concerns related to the thermal instability of LiCoO_2 at high states of charge, high material costs due to cobalt content [14], and a relatively modest capacity constrained by the graphite anode's theoretical limit of 372 mAh/g. [15] In response to these challenges, the *second generation* of lithium-ion batteries emerged in the early 2000s, introducing more cost-effective and thermally stable cathode chemistries. Layered oxides such as $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) [13,16] and LiNiCoAlO_2 (NCA), spinel structures like LiMn_2O_4 [17-19], and olivine-based materials such as LiFePO_4 began to replace or complement LiCoO_2 . [20,21] [22-24] These new materials offered improved safety profiles, reduced reliance on cobalt, and enhanced capacity retention over extended cycling.

Despite these advances, the graphite anode remained a limiting factor in the demand for higher energy density, motivating further innovation. [25,26] This demand led to the *third generation* of lithium-ion batteries, which focused on enhancing anode performance. [27,28] The incorporation of high-capacity materials such as silicon (Si), silicon oxide (SiO_x), and silicon-carbon (Si/C) composites aimed to overcome the limitations of graphite [29]. Silicon, in particular, offers a theoretical specific capacity of approximately 4200 mAh/g, an order of magnitude higher than that of graphite. [30] However, the practical implementation of silicon-based anodes is challenging due to a significant volume expansion, up to 300% during lithiation, which leads to mechanical degradation, electrode pulverization, and unstable SEI formation. [31] These issues result in rapid capacity fading unless mitigated by strategies such as nano structuring, composite design, flexible binders, and tailored electrolyte systems. The third generation represents the current state-of-the-art in commercial lithium-ion battery technology, with continued development focused on achieving higher energy densities, longer cycle life, and safer operation under demanding conditions.

To provide a comprehensive comparison of the electrochemical performance of various electrode materials used across different generations of lithium-ion batteries, a Ragone plot is presented in Figure 3 [32]. This plot visually highlights the trade-off between energy density and power density for a selection of commonly employed cathode and anode

materials [33]. Cathode materials such as LiFePO_4 (LFP), LiCoO_2 (LCO), NMC families (NMC111, NMC622, NMC811), and high-voltage spinels (e.g., $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$) [34,35] are compared with anode materials like graphite, lithium titanium oxide (LTO), silicon (Si) and silicon composites. [36] As shown in figure 3, graphite is positioned at relatively low anode capacity values (~ 372 mAh/g) with a lithiation potential close to 0.1 V vs. Li/Li^+ , which enables a high operating voltage of the full cell when coupled with common layered oxide cathodes. Moreover, graphite remains a widely used anode material due to its excellent cycling stability, though its limited capacity constrains further improvements in energy storage. [37,38]

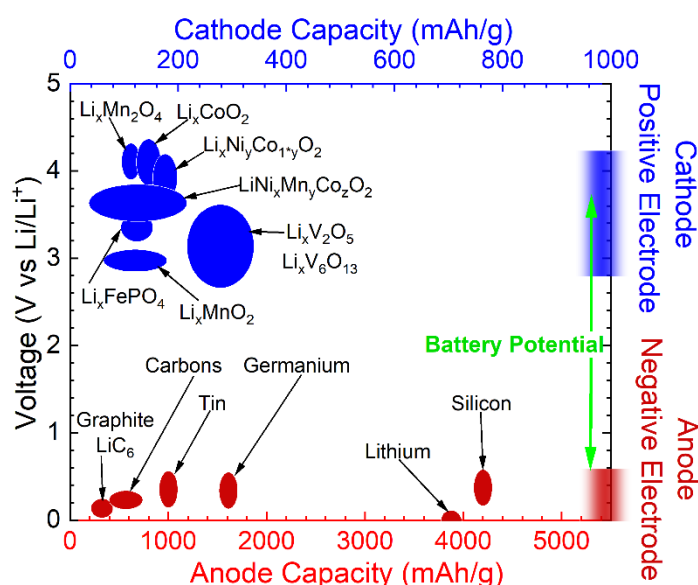


Figure 3. Ragone plot of representative anode and cathode materials employed in lithium-ion batteries across three technological generations (rearranged from [38]).

Since battery research continues its progress, efforts are increasingly directed toward pushing the boundaries of energy storage beyond the limits of conventional LIBs. However, understanding the generational development and fundamental working principle of lithium-ion systems remains essential, both for the advancement of current technologies and the design of future energy storage solutions. [38]

1.2. LIB structure: fundamental components evaluation

A lithium-ion battery can be schematically represented as two electrodes, physically separated by an electrically insulating membrane, all permeated by an electrolytic medium as shown in Figure 2. LIB functioning relies on redox reactions that occur within the system; during spontaneous redox reactions, typically referred as a discharge process, electrons flow through the external circuit, generating an electric current; the chemical energy stored in the electroactive materials is converted into usable electrical energy. Then, in order to restore the system to its initial state, a subsequent redox reaction is required. This reaction, associated with the charging process, needs the input of electrical energy, which is thereby converted back into chemical energy. These reversible redox reactions therefore enable the development of rechargeable batteries, which function as efficient energy storage/conversion systems and are capable of withstanding prolonged cycling.

Figure 2 represents the fundamental electrochemical cell of a LIB, which consist of four essential components: anode, cathode, electrolyte, and separator. During operation, lithium ions shuttle between the electrodes through the electrolyte, while electrons flow through the external circuit, enabling the redox reactions that drive charge and discharge processes. This reversible lithium-ion insertion/deinsertion mechanism underlies the energy storage and release processes in lithium-ion batteries. [39] Each component plays a critical role in ensuring the proper functioning of the cell, and their design and integration significantly influence the overall performance. Thus, extensive research has been devoted to optimizing these elements to achieve a balance among cost, safety, energy and power densities, and long-term stability.

The selection of suitable electrode materials in lithium-ion batteries is governed by a series of fundamental criteria that directly impact both cell performance and long-term stability. In addition to the two electrodes, a typical LIB includes a porous separator and an organic electrolyte. [40] The electrolyte serves as an ionic conductor, typically composed of lithium salts (e.g. LiPF_6) dissolved in organic carbonate solvents (e.g., ethylene carbonate (EC) and dimethyl carbonate (DMC)). This medium facilitates the transport of lithium ions between the electrodes, while remaining electronically insulating, thereby preventing self-discharge and internal short circuits. [41]

The separator is a porous polymeric membrane, commonly made of polyethylene (PE), polypropylene (PP), or alternatively, composite inorganic/organic-polymer materials. The choice of separator depends on the specific requirements of the cell chemistry and application. Its primary functions are to physically separate the electrodes, preventing direct contact that could lead to short circuits, while still allowing for the free movement of lithium ions through its porous structure. Indeed, the separator plays a critical role in maintaining cell safety and electrochemical performance.

The performance and longevity of LIBs depend on several critical factors, including the chemical and morphological stability of the electrode materials, the compatibility and decomposition behaviour of the electrolyte, the nature of the solid electrolyte interphase (SEI) layer formed at the anode–electrolyte interface, and the operating conditions such as temperature and charge/discharge rates. Engineering solutions to these challenges are essential to enable the development of next-generation LIBs with enhanced specific energy, power capability, and operational safety. To this purpose, the selection of suitable electrodes must be guided by their electrochemical compatibility with the electrolyte.

In addition, electrode materials should undergo minimal volume changes during lithiation and delithiation processes, thereby preserving mechanical integrity and maintaining stable electronic contact over extended cycling. High specific capacity is also essential and is generally achieved by employing lightweight materials, which contribute to enhanced gravimetric energy density. Furthermore, both electronic and ionic conductivities must be sufficiently high to support rapid charge transport and minimize polarization, ensuring efficient battery operation under high power demands. Finally, environmental sustainability and economic feasibility are increasingly important criteria, driving the development of materials and manufacturing processes that are both cost-effective and environmentally beneficial. These considerations collectively inform the rational design of next-generation electrode materials.

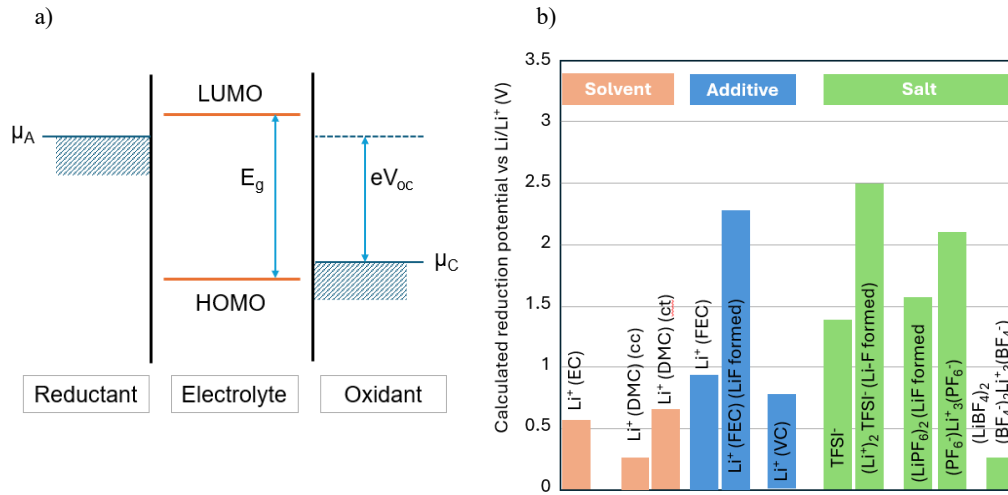


Figure 4. Schematic open-circuit energy diagram showing the alignment between electrode work functions (Φ_A and Φ_C) and the electrolyte's electrochemical stability window (reproduced from [38], b) Calculated reduction potentials of common solvents, additives, and desolvated ions (rearranged from [41])

1.2.1. Electrolyte

The electrolyte is a crucial component responsible for facilitating ionic conductivity between electrodes and ensuring electrochemical stability throughout the battery operation. Typically, an electrolyte comprises three main components: lithium salts, organic solvents, and functional additives. Lithium salts provide ion transport in solution, closing the circuit, in addition to provide Li ion that can be inserted in cathode or anode materials, or react at the electrodes; common salts include lithium hexafluorophosphate (LiPF₆), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Organic solvents, usually carbonates such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), dissolve the lithium salts and facilitate ion transport. Functional additives, such as vinylene carbonate (VC) [42,43] and fluoroethylene carbonate (FEC) [42-46] enhance the electrolyte properties by stabilizing the SEI, a protective passivation layer that prevents ongoing electrolyte decomposition and improves battery longevity and efficiency. [47-49] Electrolyte details are listed in Table 1.[50-52]

Table 1. Physico-chemical properties of solvent components

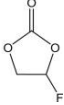
Solvent [50]	Structure	M.W. [g/mol]	Dielectric constant	Viscosity [mPa]	Density [g/cm ³]
EC		88	90.0	1.9	1.327
DMC		90	3.12	0.63	1.063
Salts [51,52]	Structure	M.W. [g/mol]	T _m (°C)	T _{decomp} (°C)	Ionic Conductivity (mS/cm) (1M, 25°C)
LiPF ₆		151.9	200	~80(in EC/DMC)	10.9 (in EC/DMC)
Additives	Structure	M.W. [g/mol]	T _m (°C)	T _b (°C)	Density [g/cm ³]
VC [53]		86.10	19~22°C	162°C	1.355 (at 20°C)
FEC [54]		106.05	18~23°C	249°C	1.48

Figure 4a illustrates the energy levels of the electrolyte components, highlighting the critical importance of forming a stable SEI. This stability is essential in guiding the selection of compatible electrode materials and ensuring efficient and safe battery operation. Additionally, Figure 4b shows the calculated reduction potentials of various electrolyte components, highlighting their electrochemical reactivity. This analysis directly shows the selection of a specific electrolyte composition optimized for silicon-composite anodes, 1M LiPF₆ dissolved in an EC:DMC solvent mixture (1:1 v/v) with 2 wt% VC and 10 wt% FEC. [55,56] This formulation was specifically chosen since EC and DMC solvents offer a stable medium for ion transport; VC, with its moderate reduction potential, polymerizes to form a robust, mechanically resilient polymer-rich SEI; this layer effectively mitigates mechanical stress, reducing particle fracturing and electrolyte degradation. FEC, characterized by a relatively higher reduction potential, facilitates the early formation of a dense LiF-rich SEI, which is characterized by a uniform, smooth, and dense morphology.

[57] This LiF-rich SEI significantly enhances mechanical and chemical stability, thereby reducing silicon particle cracking and increasing cycle stability and coulombic efficiency.

1.2.2. Positive electrodes

The performance, energy density, and stability of LIBs are strongly influenced by the choice of cathode material. As the cathode operates at high potentials relative to lithium, it largely determines the overall cell voltage and hence the energy output of the battery. Therefore, the development of high-capacity, high-voltage cathode materials is needed to meeting the growing demands for energy storage in portable electronics, electric vehicles, and stationary grid applications.

Lithium cobalt oxide (LCO) was the first commercialized cathode material and has been commercialized on the LIB market for decades due to its excellent capacity retention and high operating voltage (~ 3.9 V vs. Li/Li⁺). LCO suffers from significant drawbacks, including high cost, thermal instability at high states of charge, and most critically, the ethical and environmental concerns associated with cobalt mining. These issues have driven the research community and industry toward alternative cathode chemistries with reduced or eliminated cobalt content.

A prominent class of alternative cathode materials is the layered nickel–manganese–cobalt oxides, generally represented by the formula $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC). (Figure 5) These compounds maintain a similar layered structure to LCO, but with a tailored transition metal composition that improves performance and reduces dependence on cobalt. Each transition metal plays a specific role: nickel contributes to high capacity through redox activity ($\text{Ni}^{2+}/\text{Ni}^{4+}$), manganese enhances structural stability without participating directly in charge compensation, and cobalt maintains electronic conductivity and stabilizes the layered phase. [58-60]

In the early 2000s, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) became the dominant cathode material for electric vehicle (EV) batteries. [61-64] NMC111, a layered oxide, prompted research into various NMCs compositions to optimize battery performance and reduce costs, particularly by lowering cobalt content. [65] The state-of-the-art of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) delivers a specific capacity of more than 170 mAh/g in the voltage range between 3.0 and 4.3 V vs Li/ Li⁺. However, since the increasing demand in energy density,

the composition is pushed toward Ni-rich materials. [66,67] Ni-rich NMC (Ni content $\gg 1/3$) allows for higher degrees of delithiation due to two-electron transfer via $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, thus enabling specific capacities in excess of 190 mAh/g.

A major breakthrough came with the development of Ni-rich cathodes, such as NMC811 ($\text{LiNi}_{0.1}\text{Mn}_{0.1}\text{Co}_{0.18}\text{O}_2$), which offers excellent specific capacity (over 200 mAh/g), high voltage (over 3.8 V vs. Li/Li^+), and good cycle life. Compared to other cathode materials like LiFePO_4 (170 mAh/g) or spinel oxides (147 mAh/g), Ni-rich NMCs stand out for their high specific capacity and lower cost. [68-70]

Nevertheless, high-Ni NMCs suffer from severe capacity fading and degradation, which is believed to be associated with structural changes during cycling (contraction of c-axis and unit cell volume with delithiation and collapse of Li–O layers at high state of charge (SOC). [71] In addition to structural instability, high-Ni NMCs also exhibit lower thermal stability, nearly 100 °C lower than those of NMC111. This significant reduction in thermal robustness leads to serious safety concerns, especially under abusive conditions or elevated temperatures, where exothermic reactions may be triggered more easily. Moreover, the high reactivity of Ni^{4+} ions during charge/discharge cycles limits the cycling stability, making capacity retention a challenge. High lithium utilization, or SOC, can negatively impact capacity retention. To minimize degradation and extend battery life, it is generally recommended to operate batteries within an SOC range of 20%-80%. For this reason, manufacturers commonly reference 80% SOC in their specifications, and also in this project, we will focus on life cycle testing up to 80% SOC. Compared to NMC111, NMC622 offers improved energy density and lower irreversible capacity loss. (Figure 5, Ref:[72]) [67][73]

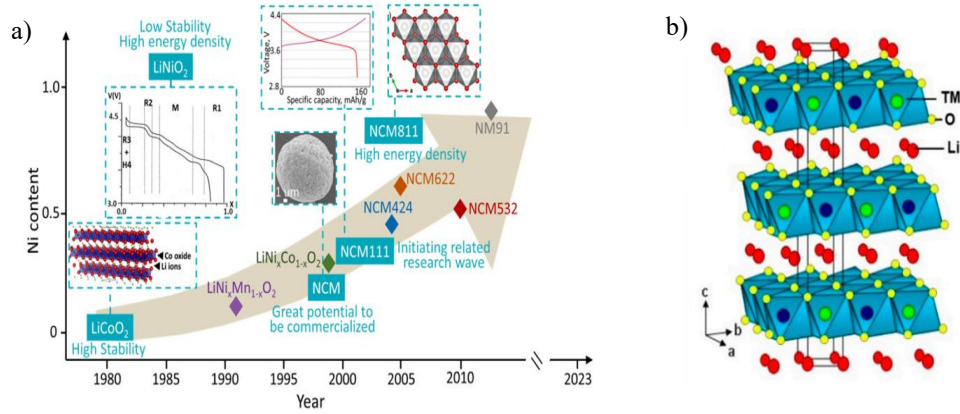


Figure 5. a) Ni-rich NMCs development over historical background. Abbreviations used for NMCs, NMC111, NMC424, NMC532, NMC622, NMC811, NMC91 stands for $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) (reproduced from [72]); b) Layered structure on NMC compound. Transition-metal cations coloured are: Li (green), O (red), Ni/Mn/Co (silver/purple/blue) (reproduced from [71])

In pursuit of completely cobalt-free solutions, several other positive electrode materials have been investigated in literature:[74,75]

- LiMn_2O_4 (LMO): A spinel-structured oxide offering high rate capability and low cost but limited by manganese dissolution and moderate cycle life. [76,77]
- $\text{Li}_2\text{Mn}_3\text{NiO}_8$ (LMNO): A lithium-rich layered oxide with high theoretical capacity, though still facing issues with voltage fade and poor first-cycle efficiency. [78-80]
- LiFePO_4 (LFP) and $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ (LFMP): Belonging to the olivine family, these materials are known for excellent thermal stability, flat voltage profiles (~ 3.4 V vs. Li/Li^+), and outstanding cycle life, but allow batteries with relatively lower energy densities due to lower operating voltages and capacities. [81-83]

Each of these alternatives brings trade-offs between cost, safety, energy density, and scalability. The choice of cathode material is ultimately critical, as it largely determines the specific capacity and, consequently, the overall specific energy of the cell.

The electrochemical performance of cathode materials is intimately linked to their crystallographic structure. The three major cathodes crystallographic frameworks used in LIB are layered, spinel, and olivine structures, each with distinct lithium-ion diffusion pathways and electrochemical characteristics.

The spinel structure, showed by LiMn_2O_4 (Figure 6b), adopts a cubic arrangement in which lithium ions occupy the tetrahedral sites of the face-centered cubic oxygen framework, while transition metal cations (e.g., $\text{Mn}^{3+}/\text{Mn}^{4+}$) occupy the octahedral sites. This configuration enables three-dimensional lithium-ion diffusion, which supports high-rate performance. However, spinels often suffer from capacity fading due to Mn dissolution and structural instability under prolonged cycling.

The olivine structure, represented by LiFePO_4 (Figure 6c), consists of FeO_6 octahedra and PO_4 tetrahedra interconnected to form a robust polyanionic network. Lithium ions diffuse along one-dimensional channels aligned with the $[010]$ direction. While olivine materials exhibit excellent thermal and cycling stability, their limited electronic and ionic conductivity necessitates carbon coating or doping strategies to enhance rate capability.

Layered oxide cathodes, such as LCO and NCMs materials are characterised by a layered crystal structure in which lithium ions and transition metal cations (Ni, Co, Mn) are arranged in alternating atomic layers within a close-packed oxygen framework. In this structure, lithium occupies octahedral sites between the transition metal oxide layers, forming a two-dimensional network that allows lithium ions to easily migrate within the interlayer spaces during charge and discharge. (Figure 6)

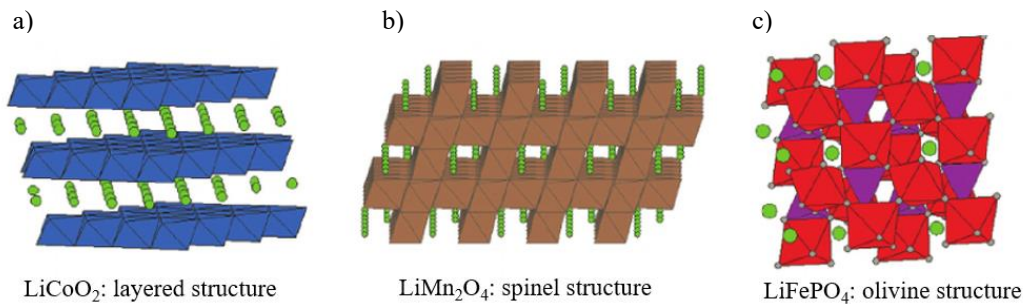


Figure 6. Comparison of the crystal structures of layered (a), spinel (b), and olivine-type (c) cathode materials, highlighting their distinct lithium transport characteristics and structural stabilities. (reproduced from [84])

This layered arrangement supports high lithium mobility and high specific capacity, typically ranging from 150 to 200 mAh/g, making these materials ideal for applications requiring high energy density. With increasing demand for higher energy density and lower environmental impact, nickel-rich NMC materials, especially NMC622, are gaining widespread adoption in electric mobility and energy storage sectors. Nevertheless, future research must address remaining challenges such as thermal stability, electrolyte

compatibility, and capacity fading at high states of charge. Emerging approaches include surface coatings, doping, and the development of hybrid structures that combine the advantages of multiple chemistries. This project is totally focused on NMCs materials, in particular NMC622 and NMC811. Moreover, in this work, we will use NMC622 for lab scale coin cell CR2032 assembling and NMC811 for pilot scale with pouch cell testing.

1.2.3. Negative electrodes

In LIBs, the anode, conventionally referred to as the negative electrode, plays a fundamental role in ensuring the efficient storage and release of lithium ions during the charge–discharge cycle. The selection of an appropriate anode material is thus a key point in the overall performance energy density, and cycling stability of lithium-ion batteries (LIBs). Based on their reaction mechanisms with lithium ions, anode materials can generally be classified into three main categories: *intercalation*, *conversion*, and *alloying* materials (Figure 7). Each category is defined by a distinct lithium storage mechanism and offers a unique balance of advantages and challenges.[85,86]

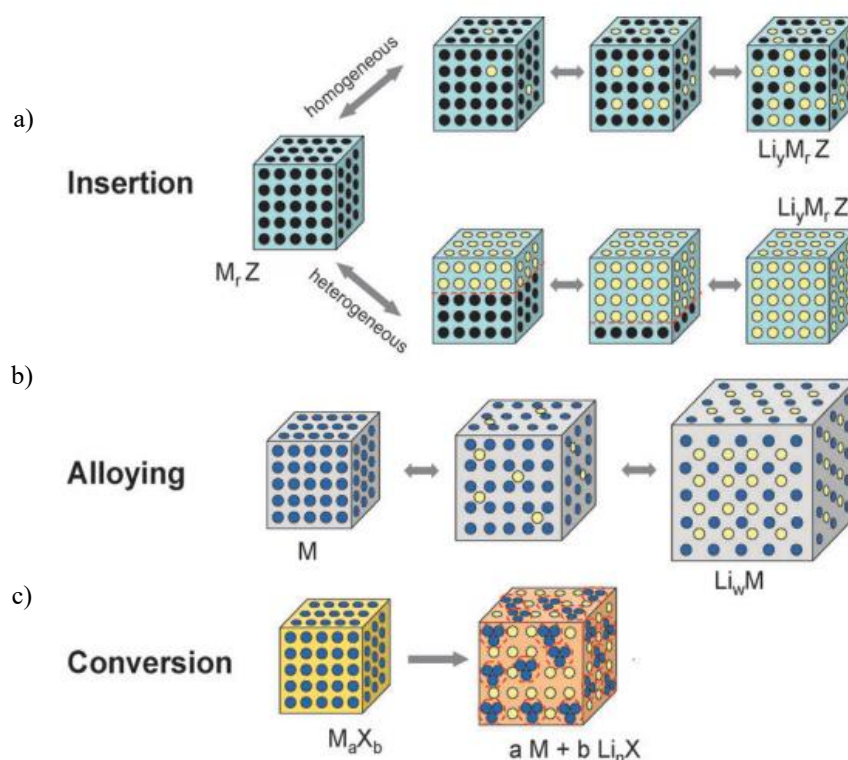


Figure 7. Schematic representation of the different reaction mechanisms of anode materials for LIBs: a) insertion type, b) conversion and c) alloying type anodes (rearranged from [87])

Intercalation anodes

Insertion-type anodes are characterized by a mechanism in which lithium ions are reversibly inserted into and extracted from the crystal lattice of a host material. This process involves the movement of lithium ions into specific interstitial sites within the layered, tunneled, or spinel frameworks of the electrode material (Figure 7a). Since the host structure remains largely intact during cycling, these materials generally offer good structural stability, long cycle life, and high coulombic efficiency. [88]

Among insertion-type materials, graphite remains the most widely adopted anode material due to its well-ordered layered structure and favourable electrochemical properties. Usually, talking of layered materials, we can use the term “intercalation”. Graphite is composed of stacked graphene layers arranged in a hexagonal A–B–A–B stacking sequence (Figure 8b). In this configuration, carbon atoms in adjacent layers are offset, allowing for the formation of interlayer ‘space’ where lithium ions can reversibly insert during battery charging. The pristine interlayer spacing in graphite is approximately 3.35 Å, which increases upon lithium intercalation due to electrostatic repulsion and lattice expansion. [89]

The electrochemical storage of lithium in graphite via an intercalation mechanism is a multi-step and concentration-dependent process, characterized by distinct structural transitions known as “staging mechanism”. [90] Its layered carbon structure enables the formation of LiC_6 during full lithiation, with a low operating potential below 0.2 V vs. Li/Li^+ . These characteristics contribute to good rate capability and long-term cycling under standard conditions. [91,92]

Each stage is described by the degree of ordering of lithium ions within the graphite structure, as determined by the number of graphene layers (n) separating two lithium-filled layers.[93]

As illustrated in Figure 8a, the voltage profile versus specific capacity can be directly correlated with the formation of these stages:

- Stage IV: in this first stage lithium ions occupy every fourth interlayer gallery, forming an ordered, dilute phase. This arrangement maximizes Li layers separation, minimizing Li–Li electrostatic repulsion and graphite structure experiences only a slight expansion. Thermodynamically, the formation of Stage IV is a two-phase

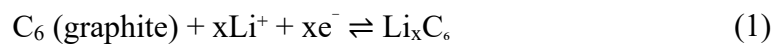
process, since it involves both nucleation and growth of Stage 4 domains within the pristine graphite lattice. This process occurs at a specific, constant voltage, visible as a voltage plateau, which signifies that both pristine graphite and the new Stage IV compound coexist.

- Stage III: As lithiation proceeds, lithium ions populate every third interlayer gallery. This change increases the overall density of the intercalated lithium, and the ordered arrangement of the ions becomes more pronounced. Compared with Stage 4, the expansion is larger, staging peaks intensify, and the voltage curve shows a distinct plateau associated with the transformation from Stage IV to Stage III. [94]
- Stage II: Since the insertion continues, it lowers the free energy by establishing Li in alternate interlayers, forming an ordered lattice. Electrostatic repulsion among Li is overcome by the free-energy gain associated with greater interlayer occupancy, to which the graphite lattice responds by expanding along the c-axis and exhibiting more pronounced staging features. Indeed, the voltage–capacity plot exhibits a well-defined plateau for the two-phase region from Stage III to Stage II.
- Stage I: this is the last first-order transition (LiC_6), in which each interlayer gallery hosts Li ion. This step is associated with an abrupt increase of interlayer spacing from $\sim 3.35 \text{ \AA}$ (graphite) to $\sim 3.70 \text{ \AA}$, as indication of complete gallery filling. Electrochemically, this corresponds to the lowest anode potential and a characteristic plateau in the voltage profile. In this state, the layered arrangement of Li is thermodynamically most stable at high Li activity; on delithiation, the reverse sequence of stages is observed.

These transitions are observable as characteristic voltage plateaus or slopes in the discharge curve, as shown in Figure 8a. [95,96]

The final intercalated compound, LiC_6 , corresponds to a theoretical capacity of 372 mAh/g and is achieved under ambient conditions.[97]

The overall reversible intercalation reaction in graphite can be summarized as reported in equation (1):



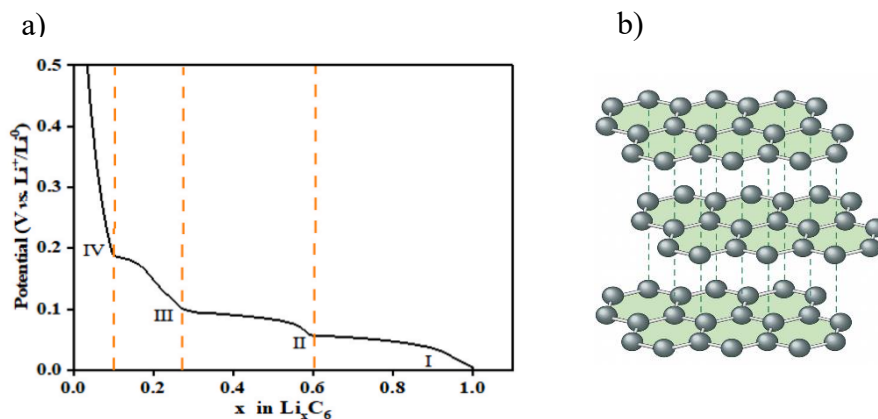


Figure 8. a) Graphite lithiation potential (V vs. Li/Li^+) as a function of x in Li_xC_6 ; dashed lines mark staging boundaries (IV $\rightarrow$ III $\rightarrow$ II $\rightarrow$ I) (adapted from [93], used with permission. License No. 6135830199241, Copyright Clearance Center); (b) Schematic of the staged structure of lithiated graphite.

Despite the high stability and reversibility of graphite as the anode in LIBs, graphite presents several drawbacks. The slow solid-state diffusion of lithium ions within its structure limits high-rate performance. Furthermore, the intercalation potential of lithium in graphite is close to that of lithium plating, raising concerns about dendrite formation, particularly during fast charging. Additionally, solvent co-intercalation and subsequent graphite exfoliation can occur due to reactions between the electrolyte and graphite layers, compromising mechanical integrity and capacity retention.

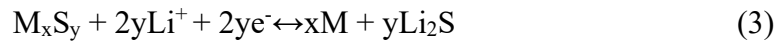
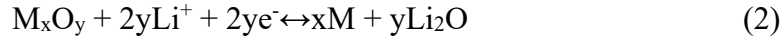
Moreover, its relatively low theoretical specific capacity is not suitable for high-energy-density applications such as transport electrification, and other types of anode materials have been progressively studied, considering performance as well as sustainability, stability, cost and safety.

Conversion anodes

Conversion-type anode materials (CTAMs) encompass a broad class of compounds, primarily including transition metal oxides [98], sulfides [99], phosphides, and certain nitrogen-based compounds, typically involving metals such as Co, Ni, Fe, or Mn. Transition metal oxides such as Fe_2O_3 , Co_3O_4 , and Mn_3O_4 exemplify this class of materials.

Unlike intercalation-based materials, CTAMs undergo a conversion reaction during lithiation and delithiation processes. This mechanism involves the complete reduction of the metal compound into metallic nanoparticles dispersed in a Li₂O (or analogous) matrix, and the reverse oxidation upon delithiation. [100]

The transformation reaction of metal oxides and sulfides with Li⁺ is as follows (equations (2) and (3)): (Figure 7b)



This mechanism can deliver high specific capacities, often exceeding 600 mAh/g, due to multi-electron transfer processes. However, conversion reactions are often accompanied by significant volume changes, sluggish kinetics, and poor cycling stability.

Alloying anodes

Alloying anode materials operate through a mechanism in which lithium ions chemically react with the host material to form lithium-rich alloys during the lithiation process (Figure 7c). This reaction is distinct from the intercalation mechanism. In alloying anodes, the lithiation process induces substantial structural and compositional changes as new alloy phases are formed. These transformations involve the breaking and reforming of chemical bonds, which allow for the storage of a much higher quantity of lithium per unit mass compared to intercalation anodes. The potential of alloying anode materials lies not only in their high energy density, but also in their adaptability to diverse structural and compositional modifications, enabling tailored solutions for various energy storage applications. These materials represent a critical focus area in the pursuit of high-capacity and high-performance LIBs, offering transformative potential for the future of energy storage.

The alloying process typically involves the formation of Li_xM-type alloy phases, where the alkali metal (Li) is progressively incorporated into the host material (M) during lithiation. This reaction is governed by the general equation (4):



where M represents the host material and it might be $M = \text{Si, Sn, Ge, Sb, P}$, and x indicates the stoichiometric ratio of the alkali metal incorporated into the alloy phase. This mechanism enables high-capacity energy storage by allowing multiple alkali metal atoms to bond with each host atom (Figure 9). [101]

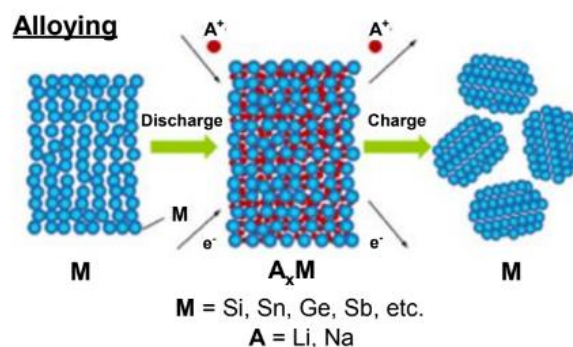


Figure 9. Illustration of alloying mechanism reaction and A_xM -type alloy formation for Li^+ . (reproduced from: [102] used with permission. license No. 613561344816, Copyright Clearance Center.)

This mechanism enables alloying materials to achieve significantly higher theoretical capacities, often an order of magnitude greater than those of traditional intercalation materials like graphite. For instance, silicon, a leading candidate in alloying-based anodes, boasts an impressive theoretical capacity of $\sim 4200 \text{ mAh/g}$, far surpassing 372 mAh/g of graphite. This superior performance, combined with the abundance, safety, environmental friendliness, and low cost of elements such as Si, has garnered considerable attention making alloy-type anodes highly appealing for next-generation LIBs aimed at applications requiring increased energy densities, such as electric vehicles and portable electronics. [103]

However, the structural changes accompanying lithiation in alloying materials are not without challenges. The repeated formation and decomposition of lithium-rich alloys during cycling lead to drastic volume changes, causing severe mechanical stress, particle pulverization, and loss of electrical contact within the electrode. These issues can result in rapid capacity fading and poor long-term cycling stability. Despite these challenges, significant advancements have been made in developing nanostructured materials, composites, and novel binder chemistries to mitigate the mechanical degradation and improve the electrochemical performance of alloying anodes.

1.3. Silicon-Based Anodes: challenges and advances through composite architectures

Silicon has emerged as one of the most promising anode materials for next-generation LIBs, primarily due to its exceptionally high theoretical specific capacity, ranging from approximately 3579 to 4200 mAh/g for the fully lithiated $\text{Li}_{15}\text{Si}_4$ phase. This value far exceeds that of conventional graphite (372 mAh/g), highlighting the promise of high-capacity anodes. However, in a full cell, any increase in anode capacity must be balanced by a proportional increase in cathode mass to maintain the correct capacities (N/P ratio). Consequently, the specific capacity of the cathode ultimately defines the upper limit of the cell energy and improvements to the anode can only enhance overall energy density [104-107]

Such a substantial increase in capacity positions silicon as a transformative material for LIBs, capable of meeting the growing demands of electric vehicles (EVs), grid-level energy storage, and advanced portable electronics. [108,109]

In addition to its remarkable capacity, silicon offers several other compelling advantages. It is the second most abundant element in the Earth's crust, readily available and inexpensive compared to transition metals used in other battery components. [105,110] Silicon is also non-toxic and environmentally benign, which aligns with the growing focus on sustainable and eco-friendly energy technologies. Furthermore, it exhibits a relatively low average lithiation potential of ~ 0.4 V vs. Li^+/Li , which helps maximize the operating voltage of full cells, thereby improving overall energy density. [110,111]

Another strategic benefit of silicon lies in its compatibility with existing semiconductor processing infrastructure. This opens pathways for advanced manufacturing techniques, such as vapor deposition, ball milling, and scalable solution-based synthesis, to be adapted for battery-grade silicon materials. [112-115] These techniques enable precise control over particle size, morphology, and surface chemistry, which are all crucial for optimizing the electrochemical behaviour of silicon-based anodes. [116,117]

However, despite its theoretical advantages, the practical implementation of silicon anodes is severely constrained by intrinsic limitations. The most critical issue is the dramatic volume expansion, up to 300–400%, that silicon undergoes during the lithiation process. [118] This repeated expansion and contraction induces intense mechanical stress, leading

to particle pulverization, loss of electrical contact with the conductive matrix, and structural collapse of the electrode. [119-121]

Moreover, such mechanical degradation causes continuous fracture and reformation of the SEI layer, which consumes both lithium and electrolyte and results in increased impedance and rapid capacity fading. [122,123]

This phenomenon is well illustrated in Figure 10, which summarizes the three most critical degradation mechanisms affecting silicon-based anodes: particle pulverization due to repeated volume expansion, electrode delamination leading to electrical isolation, and the continuous formation and thickening of an unstable SEI layer over cycling.

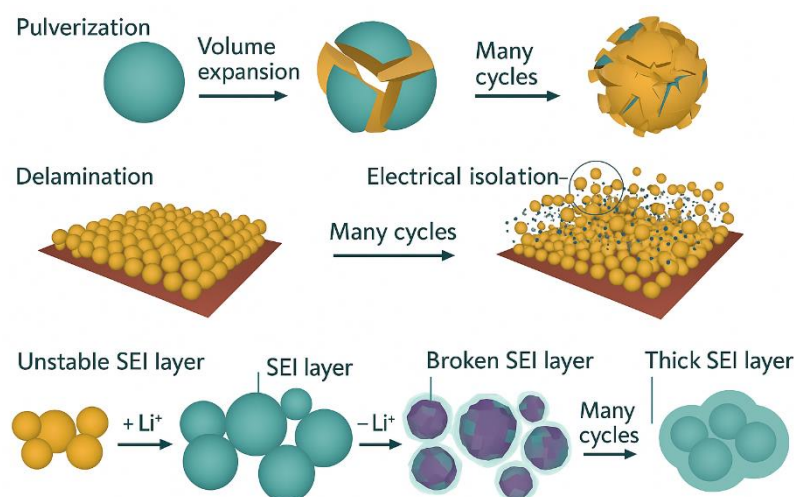


Figure 10. Schematic diagram of the main degradation mechanism of silicon anode due to the large volume expansion of silicon during lithiation process. (adapted from [124])

As shown in Figure 10, the instability of SEI on silicon-based anodes represents one of the most critical limitations to their practical application in lithium-ion batteries, particularly due to its strong impact on the initial coulombic efficiency and long-term cycling stability. [123,126] During the first lithiation cycle, the highly reactive surface of silicon promotes substantial electrolyte decomposition, leading to the formation of the SEI layer. This repeated volume fluctuation induces mechanical stress and fracturing of both the active material and the SEI layer. [127,128] As a consequence, the SEI must reform continuously during each cycle to re-passivate newly exposed surfaces, resulting in a self-perpetuating cycle of electrolyte decomposition and consumption of active lithium ions. This phenomenon has a direct and deleterious effect on the initial coulombic efficiency

(ICE), which is defined as the ratio between the charge extracted from the anode during the first delithiation (discharge) and the charge inserted during the initial lithiation (charge). In silicon anodes, ICE values are typically low, often ranging from 50% to 70% depending on material design and surface engineering, because a significant portion of the inserted lithium is irreversibly consumed in the formation of the SEI and cannot be recovered. This loss is particularly critical in full-cell configurations, where the amount of lithium available is fixed by the cathode capacity. Unlike half-cells that use excess lithium metal, full cells cannot compensate for the initial lithium loss, leading to a permanent reduction in the cell's reversible capacity.

Furthermore, the continuous breakdown and reformation of the SEI throughout cycling not only lead to progressive lithium and electrolyte consumption but also generate electrically insulating debris that can increase the cell impedance and hinder charge transport. Over time, this degrades the electrode structural integrity, reduces lithium-ion diffusion kinetics, and accelerates capacity fade, thus impairing both energy density and battery lifespan. These challenges make it extremely difficult to implement pure or high-loading silicon anodes in commercial cells, especially for applications demanding long-term reliability, high ICE, and stable performance over hundreds or thousands of cycles, such as electric vehicles or grid storage systems. [109], [129,130] Therefore, improving ICE is not only a matter of maximizing energy density but is also crucial for ensuring lithium economy, extending cycle life, and enabling full-cell viability.

To address these multifaceted challenges, researchers have pursued a range of strategies aimed at mitigating the mechanical and electrochemical degradation of silicon anodes. These approaches span from material design to electrode architecture and electrolyte formulation. A key focus has been placed on the *selection and optimization of binders*, which play a crucial role in maintaining electrode integrity under the mechanical strain of cycling. [115], [131,132]

Another crucial avenue involves *surface engineering techniques*, including carbon coating and the application of artificial SEI layers, which serve to stabilize the interface between silicon and the electrolyte. [133-136] By preventing continuous SEI rupture and reformation, these modifications contribute to higher Coulombic efficiency and longer cycle life. [114,137]

Furthermore, *nanoscaling of silicon particles* helps limit the absolute expansion of individual particles, although it often leads to challenges related to high surface area and increased side reactions. [117,120] As such, engineering *composite structures* that embed silicon within conductive and elastic carbon matrices has emerged as a highly effective approach. [126,129,138]

Finally, *modifying the silicon at the chemical level*, through alloying, doping, or forming silicon oxides (SiO_x), offers a promising path to structural and electrochemical stability. These modifications help to buffer volume changes, enhance electronic conductivity, and reduce irreversible reactions. [105,111,130]

Within this broader framework, two principal and complementary material engineering strategies have gained widespread attention: (i) *silicon-carbon (Si/C) composites*, and (ii) *silicon oxide-based carbon coated ($\text{SiO}_x\text{@C}$) composites*, often in conjunction with prelithiation, (iii) *magnesium silicon oxide composite (Mg-SiO_x)*. These material systems aim to buffer the mechanical strain during cycling, enhance electrical conductivity, and stabilize interfacial chemistry, thereby improving the viability of silicon as an anode material in practical LIB systems. [139]

1.3.1. Silicon-Carbon Composites: mitigating volume change with conductive matrix

A significant strategy to address the inherent drawbacks of silicon-based anodes is through the integration of carbon coatings, resulting in silicon-carbon (Si/C) composites. These composites leverage silicon exceptional theoretical capacity alongside the mechanical and conductive benefits of carbonaceous materials. [129,136,140] Carbon provides a robust structural support that mitigates the volumetric expansion of silicon particles during lithiation, thus preserving electrode integrity over prolonged cycling. [130] Various Si/C architectures, including uniform carbon coatings, embedded silicon structures within carbon matrices, and hollow configurations, have been extensively investigated. Carbon coatings specifically serve as protective barriers, reducing direct electrolyte exposure of silicon particles, stabilizing SEI, and enhancing cycling stability. [111,112]

Embedded and hollow configurations offer additional mechanical flexibility, effectively accommodating the substantial swelling of silicon particles during repeated cycling. [133,138]

The presence of *carbon-coated* silicon nanoparticles significantly influences slurry formulation and mixing procedures. The carbon coating significantly enhances particle dispersion, promoting a homogeneous distribution of silicon and conductive additives within the slurry. Improved dispersibility aids in preventing agglomeration, ensuring a uniform and consistent particle distribution throughout the electrode matrix. Nonetheless, the inherently hydrophobic nature of certain carbon coatings can present challenges by impeding effective binder interaction, particularly within aqueous-based slurry formulations. To overcome this issue, precise adjustments to slurry pH and careful selection of binder systems, particularly combinations like carboxymethyl cellulose (CMC) with styrene-butadiene rubber (SBR), are essential. These binder systems improve adhesion, contribute to slurry stability, and ultimately enhance the structural robustness of the electrodes. Additionally, the presence of carbon demands careful control during slurry mixing processes; parameters such as mixing time, rotational speed, and vacuum conditions require optimization to prevent air entrapment, ensuring consistent coating properties and minimizing defects.

Moreover, the rheological behaviour of slurries containing Si/C composites is significantly affected by the characteristics of carbon coatings. Ideal carbon coatings enhance slurry viscosity stability, thus facilitating precise control over electrode coating thickness and uniformity. Optimized viscosity conditions also contribute to improved drying consistency, resulting in more homogeneous and defect-free electrode coatings on current collectors. However, attention is necessary during slurry processing, particularly during pilot-scale electrode manufacturing, to manage residual solvent evaporation and prevent excessive gas evolution during drying and calendaring processes. Accurate control of temperature, humidity, drying speeds, and calendaring pressure is critical to maintaining structural integrity and achieving uniform electrode thicknesses and porosities. Such meticulous control prevents common defects such as delamination, cracking, or gas entrapment, which could significantly degrade the electrochemical performance of the resulting electrodes.

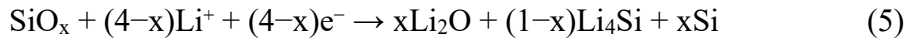
Electrochemical evaluations emphasize the superior performance potential of meticulously designed Si/C composite electrodes. Cells incorporating these composites demonstrate remarkable cycling stability, maintaining capacities around 1000 mAh/g over extended cycling durations with minimal degradation. [114]

Notably, advanced architectures like yolk-shell designs have showcased exceptional resilience, delivering capacities around 2800 mAh/g with 74% retention after 1000 cycles and consistently achieving Coulombic efficiencies above 99.8%. Such results underscore the critical importance of structural optimization coupled with effective carbon coatings in enhancing electrode longevity. However, certain challenges persist, including limitations in rate capabilities due to slower lithium-ion diffusion through thicker carbon layers and potential interfacial delamination under extensive cycling conditions. [140] Continuous research efforts are therefore required to refine Si/C composite structures further, enhancing diffusion kinetics and interfacial stability to achieve comprehensive improvements in long-term durability and electrochemical performance.

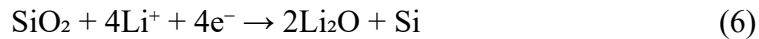
1.3.2. Silicon Oxide-Carbon (SiO_x@C) Composites: structural buffering and prelithiation

Silicon oxide (SiO_x) has emerged as a promising high-capacity anode material for lithium-ion batteries. However, Si and SiO_x particles undergo enormous volumetric expansion upon full lithiation, which causes several challenges in silicon anodes, as previously mentioned. Indeed, one primary challenge of using SiO_x as an anode material lies in its intrinsically low ICE.

Considering SiO_x-composite anodes, additional lithium is irreversibly consumed during the first lithiation process due to the decomposition of SiO_x into electrochemically inactive lithium-containing species. The representative reaction occurring during initial discharge (lithiation) can be simplified as equation (5):



Depending on the value of x (i.e., the oxygen content in the SiO_x material), the reaction yields a mixture of lithium oxide (Li₂O), lithium silicates (e.g., Li₂Si₂O₅, Li₄SiO₄), and lithium-rich silicon alloys (such as Li_{4.4}Si). These reactions are largely irreversible and consume a substantial portion of lithium from the cathode. As a consequence, the ICE drops significantly, especially for high- x SiO_x compositions (oxygen-rich materials), where more lithium is diverted toward the formation of Li₂O and silicate species as reported in equation (6):



(followed by alloying with additional Li to form Li_xSi)

However, the same Li₂O and lithium silicate phases formed in situ create a robust, inactive matrix that mechanically buffers the active silicon domains during repeated charge/discharge cycles, thereby mitigating the pulverization typically observed in pure silicon anodes. This structural stabilization enhances long-term cycling performance. Thus, there exists a fundamental trade-off in SiO_x anode design. A higher oxygen content (higher x) in SiO_x results in more extensive formation of lithium silicates and Li₂O, which benefits cycling stability by providing structural reinforcement but simultaneously reduces ICE due to greater lithium consumption in irreversible reactions. Conversely, a lower oxygen

content (approaching pure Si) minimizes the formation of inert byproducts, thereby improving ICE, but leads to less structural buffering, which worsens volume expansion and reduces mechanical integrity during cycling. The optimization of the oxygen-to-silicon ratio in SiO_x is therefore critical to balance initial efficiency with long-term stability in lithium-ion battery applications.

To overcome these challenges, researchers have investigated both *carbon coating* of SiO_x particles and *prelithiation* of the SiO_x active material as key strategies.[141-149]

Each of these treatments targets a different aspect of the problem: *carbon coatings* enhance electrode conductive network and provide mechanical confinement, while *prelithiation* compensates the initial lithium loss and pre-stabilizes the anode interface. The deposition of a carbon coating onto SiO_x particles is an effective way to improve their electrochemical performance and processability. In general, rational design of silicon-composite anodes often employs carbon coatings to mitigate silicon's drawbacks. Thus, the carbon coating layer on SiO_x serves multiple functions. Firstly, it greatly increases the electrical conductivity of the active material, ensuring that SiO_x particles remain electronically percolated throughout the electrode. Second, the carbon shell acts as a physical buffer that can accommodate some of the volume changes during lithiation/delithiation, thereby relieving stress on the SiO_x core and preserving structural integrity. Third, it forms a protective interface that can reduce direct contact between the electrolyte and the SiO_x surface, which in turn moderates undesirable side reactions and SEI growth on the active material. Notably, the carbon content must be optimized: an excessively thick carbon layer, while benefiting mechanical stability, adds electrochemically inert mass that dilutes the cell capacity. It has been observed that beyond an optimum, increasing the carbon coating thickness actually reduces the composite anode's capacity, since amorphous carbon contributes only ~ 25 mAh/g of its own storage. Thus, a thin and continuous carbon coating is desired to maximize electronic connectivity and structural support without sacrificing too much energy density.

Carbon coating of SiO_x ($\text{SiO}_x@\text{C}$) also has important implications for electrode fabrication from slurry formulation to the quality of the finished coated electrode. In a typical water-based slurry with polymer binder and conductive additives, pristine SiO_x powders tend to have high surface energy and often aggregate in suspensions, making it challenging to achieve a uniform dispersion in the anode slurry and poor rheological behaviour (e.g. inconsistent viscosity). On the contrary, carbon-coated SiO_x is generally easier to disperse

because the hydrophobic carbon surfaces and reduced van der Waals forces between coated particles lessen the strong self-aggregation seen in bare SiO_x . This brings to a well-dispersed anode slurry, then coated onto Cu foil without issues like particle sedimentation or binder separation, even at relatively high solid loadings. After drying and mechanical pressing, the carbon-coated SiO_x containing electrodes exhibited good adhesion to the current collector and resisted ‘peeling’ or ‘cracking’. The carbon matrix helps bind the active material together and to the copper substrate, effectively reinforcing the electrode against the strains of solvent evaporation and later electrochemical cycling. The ability to formulate carbon-coated SiO_x electrodes with >90% active material is highly attractive for achieving higher areal capacities and energy density. Crucially, these carbon-coated electrodes have demonstrated markedly improved electrochemical performance over their uncoated counterparts. [111][116-117][147][150-153]

According to earlier generations patents, the vapor-phase synthesis of bulk SiO_x through co-evaporation involved vaporizing a mixture of high-purity silicon dioxide (purity 99.9%; $D_{50} \approx 10 \mu\text{m}$) and elemental silicon (purity 99%; $D_{50} \approx 10 \mu\text{m}$) within a reactor maintained at approximately 1340 °C under a vacuum pressure of 10 Pa. [154,155]

Upon cooling, the vapor-phase material condensed and deposited as bulk silicon monoxide (SiO) onto a substrate. The resulting SiO solid was subsequently ground via mechanical ball-milling to obtain a powder with a median particle size of approximately 6.5 μm . To enhance its electronic conductivity, the SiO powder underwent a carbonization step in a methane (CH_4)-rich atmosphere at around 1000 °C for three hours, where active material particles were uniformly exposed to the decomposing hydrocarbon gas. Methane pyrolyzes at this temperature, releasing reactive carbon species (primarily C and CH_x radicals), which deposit onto the particle surface forming an amorphous carbon layer. This results in a conformal, homogeneous coating with a thickness of approximately 30–50 nm, depending on process parameters such as gas flow rate, temperature stability, and residence time. [151] While carbon coatings address the conductivity and stability issues, they do not directly solve the initial lithium loss problem. This is where *prelithiation* becomes indispensable. [156]

Prelithiation of SiO_x active materials represents a critical strategy to address their intrinsically low ICE, which typically ranges from 50–70% in untreated materials, due to substantial irreversible lithium loss during the first discharge cycle.[144] [157-159]

This loss is primarily attributed the irreversible lithiation of SiO_2 domains, resulting in the formation of electrochemically inactive compounds such as lithium silicates ($\text{Li}_2\text{Si}_2\text{O}_5$, Li_4SiO_4) and lithium oxide (Li_2O) [128,141,143,160]

To address this, several solid-state prelithiation methodologies have been proposed, allowing lithium incorporation directly into the active material. (Figure 11) [161-164]

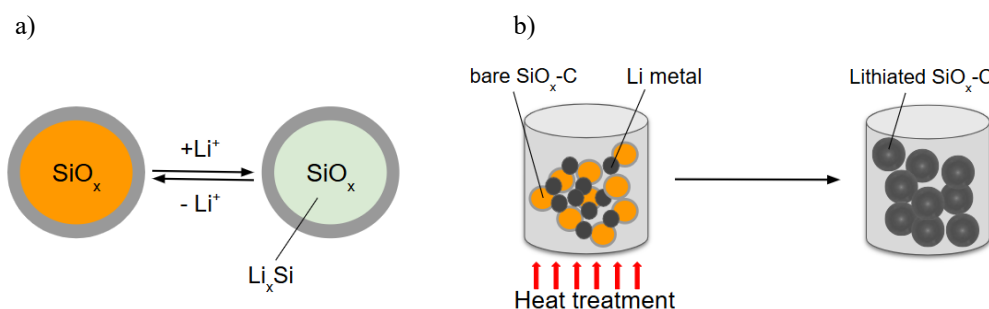


Figure 11. a) Lithiation–delithiation process of SiO_x ; b) Prelithiation treatment of Si active material via a ball-milling process. (rearranged from [165])

Among these, a highly effective approach involves thermal lithium-metal-free solid-state prelithiation of SiO using lithium hydride (LiH) as the lithium source.[166] In this method, carbon-coated SiO_x ($\text{SiO}_x\text{@C}$) particles, generally obtained via pyrolytic carbon coating in a methane atmosphere at $\sim 1000^\circ\text{C}$, are mechanically mixed with LiH and subjected to mild heating at temperatures between 300 and 400°C under inert atmosphere.

Under these conditions, LiH decomposes, releasing atomic lithium, which diffuses through the conformal carbon coating (typically $30\text{--}50\text{ nm}$ thick) and reacts with the underlying SiO_x matrix. This reaction leads to the formation of Li_2O and lithium silicates, while simultaneously generating Li_xSi nanodomains, which are electrochemically active. This method enables high lithiation efficiency (up to 98%) and significantly improves ICE values, often exceeding 90% in half-cell configurations. [167]

An alternative solid-phase prelithiation route involves the use of *stabilized lithium metal powder (SLMP)*, composed of sub-micron lithium particles passivated with a surface layer of lithium carbonate or lithium hydroxide. [168-170] The SLMP is uniformly distributed over the surface of the $\text{SiO}_x\text{@C}$ powder, and lithium is subsequently activated via mild thermal annealing ($\sim 200\text{--}250^\circ\text{C}$) or mechanical pressure. Upon activation, lithium diffuses

into the carbon-coated particles and reacts with the SiO_x core to form a passivated, lithiated shell. This method allows for precise control over the quantity of lithium introduced by adjusting the SLMP-to- $\text{SiO}_x@\text{C}$ ratio, and it does not require high temperatures or complex instrumentation. SLMP-based prelithiation has demonstrated ICE values from $\sim 70\%$ to $>85\%$ and often exceeding 90% , without carbon shell degradation or dendrite formation, with full-cell reversibility maintained over hundreds of cycles. [145,171]

1.3.3. Mg-Doped $\text{SiO}_x@\text{C}$ Composites: Industrial viability and stability enhancement

Among the emerging silicon-based anode materials for next-generation lithium-ion batteries, magnesium-doped carbon-coated silicon suboxide ($\text{Mg-SiO}_x@\text{C}$) composites have gained particular interest due to their promising balance between performance and process compatibility. Compared to conventional Li-doped $\text{SiO}_x@\text{C}$ materials, which, although electrochemically efficient, are prone to significant gas evolution during aqueous slurry preparation, $\text{Mg-SiO}_x@\text{C}$ offers superior chemical stability, making it better suited for industrial-scale electrode manufacturing processes that involve high shear mixing and elevated temperatures. The introduction of magnesium into the SiO_x matrix is typically performed via solid-state magnesiothermic reaction, in which Mg powder reacts with SiO_2 species within SiO_x to generate embedded Mg silicates such as MgSiO_3 and Mg_2SiO_4 . These magnesium compounds, predominantly located near the particle surface, serve to partially reduce SiO_2 to Si and mitigate the irreversible formation of lithium silicates during the first cycle, thereby enhancing the ICE and mechanical integrity of the active material.[172]

In their 2023 study, Liu et al. demonstrated that by carefully tuning the Mg doping process, they were able to achieve ICE values as high as 84.12% for $\text{Mg-SiO}_x@\text{C}$ (compared to $\sim 50\%$ for undoped SiO_x), with a corresponding specific capacity of 1226 mAh/g . Further prelithiation of this $\text{Mg-SiO}_x@\text{C}$ material resulted in a remarkable capacity of 1477 mAh/g while maintaining a high ICE of 83.77% , indicating a synergistic benefit of Mg doping and prelithiation strategies.[172]

From a structural perspective, Oh S. et al. disclose that $\text{Mg-SiO}_x@\text{C}$ composites typically consist of nanocrystalline MgSiO_3 domains ($\sim 1\text{--}25 \text{ nm}$) embedded within a SiO_x matrix,

with a uniform carbon coating enveloping the particles.[173] This architecture enhances both electrical conductivity and structural stability during cycling. Additionally, the carbon shell contributes to improved electronic pathways and mitigates direct contact between the SiO_x core and electrolyte, thus reducing SEI growth and improving long-term cycle performance. As a particularly innovative and industrially viable variation of SiO_x -based anode materials, the $\text{Mg-SiO}_x@\text{C}$ architecture retains the electrochemical and mechanical advantages of conventional $\text{SiO}_x@\text{C}$ composites while introducing specific improvements critical for pilot and large-scale manufacturing.[174] Doping SiO_x with magnesium modifies the internal structure and chemical composition of the composite, enhancing both its mechanical robustness and its electronic/ionic conductivity. Magnesium atoms are believed to partially substitute for silicon or occupy interstitial sites, helping to reduce the formation of brittle lithium silicate domains while preserving the buffering action necessary for long-term cycling. The result is a composite with a better balance of capacity retention, Coulombic efficiency, and thermal/mechanical stability.

From an electrochemical prospect, Mg doping has been reported to lower the overpotential of lithiation, improve lithium diffusion kinetics, and stabilize the SEI layer due to a modified surface environment. These effects combine to produce a more stable cycling profile and improved performance under high-rate and long-term cycling conditions. However, the most significant benefit of $\text{Mg-SiO}_x@\text{C}$ composites emerge in the context of industrial slurry processing and pilot-scale electrode manufacturing. Unlike lithium-doped or prelithiated SiO_x materials, which often release hydrogen or other gases upon contact with water-based binder solutions, Mg-doped materials exhibit far better chemical stability. In large-scale slurry mixing operations, high shear rates and elevated mixing temperatures can induce gas evolution from lithium-doped particles, leading to bubble formation that disrupts slurry homogeneity, coating uniformity, and ultimately cell performance. Magnesium doping, by contrast, avoids this problem, enabling stable, scalable processing without foaming or gas evolution. Additionally, $\text{Mg-SiO}_x@\text{C}$ materials show enhanced compatibility with a broader range of aqueous binder systems (e.g., CMC/SBR, alginate blends, etc), simplifying the formulation protocol and improving the shelf-life and robustness of the electrode slurry.

On the downside, magnesium does not participate in lithium storage in the same way lithium dopants do, so a slight compromise in initial capacity may occur. Nonetheless, this trade-off is usually acceptable in high-throughput manufacturing settings, where process reliability and electrode uniformity are prioritized over maximizing theoretical capacity.

Altogether, Mg-SiO_x@C composites represent a strategically engineered class of materials that overcome the limitations of both pristine and Li-doped SiO_x systems. Their combined electrochemical reliability, structural integrity, and processing compatibility make them highly promising candidates for commercial-scale lithium-ion battery production.

1.4. Selection and optimization of polymeric binders for Silicon-based anodes

To effectively address and mitigate the challenges associated with silicon-based anodes, the binder plays a crucial role in ensuring the structural integrity and long-term performance of the electrode; the critical function of the binder lies in its ability to create a matrix that interconnects all active material particles. [175]

A well-designed binder is essential not only for accommodating the volumetric expansion of silicon, but also for enhancing its physicochemical properties, including mechanical stability, adhesion strength, and ion transport. [176]

By reinforcing the electrode structure, the binder helps mitigate the detrimental effects of silicon fracturing and delamination, both of which contribute to rapid capacity fade in lithium-ion batteries. This structural stability is achieved through a combination of mechanical entanglement, chemical interactions, van der Waals forces, and electrostatic attractions, all of which contribute to the overall durability of the anode throughout prolonged cycling. [177] Given the substantial impact of binder properties on electrode performance, recent research has focused on tailoring polymer binders to meet the specific requirements of silicon-based anodes.

The performance of polymer binders in silicon-based anodes is primarily dictated by their backbone structure and functional groups, which influence critical properties such as adhesion strength, elasticity, and electrochemical stability. To optimize binder functionality, various strategies have been explored, including copolymerization, polymer blending, and structural modifications. [178]

These approaches are specifically designed to enhance the binder's chemical stability, mechanical robustness, and interfacial adhesion, thereby improving the overall structural integrity of the electrode. [179]

Beyond improving mechanical and adhesive properties, the incorporation of specific functional groups, such as carbon-carbon double bonds (C=C), cyano groups (–CN), carboxyl groups (–COOH), and hydroxyl groups (–OH), has led to the development of advanced functional binders. [180,181]

By strategically designing and engineering polymer binders, it is possible to overcome the limitations of silicon anodes, enabling the development of high-performance, high-loading electrodes in next-generation lithium-ion batteries.

This work is focused on selecting and developing the optimal binder for silicon composite anode, in order to improve anode integrity and stability over prolonged lifecycle. The following section provides an overview of the conventional binders used in the production of silicon-based composite anodes.

The most widely recognized and commonly used binders in silicon-based anodes for LIBs include polyvinylidene fluoride (PVDF), carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), polyvinyl alcohol (PVA), polyacrylamide (PAM) and polyacrylic acid (PAA). [182,183] PVDF is a widely used binder for both LIBs cathode and anode, since it is stable over a wide range of operating potentials and provides good processing characteristics. Moreover, it possesses good adhesion strengths ranging from 0.5 to 2.5 MPa, high elasticity (Young's modulus between 500 and 1500 MPa) and good thermal stability (up to 350°C). [184] Despite these pros, the use of toxic solvents such as N-methyl-2-pyrrolidone (NMP) is required, which complicates its use in environmentally sustainable battery manufacturing. PVdF binders form relatively weak interactions with active materials and conductive agents, which compromises the mechanical integrity of silicon anodes. As a result, they are ineffective at accommodating the large volume changes of silicon during cycling, leading to rapid structural failure and capacity fade. Consequently, PVdF is not suitable for silicon-based alloy anodes. In contrast, silicon-based anodes rely on an aqueous fabrication process, making water-based binders the most suitable and sustainable choice. These binders not only align with environmentally friendly manufacturing processes, but also enable the formation of hydrogen bonds with the silicon surface, thereby significantly enhancing both the mechanical stability and the electrochemical performance of the silicon-composite anode.[185-188]

PAA [189-191], PVA [191,192], PAM [193,194], and polysaccharide-based polymers such as CMC [195-197] and SBR represent some of the most outstanding and commonly employed aqueous polymer binders for silicon-based anodes.

CMC is a water-soluble binder that significantly improves slurry viscosity and adhesion while maintaining good mechanical flexibility. It provides an adhesion strength between 1.5 and 4.0 MPa and has a Young's modulus ranging from 50 to 300 MPa. Although CMC is not intrinsically ionically conductive, its hydrophilic nature can facilitate ion transport when in contact with liquid electrolytes. As a result, in the presence of electrolyte, the effective ionic conductivity of CMC-containing interfaces can reach values in the range of 10^{-6} to 10^{-4} S/cm, significantly higher than that of dry PVDF-based binders. However, its thermal stability is low, reaching approximately 250°C. [198-202]

SBR is known for its high elasticity and ability to enhance the electrode cohesion. It is typically used in combination with CMC to improve mechanical stability and processability. SBR provides an adhesion strength between 1.0 and 3.5 MPa and has a relatively low Young's modulus ranging from 1 to 10 MPa. While SBR does not exhibit intrinsic ionic conductivity due to its non-polar and non-ionic nature, its flexible network structure supports electrolyte penetration, enabling effective lithium-ion transport at the electrode interface. In terms of thermal stability, it can withstand temperatures of approximately 300°C. [200,201,203,205] PVA is another widely used binder that offers an adhesion strength between 1.0 and 3.0 MPa. Its elasticity is relatively low, with Young's modulus between 10 and 100 MPa. [202] The hydroxyl groups (–OH) within the PVA structure facilitate intermolecular bonding, promoting both electrode cohesion and resistance to particle detachment. However, PVA binders also present several critical drawbacks. They are highly sensitive to moisture, which can lead to swelling, reduced mechanical stability, and degradation of performance over time.[203] Their thermal stability is relatively limited, with degradation typically occurring around 250 °C, thus restricting their use in high-temperature processing environments.[204] In addition, although PVA has a higher ionic conductivity than PVDF (ranging around 10^{-6} S/cm), this value remains modest and may not fully support rapid ion transport in high-rate applications.[205,206] Furthermore, excessive incorporation of PVA in electrode formulations can lead to increased brittleness, reducing elasticity and ultimately accelerating capacity fade during cycling. [207]

Among polymeric binders investigated, PAM and PAA have emerged as effective alternatives to conventional PVdF, offering unique and complementary physicochemical properties.[208] PAA is characterized by a high density of carboxylic acid groups (-COOH), which provide strong hydrogen bonding interactions with the hydroxylated surface of SiO_x or silicon nanoparticles.[209,210] These interactions contribute to improved adhesion to the active material and enhanced structural integrity during cycling. Moreover, PAA exhibits high ionic conductivity, ranging from 10^{-2} to 10^{-4} S/cm, and its mechanical properties, including Young's modulus (10–100 MPa), can be modulated by pH control, allowing tailored viscoelastic responses to accommodate the anisotropic volume expansion of silicon during lithiation/delithiation cycle. [211,212]

Its adhesion strength can reach values between 3.0 and 6.0 MPa, and its thermal stability of approximately 280°C makes it compatible with industrial electrode drying processes. Studies have shown that PAA coatings contribute to the formation of stable SEI layers and suppress electrode degradation, especially in Si-graphite composites. In contrast, PAM enables extensive intra- and intermolecular hydrogen bonding and dipole–dipole interactions within the polymer matrix, owing to the presence of amide groups (-CONH_2). These interactions contribute to its high-water absorbency, film-forming ability, and mechanical ductility. However, when interacting with silicon-based active materials, the hydrogen bonds formed between the amide groups of PAM and the silanol (Si-OH) or oxide surface of Si/SiO_x are generally weaker than the strong ionic or hydrogen bonding interactions established by carboxylic groups (-COOH) present in PAA. While PAM can form numerous hydrogen bonds, particularly within the binder network itself, these are less effective in anchoring the polymer to the silicon surface during cycling. As a result, PAM-based binders typically exhibit lower interfacial adhesion to silicon compared to PAA, leading to reduced structural stabilization upon prolonged cycling. Nevertheless, PAM remains attractive for its flexibility, low toxicity, and ease of processing, and is often explored in combination with more strongly interacting functional groups to improve adhesion performance.

Additionally, PAM has moderate thermal stability ($\sim 250^\circ\text{C}$), limiting its applicability in high-temperature processing conditions. While both polymers individually show promise, recent binder systems have focused on combining PAA and PAM to exploit their synergistic advantages. This strategy allows the engineering of polymer matrices that balance high adhesion and interfacial stability (from PAA) with improved ductility and

swelling behaviour (from PAM). The introduction of amide groups helps modulate the elasticity of the polymer network, which is particularly beneficial for accommodating the volumetric strain of silicon particles without causing electrode delamination. Furthermore, this blend enhances electrolyte uptake while mitigating binder dissolution, contributing to more consistent ionic transport across cycles.

In this research, a linear terpolymer binder comprising PAA, PAM, and a third confidential monomer was employed. The linear configuration of the polymer is particularly advantageous for electrode fabrication, as it ensures homogeneous distribution within the slurry, promotes interparticle binding, and facilitates the formation of a continuous polymeric network throughout the electrode matrix. Linear binders also exhibit predictable viscoelastic behaviour, which is crucial for controlling slurry rheology and ensuring uniform coating during electrode fabrication. Such architectural control is essential for achieving high active material loading, minimal cracking during drying, and optimal interfacial contact between the active material and the current collector.

In addition, the selected terpolymer binder features a high density of functional groups, particularly carboxylic acid moieties (-COOH) and amide groups (-CONH₂), which enable extensive hydrogen bonding within the electrode matrix. These functionalities not only ensure strong adhesion to silicon-based particles, but also allow for chemical modification that enhances electrochemical performance. Specifically, through a neutralization reaction using lithium hydroxide (LiOH), the distribution between -COOH and -COO⁻ groups along the polymer backbone can be precisely adjusted, thereby controlling the degree of neutralization of the aqueous polymer solution. This modulation has a direct impact on the chemical and physical properties of both the slurry and the resulting electrode. [213]

This process, commonly referred to as *binder prelithiation treatment*, is increasingly recognized as it contributes significantly to improving the first-cycle Coulombic efficiency and long-term cell stability.[212-215]

Indeed, this *prelithiation treatment* offers several key advantages. Firstly, it directly contributes lithium ions that can participate in SEI formation or compensate for the irreversible lithium consumption associated with the lithiation of silicon active materials during the initial cycles. This reduces the net lithium loss from the cathode and enhances the capacity retention of the full cell from the very first cycle. Then, the presence of Li⁺ in the binder matrix improves ionic conductivity within the electrode, facilitating better ion

transport during cycling. Moreover, the lithiated binder leads to earlier stabilization of the electrode–electrolyte interface by forming a more uniform and stable SEI, which mitigates ongoing parasitic reactions and helps preserve electrode integrity over prolonged cycling. Finally, the ionic structure of the binder modifies the electrostatic interactions within the slurry, which can lead to more favourable rheological properties, improved coating uniformity, and reduced electrode swelling during operation.

However, this chemical modification also affects the final pH of the binder solution, which in turn influences the entire electrode fabrication process. The degree of neutralization alters the ionization state and solubility of the binder, impacting slurry viscosity, solid dispersion, and drying behaviour. A finely tuned pH is therefore essential to maintain a balance between processability, film-forming ability, and electrochemical stability. The synergistic integration of lithium-containing functional groups, optimal pH control, and linear polymer architecture in the terpolymer system enhances interfacial bonding, reduces mechanical degradation, and enables the fabrication of high-loading, high-performance silicon anodes.

In addition to prelithiation treatment, optimization of the polymer binder's molecular weight (MW) is of fundamental importance for silicon-composite anodes in lithium-ion batteries (LIBs). [216]

The choice of molecular weight significantly influences the mechanical, rheological, and consequently, electrochemical properties of these anodes. Specifically, molecular weight affects polymer chain entanglement density, directly impacting the electrode's ability to accommodate repeated volumetric expansion during lithiation and delithiation cycles. A binder with low molecular weight typically exhibits lower viscosity, enhancing slurry processability, facilitating mixing, and improving the dispersion uniformity of silicon particles, thereby leading to more homogeneous coating and better electrode manufacturing. However, such low molecular weight binders often exhibit significant drawbacks, primarily their insufficient mechanical strength and cohesive properties, which are crucial during extensive cycling of silicon-based anodes. This mechanical inadequacy may lead to rapid degradation of electrode integrity, increased electrode cracking, delamination, and ultimately pronounced capacity fading during prolonged cycling. [217] On the other hand, binders with higher molecular weight tend to offer increased mechanical robustness due to enhanced polymer chain entanglement, which supports stronger interparticle cohesion and better electrode stability. Higher molecular weight polymers

significantly improve electrode integrity, reducing particle detachment and ensuring consistent electrical contact within the electrode matrix, thereby preserving electrochemical performance over extended cycling. Nonetheless, excessively high molecular weights introduce considerable limitations, notably increased slurry viscosity. This high viscosity can hinder efficient mixing and homogeneous dispersion of active particles, complicate slurry preparation, and result in non-uniform particle distribution within the electrode. Such challenges negatively affect electrode coating uniformity, potentially leading to uneven lithiation/delithiation reactions and compromised electrochemical performance.

Therefore, selecting an optimal molecular weight for the binder is critical to balancing mechanical integrity and processing efficiency. Intermediate molecular weights are typically considered ideal, as they strike an effective compromise, ensuring sufficient mechanical strength to accommodate silicon's volumetric expansion, while maintaining manageable viscosity and processability for slurry preparation. Empirical studies, such as those by Jolley et al. [218] and Zhao et al. [219] underscore the advantages of intermediate molecular weight PAA binders, demonstrating improved electrode performance with sustained capacity retention and reduced mechanical degradation.

Therefore, optimizing the binder design by carefully controlling both prelithiation treatment and molecular weight is essential for developing robust, high-performing silicon-composite anodes for next-generation lithium-ion batteries.

1.5. Electrode production: from electrode architecture to testing

Electrode production is a critical step in lithium-ion battery manufacturing, as it directly influences the cell performance, stability, and scalability. This process includes the design of the electrode architecture, material formulation, coating and drying procedures, and subsequent electrochemical testing to evaluate functionality and stability.

1.5.1. Theoretical electrode architecture

The design and manufacturing of LIB electrodes follow a structured, multi-step workflow that begins with theoretical considerations and culminates in full-cell assembly and testing. Figure 12 illustrates the theoretical workflow typically followed for the development and production of lithium-ion battery electrodes, culminating performance evaluation.

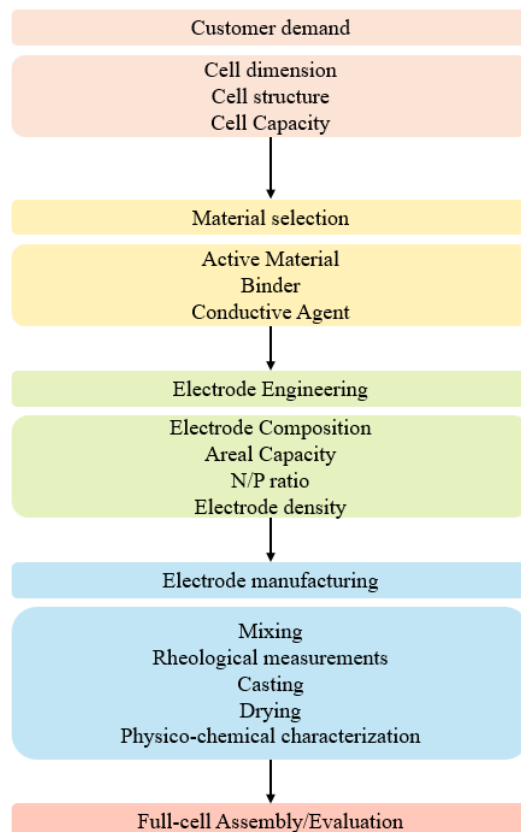


Figure 12. Cell manufacturing workflow, from electrode design to cells assembly

In this doctoral research project, each of these steps was systematically executed, based both on specific customer requirements and on additional technical needs related to electrochemical testing and prototype cell development.

The process began with the definition of the final application goals, which included the specification of binder chemistry, electrode composition, and overall cell format. Once the performance targets were established, the first step was the theoretical design of the cell, involving the definition of its dimensions, architecture, and energy capacity. This was followed by careful material selection. In particular, the active materials based on silicon (as detailed in Section 1.3) and the optimized binder systems (introduced in Section 1.4) were chosen according to their electrochemical and mechanical compatibility. Subsequently, individual characterizations necessary for the study and optimization of the slurry itself has been evaluated before proceeding with electrode assembly.

1.5.2. Electrode Manufacturing: a workflow from formulation to the final electrode properties

Once the polymeric binder and active materials have been selected, and the theoretical electrode architecture has been established, the subsequent stage involves the practical preparation of the slurry, followed by coating, calendaring, and ultimately cell assembly.[220] (Figure 13)

Despite scale-dependent adjustments, both laboratory- and pilot-scale manufacturing share a common fundamental workflow comprising key stages: formulation, mixing, coating, drying, and calendaring. These steps, though often standardized in principle, involve numerous critical variables that must be finely controlled to ensure high-quality electrode fabrication. [221-223]

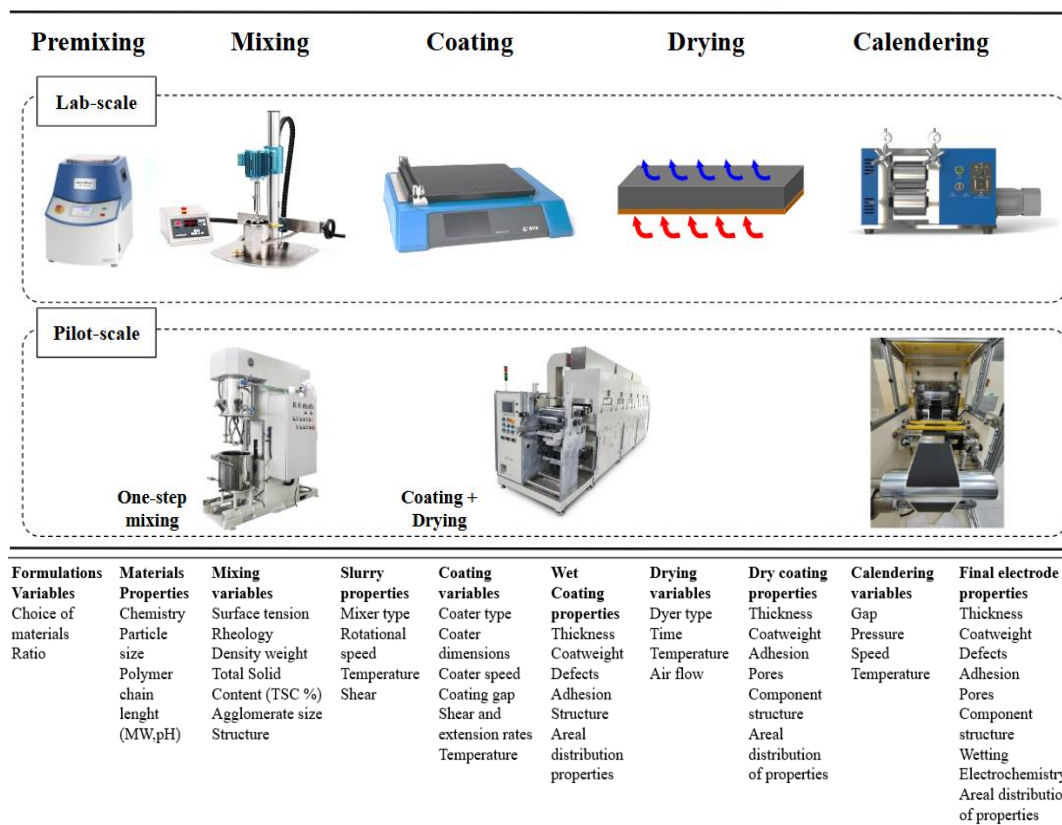


Figure 13. Lab-scale and Pilot-scale electrode manufacturing production; each step reports its own properties. (rearranged from [220], Licensed under CC BY 4.0.)

The first step, *mixing*, is carried out to achieve a homogeneous slurry.

In this stage, the binder solution, conductive agent, and active material are thoroughly mixed to ensure uniform dispersion of the components. The selection of the appropriate mixer type and rotational speed is crucial, as shear forces influence both the degree of dispersion and the rheological behaviour of the slurry. An optimal mixing protocol prevents agglomeration, ensures uniform distribution of components, and enables a processable viscosity profile suitable for high-quality coating. Differences between lab-scale and pilot-scale mixing become apparent here: while lab-scale setups allow for parameter flexibility, pilot-scale systems demand stringent control over dispersion homogeneity and batch consistency. Moreover, additional differences between laboratory- and pilot-scale production arise from the distinct operational speeds achievable by their respective mixing equipment. Nevertheless, in both cases, employing a more intensive mixing protocol, characterized by higher rotational speeds and extended mixing time, can yield beneficial effects. In particular, it facilitates the breakdown of potential agglomerates formed during the mixing process, thereby leading to a slurry with optimized rheological behaviour,

typically exhibiting a shear-thinning trend, so a decrease of viscosity under higher shear rates, which is advantageous for high-speed coating applications. [224,225]

The as-prepared mixture is then coated onto current collectors using techniques like doctor blade and slot-die or reverse comma-roll, which are used in lab-scale and pilot-scale production line. The casting step plays a fundamental role in electrode fabrication, involving the uniform deposition of the slurry onto the current collector, significantly influencing the final microstructure of the electrode. The quality of casting is strongly influenced by key slurry parameters such as particle size, viscosity, and solid content. Smaller particles offer smoother coatings due to their higher surface area, but they can also increase viscosity and reactivity, requiring careful control of coating speed and gap settings. Additionally, they may promote rapid surface drying, leading to binder migration and particle segregation that compromise electrode uniformity and performance.

Coating can be carried out using various methods. For small-scale coatings, a doctor-blade on a draw-down coater (Figure 14) is commonly used in research labs; while, for larger-scale within industrial applications, it usually takes place in a roll-to-roll configuration, and employs coating techniques like slot die and comma reverse. [220]

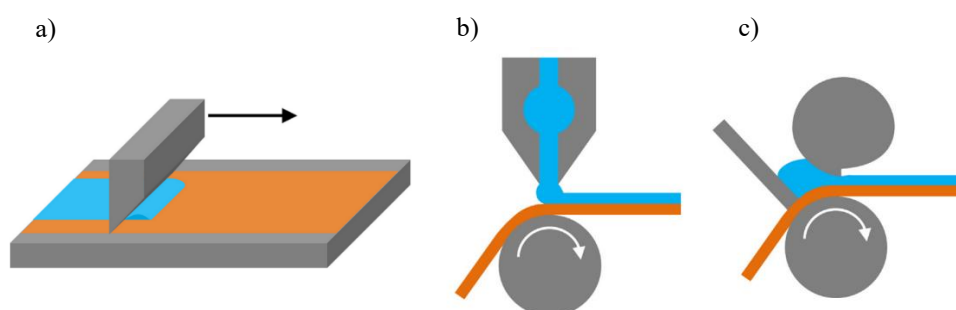


Figure 14. Schematic comparison of three electrode-coating geometries. (a) Draw-down coater equipped with a doctor blade, typically used for laboratory screening; (b) Slot-die head for roll-to-roll processing, where slurry is metered through a precision die and deposited onto a moving foil, enabling uniform, closed-loop thickness control. (c) Comma-bar (Meyer-rod) coater, in which a rotating bar drags excess slurry away from the foil to define the coating height while permitting high-speed continuous production. (rearranged from [220], Licensed under CC BY 4.0.)

In pilot-scale manufacturing of lithium-ion battery electrodes, *reverse comma-roll coating* is one of the most effective and widely adopted techniques due to its high precision and scalability. Unlike doctor-blade methods commonly used in laboratories, which rely on manual or semi-automated spreading of the slurry across a substrate, the reverse comma-roll setup enables continuous, high-speed, and highly uniform coating suitable for industrial-level electrode production.

The reverse comma-roll system comprises a metering roll that rotates in the opposite direction to the moving substrate (typically the current collector foil), creating a controlled shear gap between the roll and the substrate. Slurry is fed into this gap, and the thickness of the coated layer is primarily determined by two factors: the gap height between the roll and the comma blade, and the roll-to-web speed ratio, which defines the relative motion between the coating roll and the moving substrate. By adjusting these parameters, it is possible to finely tune the wet film thickness, which directly influences the dry electrode thickness after solvent evaporation. This configuration allows for excellent control over coating uniformity and is especially well-suited for high-viscosity slurries, such as those based on silicon-composite systems. During pilot-scale processing, *real-time thickness monitoring* is critical to ensure that the coated electrode meets target specifications. This is often achieved using a dial gauge micrometer, mounted downstream of the coating station, which measures the dry film thickness directly on the calendered electrode foil. These contact-based gauges allow for rapid adjustments of process parameters (e.g., slurry flow rate, gap setting, or roll speed) based on live feedback. This is particularly important when dealing with thick electrodes ($>100\text{ }\mu\text{m}$), where minor deviations in thickness can lead to substantial inconsistencies in areal loading and electrochemical performance. Furthermore, the reverse comma-roll setup is compatible with inline drying ovens, allowing the entire process, from slurry deposition to solvent removal, to occur in a controlled and continuous manufacture. This integration ensures not only scalability, but also reproducibility and quality control across large electrode batches. Such process is essential when transitioning from laboratory-scale proof-of-concept electrodes to pilot-scale production lines intended for pre-industrial validation.

The third critical step is the *drying* phase, where the solvent must be fully removed to ensure a stable electrode structure prior to calendaring and cell assembly. [226]

In laboratory-scale production, drying is typically conducted inside a vacuum oven. Vacuum drying is particularly beneficial as it helps control solvent evaporation rates uniformly throughout the electrode thickness, mitigating concentration gradients that cause binder migration and uneven particle distribution. The control, provided by vacuum drying, maintains the microstructural uniformity established during the casting step, ensuring optimal interfacial stability between the active materials, conductive additives, and binder. While this approach is practical for small batches and allows for solvent evaporation under controlled pressure and temperature, it is inherently slower and less uniform compared to pilot-scale systems. Moreover, the physical transfer of the wet electrode film into the vacuum oven introduces risks of slurry redistribution or flow distortion, potentially leading to surface irregularities or delamination. Additionally, uneven solvent evaporation during static vacuum drying can result in binder migration toward the top surface, compromising the homogeneity of the electrode and adversely affecting adhesion and electrochemical performance.[227-229]

In contrast, pilot-scale manufacturing integrates the drying step directly into the continuous coating line through multi-zone heating systems, combining infrared (IR) and convective air drying. These inline ovens achieve significantly faster solvent removal, typically within few minutes, while preserving the structural uniformity of the electrode film. The gradual temperature gradient and controlled airflow within the drying chambers prevent the formation of gradients in binder or conductive additive distribution, thereby maintaining film integrity.

After illustrating the individual steps involved in electrode fabrication at both laboratory and pilot scale, the following sections present the characterizations performed after each corresponding stage.

1.5.3. Viscosity: a study on slurry processability

Following the mixing step, one of the first characterizations performed to assess and validate the quality of the slurry, ensuring its suitability for the subsequent manufacturing stages, is the study of its rheological behaviour, commonly referred to as viscosity. Rheological characterization of electrode slurries is essential for optimizing their processing and ensuring high-quality electrode manufacturing. For silicon-based electrode slurries, precise viscosity control is particularly important due to the material complex behaviour associated with significant particle-particle interactions, high surface area, and the considerable structural changes during slurry preparation. Within the process (Figure 13), an optimal slurry formulation is developed with the aim of achieving target electrode parameters, such as areal capacity, negative-to-positive (N/P) electrode ratio, and bulk electrode density. The designed formulation is subsequently produced and processed through a series of experimental stages: optimized slurry mixing was conducted, and its rheological properties were measured to assess dispersion stability and coating quality. [230,231]

Rotational rheology, a common method for characterizing the viscosity of electrode slurries, typically employs coaxial cylinders or also called cup-bob geometry. (Figure 15a) This geometry involves a rotating element (bob) and a stationary counterpart (cone), with the slurry contained within the narrow gap between them.

The cone-bob setup is advantageous because it ensures uniform shear rates throughout the sample, providing reliable, accurate, and reproducible viscosity measurements even for highly heterogeneous and complex suspensions.

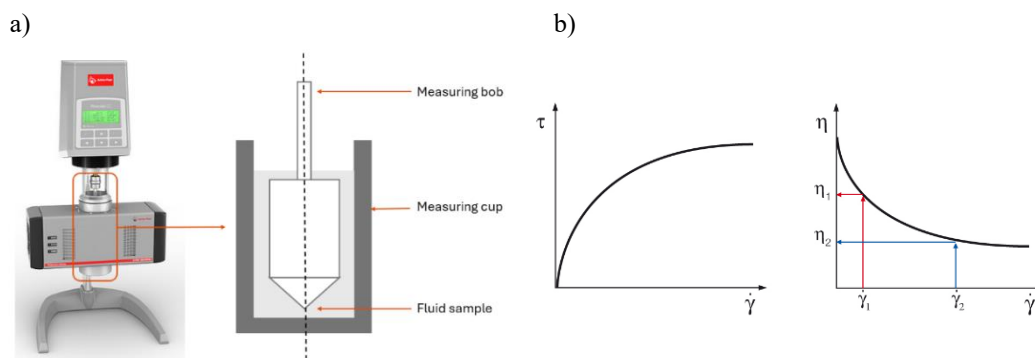


Figure 15. a) Rotational Viscometer RheolabQC, within its cup-bob geometry; b) Typical flow curve of a shear-thinning material.

The fundamental rheological measurements in rotational rheology involve applying a known torque to rotate the geometry at a specific angular velocity (ω , rad/s). This action generates a shear stress (τ) within the slurry, measured from the torque (T) according to the geometry-specific relationship (7)

$$\tau = \frac{T}{2\pi R^2 h} \quad (7)$$

where R is the radius of the rotating element, and h is the height of the cylindrical region being sheared.

The shear rate ($\dot{\gamma}$), another critical parameter, is directly derived from the angular velocity (ω) and the geometric dimensions of the cone-bob setup. Specifically, it is calculated using the equation (8):

$$\dot{\gamma} = \frac{\omega R}{d} \quad (8)$$

where R is the radius of the bob and d is the gap between the rotating cone and the stationary bob.

From these parameters, Equation (9) reports the viscosity (η) defined as the ratio between shear stress and shear rate:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (9)$$

In a rotational test, the shear rate is preset. So, the viscometer sets the desired shear rate by adjusting the rotational speed, measures the resulting torque, and converts this torque into shear stress; this measurement is a flow curve. Materials may exhibit Newtonian (ideally viscous), shear-thinning (pseudoplastic), or shear-thickening (dilatant) flow behaviour. A flow curve (viscosity vs. shear rate) is obtained by increasing the shear rate stepwise with a fixed dwell time at each step, while maintaining constant temperature and ambient conditions. Silicon-based electrode slurries commonly exhibit non-Newtonian behaviour, typically characterized by shear-thinning (pseudoplastic) characteristics (Figure 15b). Shear-thinning implies that viscosity decreases with increasing shear rate, a behaviour attributable to the progressive alignment of suspended particles and the disruption of particle aggregates under increased shear stress. Hence, shear-thinning behaviour is characterized by a steep decline in viscosity once the shear rate exceeds roughly $1\text{--}10\text{ s}^{-1}$.

Under steady-shear conditions, the slurry viscosity curve typically displays four regimes: (i) a high -viscosity plateau at low $\dot{\gamma}$, reflecting that the flocculated particle network is still intact; (ii) a sharp drop at the apparent yield point as the network fractures; (iii) a power law region indicating well-dispersed particles; and (iv) a second plateau at very high $\dot{\gamma}$, where hydrodynamic interactions dominate. This response arises from few microstructural changes. At rest, silicon particles, conductive carbon, and polymeric binders form a weak, space spanning network held together by hydrogen bonding, electrostatic attractions and van der Waals forces; this flocculated structure entraps solvent and yields a high apparent viscosity. [232,233]

Makino et al demonstrate that when shear is applied, those interparticle links break progressively, the aggregates disperse and polymer chains adsorbed on the particle surfaces stretch and align with the flow, which lowers their hydrodynamic volume and, in turn, the bulk viscosity.[230]

Moreover, other researchers found out that rheo-small-angle light scattering (-rheoSALS) and -cryoSEM studies further show that the average agglomerate diameter decreases logarithmically with increasing shear rate, while zeta -potential magnitudes rise as binder layers re-orient, confirming a strong correlation between microstructural evolution and macroscopic viscosity decay. [234]

Excessive mixing energy, however, can mechanically degrade high molecular weight binders, permanently reducing low-shear viscosity, yield stress and the overall degree of shear thinning, thus narrowing the acceptable viscosity window. Indeed, controlled shear thinning is advantageous both in lab-scale and pilot-scale productions: low viscosity at processing shear rates (10^2 – 10^3 s⁻¹) ensures reliable pumping and uniform coating, while rapid viscosity recovery at rest minimizes sedimentation during drying. Consequently, quantitative rheological profiles guide optimization of mixing energy, solids content, and binder chemistry, leading to optimized processing parameters such as mixing speed, coating methods, and drying conditions. Proper rheological characterization thus ensures uniform coating thickness, electrode homogeneity, and optimal mechanical, directly guiding formulation refinement and process optimization for manufacturing robust and high-performance silicon-based lithium-ion battery electrodes.[235]

1.5.4. Final electrode obtained

A typical anode consists of three main components: the active material (Si-composite, graphite), a conductive agent (e.g., carbon black), and a polymeric binder that provides mechanical cohesion and adhesion to the current collector. The binder plays a crucial role in maintaining the structural integrity of the electrode during cycling, especially for silicon anodes, due to their significant volumetric change.

Figure 16 shows the typical microstructure of an as-prepared LIB electrode, composed of active material, conductive carbon, and polymeric binder. In this structure, the binder (typically pre-dissolved in a solvent) functions as a mechanical matrix that anchors the particles to the current collector and form an interconnected electronic network, often referred to as the carbon-binder domain.

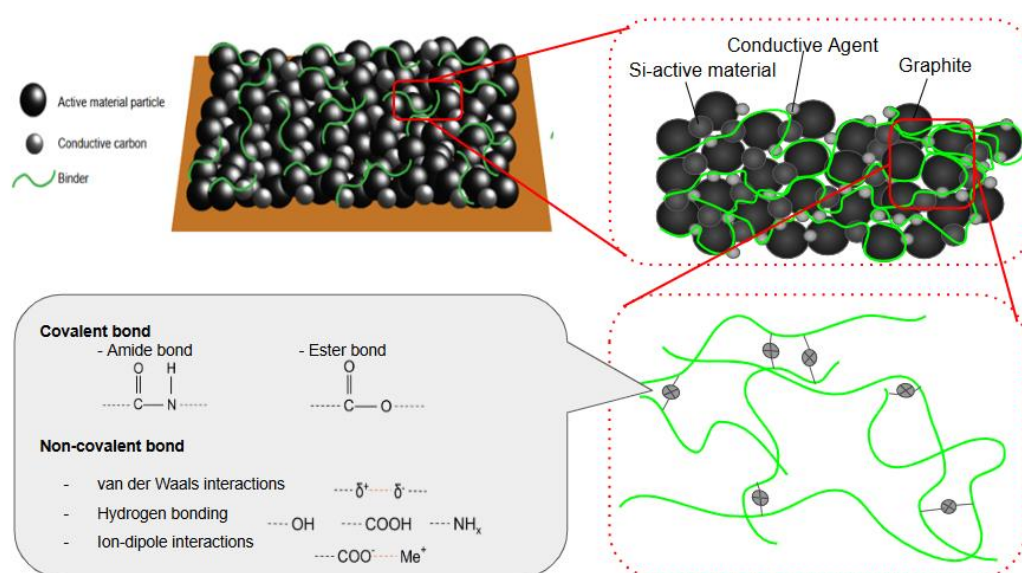


Figure 16. Electrode structure: binder behaviour for Si-composite anodes.

In the illustrated structure, the green polymeric chains represent the binder network, which interpenetrates the matrix of conductive carbon and active particles. This network is responsible not only for holding the electrode components together, but also for facilitating mechanical flexibility and buffering the internal stresses caused by silicon volume changes. The zoomed-in view highlights how the binder physically and chemically interacts with both the active material and the conductive phase.

The chemical nature of the binder determines the types of interactions it can form. In this case, as mentioned in Section 1.4, the binder is composed of PAA, PAM, and a third confidential monomer, which enable the formation of both covalent and non-covalent bonds. Covalent interactions may include the formation of amide bonds (between -COOH groups of PAA and -NH_2 groups of PAM or other additives) and ester bonds (between carboxylic acids and hydroxyl-containing moieties). These covalent bonds improve the network mechanical stability and chemical anchoring to the active material surface.

In addition to covalent bonds, a variety of non-covalent interactions further contribute to electrode cohesion and performance. These include hydrogen bonding between polar groups such as -COOH , -NH_2 , and -OH ; ion-dipole interactions between carboxylate anions (-COO^-) and metal cations (Me^+), possibly present at the surface of silicon oxides or dopants; van der Waals forces, which, although weaker, still play a role in binder adhesion and flexibility. These interactions collectively enhance binder affinity to the Si surface and maintain electrical contact with the conductive network during electrochemical cycling, accommodating mechanical stress. Such a multifunctional binder architecture is particularly advantageous for silicon-based anodes, as it mitigates its intrinsic challenges.

Considering the designed anode, it is necessary to step back adopting a bottom-down approach. It is critically important to evaluate the electrode after the casting and drying stage by systematically characterizing its structural and electrochemical properties. Among these, three parameters are essential for qualifying the electrode before subsequent cell assembly: *areal capacity density*, *porosity*, and *final electrode thickness*.

The *areal capacity density* provides a direct measure of the amount of active material available per unit surface area, and it is a key determinant of the energy density and scalability of the electrode. It must be optimized to ensure a balance between high capacity and manageable mechanical stress during cycling. Vacuum drying promotes consistent and homogeneous pore formation, essential for uniform electrolyte distribution and efficient ionic transport. Porosity, largely due to drying conditions, plays a key role in ensuring adequate electrolyte infiltration and lithium-ion transport, and it also directly influences the areal capacity density. A higher porosity generally improves ion accessibility and facilitates electrolyte uptake, which can enhance rate capability and cycling stability. [237,238] However, it simultaneously reduces the volume fraction of active material per unit area, thereby decreasing the areal capacity. On the other hand, a lower porosity boosts the active

material loading and thus the areal capacity, but it may compromise ionic conductivity and lead to performance losses at high rates. Therefore, achieving an optimal porosity is crucial for maximizing the trade-off between high areal capacity and efficient lithium-ion diffusion, ensuring balanced performance in both energy and power delivery without sacrificing electrode integrity.

Finally, accurate measurement of the *final electrode thickness* is indispensable, as it directly affects ionic resistance, energy density, and mechanical integrity. In particular, electrode thickness plays a crucial role as it directly impacts various properties of LIBs, such as active material mass loading, ionic transport, ohmic resistance, and mechanical integrity.

Thicker electrodes increase the mass loading of active materials, improving areal capacity and energy density, particularly at low current rates, while also reducing the proportion of inactive components. However, they can hinder lithium-ion transport due to longer diffusion pathways and increased resistance, resulting in lower power performance and a greater risk of cracking or delamination during processing.

Commercial silicon-composite anodes typically present post-calendering thicknesses in the range of approximately 50 to 100 μm , a compromise between maximizing areal capacity and maintaining efficient ion transport. Lab-scale studies illustrate that increasing electrode thickness enhances energy density, but also introduces challenges. For example, Li et al investigated electrodes at 20, 40, and 60 μm thicknesses and observed that while thicker electrodes improved capacity per area, they suffered from poorer lithium-ion diffusion and higher impedance resulting in faster performance degradation. [239-241]

In industrial pouch cells, a careful balance is essential. Studies on commercial $\text{SiO}_x\text{/C}$ /graphite pouch cells reveal that post-calendering stack thickness must be precisely managed, due to its direct impact on cell swelling behaviour and mechanical integrity under cycling. [242,243]

For example, typical commercial electrodes for these designs are optimized around 70–80 μm thick enough to deliver high areal capacities ($>3 \text{ mAh/cm}^2$), but thin enough to minimize ionic resistance and mechanical strain. [244]

Critically, however, the mechanical and electrochemical performance of electrodes at such commercially relevant thicknesses is strongly modulated by the particle size and morphology of the active material. Indeed, as electrode thickness increases, lithium-ion diffusion limitations become more pronounced, making the intrinsic transport properties of the constituent particles increasingly important. Larger active material particles, while

potentially beneficial for areal capacity density, introduce longer lithium-ion diffusion paths and are more prone to mechanical fracture during cycling, particularly in thick films. Conversely, nanosized particles facilitate faster ion transport and better mechanical compliance, which is essential to maintain structural integrity and electrochemical performance in thicker electrodes. Moreover, the increased surface area associated with smaller particles enhances interfacial reactivity but can lead to parasitic side reactions and electrolyte decomposition, especially at high electrode loadings. Therefore, to optimize thick electrodes for industrial application, not only the electrode architecture but also the particle size distribution must be finely tuned. Primary particles, typically smaller in dimension, significantly influence the kinetics of lithium-ion solid-state diffusion due to their reduced diffusion pathways. Secondary particles, usually larger and composed of agglomerates of primary particles, support structural stability, mechanical robustness, and improve electrode wettability during slurry processing. Empirical studies indicate that ratios such as 10:90 or 20:80 between primary and secondary particles can improve lithium-ion transport, slurry rheology, and structural robustness across the electrode thickness. [245] Thus, the selection of particle size and morphology must be precisely engineered to achieve an optimal balance between mechanical durability, ionic transport efficiency, volumetric energy density, and overall electrochemical performance. The dried electrodes underwent calendering (to control porosity and thickness), punching (to define geometry), and cell assembly. Process parameters were rigorously monitored and adjusted (Chapter 2) to ensure lab- and pilot-scale compatibility.

1.5.5. 180° Peel test on anode: study of the coating-collector adhesion

The as-prepared electrode was finally obtained after the assessment of slurry behaviour thanks to rheological measurements and casting and drying of the electrode films. After those steps, the electrode was analysed to verify its quality and confirm that it met the pre-defined structural and mechanical targets (Section 1.5), using peel test measurements.

Peel testing is a standard method for quantifying adhesion strength in bonded assemblies, with the test geometry selected according to flexibility and adhesive characteristics. [246,247]

In the battery industry, peel tests are the benchmark for monitoring electrode-coating adhesion. Although interfacial cracks can be driven at any angle from 0° to 180°, industrial practice almost exclusively adopts the 90° and 180° configurations. It is used a commercial double-sided adhesive tape laminated onto the electrode surface and peeled using a Instron 5943 with a 10N load cell, to produce a force–displacement curve that reflects stable crack propagation.[248,249] To avoid artefacts, the tape is pressed firmly on an aluminium support to expel trapped air; the reverse side of the electrode may be stripped to expose the copper foil, and both foil and tape are gripped to the upper grip. As the cross-head advances at constant speed, the load cell records the peeling force, which is reported as the steady-state force per unit tape width (N m) and directly represents the coating's adhesion strength (Equation 10).

$$Peel\ strength\ (N/m) = \frac{Peeling\ Force\ (N)}{Specimen\ width\ (m)} \quad (10)$$

Peel-adhesion strength is influenced by test parameters, such as peel rate and angle, and by experimental conditions like tape type, interfacial contact quality, dwell time before testing, ambient temperature and humidity, and the calibration and sensitivity of the testing device.

In the 180° peel test, the electrode is bonded to an aluminium backing plate with commercial double-sided adhesive tape (Tesa), after which the assembly is mounted vertically, as depicted in Fig. 17. The copper foil is manually lifted from the coating over a short starter length and secured in the upper grip of the universal testing machine. During

the test the cross-head travels upward, bending the foil through a full 180 ° while steadily separating it from the coating. The electrode specimen must be sufficiently flexible to accommodate this tight bend without kinking, thereby ensuring uniform curvature and a well-defined crack front throughout the pull.

Specifically, a 180° peel test was performed on a 2 cm × 10 cm electrode sample to assess its adhesion properties and validate the effectiveness of the previous processing steps.

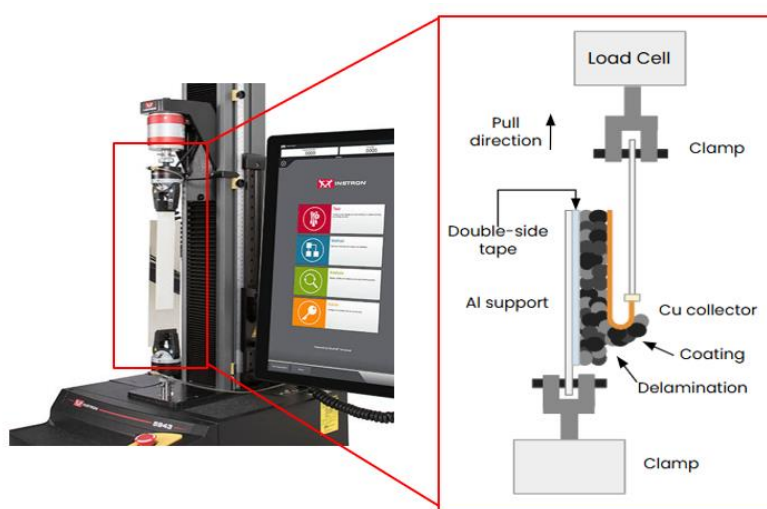


Figure 17. Peel test instrument and geometry used for silicon-composite anodes tests

1.5.6. Cells assembling for electrochemical tests

This chapter introduces the assembly strategies adopted for electrochemical cells at two scales. It first outlines the assembling of CR2032 coin cells, the milligramlevel- format used for lab-scale material screening. It then summarizes the prismatic pouch cells manufacturing at pilot scale. These two illustrate how design constraints evolve from laboratory experiments to ampere-hour devices ready for industrial validation.

Lab-scale electrochemical testing

The electrochemical performance of the silicon-based composite anodes developed in this work was assessed at laboratory scale, using CR2032 coin cells. Figure 18 schematically summarizes the entire workflow, from electrode manufacture to galvanostatic cycling, and distinguishes the two cell configurations adopted: full cells (Si-composite anode|NMC622 cathode) and half cells (Si-composite anode|Li metal).

In a first stage, after casting the slurry of silicon/graphite composites and electrode manufacturing, working electrodes (WE) and counter electrodes (CE) (e.g., NMC622) were produced as presented in Section 1.5.2. Electrodes of 14 mm diameter for anode and 12 mm diameter for cathode were then obtained by precision punching using El-Cut (EL-CELL, Germany).

A polyethylene separator of 16 mm disk was used, and the preferred electrolyte was selected.

All components converged in a dedicated coin cell assembly line (Figure 16a). Individual parts were weighed in an argon-filled glovebox ($O_2 < 0.5$ ppm, $H_2O < 0.5$ ppm) and then stacked as follows:

- *Full cells* (Figure 18a): case bottom/wave spring/Si composite anode/separator (soaked with 300 μ L electrolyte)/NMC622 cathode/spacer/case top.
- *Half cells* (Figure 18b): identical stack, except that the CE was replaced by a 12 μ m lithium metal.

This laboratory-scale methodology offers several advantages. Coin cells require only milligrams of active material, enabling rapid iteration of compositional variables (binder chemistry, conductive carbon fraction, prelithiation strategies) while delivering

reproducible electrochemical metrics: specific capacity, coulombic efficiency, that translate reliably to larger formats.

The detailed electrochemical protocols, cutoff voltages, current densities, and data- - analysis procedures will be presented in the subsequent chapters; the present section serves to frame the experimental setup on which the performance of the silicon composite anodes was quantitatively benchmarked against both lithium metal- and commercial NMC622 cathodes.

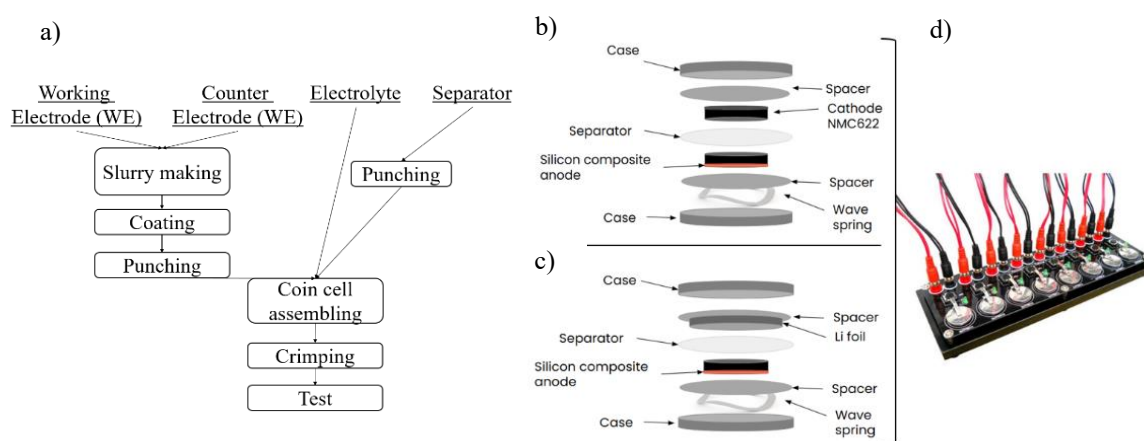


Figure 18. a) Flowchart summarizing the laboratory workflow from slurry preparation, coating and punching of the working and counter electrodes, through separator punching and electrolyte preparation, to coin-cell assembly, crimping and electrochemical testing; b) Geometry of a full-cell CR2032 configuration (silicon-composite anode|NMC622 cathode); spacers and a wave spring ensure uniform stack pressure inside the stainless-steel case; c) Half-cell configuration (silicon-composite anode| Lithium-metal); d) Multi-channel BioLogic test rack with crimped CR2032 cells, illustrating the parallel galvanostatic cycling set-up used throughout this work.

Pilot-scale electrochemical testing

After a first step of binder and slurry production screening, the most promising binder generations were transferred to pilot line for the fabrication of silicon-rich composite anodes in prismatic pouch format. Each anode was paired with a nickel-rich NMC811 cathode of matched areal capacity and stacked into aluminium laminate pouches to yield single cell prototypes with a nominal capacity of ~ 1 Ah. Formation, ageing and long term cycling were conducted under tightly controlled temperature and pressure conditions that mimic industrial practice. Compared with coin cells, these prismatic devices offer several advantages: the larger footprint allows a realistic electrode area-to-current collector ratio, the stack pressure imposed by vacuum lamination reproduces the mechanical constraints of automotive modules, and the higher capacity amplifies degradation signatures, such as impedance rise or gas generation, thereby providing a more stringent assessment of binder robustness. Moreover, the pouch geometry permits in situ thickness monitoring and precise degassing steps, tools that are impracticable at coin scale yet critical for silicon based electrodes prone to swelling. The full processing sequence for the 1 Ah prototypes, from slurry preparation and stacking to vacuum filling, thermal sealing and post formation degassing, will be detailed in the Materials and Methods Section; the present overview simply demarcates the bridge between milligram-scale screening and ampere-hour level validation.

2. Materials and Methods

2.1. Lab-scale manufacturing: SiO_x@C/graphite and Si/C

2.1.1. Slurry formulation and electrode preparation

In this study, we investigated a terpolymer binder, composed of polyacrylic acid, polyacrylamide, and a third confidential monomer. Three different binder formulations were evaluated, referred to as terpolymer **Generation 1** (1M Da, pre-lithiated, pH of 7.5, total solid content (TSC) 8.12 wt%, viscosity (η) at 25 °C $\sim$ 25000 cP), terpolymer **Generation 3** (700k - 800k Da, pre-lithiated, pH = 7, TSC = 7.94 wt %, η at 25°C $\sim$ 10000 cP) and terpolymer **Generation 3 acidic** (700k - 800k Da, pre-lithiated, pH = 6, higher degree of branching). SBR (BM480B, TSC = 38 wt%, density = 0.928 g/cm³) was purchased from Zeon Co., Japan.

CMC (MAC500LC) was purchased from Nippon Paper, and it is a special grade with minimized particle size ($\eta \sim$ 3000-5000 cP, Degree of Substitution (DS) (mol/C₆) = 0.65 - 0.75). Conductive agent, carbon black SC45 (C-ENERGY, Imerys Graphite & Carbon, Switzerland, SA-Bodio-Switzerland) and C-ENERGY™ Actilion GHDR 15-4 graphite (D90 (μ m) = 23, BET surface = 4 m² /g, Tap density = 1.1 g/cm³, Capacity = 364 mAh/g, Initial Coulombic Efficiency (ICE) = 93.0%) were purchased from Imerys. Pre-lithiated and carbon coated silicon oxide commercial active material, Li-SiO_x@C (D90(μ m) = 12.5, area BET surface = 1 m²/g, specific capacity = 1500 mAh/g) was received.

Silicon-carbon active material, Si/C (DXB8), was purchased from BTR New Materials Group.,Co.LTD.; its properties are: 40.09 g/mol, D50 (μ m) = 16.0 $\pm$ 2.0, Specific Surface Area (SSA) $\leq$ 3.0 m² /g, tap density = 0.9 $\pm$ 0.10 g/cc, specific capacity = 650 $\pm$ 10 mAh/g, ICE $\geq$ 91.5 %.

Composite electrodes were fabricated using a blend of lithium doped silicon oxide carbon coated, Li-SiO_x@C and graphite (80%wt), or silicon carbon, Si/C, carbon black SC45, and different binders, including polyacrylic binders and SBR/CMC as reference. For Li-SiO_x@C active material, the standard component ratio for was 95:1:4 = active material: carbon black: binder by weight, unless otherwise specified (for a total theoretical capacity of 591.2 mAh/g); for instance, for the SBR/CMC binder, the composition ratio used was

96:1:1:2 = active material (blend Li-SiO_x@C and graphite GHDR 15-4) : SC45: (CMC:SBR).

In contrast, for Si/C-based electrodes, the standard formulation kept a 95:1:4 ratio, but the active material consisted exclusively of Si/C, without any graphite blend; therefore, the theoretical capacity of the electrode was equal to 650 mAh/g. This was done both in accordance with customer specifications and in consideration of the intrinsic properties of the Si/C material, which does not require graphite addition due to its already enhanced electronic conductivity and structural stability. Deionized water was used as the solvent.

Table 2. Slurry Composition ratio reported.

Slurry Name	Binder 1 amount (%wt)	Binder 2 (%wt)	SC45 (%wt)	Active Material (%wt)
S1	2% SBR	1% CMC	1	96
S2	4% Generation 1	-	1	95
S3	4% Generation 3	-	1	95
S4	4% Generation 3 acidic	-	1	95

For both active materials, the same processing protocol was applied for slurry preparation and all subsequent characterizations, ensuring consistency and comparability across formulations (Table 2).

Initially, the binder material and solvent were combined for dilution (6 wt%). The binder was dissolved using a laboratory SpeedMixer (DAC 400, Hauschild, Germany) operating at 800 rpm for 10 minutes. Following this, the remaining powder components were introduced into the mixture. The solution underwent an initial mixing (Step 1) using SpeedMixer at different speeds (1500 rpm per 1 min; 2000 rpm per 3 min; 800 rpm per 2 min; 2500 rpm per 3 min; 1500 rpm per 1 min) for 10 minutes. Subsequently, the water quantity was adjusted according to the formulation and the desired TSC for slurry preparation. The adjusted slurry was then mixed in the SpeedMixer (Step 2) at different speeds for 10 minutes (1200 rpm per 1 min; 2000 rpm per 3 min; 800 rpm per 1 min; 2000 rpm per 3 min; 2100 rpm per 2 min).

After the initial mixing steps, the slurry was further processed to enhance dispersion using a Dispermat (CV3 plus, VMA-Getzmann, Germany) at 25 °C at 600 rpm for 1 hour, followed by an additional hour at 300 rpm. The prepared slurry was characterized by measuring its TSC using Mettler-Toledo moisture analyser HX204, at 120 °C until mass change ± 0.1 mg. Slurry pH was measured using a V20 Volumetric Compact KF (Mettler-Toledo International Inc.) Then, slurry viscosity was measured using a rotational rheometer (RheolabQC, Anton Paar) with coaxial cylinders geometry at 25 °C, maintained by a Peltier chamber C-PTD 180/AIR/QC.

The obtained slurry was casted onto a 10 μm copper foil using a doctor blade coater (film applicator, BYK byko-drive XL Automatic) with adjustable thickness settings at 100 mm/s, allowing for precise control of the wet coating thickness. The composite electrode was then dried under dynamic vacuum for 25 minutes at 60 °C with airflow at 10 L/min, followed by an additional static vacuum drying for 45 minutes at 60 °C without airflow. From the dried slurry coating, three samples, with dimension 2 cm by 10 cm, were characterized by measuring their thickness and weight to evaluate the quality and uniformity of the coating in order to have a total target area capacity of $3.6 \text{ mAh/cm}^2 \pm 0.09$, a target density of $1.1 - 1.05 \text{ g/cm}^3$ and total target mass loading $6.27 - 6.58 \text{ mg/cm}^2$. After the physicochemical characterizations, electrodes were calendered at 8 mm/s to a target density of 1.6 g/cm^3 at 60 °C, then electrochemical tests were conducted in coin cells CR2032 to assess capacity retention and specific discharge capacity for each binder formulation with both $\text{Li-SiO}_x\text{@C}$ and Si/C as active materials.

2.1.2. Characterization of the slurry and as-prepared anode

Viscosity

Rheological measurements were conducted on four different silicon–graphite slurry formulations (Table 2), with three independent trials performed for each formulation to ensure reproducibility and reliability of the data. The viscosity of the slurries was evaluated using rotational rheology, a standard and widely adopted technique for characterizing the flow behaviour of battery electrode suspensions. Measurements were carried out using a rotational viscometer (RheolabQC, Anton Paar, Figure 15) equipped with cup-bob geometry, which is particularly well-suited for semi-solid, heterogeneous systems like electrode slurries.

The complete flow curves were recorded across a broad range of shear rates, from 1 Hz to 1000 Hz, to fully capture the shear-thinning behaviour and viscoelastic properties of each suspension. All tests were performed at a controlled temperature of 25 °C, by a C-PTD 180/AIR/QC temperature control Peltier, ensuring consistent thermal conditions and minimizing variations due to temperature-dependent viscosity changes. These rheological measurements were critical for assessing the processability of each formulation, particularly in relation to coating uniformity and slurry stability.

Peel Test

The 180° peel test was conducted using an Instron 5943 testing machine, equipped with a 10 N load cell to measure the applied force accurately (as reported in Section 1.5.5.). Adhesion testing was conducted on samples measuring 2 cm by 10 cm, prepared as mentioned previously. To evaluate the adhesion performance, the electrodes were carefully adhered to aluminium plates using Tesa 4970 25mm x 50m double-sided adhesive tape, ensuring a strong and uniform bond between the electrode and the substrate.

Electrochemical tests

Initially, cyclic voltammetry (CV) was performed in a three-electrode T-shaped BOLA (Bohlender, Germany) cell to characterize the produced silicon-composite anodes. Electrodes derived from formulations S1, S2, S3, and S4, with a diameter of 9 mm, were tested against two metallic lithium electrodes (diameter $\varnothing \approx 11$ mm), which served one as counter electrode and the other as reference electrode. All cells were assembled in a glovebox (MBraun Inertgas-System GmbH, Germany) under an argon atmosphere (O_2 , $\text{H}_2\text{O} < 0.1$ ppm) and 600 μL of an electrolyte solution (Solvionic, France), 1 M LiPF_6 dissolved in a 1:1 (v:v) mixture of EC: DMC with 2 wt% VC and an additional 10 wt% FEC, was employed. For CV tests, a Whatman GF/A separator ($\varnothing \approx 12$ mm) was used. The cells underwent cyclic voltammetry at 30°C at a scan rate of $50 \mu\text{V/s}$ for a total of 4 cycles in the potential range of 1.5 V to 0.025 V, thereby adopting a conservative lower potential cutoff.

Subsequently, coin cells CR2032 (Hohsen Corp., Japan) were assembled under an argon atmosphere (O_2 , $\text{H}_2\text{O} < 0.1$ ppm) inside a glovebox (MBraun Inertgas-System GmbH, Germany). Three coin-cells were built for each formulation according to the different binder used. The results of all coin cells pairs were in good agreement, so the average result of three cells per composite will be presented hereinafter.

Two different coin cells configurations were tested:

- i) half-cell configuration to investigate the stability of the anodes produced for each formulation; each silicon-graphite anode ($\varnothing \approx 10$ mm) was paired with a metallic lithium counter electrode ($\varnothing \approx 12$ mm, Alfa Aesar 10769, 99.9%, thickness: 750 μm);
- ii) full-cell configuration, by coupling each anode with an NMC622 cathode.

The full configuration coin cells were composed of a silicon-graphite composite anode ($\varnothing \approx 14$ mm) as a counter electrode and NMC622 with $\varnothing \approx 12$ mm as a working electrode. Polyethylene separator (PE, $\varnothing \approx 16$ mm, thickness=150 μm) and 300 μL of the same electrolyte of CV tests, were used for both cell configurations.

For full-cell evaluation, the balance between the silicon-graphite anode and the NMC622 cathode was quantified through the N/P ratio, calculated as (11):

$$\frac{N}{P} = \frac{Q_N}{Q_P} \quad (11)$$

Where Q_N is the capacity of the negative electrode (anode), Q_P the capacity of the positive electrode (cathode). The N/P ratio was set between 1.1 to 1.2; maintaining an N/P ratio slightly above unity ensures that the anode retains a small excess capacity throughout cycling, thereby preventing lithium plating while minimising unnecessary inactive mass.

Electrochemical measurements were performed using a battery cycler (BCS-805, BCS-810 Bio-Logic SAS, France), controlled via ECLab v11.36. Cell temperature was kept at 25 °C thanks to an actively ventilated chamber.

The cells were cycled, in voltage window 4.2 V – 3V, with a precise formation and cycling protocols:

- (i) a 12 h equilibration at open circuit voltage (OCV) to allow partial wetting of the separator;
- (ii) a first formation cycle at C/20 and then, three low current formation cycles at C/10: the cells were charged under a constant current/constant voltage (CCCV) regime, on charge with current limit < C/20, CC on discharge) to stabilize the SEI;
- (iii) a rest of 10 hours and then, three cycles at C/2 under a CCCV regime on charge with current limit at C/20, CC on discharge), where the last discharge capacity was taken as the ‘real’ cell capacity;
- (iv) long-term galvanostatic cycling at 1C: cells were charged under a CCCV regime during the charge, with current limit at C/20, and discharged at 1 C. Cycling underwent 400 - 500 cycles, until the capacity retention fell to 80 % of the initial value.

The specific capacity delivered by the cells varied according to the silicon content of the anodes, leading to C-rates in the range of approximately 0.05 C to 1C.

2.2. Pilot-scale production: Mg-SiO_x/Graphite composite anode

For the anode formulation, Super P conductive carbon black (SP, CAS 215-609-9, Timcal) was employed as the electronic conductive additive. The active materials consisted of magnesium-doped silicon oxide (Mg-SiO_x, 20 wt%, DMSO, supplied by Daeju), blended with a graphite mixture composed of natural graphite (NG, BTR 918-2, D50 (μm) = 16.846, D90 (μm) = 27.048, BET surface = 2.041 m²/g) and artificial graphite (AG, Shanshan FSNC-4, D50 (μm) = 18.159, D90 (μm) = 35.333, BET surface = 2.113 m²/g) in a 3:7 weight ratio. The binder system evaluated included SBR (BM451B, total solids content = 40 wt%, BTR) combined with CMC (MAC350HC, supplied by Powder). Additionally, Syensqo polymer binders Generation 1 and Generation 3, previously screened and validated at laboratory scale, were also incorporated. The acidic variant of Generation 3 remains currently under evaluation and it is not reported here.

The anode formulation used for pilot-scale testing consisted of 98 wt% active material, including Mg-SiO_x, natural graphite and artificial graphite, blended in a fixed ratio of 20:24:56 by weight, respectively. The conductive agent, SP was added at 1 wt%, while the binder system accounted for the remaining 5 wt%, composed of 4 wt% of terpolymer (Generation 1 or Generation 3) or SBR and 1 wt% CMC (TSC = 1.4%). The electrode was calendered to a final density of 1.5 g/cm³, with a single-sided active material loading of 9.2 mg/cm².

The cathode employed for the pilot-scale testing was a double-side coated electrode. The cathode formulation consisted primarily of the active material NCM811 (Cosmo; 97.6 wt%), combined with multi-walled carbon nanotubes MWCNT (ANP; 0.9 wt%) as a conductive agent, and PVDF (Solef® 5130, 1.5 wt%, Solvay Specialty Polymers S.p.A.) as the binder. This cathode exhibited an active material reversible capacity of approximately 210.08 mAh/g, with a single-side loading level of 20 mg/cm², and was calendered to a target electrode density of 3 g/cm³.

Table 3 reports both anode and cathode formulations used for the manufacturing and electrode specifications required for testing.

Table 3. Anode and cathode formulations

	Anode			Cathode		
Design Parameter		Material	Ratio (wt%)		Material	Ratio (wt%)
Electrode composition	Active Material	Mg-SiO _x	94	Active Material	NCM811	97.6
		NG				
		AG				
	Conductive Agent	Super P	1	Conductive Agent	MWCNT	0.9
	Binder 1	SBR/Gen1/Gen3	4	Binder	PVDF	1.5
	Binder 2	CMC	1			

Once the slurries were prepared according to the formulations described, the electrodes were cast and processed to meet specific target specifications. For the anode, the electrode was formulated with a reversible specific capacity of 500.65 mAh/g, a single-side loading of 9.2 mg/cm², electrode thickness of 51 mm, and was calendered to reach a final electrode density of 1.5 g/cm³. The total electrode length was 350 mm, with 320 mm of coating on side A and 263 mm on side B. For the cathode, the electrode had a reversible specific capacity of 210.08 mAh/g, a single-side loading of 20 mg/cm², electrode thickness equals to 48 mm, and a final electrode density after calendering of 3.0 g/cm³. The total length of the cathode foil was 336 mm, with 315 mm coated on side A and 245 mm on side B.

These dimensional and performance targets were established to ensure compatibility with pilot-scale pouch cell assembly and to reflect industrially relevant processing parameters.

2.2.1. Slurry preparation at pilot scale

For the pilot-scale production of water-based anode slurries, a series of well-defined processing steps were implemented to ensure reproducibility, scalability, and consistency with industrial standards. These steps include raw material preparation, sequential mixing protocols, slurry homogenization and degassing, as well as casting, drying, and post-processing of the electrodes. Each of these stages played a critical role in determining the final electrode quality and those are presented in detail in the following sections of this chapter.

For the preparation of the slurries, each formulation was processed using a planetary mixer, employing a sequence of mixing steps at controlled speeds, followed by a final 30-minute degassing stage. This procedure ensured proper dispersion of all components and minimised entrapped air, as further described below. Figures 19 and 20 illustrate the initial process workflow, starting from the selection of active materials and binders through to the mixing stages leading up to slurry homogenisation.

2.2.1.1. Slurry Mixing: considering a standard slurry with SBR/CMC binder

Firstly, a CMC solution was prepared. CMC powder was dissolved in deionized water, while operating IKA homogenizer at 600-700 rpm to ensure uniform dispersion of the powder. The CMC solution (TSC=1.4 wt %) was kept under mixing overnight until CMC powder was fully dispersed and solubilized. Slurries were prepared with 94 wt% active material mixture (Mg-SiO_x + AG:NG), 1 wt% SP and 4 wt% SBR + 1 wt % CMC. Deionized water was used as the solvent. Three pilot-employed mixing sequences were used to prepare the slurry for the reference anode (Figure 19).

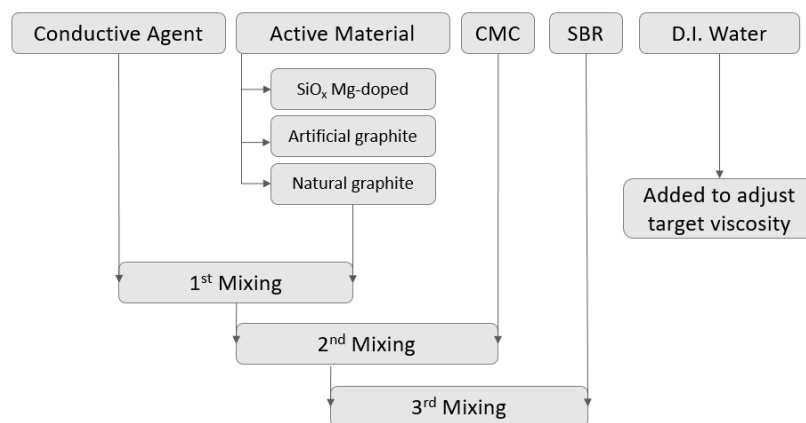


Figure 19. Illustration of the mixing sequence for preparing the reference SBR/CMC electrode slurry.

The slurry procedure illustrated shows several mixing steps. In the first step, conductive agent SP and active material powders (Mg-SiO_x + NG:AG=3:7 w/w) were firstly dry mixed in the planetary mixer at 17 °C for 20 minutes at 20 rpm revolution and at 100 rpm rotation. Then, they were mixed with the CMC solution previously prepared for 120 minutes at different rates, i.e. 25-40 rpm revolution and 500-1000 rpm rotation. The slurry was kept under mixing overnight, then, a SBR solution (TSC=40 wt%) was added in the slurry and all mixed for 15 minutes at 20 rpm revolution and 500 rpm rotation. The last step was the defoaming: anode slurry underwent vacuum defoaming in air flux at 1 bar for 30 minutes at 20 rpm revolution and 500 rpm rotation, to remove the gas bubbles formed during mixing. Slurry defoaming is a main step for pilot scale production, especially for a water-based anode: it is essential to defoam under vacuum at 1 bar pressure to eliminate possible air trapped in the slurry; otherwise, air could cause visible bubbles during the coating process leading to a non-optimized and usable electrode. This method ensures that the slurry is homogeneous, defect-free, and suitable for large-scale anode production.

During the process, the slurry was subjected to viscosity measurements after each addition to monitor the target value, using a Brookfield viscosimeter. To achieve the initial desired viscosity (after the addition of CMC solution), 4000 ± 1000 cP, adjustments was made by adding deionized water (as indicated in the figure 19).

2.2.1.2. Slurry mixing using Syensqo Generation 1 and Generation 3 binders

Slurries were prepared with 94 wt% active material mixture (Mg-SiO_x@C + Graphite), 1 wt% SP and 4 wt% Syensqo binder (Generation 1 or Generation 3) and 1 wt% CMC. Deionized water was used as the solvent.

The pilot scale slurry production for Syensqo anode electrode slightly differs for the reference SBR/CMC electrode, due to optimized several steps of materials addition and mixing. Figure 20 shows the mixing procedure for a general Syensqo binder anode.

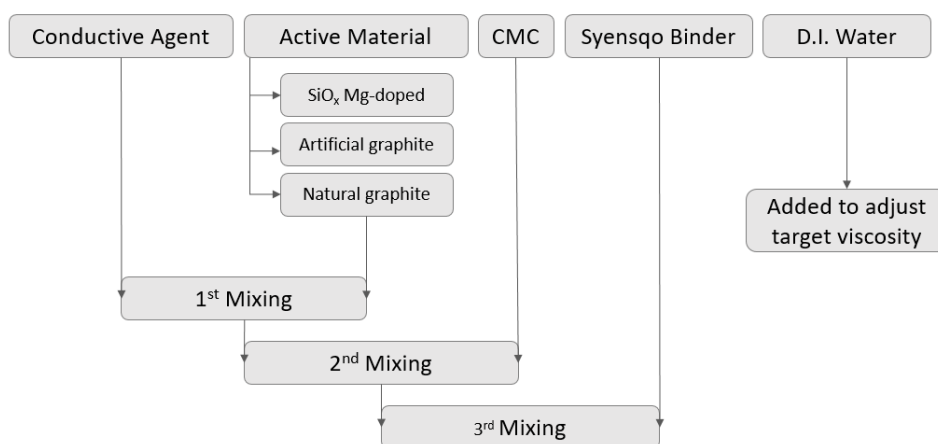


Figure 20. Syensqo binder slurry step by step mixing process: several additions starting from only powder mixing

The conductive agent SP and active material powders were firstly dry mixed in a planetary mixer at 17 °C for 20 minutes, using a revolution speed of 20 rpm and a rotation speed of 100 rpm. Next, the CMC solution (TSC=1.4 wt%, firstly prepared) was added in three stages over a total of 120 minutes, with revolution speeds ranging from 25 to 40 rpm and rotation speeds maintained at 500 rpm. Then, Syensqo terpolymer binder was gradually added, and the slurry was kept under mixing for another 120 minutes at the same revolution and rotation rates. After the binder was incorporated, deionized water was added to adjust the slurry viscosity to the target level. This was followed by an additional mixing step of 15 minutes at 20 rpm revolution and 500 rpm rotation.

Finally, the slurry undergoes vacuum defoaming at 1 bar pressure for 20 minutes under an air flux at 20 rpm revolution and 500 rpm rotation.

2.2.2. Slurry Coating

Following slurry preparation and degassing under vacuum for 30 minutes, the anode slurry was transferred to an industrial reverse comma-roll coating machine for pilot-scale processing. (Figure 21) Before coating, the gap between the comma roll and backing roll was carefully adjusted in the range of 120–130 μm to control the wet coating thickness. The slurry was deposited onto a 10 μm thick copper current collector at a line speed of 0.6 m/min, with a cylinder tension of 60 N and a dancer roll tension of 120 kPa. The coating thickness was continuously monitored in real time using laser displacement sensors, ensuring uniform film deposition and consistent thickness across the all production (Figure 21b).

The coated foil was conveyed through a three-stage drying system, with chambers set at 35 °C (Chamber 1), 48 °C (Chamber 2), and 43 °C (Chamber 3), respectively (Figure 21a). This gradient drying profile enabled controlled solvent evaporation, minimizing binder migration, pore collapse, or crack formation. A dry supply fan operating at 21 Hz ensured stable airflow through the chambers.

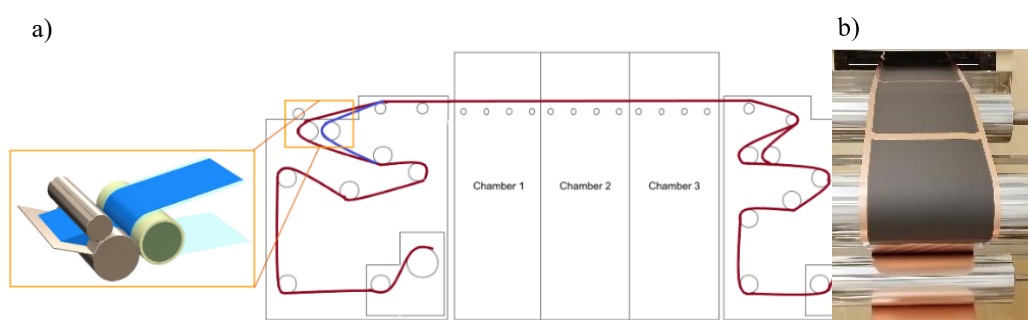


Figure 21. a) Reverse comma-roll reconstruction and inset on slurry position and comma roll; b) Anode prepared at the end of the drying step

After complete drying, the mass loading of the anode on Side A was measured and compared with the target specification of 9.2 mg/cm². If the measured value met the required threshold, the coated foil was re-rolled and re-fed back into the reverse comma-roll coater to proceed with the deposition of Side B. This second coating was carried out under the same processing conditions, including line speed, cylinder tension, and dancer roll pressure, to ensure consistent coating quality and reproducibility across both sides.

2.2.3. Final electrode preparation

This chapter describes the final preparation and processing steps carried out at pilot-scale to obtain the final electrodes implemented in pouch cells assembling. Firstly, the calendering procedure applied to the coated electrodes is presented, together with the resulting electrode thicknesses and densities measured on both the A and B sides. The subsequent tab welding process used to establish electrical contact is then detailed. In addition, a transmission electron microscopy (TEM) characterization performed on one of the produced anodes is reported to evaluate the electrode microstructure after processing. Finally, the full pouch cell assembly workflow is outlined, from electrode cutting and stacking, electrolyte filling, cell sealing to cell testing.

Electrodes calendering

After obtaining a uniform and well-calibrated double-sided anode, the calendering process was subsequently carried out on individual anode coating patterns using a laboratory-scale calendering machine. The operation was performed at room temperature, and the electrode thickness was measured both before and after calendering using a tactile dial gauge to ensure dimensional accuracy. The target electrode density after calendering was set at 1.5 g/cm^3 , corresponding to an average double-coated thickness of $133 \pm 5 \text{ }\mu\text{m}$. As previously described, the cathode electrodes were already manufactured and pre-calendered. They were processed to achieve a final electrode density of 3.0 g/cm^3 , with a single-side mass loading of 20 mg/cm^2 .

Electrodes obtained

Following calendering, the anode was cut to the required dimensions for subsequent electrochemical testing. As shown in Figure 22, the total electrode length was set to 350 mm, with an electrode width of 51 mm. On Side A, the coating covers a length of 320 mm, intentionally leaving a 30 mm section of bare copper foil at one end to enable tab welding and ensure reliable electrical contact. On the reverse (Side B), the coating extended for 263 mm, resulting in an uncoated copper segment of 87 mm. This asymmetric design was specifically engineered to meet the requirements of cell stacking and heat sealing during pouch cell assembly, while maintaining precise alignment between the coated regions and the electrode tabs.

Throughout the entire electrode length, the 10 μm thick copper current collector ensured mechanical robustness and uninterrupted electrical continuity. Once all dimensional and mass loading specifications were confirmed, the final double-sided electrode was processed for calendering and integrated into the subsequent pouch cell fabrication workflow. This electrode geometry was meticulously preserved across all production steps to guarantee reproducibility and compatibility with pilot-scale manufacturing protocols.

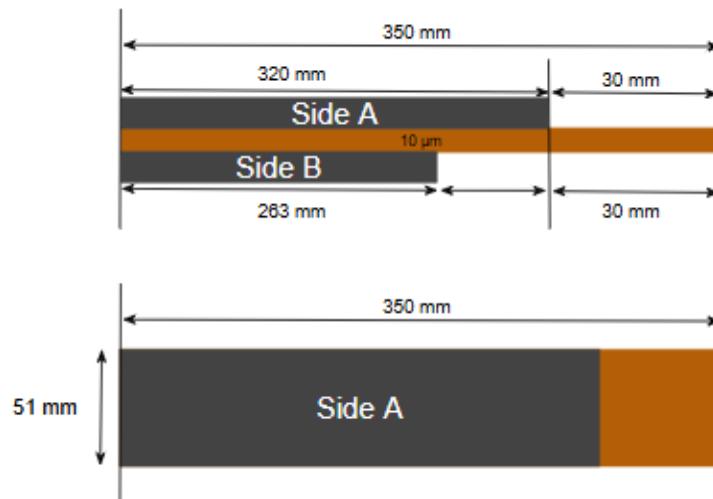


Figure 22. Anode Coating dimensions considering both side A and side B.

Once measured and cut to the desired dimensions, the anodes were dried in a vacuum oven at 60 °C overnight to remove residual moisture. Following the drying step, they were stored in a dry room environment at –60 °C dew point, ensuring that all subsequent processing and cell assembly steps were carried out under controlled low-humidity conditions to prevent moisture-induced degradation and ensure consistent electrode quality.

Electrodes tab-welding

The ultrasonic tab welding process was carried out using a ultrasonic welding machine (Branson Ultraweld, Emerson Electric Co., USA) (Figure 23).

Distinct welding parameters were applied for the positive and negative electrodes, aluminium (Al) and nickel (Ni) tabs, respectively, with welding and holding times appropriately calibrated to ensure robust and reliable bonding. For the positive electrode (Al tab), weld and hold times were set to 0.170 s and 0.220 s, respectively, with an amplitude of 33%. For the negative electrode (Ni tab), weld and hold times were 0.100 s and 0.150 s, respectively, at a higher amplitude of 40% to accommodate the differences in material properties. In terms of geometry, the anode had a total length of 350 mm, with the coating on Side B extending for 263 mm and leaving an 82 mm non-coated region. The Ni tab was welded 3 mm from the edge of the electrode and positioned 1.5 mm from the start of the non-coated copper area. For the cathode, the total length was 336 mm, with a 315 mm coated region on Side A; the Al tab was welded precisely 6 mm from the start of the uncoated region. These tab locations were chosen to ensure proper electrical connectivity, alignment, and compatibility with the pouch cell stacking and sealing process.

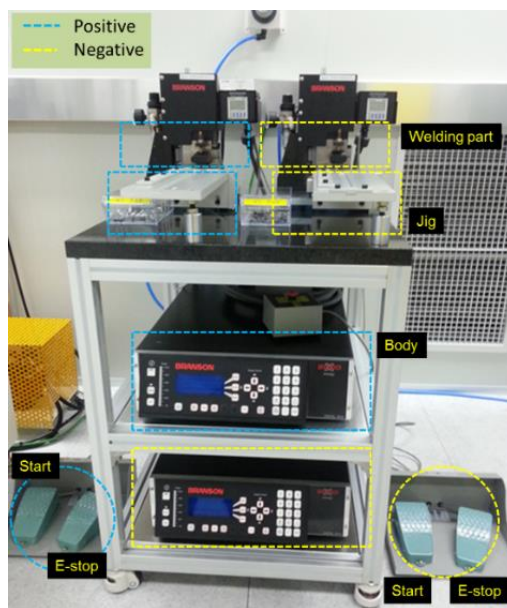


Figure 23. Ultrasonic welding station used for tab attachment. The system comprises two separate welding heads for the positive (Al) and negative (Ni) electrodes, each equipped with its own welding jig and horn (labeled as "Welding part"). The control units (labeled as "Body") allow independent adjustment of welding parameters such as weld time, hold time, and amplitude. Safety features include dedicated "Start" and "Emergency stop (E-stop)" pedals for each unit. The workstation is designed for stability and precision, with color-coded labels distinguishing between the two welding positions

During standard operation, the electrode was placed on the jig with proper alignment: the cathode with the side A facing up and the anode with the side B facing up, as shown in Figure 24. The metallic tab was positioned precisely over the exposed current collector foil to ensure a clean weld and to meet the reference dimensions for 1Ah-class pouch cell assemblies. Specifically, the Al tab for the cathode was aligned to leave a 10 mm extension from the edge, while the Ni tab for the anode was positioned on the 3 mm from the edge of uncoated copper segment.

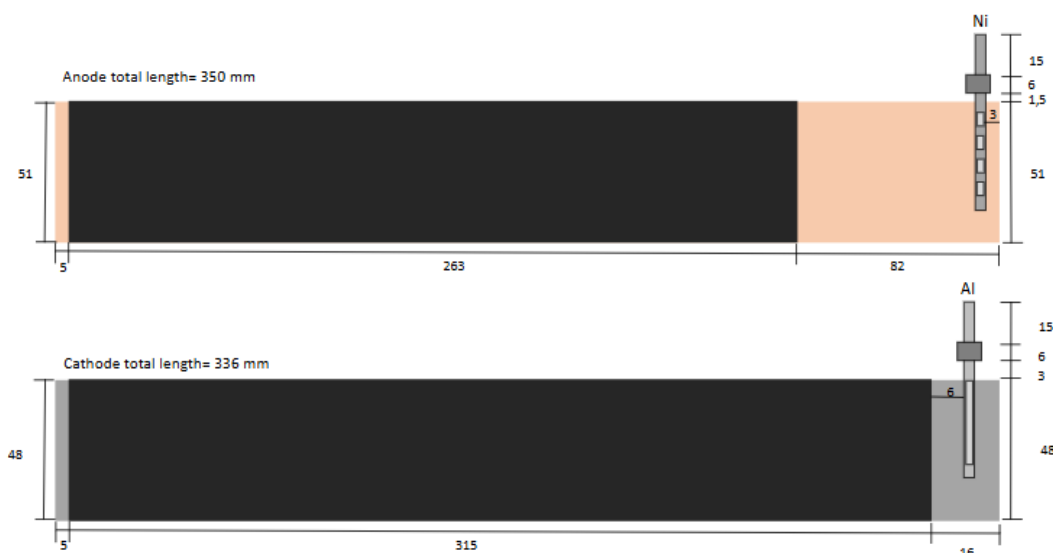


Figure 24. Final dimensions and tab positions of the anode and cathode electrodes used for pouch cell assembly. The top view shows the anode (total length 350 mm, width 51 mm) with a Ni tab welded onto the uncoated copper region. The bottom view shows the cathode (length 336 mm, width 48 mm) with an Al tab attached to the exposed current collector. The layout ensures correct alignment, tab positioning, and compatibility with cell stacking requirements.

2.2.4. TEM anode characterization

High-resolution Transmission Electron Microscopy (TEM) was employed to investigate the microstructural organization and interfacial architecture of the pilot-scale anode. This technique was selected due to its superior spatial resolution compared to conventional SEM, enabling direct observation of nanoscale features such as binder coating continuity, interparticle interfaces, and phase boundaries within the electrode composite.

The objective of this characterization was to examine the surface morphology and coating uniformity of the binder layer (Figure 25), focusing specifically on the interfacial junctions between SiO_x and graphite active material particles within the composite matrix.

TEM lamellae were prepared using a Focused Ion Beam (FIB) instrument (*Thermo Scientific Nova600*), allowing precise site-specific sampling of the electrode cross-section. During sample preparation, a thin protective layer of platinum (Pt) was deposited on the electrode surface to prevent ion-beam-induced damage. The FIB operation was carried out at an acceleration voltage of 30 kV and a beam current of 0.1 nA, ensuring optimal milling precision and minimal alteration of the electrode microstructure.

The analysed electrode corresponds to the pilot-scale pristine anode produced using the Generation 3 lithium-doped binder, incorporating Mg-SiO_x@C active material. This configuration was selected as representative of the optimized slurry formulation developed at pilot scale, aimed at evaluating binder coating behaviour and interfacial compatibility between the active phase and conductive graphite domains.

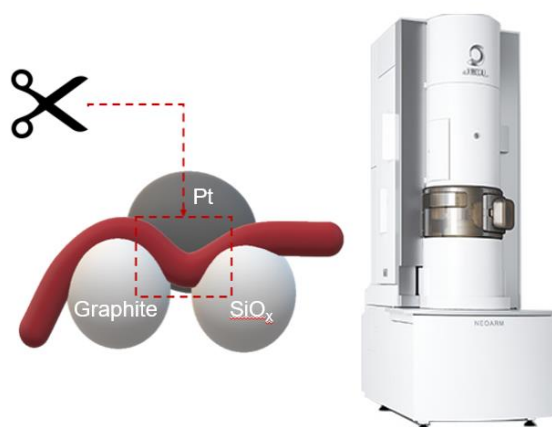


Figure 25. Schematic representation of the focused ion beam (FIB) sampling process used for TEM characterization of the pilot-scale SiO_x–graphite composite anode. The red polymer segment represents the binder coating bridging graphite and SiO_x particles. A protective Pt layer is deposited before FIB milling to prevent ion-beam damage. The prepared region (highlighted by the dashed red box) is then extracted and analyzed in the TEM system (right).

2.2.5. Pouch cells: assembling and testing

Prior to assembly, both prepared anode and cathode electrodes were dried under vacuum at 100 °C overnight under a pressure of 10 mbar. This step was essential to eliminate any residual moisture from the electrodes and ensure stable electrochemical performance, particularly in moisture-sensitive lithium-ion systems. Once dried, the electrodes were handled exclusively in a dry room environment (dew point < – 60 °C) to prevent reabsorption of humidity and to proceed with cell fabrication under controlled conditions.

The pouch cell assembly process began with the preparation of a preformed aluminium-laminate pouch. Individual film sheets were cut to the required dimensions and positioned onto the forming mold of the Pouch Forming M/C at room temperature (RT). A pressure of 0.6 MPa was applied to press the film into the mold cavity, shaping it into a three-dimensional preformed pouch. This process produced a cavity precisely dimensioned to accommodate the as-prepared jelly roll while ensuring compatibility with subsequent sealing and electrolyte filling steps. This pouch not only serves as a mechanical enclosure but also ensures an effective barrier against moisture and air, which is critical for the long-term stability of the cell.

The electrode stack was assembled through a winding process at room temperature, in which the coated electrodes and separators (polyethylene) were arranged in the sequence *cathode / separator / anode / separator* and wound together in the specified direction to form the jelly roll structure. Careful alignment of the electrode edges and tabs was maintained throughout the process. The Al tab (cathode) and Ni tab (anode) were positioned to emerge on opposite sides of the roll, ensuring electrical isolation and compatibility with later packaging steps. The web tension was precisely regulated during the winding step to ensure proper alignment of all layers. This control was critical to prevent telescoping, lateral displacement or misalignment of layers that leads to instability, and to maintain uniform interfacial contact between each electrode and separator layer. Moreover, a consistent layer contact is essential for preserving the mechanical integrity of the wound structure and ensuring homogeneous ionic pathways throughout the jelly roll.

Once winding was completed, the free end of the jelly roll was secured using a strip of adhesive tape, applied longitudinally in the winding direction. This step was necessary to prevent unwinding, maintain compression, and protect the exposed edge. The taped jelly

roll, with final dimensions of approximately 54 mm in width, tab distance of 12 mm and thickness of 38 mm and 35 mm in length. The initial preparation steps, including winding, taping, and pouch insertion, are illustrated in Figure 26.

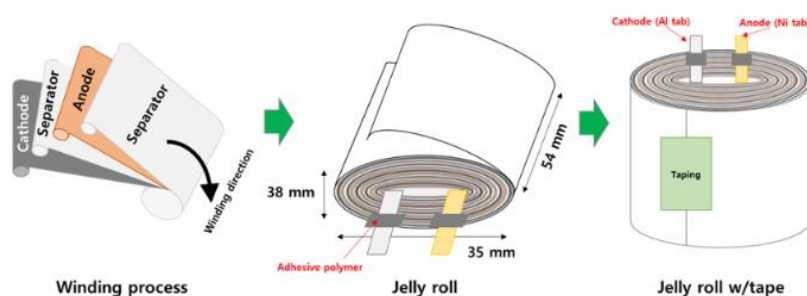


Figure 26. Preparation of the jelly roll: The figure shows the winding sequence of cathode, separator, and anode layers to form the jelly roll. After winding, the roll is secured with adhesive tape to maintain its shape and tab alignment, preparing it for insertion into the preformed pouch cell housing.

Once the jelly roll was formed, it was subjected to a compaction step to improve internal packing density and eliminate void spaces between layers. This was performed using a Hot Press M/C at 60 °C and applying a pressure equivalent to 400 kg for approximately 10 seconds. The freshly wound jelly roll was placed on the press platform and automatically compressed under the defined conditions.

Immediately after hot pressing, the jelly roll was then inserted into the pouch cavity, and it was centred and laid flat at the bottom of the cavity, with the Al and Ni tabs aligned with the corresponding notches to allow correct placement for welding, electrolyte filling, and top sealing; the jelly roll was oriented with the cathode tab (Al) positioned to the left and the anode tab (Ni) to the right. The two tabs were then clearly marked or labeled to identify the polarity and facilitate tab recognition after final pouch sealing. (Figure 27)

The flexible coffee bag laminate was then folded over the inserted jelly roll, aligning the edges to fully enclose the electrode assembly. Subsequently, two sides of the pouch were sealed using a 2-side sealing M/C, operating at 180 °C for 10 seconds, to ensure robust thermal bonding and hermetic encapsulation. After sealing, a slight trim was performed on the cathode side of the pouch to remove excess material. However, sufficient space was

deliberately left on this side to accommodate electrolyte filling in the next processing steps, as this region corresponds to the cathode tab and electrolyte injection zone.

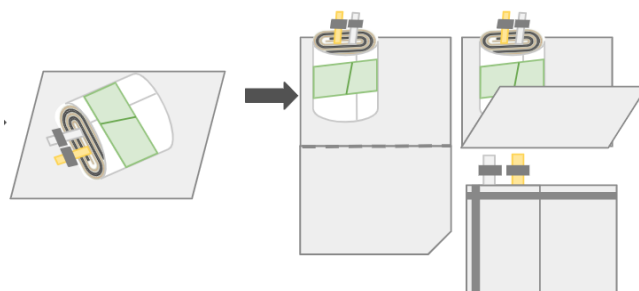


Figure 27. Schematic representation of the insertion of the jelly roll into a preformed pouch.

After the initial sealing on two sides, the pouch cells were subjected to a controlled drying process in a vacuum oven (20 mbar) set at 55 °C for 76 hours. This prolonged thermal treatment was crucial to eliminate any residual moisture from the electrodes, separators, and packaging materials, thereby minimizing the risk of side reactions during electrolyte filling and subsequent electrochemical operation.

In parallel, the electrolyte was prepared inside an argon-filled glove box maintained under strictly controlled conditions, H_2O , $\text{O}_2 < 0.1$ ppm and an internal pressure of approximately 2.7 mbar. The electrolyte solution composed of 1 M LiPF_6 dissolved in a solvent mixture of EC and ethyl methyl carbonate (EMC) in a 3:7 volume ratio, was supplied pre-mixed, from which 60 g was taken. To this solution, 3 g of FEC and 0.3 g of propane sulfone (PS) were added as electrolyte additives to enhance SEI formation and improve high-voltage stability. All components were obtained from the same manufacturer to ensure chemical compatibility. The complete solution was stirred overnight at RT to guarantee thorough homogenization, making it ready for injection on the following day.

Electrolyte filling was carried out using a Pasteur pipette, with a precisely measured amount of $3.5 \text{ g} \pm 0.01$ of the pre-prepared electrolyte injected directly into each pouch cell. The process was performed on a calibrated balance to ensure mass accuracy. Once electrolyte injection was completed for each cell, they were individually placed into a vacuum chamber, where a sequence of three vacuum cycles was applied. Each cycle involved reducing the pressure to 10 mbar using a high-vacuum pump, followed by gradual venting to atmospheric pressure before repeating the process. This vacuum treatment promotes effective infiltration of the electrolyte into the electrode stack and facilitates the removal of trapped air pockets. Notably, upon initial vacuum application, visible bubbling within the pouch was observed due to gas displacement by the injected electrolyte. Subsequent cycles were aimed to minimize residual bubbling and enhance electrolyte penetration and wetting of the internal cell components. After completing the three vacuum cycles, the cells were allowed to rest for 20 minutes to stabilize before proceeding to the next processing step. (Figure 28)

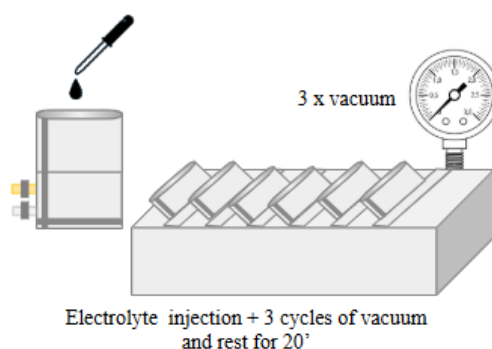


Figure 28. Schematic representation of the electrolyte injection process.

Following electrolyte infiltration and resting, each pouch cell was individually subjected to a vacuum sealing and degassing procedure to remove residual gases and seal the electrolyte inside the cell. The process was performed using a dedicated vacuum heat-sealing unit, equipped with a sample holder to ensure correct pouch alignment and uniform sealing pressure.

The pouch was sealed at 180°C , applying vacuum in a stepwise pressure reduction sequence to gradually extract internal gas while minimizing disturbance to the internal structure and electrolyte distribution. The vacuum pressure was lowered in five controlled stages: (1) 500 Torr, (2) 300 Torr, (3) 200 Torr, (4) 100 Torr, and (5) 50 Torr. Each stage

contributed to efficient gas removal, and the entire vacuum application and sealing sequence was completed within a total residence time of approximately 10 seconds.

Once sealing was complete, the cell was removed from the chamber and stored under dry conditions. This procedure was repeated for all remaining cells to ensure consistent processing and reproducibility. (Figure 29)

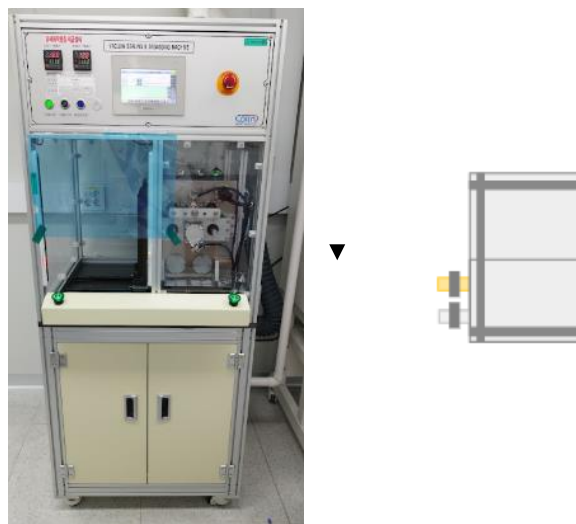


Figure 29. Vacuum sealing equipment used for final cell encapsulation at 180 °C. The image illustrates the sealing machine and the schematic of a fully sealed pouch cell after electrolyte injection and degassing.

After electrolyte filling and vacuum degassing, each cell was positioned between two rigid plastic plates to apply uniform mechanical constraint during the subsequent steps. This setup is critical to prevent excessive pouch swelling due to gas evolution, particularly during the high-temperature rest and formation protocol. The pressure applied by the clamps ensures mechanical stability and helps maintain electrode contact. Each cell was labelled, clamped, and then connected to a specific channel of the PNE battery cycler at room temperature for 24h rest. The primary goal was to charge each cell to approximately 30% State of Charge (SOC), corresponding to a single charge cycle at 0.1C.

Then, the formation protocol consisted of two main charging steps: an initial CCCV charge to 4.2 V with a 0.1C ($t > 10$ s), followed by a rest period of at least 22.5 h to reach ~24 h from the sealing time. An additional CC charge cycle at 0.1C until 4.35 V ($t > 3$ h) was then applied, followed by a 30-minute rest.

Following the electrochemical formation, the cells underwent two aging steps protocol: first, a 12-hour rest at room temperature while still connected to the PNE cyclers and then at 60 °C in a thermal chamber for additional 12 hours. Those thermal aging steps were crucial for stabilizing the SEI layer formed during formation and ensuring uniform electrolyte wetting throughout the cell. (Figure 30)

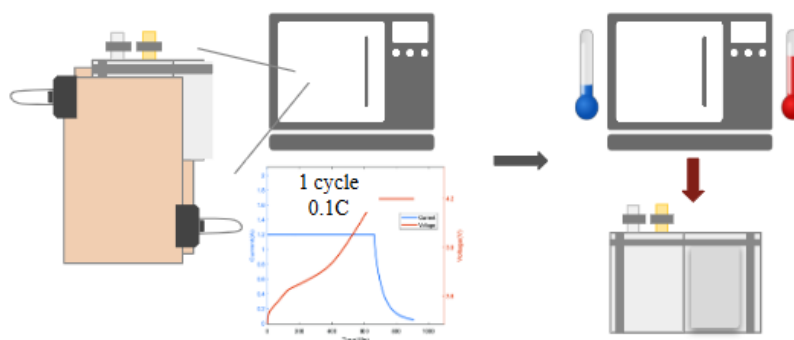


Figure 30. Formation and aging steps of pouch cells. After one 0.1C formation cycle at 25 °C (24 h total), cells were aged in two steps: 12 h at 25 °C and 12 h at 60 °C to promote gas evolution and SEI stabilization.

Once performed the aging steps, cells were removed from the oven, the external plastic supports were detached, and the pouches were opened to inspect gas evolution. As expected, gas accumulation was observed in the free volume intentionally left during electrolyte filling. The cells were allowed to cool down at room temperature for 20 minutes in a dry room -60 °C dew point. Following this rest period, the gas pocket area was carefully trimmed to enable degassing. The cells were then resealed using the vacuum sealing machine at 180 °C, completing the final degassing and sealing process. (Figure 31)

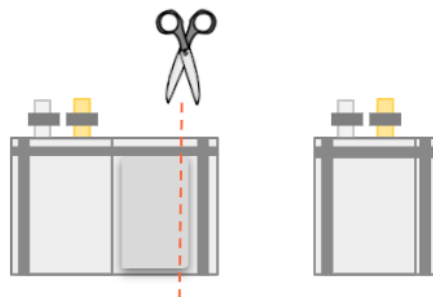


Figure 31. Final vacuum degassing and resealing at 180 °C to remove excess gas and electrolyte before electrochemical testing.

Subsequently, each pouch cell was positioned again between two rigid compression plates to maintain consistent mechanical pressure during the following electrochemical testing phases. This step was essential to prevent internal delamination or swelling, particularly in the case of silicon-containing anodes, which are prone to significant volume expansion. The fixed configuration ensured geometric stability throughout charge/discharge processes and minimized variability caused by external mechanical deformation.

Once stabilized, the cells were individually connected to the PNE cycler for a standardized *capacity check* (CD) protocol.

This consisted of an initial cycle at 0.1C in the voltage window 4.2 V-2.5 V (CCCV in charge, at C/20 and 2.5 V), followed by four charge/discharge cycles at 0.2C (CCCV in charge at C/20 and 2.5 V), and three additional cycles at 0.5C in voltage window 4.2V – 3V with a 10 minutes rest among each cycle. This multistep approach enabled precise evaluation of the effective capacity under controlled conditions, while also serving as a diagnostic step to screen for any anomalous cell behaviour (e.g., abnormal voltage drop, gas evolution, or impedance rise).

Following the completion of the *capacity check*, each cell was charged to a 30% SOC. Subsequently, two additional charge–discharge cycles were performed at 0.5 C, followed by a further charge step to reach 50% SOC. At this intermediate state, the Direct Current Internal Resistance (DCIR) was measured at different time intervals (e.g., 0 s, 10 s) and under different current rates to quantify the internal resistance of the cell at cycle zero. This same DCIR procedure was repeated every 100 cycles throughout the long-term cycling protocol, in order to monitor and compare the evolution of resistance with aging.

The assembled pouch cells were then divided into two temperature-controlled batches: one undergoing cycling at room temperature (25 °C), and the other exposed to elevated temperature conditions (45 °C).

This comparative cycling study was designed to assess the impact of thermal stress on performance degradation, capacity fade, and stability of the SEI, particularly relevant for next-generation silicon-based anodes (Figure 32).

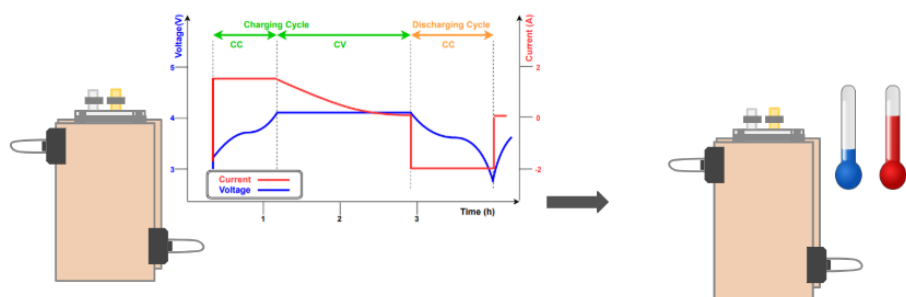


Figure 32. Schematic representation of the capacity check protocol (4 cycles at 0.2C, followed by 3 cycles at 0.5C) performed after final sealing. Afterward, cells were subjected to long-term cycling either at room temperature (RT, 25 °C) or at elevated temperature (HT, 45 °C) to evaluate thermal effects on performance.

Each thermal batch was subjected to a distinct electrochemical protocol: *Reference Performance Test (RPT)* was carried out to establish the baseline electrochemical performance of the pouch cells at 25 °C. *RPT protocol* began with a rest period of more than four hours, followed by a CC discharge at 0.5C to 2.5 V, with a voltage cutoff of 2.8 V or a time limit of four hours. After a 30-minute rest, two identical cycles were performed consisting of a CCCV charge to 4.2 V at 0.5 C (cutoff: current < 0.05 A or time > 4 h), a rest of 30 minutes, then a discharge cycle to 2.5 V at 0.05 C (cutoff: V < 2.8 or time > 4 h), and another rest of 30 minutes.

A third cycle was then performed according to the following sequence:

- a CCCV charge to the average target voltage specific to each binder generation (3.802 V for Generation 1 and 3.840 V for Generation 3, values determined from the initial capacity check), at 0.5C, followed by a 30 min rest.
- a CC discharge to 2.5 V at 0.5C, followed by a 30 min rest.
- a CC charge to 4.2 V at 0.2C, followed by a 30 min rest.

- A high-rate CC discharge to 2.5 V at 2C, applying the cutoff condition $V < 2.8 \text{ V}$ or $t > 10 \text{ s}$, followed by a 30 min rest.
- final CC discharge to 2.5 V at 0.5C, with 30 min rest.

After this step, the long-term cycling sequence was initiated and repeated for 300 cycles. This consisted of CCCV charging to 4.2 V at 1C (cutoff: current $< 0.05 \text{ A}$ or $t > 4 \text{ h}$), followed by 30 minute rest, then a CC discharge to 2.5 V at 1C (cutoff: $V < 2.8 \text{ V}$ or $t > 4 \text{ h}$), and a final rest of 10 minutes.

In contrast, the cells cycled at 45 °C were subjected only to galvanostatic cycling, with no RPT steps. These cells underwent a simpler protocol: a CCCV charge to 4.2 V at 1C (cutoff: current $< 0.05 \text{ A}$ or $t > 4 \text{ h}$), followed by a 30-minute rest, and a CC discharge to 2.5 V at 1C (cutoff: $V < 2.8 \text{ V}$ or $t > 4 \text{ h}$), completed by a 10-minute rest. The implementation of the DCIR measurement at 25 °C allowed for real-time tracking of internal resistance evolution throughout the cycling process, thus offering valuable insight into degradation mechanisms affecting internal conductivity and the electrode–electrolyte interface.

In addition to the standard electrochemical testing protocols, a separate batch of pouch cells, assembled using the three different silicon-based anodes (formulated with SBR/CMC, Generation 1, and Generation 3 binders), was subjected to a thermal storage test. Following the completion of the formation step, these cells were placed in a temperature-controlled oven at 60 °C. The purpose of this treatment was to monitor the percentage increase in cell thickness over time, as an indicator of gas evolution and mechanical swelling. To this end, the total cell thickness was measured using a micrometre immediately after formation (week 0), and subsequently at the end of each week, for a total monitoring period of four weeks.

3. Results and Discussion

3.1. Lab-scale manufacturing and testing

This section summarizes the laboratory-scale evaluation of silicon-based composite electrodes employing Li-SiO_x@C and Si/C as active materials. The primary objective of this study was to investigate the influence of various Syensqo polymeric binders on electrode formulation, processing, and performance, to identify candidates that could match or exceed the performance of the industry-standard SBR/CMC system, thereby guiding potential future scale-up. The focus was placed on four promising binder formulations. All reported data, including slurry viscosity, adhesion strength, and electrochemical performance, were averaged from three independent tests per formulation to ensure reproducibility and statistical reliability.

Finally, electrochemical testing was conducted both in half-cell and full-cell configurations. Since the primary objective of this study is the evaluation of binder performance, the focus is placed on interpreting the full-cell electrochemical response as a means to primarily discriminate the effect of the binder among the different anode formulations. Assuming that the NCM622 cathode behaves consistently across all tested cells, any observed variation in terms of electrochemical stability, capacity retention, or coulombic efficiency can be mainly attributed to the specific binder employed in the silicon-based anode compositions.

3.1.1. SiO_x@C/graphite slurry formulation

Rheological characterization

The rheological behaviour of the investigated slurries was evaluated by means of flow curve measurements, which revealed a typical non-Newtonian, shear-thinning behaviour, as illustrated in Figure 33. The flow curves correspond to the four anode slurries (S1–S4) formulated using Syensqo binders in combination with Li-SiO_x@C and graphite as active materials. As previously introduced the rheological study in Section 1.5.3. and detailed in

the Section 2.2., the shear rate domain can be conceptually divided into two distinct regions, each relevant to a specific step in the electrode production process.

The first region, spanning shear rates from 1 to 100 Hz (highlighted in green in Figure 33), can be directly associated with the slurry preparation and mixing stage. This frequency range is therefore meaningful for evaluating and optimizing the slurry formulation preparation and mixing. In contrast, the second region, between 100 and 1000 Hz (highlighted in orange), corresponds to the conditions more closely encountered during the coating and film formation step at pilot scale. Thus, considering this higher frequency range is essential for assessing slurry behaviour in view of future pilot-scale processing and coating stability. This conceptual separation aligns with practical needs: mixing occurs under lower mechanical stress (lower shear), while the coating process imposes higher shear rates due to fast doctor blade or comma-roll movements. Consequently, particular attention was devoted to the low-shear regime, as it is extremely sensitive to the physicochemical characteristics of the slurry, such as mixing efficiency, particle dispersion, and overall homogeneity. Within this range, the viscosity measured at 10 Hz was selected as a representative and discriminating parameter, given its central position in the mixing-relevant frequency domain and its reliability in capturing variations in rheological behaviour arising from formulation or processing differences. A viscosity acceptance range of 2000–8000 mPa·s at 10 Hz was established for the laboratory-scale process. Slurries falling within this range were considered adequately mixed and thus eligible for subsequent processing steps, such as coating and drying. This viscosity window not only reflects optimal mixing and homogeneity conditions, but is also consistent with values typically used in industrial-scale manufacturing of lithium-ion battery electrodes. Only slurries meeting this criterion were processed further, ensuring that electrode fabrication proceeded under controlled and reproducible conditions.

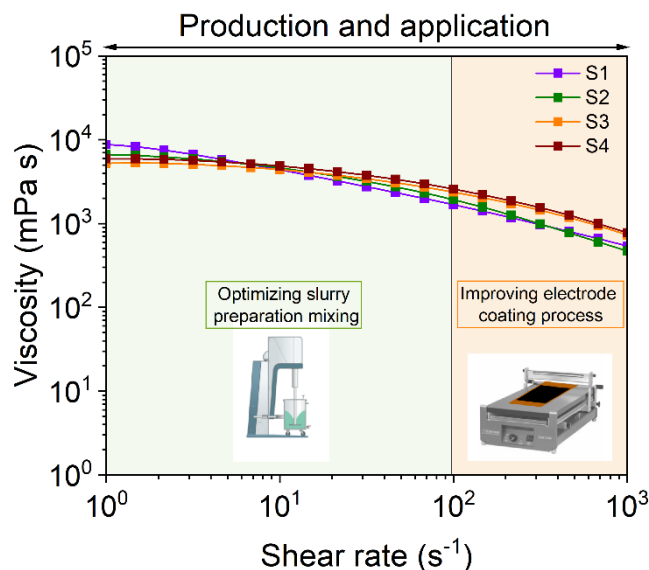


Figure 33. Flow curves of four slurries formulated with Syensqo binders (S1–S4) with Li-SiO_x@C employed, highlighting the low-shear region for mixing and the high-shear region for coating. Viscosity at 10 Hz was used as the acceptance criterion (2000–8000 mPa·s).

As shown in Figure 33, the viscosity profiles of the four investigated slurries (S1–S4) exhibit consistent shear-thinning behaviour across the entire shear rate range. The corresponding numerical values at both 10 Hz and 1000 Hz are reported in Table 4, allowing direct comparison between low- and high-shear regimes.

Specifically, values range from 4367.7 mPa·s (S1) to 4860.7 mPa·s (S4), confirming that all samples exhibit rheological properties compatible with the required standards for lab-scale processing. Moreover, the relatively narrow viscosity distribution suggests good repeatability in the mixing protocol and a high degree of formulation homogeneity.

At higher shear rates (1000 Hz), viscosity values decrease significantly, as expected from shear-thinning systems, but remain within an acceptable range for coating applications. The modest variation observed among the samples, e.g., 470.1 mPa·s for S2 vs. 780.6 mPa·s for S4, further confirms that all slurries maintain stable flow behaviour under coating-relevant conditions. This reinforces the conclusion that the slurries not only meet the acceptance criteria but also possess robust rheological profiles suitable for consistent electrode fabrication.

Table 4. Average viscosity values at 10 Hz and 1000 Hz for slurries S1–S4, representing mixing and coating regimes, respectively ($n \geq 3$).

Table 4. Rheological measurements values obtained at 25°C on several slurry formulations.

Slurry name	Viscosity (mPa·s) at 10Hz	Viscosity (mPa·s) at 1000 Hz
S1	4367.7	540.4
S2	4611.8	470.1
S3	4390.5	733.7
S4	4860.7	780.6

The favourable viscosity behaviour observed in the slurries formulated with Li-SiO_x@C can be attributed to the chemical nature of the surface functionalities of the active material and its strong interactions with the selected binders. The carbon coating of Li-SiO_x@C particles contributes to an enhanced dispersion stability by reducing surface energy and limiting particle agglomeration, while the lithiated silicon oxide core presents residual surface hydroxyl or silanol groups that can engage in hydrogen bonding or ionic interactions with the binder network.

In particular, the carboxylic (–COOH/COO[–]) and amide (–CONH₂) groups in Syensqo binders enable strong interactions with the SiO_x surface, stabilizing the slurry microstructure through a viscoelastic polymer–particle network that shear-thins under stress. The partial pre-lithiation of SiO_x further reduces surface reactivity, improving colloidal stability and preserving slurry viscosities within the optimal processing range (≈ 2000 – 8000 mPa·s), thus minimizing flocculation or gelation during large-scale electrode fabrication.

Overall, the favourable viscosity behaviour observed for Li-SiO_x@C-based slurries reflects a well-balanced combination of surface chemistry, carbon-coating effects, and binder–particle compatibility, which together promote uniform mixing, defect-free coating, and robust mechanical integrity of the final electrode layer.

Adhesion measurement

The adhesion strength of the electrode slurries formulated (S1–S4) was evaluated using a 180° peel test configuration, as previously described in Section 1.5.5 and Section 2.1. The results, shown in Figure 34 and summarized in Table 5, clearly highlight the superior adhesion performance of anodes prepared using Generation 3 (S3) and Generation 3 acidic (S4) binders compared to the ones with Generation 1 (S2) and conventional SBR/CMC (S1) samples.

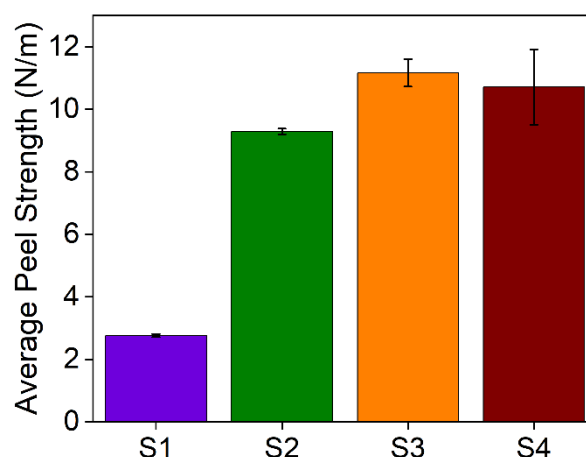


Figure 34. Average peel strength values (N/m) measured by 180° Instron peel test for slurries S1–S4. Values represent the mean of at least three replicates.

Table 5. Average peel strength and standard deviation for each anode, derived from slurry formulation (S1–S4), obtained from at least three independent 180° peel tests per sample.

Table 5. Adhesion peel test results obtained from the four anode tested

Anode tested from slurry formulation:	Average Peel Strength (N/m)
S1	2.76 ± 0.05
S2	9.29 ± 0.09
S3	11.16 ± 0.44
S4	10.72 ± 1.21

Quantitatively, the S3 and S4 formulations exhibit average peel strengths of 11.16 N/m and 10.72 N/m, respectively, higher than S2 (9.29 N/m) and especially S1 (2.76 N/m). The larger deviation observed for S4 is attributed to environmental humidity fluctuations, which, as previously discussed, can significantly influence binder-copper interfacial interactions during testing.

The enhanced adhesion of S3 and S4 can be explained by the lower molecular weight and more acidic pH of the binders themselves compared to S1 and S2. Indeed, a lower molecular weight increases binder chain flexibility and mobility, improving the wetting behaviour on the copper substrate and promoting stronger contact during the drying phase. Simultaneously, a lower pH favours greater deprotonation of carboxylic groups in the polymeric backbone, enhancing interactions with the slightly oxidized surface of the Cu current collector. This leads to the formation of hydrogen bonds or coordination complexes between carboxylate groups and surface copper oxides, improving interfacial adhesion. Additionally, acidic binders are less prone to swelling and delamination under ambient conditions, contributing to better mechanical integrity under stress. In contrast, the poor performance of S1 is consistent with the known limitations of the SBR/CMC system in terms of adhesion to metal surfaces, especially in the absence of targeted functional groups.

SEM on pristine electrodes

Scanning Electron Microscopy (SEM) measurements were performed on calendered graphite-based electrodes to assess the morphological quality of the coating and the effectiveness of the mixing process. Both dried and calendered pristine electrodes were examined to investigate the distribution of active materials across the electrode surface and detect any heterogeneities potentially linked to binder formulation or processing steps.

Figure 35 shows a progressive improvement in the homogeneity and dispersion of active material, moving from formulation S1 to S4 (Figure 35a-d). In particular, the electrodes prepared with the Generation 3 binders (S3 and S4, Figure 35c and Figure 35d) exhibit a more uniform distribution of the Li-SiO_x@C and graphite phases, with fewer agglomerates and better adhesion to the conductive matrix. In contrast, the S1 electrode (based on the SBR/CMC reference binder, Figure 35a) shows visible particle clusters and non-uniform surface features, suggesting sub-optimal dispersion during slurry preparation and coating.

This trend is further corroborated by Energy Dispersive Spectroscopy (EDS) analysis, reported in Table 6, which reveals slightly higher silicon content in electrodes S2, S3, and S4 compared to S1. The observed differences in Si content may also reflect the influence of binder chemistry on the mixing dynamics and dispersion behaviour of the active material. In particular, the lower molecular weight and higher acidity of the Generation 3 binders enhance polymer–particle interactions, resulting in better homogenization and more effective distribution of silicon-based components throughout the electrode structure.

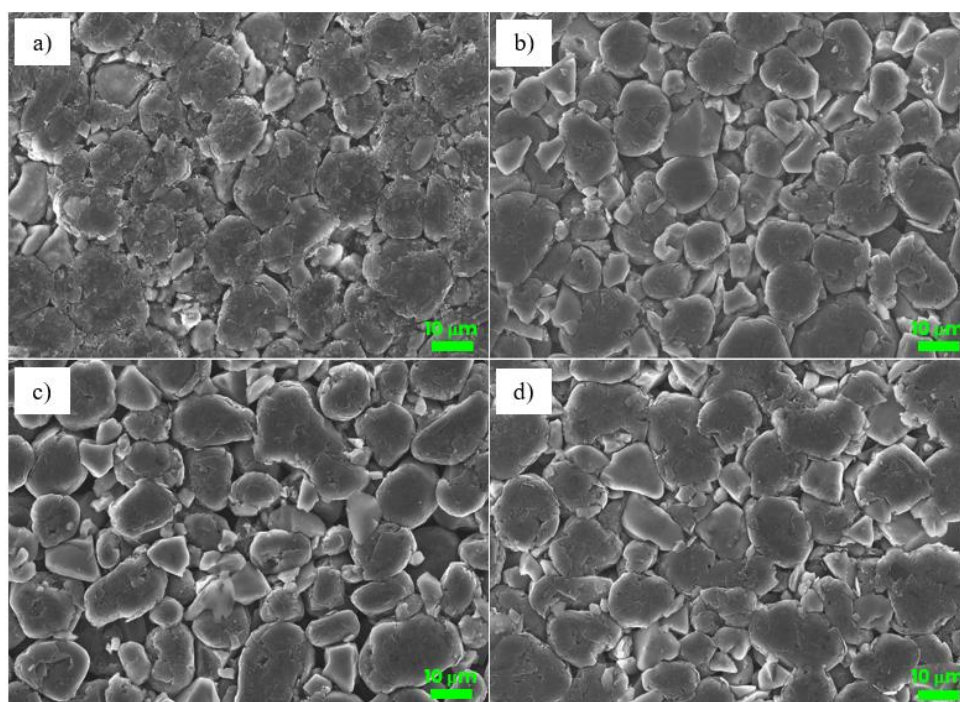


Figure 35. SEM images of pristine Li-SiO_x@C/graphite electrodes: a) S1 anode (SBR/CMC binder used within the formulation); b) S2 anode (Generation 1 binder); c) S3 anode (Generation 3 binder); d) S4 anode (Generation 3 acidic binder)

Table 6. EDS analysis on pristine electrodes

Slurry name	C Atom (%)	O Atom (%)	Si Atom (%)
S1	85.86	11.25	2.73
S2	86.02	10.14	3.68
S3	86.07	10.29	3.48
S4	85.94	9.98	3.95

Electrochemical tests

Cyclic Voltammetry

Cyclic voltammetry (CV) measurements were conducted on Li-SiO_x@C-based anodes using a three-electrode T-shaped cell (BOLA, Bohlander, Germany). Working electrode ($\varnothing=9$ mm) and counter/reference electrode lithium metal foil ($\varnothing=12$ mm) were used. A Whatman GF/A glass fiber separator ($\varnothing=12$ mm) was used, and the electrolyte used was 1 M LiPF₆ dissolved in a 1:1 v/v mixture of EC:DMC with 2%wt VC and 10wt% FEC. All measurements were performed within a potential window of 1.5 V to 0.025 V vs. Li⁺/Li, using a scan rate of 50 μ V/s to allow detailed resolution of redox events, while remaining within conservative electrochemical conditions. Each electrode (S1–S4) was tested over four cycles. In Figure 36, the first and second CV scans of the four anodes are presented. Despite the use of the same active material, differences in the electrochemical response underline how the binder not only affects the mechanical integrity of the electrode but also modulates its electrochemical response, particularly with respect to redox peak shape, intensity, and position. These variations are linked to changes in lithiation/delithiation kinetics, SEI formation dynamics, and ionic/electronic conductivity across the electrode interface.

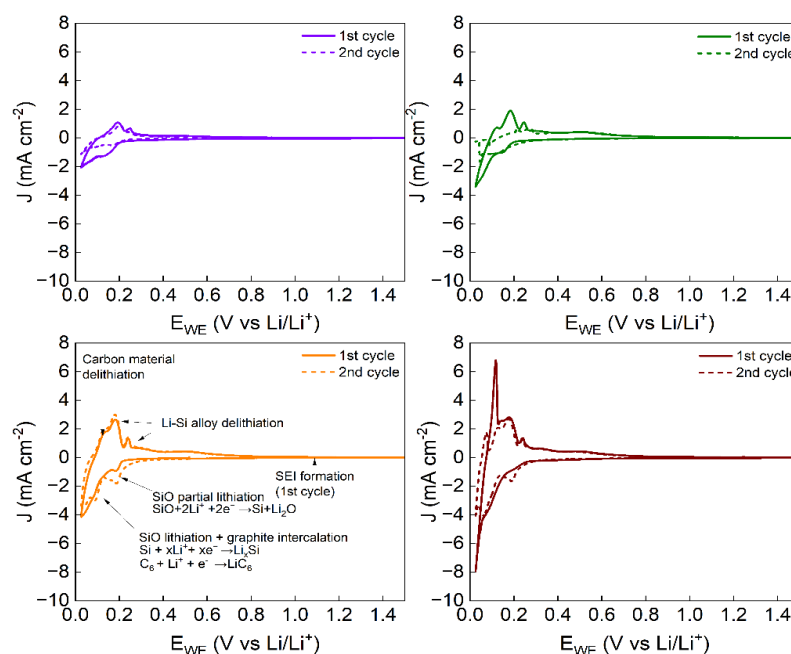
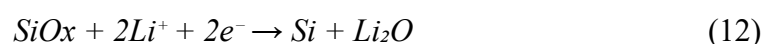


Figure 36. Cyclic voltammetry profiles (first and second cycle at 50 μ V/s) of anodes S1 (purple, SBR/CMC binder), S2 (green, Generaztion 1 binder), S3 (orange, Generation 3 binder), S4 (dark red, Generation 3 acidic binder), with Li-SiO_x@C as active material.

In the case of S1 (purple, SBR/CMC), the overall current response is significantly lower, and the redox features are less defined. During the first lithiation scan, a broad reduction shoulder between 1.0 and 0.6 vs Li^+/Li is observed, which corresponds to electrolyte decomposition and SEI formation. At 0.18 V, a weak and broad reduction peak appears, which can be assigned to the co-lithiation of graphite and amorphous silicon phases, occurring simultaneously. However, the peak is slightly shifted toward $\sim 0.1\text{--}0.15$ V, indicating delayed lithiation, possibly due to poor ionic transport through the inactive polymer matrix. On the anodic side, a broad oxidation peak centred around 0.35–0.4 V is visible, which is attributed to delithiation of Li-Si alloys. The absence of a sharp carbon-related oxidation peak around 0.2 V suggests poor interfacial contact or incomplete reversibility of lithium intercalation in graphite. Overall, these features indicate sluggish kinetics and limited active material utilization in S1.

The CV profile of S2 (green), corresponding to the Generation 1 Syensqo binder, displays an improvement in current response and peak resolution. During the first lithiation scan, the broad SEI formation band around 0.7 V persists but is slightly less pronounced than in S1, suggesting a more stable initial interface. A clearer reduction peak emerges at ~ 0.25 V, associated with the partial lithiation of SiO_x , which proceeds via the conversion reaction (equation 12):



A second peak at ~ 0.1 V corresponds to Li^+ intercalation into graphite (13):



and alloying of Si to form amorphous Li_xSi , both contributing to capacity in subsequent cycles. Regarding delithiation process, oxidation peaks appear at ~ 0.2 V (graphite delithiation) and $\sim 0.4\text{--}0.5$ V (Li-Si dealloying), indicating better electrochemical reversibility than S1 but still not ideal resolution, possibly due to the higher molecular weight and lower acidity of the binder, which limit chain mobility.

For S3 (orange), prepared using Generation 3 binder, the CV displays highly resolved and intense redox features. The first lithiation scan shows a well-defined SEI formation peak centered at ~ 0.7 V (starting from 1.1V), followed by a distinct shoulder at ~ 0.3 V, which can be confidently assigned to SiO_x reduction. As lithiation proceeds, two sharper cathodic

peaks emerge at ~ 0.2 V and ~ 0.05 V, which correspond respectively to Li intercalation into graphite and Li-Si alloying reactions forming various amorphous Li_xSi species. On the delithiation side, the broad oxidation process appears around 0.45 V, attributed to Li-Si delithiation, and a smaller but clearly distinguishable peak at ~ 0.2 V corresponds to delithiation from the graphite phase. These features indicate efficient lithiation/delithiation dynamics, a highly reversible redox mechanism, and stable SEI formation.

Lastly, S4 (dark red), employing the Generation 3 acidic binder, exhibits similar peak positions and intensities to S3 but with slightly higher current densities. The lithiation scan features a broad SEI-related peak at ~ 0.7 V, followed by well-resolved lithiation events at 0.3 V, 0.2 V, and ~ 0.05 V, corresponding respectively to SiO_x reduction, graphite lithiation, and Li_xSi alloy formation. During delithiation, two anodic peaks are visible at ~ 0.2 V and ~ 0.45 V, matching the deintercalation of Li from graphite and the delithiation of Li-Si alloys. Compared to S3, the oxidation peaks in S4 are slightly shifted to higher potentials, which may reflect a more resistive SEI layer or altered surface chemistry due to the increased acidity of the binder solution. Despite this, the overall profile remains highly reversible, and the increased peak area indicates a high degree of active material utilization. These observations confirm that binder properties, particularly molecular weight, pH, and polymer functionality, can profoundly affect the electrochemical kinetics of SiO_x based anodes.

GCD in Half-cell configuration

Following the assessment of electrode properties through both physicochemical characterization and preliminary electrochemical testing via CV, galvanostatic charge/discharge cycling (GCD) was carried out to evaluate the long-term electrochemical stability of the silicon-based anodes. These experiments were firstly conducted using a half-coin cell configuration.

The working electrode consisted of a silicon-graphite composite disk ($\varnothing = 10$ mm, theoretical capacity = 591.2 mAh/g, calculated taking into the account the relative mass percentage of $\text{Li-SiO}_x@\text{C}$ and graphite, average mass loading ≈ 6.1 mg/cm², areal capacity ≈ 3.77 mAh/cm²). The counter and reference electrode was a lithium metal foil ($\varnothing = 12$ mm), and a Whatman GF/A separator ($\varnothing = 16$ mm) was employed to ensure physical separation and ionic conductivity. The electrolyte employed was a 1 M solution of LiPF_6

in 1:1. v/v EC:DMC with 2 wt% VC and 10 wt% FEC. All galvanostatic cycling measurements were performed at a current density corresponding to 1C (approximately of 2.662 mA), under controlled temperature conditions at 25 °C.

The full experimental protocol applied for half-coin cells cycling is described in detail in Section 2.1. Figure 37a presents the long-term GCD profiles for all four binder-based formulations (S1 to S4) cycled over 150 cycles. Figure 37b shows the corresponding capacity retention values, expressed as percentages and calculated using the following equation (14):

$$\text{Capacity Retention (\%)} = \frac{Q_n}{Q_{\text{initial}}} \times 100 \quad (14)$$

where Q_n is the discharge capacity at the n -th cycle (in this case, the 150th cycle), and Q_{initial} is the discharge capacity measured at the first cycle. To evaluate long-term performance, an 80% capacity retention threshold was adopted, consistent with current industrial standards for lithium-ion battery electrodes.

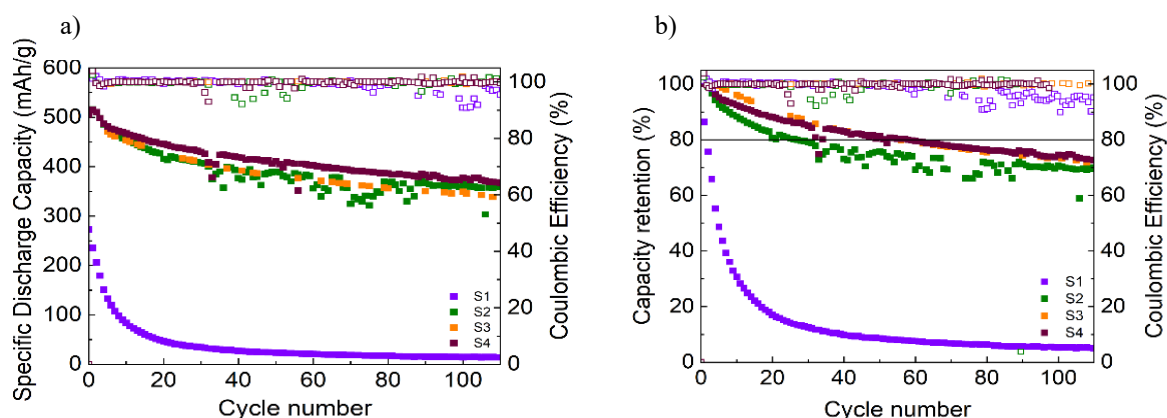


Figure 37. a) Specific capacity and coulombic efficiency of the four formulations (S1-S4); b) capacity retention and coulombic efficiency

Table 7. Initial specific discharge capacity and capacity retention are reported for each anode formulation tested.

Electrode slurry tested	Initial Specific Discharge Capacity (mAh/g)	Cycle number until Capacity retention = 80%
S1	272.60	2
S2	515.01	30
S3	471.70	56
S4	505.42	61

The values reported in Table 7 summarize the initial specific discharge capacities and the corresponding cycle number at which each electrode formulation drops below 80% capacity retention. SBR/CMC-based electrode (S1) shows both the lowest initial capacity (272.60 mAh/g) and extremely poor cycling stability, with capacity fading below the 80% threshold after only 2 cycles. In contrast, all three anode formulations (S2, S3, S4) deliver significantly higher initial specific capacities, exceeding 470 mAh/g, and exhibit markedly improved cycling performance. Notably, Generation 3 acidic binder (S4) achieves the best overall result, maintaining over 80% capacity for 61 cycles, followed closely by Generation 3 binder (S3) with 56 cycles. These findings highlight the strong influence of binder chemistry on both initial electrochemical performance and long-term stability of silicon–graphite composite anodes. The trends observed in half-coin cells cycling tests are further corroborated by the results obtained in full-coin cell configuration, as will be discussed in the following sections. This consistent behaviour confirms that the modifications introduced at the binder level lead to tangible improvements in electrochemical performance, supporting enhanced capacity retention and structural stability during cycling.

Rate Capability

Consequently, rate capability measurements were performed to further evaluate the electrochemical response of the electrodes under varying current densities. The applied current values in these experiments were calculated based on the total mass of active material (carbon and SiO_x) in each electrode. Tests were performed in coin cells CR2032 with silicon-composite working electrode ($\varnothing = 9\text{mm}$, average mass loading = 6.33 mg/cm², average areal capacity = 3.74 mAh/cm²), lithium foil ($\varnothing = 16\text{mm}$), Whatman GF/A separator ($\varnothing = 18\text{mm}$) and 150 μL of the same electrolyte previously used. The rate tests were conducted sequentially at increasing C-rates: C/20, C/10, C/5, C/2, 1C, followed by a return to C/5, with each rate held for four consecutive cycles. This protocol was designed to identify the optimal and most stable C-rate condition, which was then used as the reference for subsequent Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) measurements conducted at different states of charge.

Figure 38 shows the behaviour for all formulations, tested twice for reproducibility.

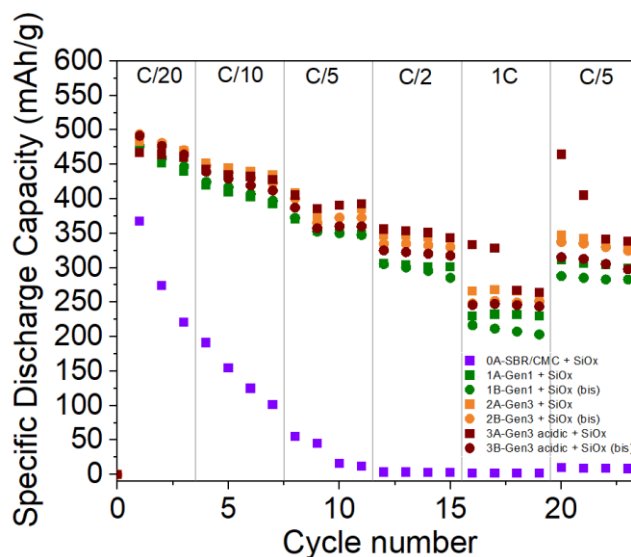


Figure 38. Rate capability tests for S1, S2, S3, S4 electrodes: square test refers to the first cell assembling and cycling, while circle to the second cells batch

Among all tested conditions, the C/2 rate exhibited the most stable and consistent electrochemical behaviour across all binder formulations. Therefore, C/2 was selected as the reference C-rate for subsequent measurements, as it provides a practical balance between electrochemical representativeness and experimental duration within a single working day. At C/2, the electrodes retain a substantial fraction of their low-rate capacity, indicating that the response remains representative of the electrode behaviour while still being sufficiently sensitive to kinetic and transport limitations compared with C/10–C/20. In addition, C/2 was adopted for subsequent PEIS performed at defined states of charge (0% SOC initial, 50% SOC, 100% SOC, and 0% SOC final), enabling impedance comparison across delithiated and lithiated states within a feasible experimental time window.

GCD in Full-cell configuration

Finally, electrochemical stability tests were performed in full-coin cell configuration to further validate the behaviour of the binder-based anodes under realistic cycling conditions. The cathodes employed were single-layer NMC622 electrodes, previously produced at pilot scale. The full-cell assembly included a working electrode (NMC622, $\varnothing = 12$ mm, theoretical capacity = 158 mAh/g, average mass loading ≈ 18.8 mg/cm², areal capacity ≈ 3.0 mAh/cm²) paired with a polyethylene separator (PE, $\varnothing = 16$ mm), and a counter electrode consisting of the silicon-graphite composite ($\varnothing = 14$ mm, theoretical capacity = 591.2 mAh/g, average mass loading $\approx 5.4 - 5.6$ mg/cm², areal capacity ≈ 3.2 mAh/cm²). The electrolyte used was 1 M LiPF₆ in EC:DMC (1:1 v/v), with 2 wt% VC and 10 wt% FEC as additives (300 μ L used per cell). The specific capacities of the full-cell electrodes were calculated based on the limiting cathode mass, using a theoretical specific capacity of 158 mAh/g for the NMC622 active material.

Cycling was conducted at 1C (≈ 3.370 mA) using the same protocol previously applied for the half-coin cells tests, ensuring consistency across half- and full-cell configurations. The electrochemical stability results, reported in Figure 39, confirm the trends observed in half-coin cells, further validating the beneficial role of binder modification in enhancing full-cell cycling performance.

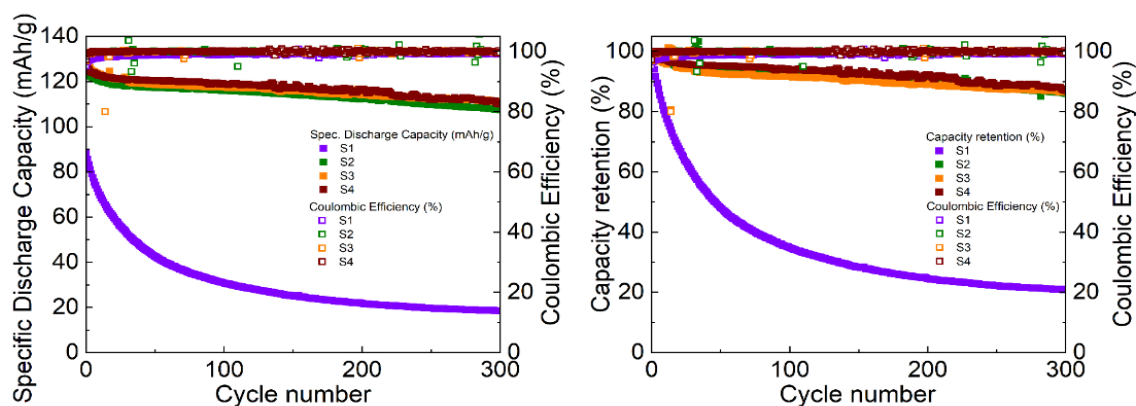


Figure 39. Specific capacity, capacity retention and coulombic efficiency for S1-S4; the behaviour showed is the average value of three electrochemical tests for each anode tested.

Table 8 shows the average value of the four formulation anodes tested. Among them, S3 and S4 once again demonstrate superior cycling stability compared to the other two formulations. This improved behaviour is directly related to the intrinsic modifications of

the binder, as previously discussed. As reported in Table 8., after 300 cycles, S3 retains a specific capacity of 111.3 mAh/g, while S4 reaches 110.0 mAh/g, confirming their enhanced long-term stability. In contrast, S1 exhibits poor cyclability from the early stages, with an initial specific capacity already significantly lower than the theoretical capacity of the cathode. This suggests a decreased electrode integrity and limited electrochemical accessibility, likely due to insufficient binder performance in maintaining electrode cohesion during prolonged cycling.

Table 8. Average values of Discharge Capacity reached at 300 cycle and cycle number until 80% of capacity retention.

Slurry tested	Discharge Capacity (mAh/g) at 300 cycles	Cycle number until Capacity retention = 80%
S1	18.5	10
S2	107.5	414
S3	111.3	495
S4	110.0	409

These results not only confirmed the distinct electrochemical behaviours between the Generation 1 and Generation 3 binder families but also validated both systems for successfully passing the laboratory-scale screening phase. Therefore, these two binder families were selected for subsequent evaluation at pilot scale, with the aim of assessing their suitability for industrial electrode production.

3.1.2. Si/C formulation

Rheological characterization

The rheological characterization of the slurries formulated with Si/C as active material was carried out following the same experimental procedure and analysis approach previously adopted for the Li-SiO_x@C-based systems. Details regarding the material properties and specific formulation of each slurry are reported in Sections 2.1 and 2.2.

As in the previous case, flow curve measurements (S1-S4) were used to evaluate the shear-thinning behaviour of the slurries and to assess their processability under mixing and coating conditions. The viscosity at 10 Hz was selected as the primary reference value, representative of the low-shear regime relevant to the mixing step. For comparison, the viscosity at 1000 Hz, corresponding to high-shear conditions typically encountered during electrode coating, was also reported.

The results of these measurements are presented in the following section, and the corresponding viscosity values at both shear rates are summarized in Figure 40 and in Table 9.

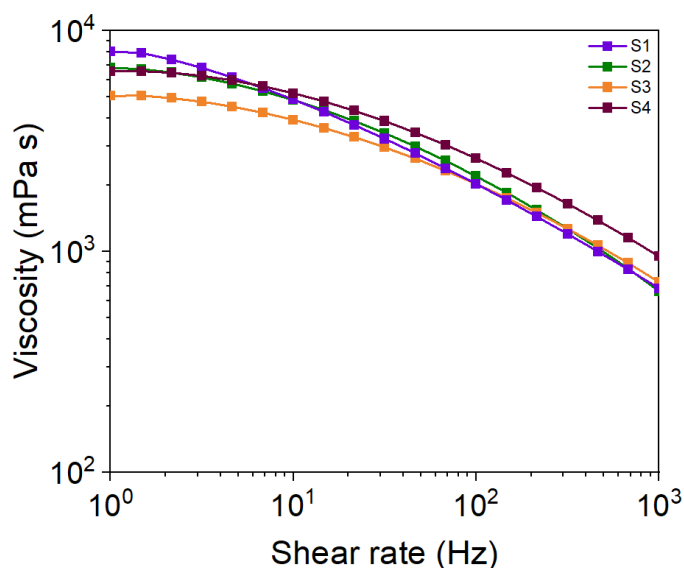


Figure 40. Flow curves of Si/C-based anode slurries (S1–S4), showing shear-thinning behaviour across the tested shear rate range.

Table 9. Viscosity values at 10 Hz and 1000 Hz were used as reference points for mixing and coating conditions, respectively.

Slurry name	Viscosity (mPa·s) at 10Hz	Viscosity (mPa·s) at 1000 Hz
S1	4871.6	681.3
S2	4850	661.1
S3	3947	727.2
S4	5207.2	951.8

The viscosity values reported in Table 9 refer to Si/C-based slurries prepared with the four binder formulations (S1–S4), measured at 10 Hz and 1000 Hz to reflect, respectively, the mixing and coating regimes. All formulations exhibit viscosities at 10 Hz within the acceptable range for laboratory processing (2000–8000 mPa·s), indicating satisfactory dispersion and compatibility with the Si/C active material. Notably, the lowest viscosity is observed for S3 (3947 mPa·s), suggesting enhanced flowability, while S4 exhibits the highest value (5207.2 mPa·s), consistent with its higher acidity and increased polymer–particle interactions.

At high shear rate (1000 Hz), the expected shear-thinning behaviour is confirmed across all samples, with viscosity decreasing significantly. S4 again shows the highest value (951.8 mPa·s), potentially reflecting a more structured slurry network.

Indeed, in Si/C-based slurries, the carbon coating on the silicon particles plays a key role in modulating the rheology. The carbon layer reduces the surface reactivity of silicon, limiting strong interactions with binder functional groups such as carboxylic acids and hydroxyls. As a result, fewer hydrogen and ionic bonds are formed between the binder and the active material, leading to a less structured polymer-particle network. This contributes to a more fluid behaviour under shear and helps maintain stable, processable viscosity values, especially under high shear conditions. Moreover, the graphitic nature of the coating improves particle dispersibility and reduces agglomeration, favouring a homogeneous slurry and enhancing its shear-thinning characteristics. These results demonstrate that, even with a different active material (Si/C), binder chemistry continues to influence slurry rheology, affecting both low-shear and high-shear processing characteristics.

Adhesion measurement

Adhesion measurements were performed using the 180° peel test method on Si/C-based electrodes prepared from the four binder formulations S1–S4. As in the case of the Li-SiO_x@C-based electrodes, each sample was tested after the complete electrode fabrication process, including coating, drying, and calendering. The methodology and test configuration were identical to those described in Sections 1.5.5 and 2.1.2.

The results of the peel tests are reported in Table 10. As in the previous analysis, the values represent the average of three independent measurements, each performed on a distinct electrode sample prepared with the same formulation. This approach was adopted to ensure data reproducibility and to minimize the influence of sample variability.

The results (Figure 41) reveal a consistent trend: electrodes prepared with S3 and S4 binders exhibit higher peel strength values compared to the reference S1 (SBR/CMC-based) and S2 (Generation 1). This confirms the enhanced adhesive interaction promoted by the Generation 3 binder family, even when switching the active material from Li-SiO_x@C to Si/C. The improved adhesion is likely related to the lower molecular weight and increased acidity of S3 and S4, which facilitate more effective binder–current collector interactions and contribute to better film cohesion during drying and post-processing.

However, it is also observed that the standard deviation of peel strength is notably higher for S3 and S4. This variability can be attributed to the influence of uncontrolled ambient humidity during testing at room temperature. As known from prior analysis, moisture uptake by the binder or by the hydrophilic components of the electrode may locally alter mechanical integrity, affecting the reproducibility of adhesion measurements. Despite this, the mean peel strength values for S3 and S4 remain superior, confirming the robustness of their adhesive properties.

These findings indicate that the binder continues to play a dominant role in determining mechanical integrity and electrode adhesion, regardless of the active material used. The adhesive performance is therefore not only a function of the slurry's rheological behaviour, but also a direct consequence of how the binder chemistry supports interfacial bonding after the electrode undergoes drying and mechanical compaction.

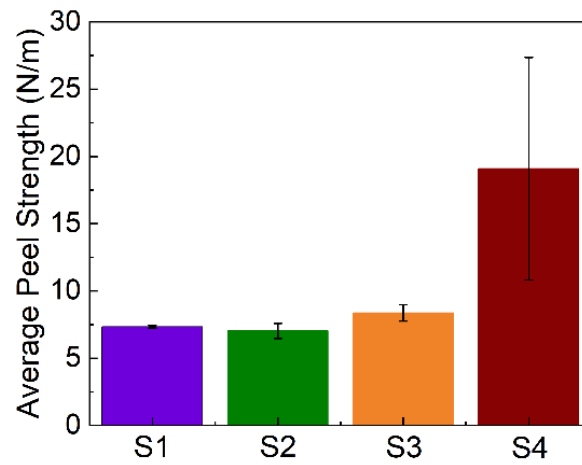


Figure 41. Average peel strength values (N/m) obtained from 180° peel tests on Si/C-based electrodes formulated with binders S1–S4. Generation 3 binders (S3 and S4) show significantly higher adhesion, despite increased variability due to ambient humidity during testing.

Table 10. Peel strength values (average and standard deviation) for Si/C-based electrodes prepared with binder formulations S1–S4.

Electrode Slurry name	Average Peel Strength (N/m)	ST DEV
S1	7.34	0.09
S2	7.03	0,57
S3	8.36	0.60
S4	19.09	8.27

Electrochemical tests

Cyclic Voltammetry

Cyclic voltammetry measurements were carried out to investigate the electrochemical behaviour of Si/C-based anodes formulated with four different binder compositions (S1–S4). The measurements were performed at a scan rate of 50 $\mu\text{V/s}$ within a potential window of 1.5 V - 0.025 (vs. Li^+/Li), using a BOLA three-electrode cell configuration. The working electrode (WE) was a Si/C-based anode disk ($\phi = 9\text{ mm}$), while both the counter and reference electrodes consisted of lithium metal disks ($\phi = 10\text{ mm}$). A Whatman GF/A glass fiber separator ($\phi = 10\text{ mm}$) was used, and the electrolyte was 1 M LiPF_6 in EC:DMC (1:1 v/v) with 2 wt% VC and 10 wt% FEC (600 μL per cell).

Figure 42a presents the first CV scan for the four anodes. A dominant reduction peak appears between 0.20 V and 0.17 V vs. Li^+/Li , associated with the lithiation of Si/C and possible formation of Li_xSi phases and the initial SEI. The peak is most intense and sharpest for S1, while S3 shows a slight cathodic shift ($\sim 0.17\text{ V}$), indicating altered reaction kinetics or earlier onset of Li insertion, potentially due to binder influence.

During delithiation, the first peak appears at $\sim 0.10\text{ V}$ for all electrodes, which may be associated with the initial extraction of lithium from amorphous Li_xSi species formed during the first cycle. This peak is particularly pronounced in the S1 electrode and is slightly shifted to $\sim 0.11\text{ V}$ in S2 and S3, suggesting variations in reversibility and kinetics among the compositions. A second feature is observed around $\sim 0.20\text{ V}$, with minor potential shifts across electrodes, indicative of multi-step delithiation reactions, possibly from more stabilized Li_xSi or interfacial species. A broader peak centered at $\sim 0.50\text{ V}$ is clearly visible for the S1 and S2 electrodes, while it appears less defined and more diffuse for S3 and S4, likely reflecting differences in surface passivation or the structural evolution of the active material during the initial cycle.

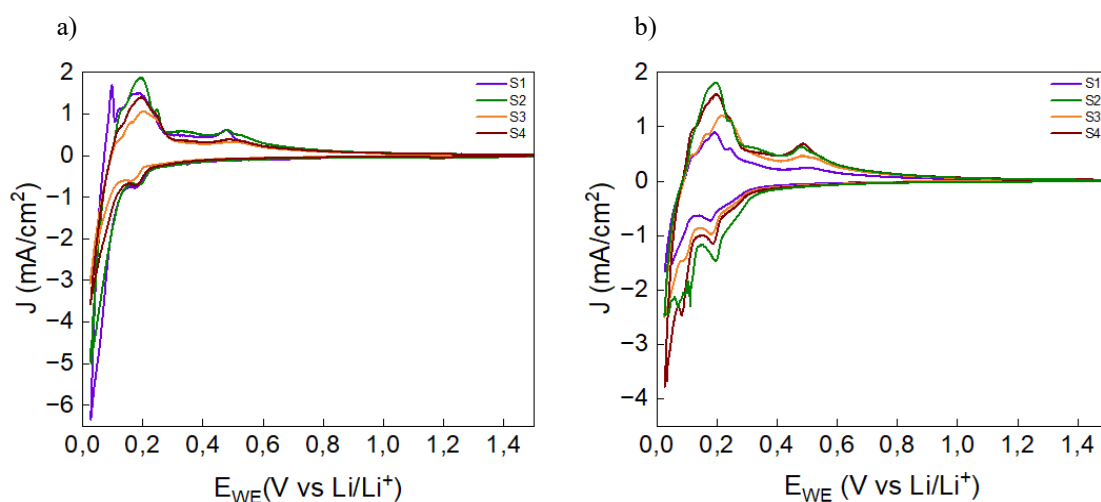


Figure 42. Cyclic voltammetry curves of Si/C-based anodes (S1–S4) recorded at a scan rate of 50 $\mu\text{V/s}$ in the voltage range 0.025–1.5 V vs. Li/Li^+ . (a) First scan, highlighting irreversible processes such as SEI formation and electrolyte decomposition during initial lithiation/delithiation; (b) Second scan, showing more stabilized and reversible redox features, with reduced parasitic currents and enhanced definition of lithiation/delithiation peaks.

In the second CV scan (Figure 42b), the electrochemical response of all Si/C-based electrodes appears more stabilized, indicating that most of the irreversible processes observed during the first largely completed. The lithiation process, occurring during the cathodic sweep, still presents a broad reduction feature centred around ~ 0.20 V for all four compositions. However, the intensity of this cathodic peak is significantly reduced compared to the first scan, particularly for S3 and S4, suggesting diminished parasitic reactions and a more efficient Li^+ insertion into the active material.

In the anodic sweep, corresponding to the delithiation process, a clearer and more reproducible set of peaks is now observed across all electrodes. A first oxidation peak appears around ~ 0.11 V, visible in each composition and particularly pronounced for S1, indicating a partially reversible delithiation from amorphous Li_xSi phases. A second oxidation feature arises at approximately ~ 0.20 V, consistent among all samples and pointing to further Li^+ extraction from more stabilized lithiated silicon environments. Additionally, a broader anodic shoulder is detected near ~ 0.5 V, slightly better resolved in S2–S4 compared to the first scan, and likely associated with the delithiation of less-ordered or surface-confined lithiated species. Overall, this second scan highlights the improved electrochemical reversibility after the initial cycle. The redox peaks are more defined and less affected by side reactions, with current densities suggesting that S1 remains the most

electrochemically active sample, followed by S2, while S3 and S4 show more moderate behaviour, potentially indicative of greater long-term stability.

GCD in Half-cell configuration

Half-coin cells were assembled to evaluate the electrochemical stability of Si/C-based anodes using a two-electrode configuration in CR2032 coin cells. The working electrode (WE) was a Si/C composite electrode ($\varnothing = 10$ mm, area = 0.785 cm², average mass loading = 5.14 mg/cm², average areal capacity = 3.34 mAh/cm², theoretical specific capacity = 650 mAh/g). The counter/reference electrode (CE) used was a lithium metal foil ($\varnothing = 12$ mm).

A Whatman GF/A separator ($\varnothing = 16$ mm, pore size = 1.6 μ m) was used to ensure ionic conduction and physical separation between the electrodes. The electrolyte was 1 M LiPF₆ in EC:DMC (1:1 v/v), modified with 2 wt% VC and 10 wt% FEC, consistent with all previously reported measurements.

The galvanostatic cycling protocol applied to these half-coin cells was identical to that used for the Li-SiO_x@C-based systems, as described in Section 2.1.2.

Figure 43 shows the electrochemical stability of the four Si/C-based anodes (formulations S1 to S4), cycled for a total of 100 cycles in half-coin cells configuration at 1C (~2.62 mA). As visible in the graph, a general performance trend can be observed among the formulations, with significant differences in terms of capacity retention and degradation behaviour. Additionally, the scattered data points observed after cycle 40 suggest the onset of lithium-related instabilities, likely due to local depletion of the lithium counter electrode, a common phenomenon in two-electrode half-coin cells configurations over extended cycling. These anomalies reflect increasing interfacial resistance or inhomogeneous current distribution caused by lithium surface degradation.

S1 electrode, based on the SBR/CMC reference binder, exhibits a steep capacity drop starting from the first cycles, with the capacity falling below 200 mAh/g after only 20 cycles, and continuing to degrade down to ~50 mAh/g by cycle 100. This behaviour is consistent with its low initial specific capacity (Table 11) and confirms its poor mechanical stability under repeated Si volume expansion.

By contrast, S2, S3, and S4 formulations display significantly improved cycling stability and higher coulombic efficiency throughout the test. Among them, S3 shows the best overall performance, with a smoother capacity decay and high retention across the full test window. S4, while performing comparably to S3 in the first 80 cycles, displays a temporary capacity drop followed by a slight rebound near cycle 95, which may be linked to dynamic changes in the SEI structure or temporary improvements in electrode–electrolyte contact, potentially due to reorganization of the binder matrix under repeated stress. Such effects have been reported in literature for silicon-based anodes with responsive polymeric binders. [250]

The coulombic efficiency remains above 98% for S2–S4 during most of the test, indicating good reversibility and stable SEI formation after the initial cycles. In contrast, S1 shows a lower and more fluctuating coulombic efficiency due to ongoing parasitic reactions and continuous SEI growth. As summarized in Table 11, all electrodes except S1 reach the 80% capacity retention threshold around cycle 40 to cycle 60, aligning with industrial acceptability standards.

Overall, these results confirm that binder formulation has a direct and measurable impact on long-term performance, even when using a different active material such as Si/C.

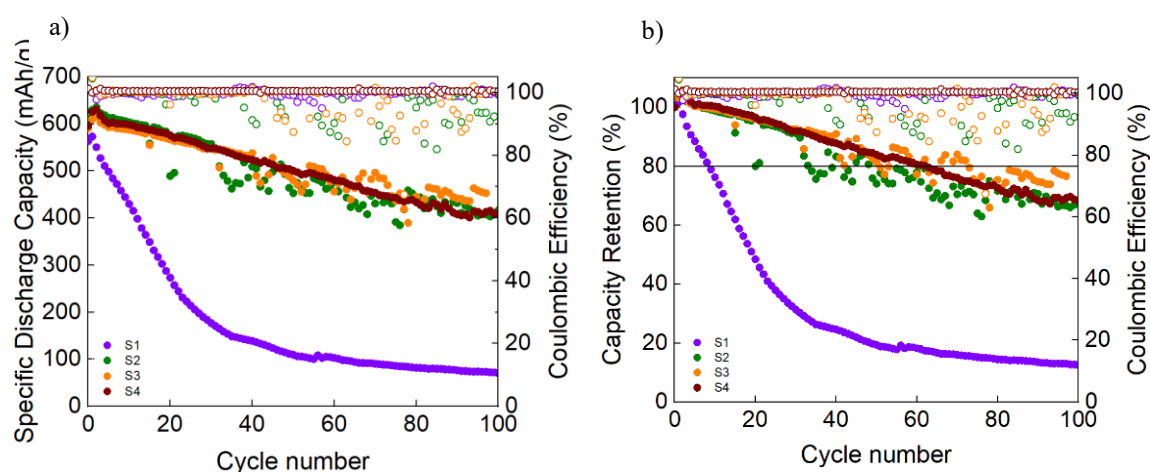


Figure 43. Electrochemical cycling performance of Si/C-based anodes (S1–S4) in half-coin cell configuration at 1C for 100 cycles: a) specific discharge capacity (in solid circle markers) and coulombic efficiency (in open circle markers) vs cycle number; b) capacity retention (in solid circle markers) and coulombic efficiency (in open circle markers) vs cycle number

Table 11. Initial specific discharge capacity and cycle number at which 80% capacity retention is reached for Si/C-based anodes formulated with S1–S4 binders.

Electrode slurry tested	Initial Specific Discharge Capacity (mAh/g)	Cycle number until Capacity retention >80%
S1	563.4	9
S2	611.1	40
S3	590.7	50
S4	596.2	62

Rate Capability

Following the evaluation of long-term electrochemical stability of the individual Si/C-based anodes, rate capability tests were performed to identify the most stable C-rate for each formulation. This analysis aimed to determine the optimal current density to be used in subsequent PEIS measurements at various states of charge.

Additional half-coin cells CR2032 were assembled for this purpose. The working electrodes (WE) were Si/C-based anodes prepared with the four different binder formulations (S1-S4) ($\varnothing = 9$ mm, area = 0.636 cm², active material mass loading = 5.45 mg/cm², areal capacity = 3.54 mAh/cm², and theoretical specific capacity = 2.25 mAh/g). The counter electrode (CE) consisted of lithium metal chips ($\varnothing = 16$ mm), and a Whatman GF/A separator ($\varnothing = 9$ mm) was used. A total of 150 μ L of electrolyte was added to each cell, using the same electrolyte formulation previously described (1 M LiPF₆ in EC: DMC (1:1 v/v) + 2 wt% VC + 10 wt% FEC).

Cells were subjected to a rate capability protocol involving progressively increasing C-rates to assess the current response and electrode performance under different kinetic conditions. The most stable C-rate observed was selected as the reference for subsequent impedance measurements.

The cycling protocol adopted was the same as that previously used for the Li-SiO_x@C-based half-coin cells, as described in Section 3.1.1. The corresponding rate capability

results for each binder formulation (S1–S4) are shown in Figure 44, where specific discharge capacities are plotted as a function of increasing C-rate.

Also in this case, C/2 was selected as the optimal C-rate for subsequent PEIS measurements at various states of charge. This choice was based on its stable performance across all tested formulations, as well as to ensure reproducibility and consistency with the tests already conducted on Li-SiO_x@C electrodes. This alignment enables a meaningful comparison between the two active material systems and further validates the influence of binder chemistry under controlled electrochemical conditions.

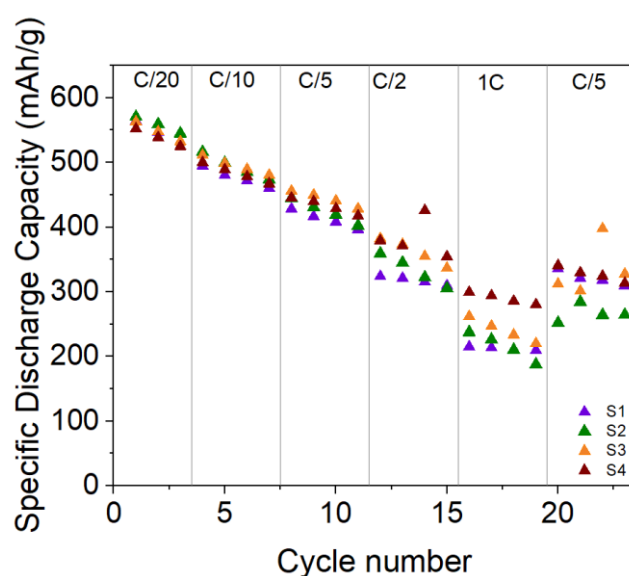


Figure 44. Rate capability at different c/rate for the four formulation electrodes.

GCD in Full-cell configuration

To assess the electrochemical stability of the four formulations under practical operating conditions, galvanostatic cycling tests were conducted in full coin-cell (FCA) configuration. The cathodes employed were single-layer NMC622 electrodes ($\varnothing = 12$ mm, average mass loading ≈ 19.23 mg/cm², areal capacity ≈ 3.0 mAh/cm²), previously produced at pilot scale. These were paired with silicon–graphite composite anodes ($\varnothing = 14$ mm, average mass loading ≈ 3.45 mg/cm², areal capacity ≈ 3.2 mAh/cm²). A polyethylene separator (PE, $\varnothing = 16$ mm) was used to ensure effective ionic conduction and mechanical separation between electrodes. The electrolyte consisted of 1 M LiPF₆ in EC:DMC (1:1 v/v) with additives (2 wt% VC + 10 wt% FEC), designed to promote stable interfacial chemistry and SEI formation. Specific capacities of the full-cell electrodes were calculated based on the limiting cathode mass, assuming a theoretical specific capacity of 158 mAh/g for the NMC622 active material. The electrochemical stability protocol followed was identical to that described in Section 2.2.1.2.3. The results presented in Figure 45 correspond to cycling tests performed at a rate of 1C (~ 3.348 mA).

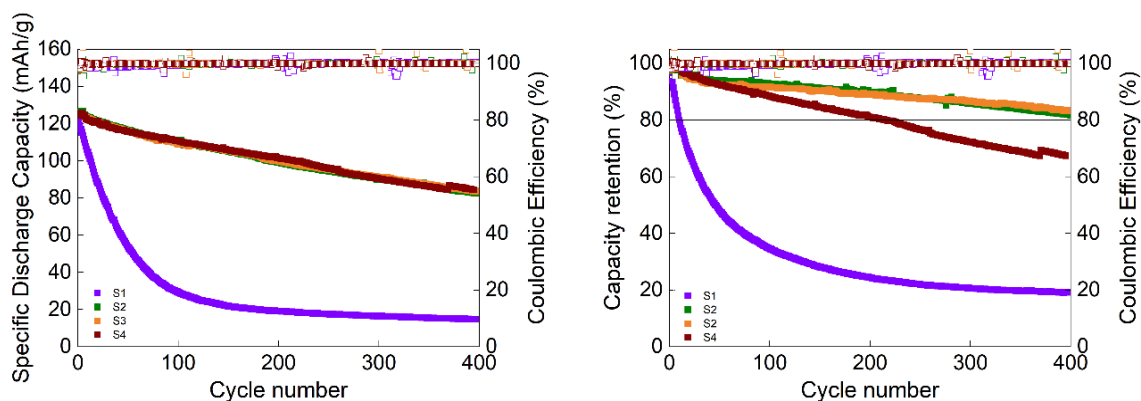


Figure 45. Galvanostatic charge–discharge performance of full coin cells NCM622|Si/C-based anodes: a) Specific discharge capacity (in solid square markers) and coulombic efficiency (in open square markers) as a function of cycle number; b) corresponding capacity retention (in solid square markers) and coulombic efficiency (in open square markers) over prolonged cycling.

Anodes formulated as S2 to S4 exhibit notably stable behaviour over extended cycling up to 400 cycles, with comparable trends that indicate good long-term electrochemical resilience. Among them, Anode S4 consistently maintains the highest specific capacity over

time, followed closely by S3, thus reinforcing the superior performance previously observed in half-cell testing. In contrast, anode formulation S1 shows rapid degradation, with a substantial drop in capacity within the first few cycles, confirming its poor electrochemical stability. Evaluating the number of cycles required to reach 80% capacity retention, used here as a standard industrial reference threshold, further supports these observations.

Table 12 reports the electrochemical stability trends observed for all assembled cells; it reports the initial specific discharge capacity (mAh/g) and the corresponding cycle number at which each anode formulation reaches a capacity retention of 80%.

Table 12. Electrochemical stability for all anodes tested

Electrode slurry tested	Initial Specific Discharge Capacity (mAh/g)	Cycle number until Capacity retention = 80%
S1	121.2	14
S2	126.8	184
S3	125.9	195
S4	125.1	222

3.2. Li-SiO_x@C vs Si/C: a comparison

A comparative evaluation of the electrochemical performance of Li-SiO_x@C and Si/C composite anodes reveals substantial differences in long-term cycling. When tested using identical full-cell configurations with NCM622 cathodes at 1C, electrodes employing Li-SiO_x@C consistently exceed those incorporating Si/C, particularly in terms of capacity fading. As shown in Figure 46, Li-SiO_x@C anodes maintain a highly stable electrochemical profile over extended cycling, with specific discharge capacity remaining relatively constant up to 400 cycles. This behaviour highlights the excellent chemical and mechanical robustness of the Li-SiO_x@C architecture, which effectively buffers volumetric changes and suppresses interfacial degradation.

In contrast, Si/C-based electrodes, while demonstrating competitive initial capacities, display a markedly different trend. A noticeable decline in capacity emerges after the first

50–100 cycles, followed by a continuous and accelerated degradation over time. This rapid drop in performance suggests that the Si/C active material itself is less capable of withstanding the mechanical stress and repeated SEI regeneration associated with continuous lithiation/delithiation. As a result, the active material becomes progressively isolated from the conductive matrix, leading to loss of capacity.

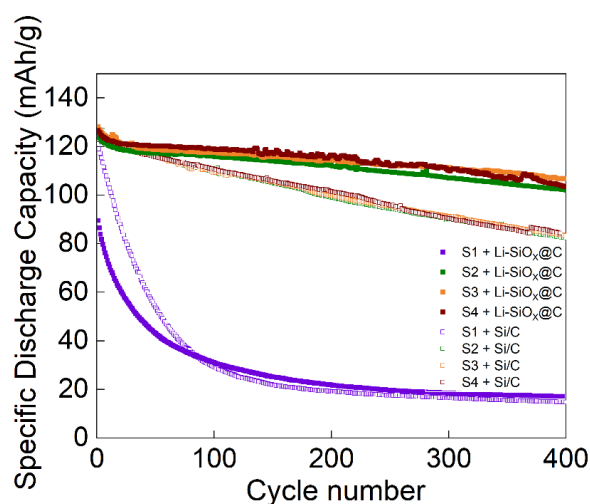


Figure 46. Comparison of Specific discharge capacity over 400 cycles at 1C for silicon composite anodes tested in full-coin cell configurations (vs NCM622), using both active material: Li-SiO_x@C (in solid square markers) and Si/C (in open square markers).

This divergence originates from intrinsic materials chemistry and interfacial mechanics. Non-stoichiometric silicon oxides (SiO_x, 0 < x < 2) undergo a smaller net volume change than elemental Si because, during the first lithiation, part of the oxide is irreversibly converted to a Li₂O/Li₄SiO₄ matrix that mechanically buffers subsequent Si expansion and helps preserve percolation within the composite; as a result, SiO_x-based electrodes typically show longer cycle life than Si at comparable loading. [251]

In Li-SiO_x@C specifically, the conformal carbon coating raises electronic connectivity and moderates electrolyte access, while prelithiation further improves the initial Coulombic efficiency and early SEI stability, both factors that suppress parasitic Li loss and delay resistance growth. [252]

By contrast, Si/C composites based on elemental Si (carbon-coated Si) still experience large, repeated volume changes of the Si core on lithiation/delithiation. These changes propagate to the surface, promoting particle cracking, SEI rupture/regrowth, and

accelerated electrolyte reduction at newly exposed surfaces; the cumulative effect is electrode swelling, loss of electrical contact, and faster capacity fade under long cycling. Comprehensive reviews of Si anodes document this sequence, pulverization, unstable SEI, and rising impedance, as the dominant degradation pathway in carbon-coated Si systems. [253]

Compared with Si/C, Li-SiO_x@C builds a more homogeneous and resilient particle-to-binder/conductive-carbon network. This translates into lower interfacial reactivity, better mechanical integrity of the composite, and superior capacity retention over extended cycling, whereas Si/C, despite its carbon shell, remains limited by surface-driven cracking and SEI growth at the particle exterior. [254]

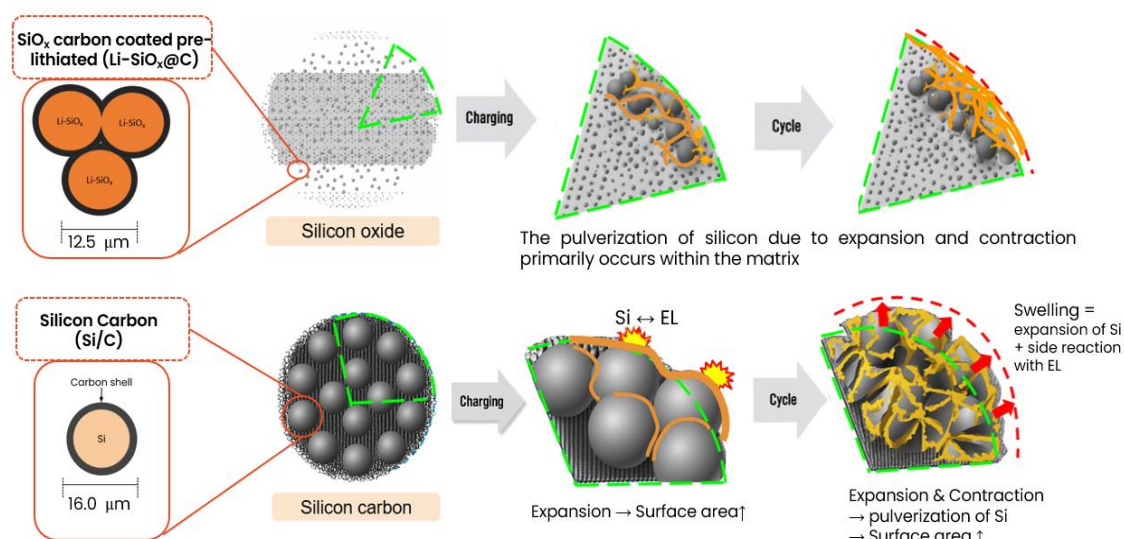


Figure 47. Schematic comparison of degradation pathways in silicon composite anodes. Li-SiO_x@C (on top): first-cycle formation of a Li₂O/Li₄SiO₄ buffer confines strain within the particle; the carbon shell and prelithiation stabilize the interface, enabling improved cycling stability. Si/C (bottom): surface-driven expansion/contraction causes particle cracking, SEI rupture/regrowth, and electrode swelling.

Figure 47 compares the electrochemical response of the two active materials at the initial charge step and after prolonged cycling. In Li-SiO_x@C, the volumetric expansion of silicon during lithiation is largely accommodated within the oxide-derived matrix, while the carbon coating and the (pre-lithiated) binder provide additional mechanical buffering. This yields a confined, more homogeneous deformation that minimizes particle cracking and limits the creation of fresh surface/interfaces exposed to the electrolyte. In contrast, Si/C (elemental Si with a carbon shell) undergoes more severe, geometry-altering expansion. Swelling

propagates to the particle surface as lithiation proceeds, imposing stress that fractures the carbon coating and induces cracking of the Si core, thereby continuously generating new interfacial area. The persistent formation of fresh interfaces accelerates parasitic reactions, promotes SEI thickening, increases porosity, and degrades electronic contact. To corroborate these mechanisms, electrochemical impedance spectroscopy (EIS) measurements were performed at different states of charge to quantify the evolution of interfacial and transport resistances.

EIS measurements at different state of charge

EIS tests were carried out in three-electrode Swagelok cells using: silicon-composite anode as WE ($\varnothing = 9$ mm; both Li-SiO_x@C and Si/C), lithium metal both as CE ($\varnothing = 11$ mm) and as RE ($\varnothing = 2$ mm); a Whatman GF/A separator ($\varnothing = 12$ mm) were used and 600 μ L of 1 M LiPF₆ dissolved in a 1:1 v/v mixture of EC:DMC with 2 % wt VC and 10% wt FEC were added.

These measurements were performed at different states of charge (SOC) following a defined electrochemical protocol. Initially, the cells were subjected to an open-circuit rest period of 12 hours to allow thermodynamic stabilization after cell assembling. This was followed by three formation cycles carried out at a constant current of C/20 in potential range: 1.5V – 0.010V vs Li/Li⁺. Subsequently, a single charge–discharge cycle was conducted at a higher current rate of C/2 (Figure 48a) in the same potential window. EIS measurements were acquired at four specific SOC during this cycle over the frequency range of 100 kHz to 100 mHz:

- 0% SOC initial: fully discharged state, after formation protocol and before starting the charge at C/2;
- 50% SOC during charging at C/2;
- 100% SOC : end of charge at C/2;
- 0% SOC final: fully discharged state after complete discharge at C/2.

The SOC-dependent evolution as a response of the two different material architecture was analysed and compared, highlighting the role of material-specific degradation mechanisms. Indeed, it was possible to compare the electrochemical behaviour of the two active materials investigated at lab scale. For this purpose, in both cases the anode formulation

employing Generation 3 acidic binder was selected, as this generation consistently exhibited the most reliable electrochemical stability.

Accordingly, two electrode formulations were tested:

- 4:1:95 = Generation 3 acidic : SC45 : (Li-SiO_x@C : graphite) (mass loading= 6.36 mg/cm²)
- 4:1:95 = Generation 3 acidic : SC45 : (Si/C) (mass loading= 5.68 mg/cm²)

For each electrode composition tested, the fitted impedance parameters corresponding to each studied SOC are reported in the following table. These values were extracted by fitting the experimental Nyquist plots using appropriate equivalent circuit models (Figure 48b) via Boukamp software (EQUIVCRT, DOSBox 0.74 environment).

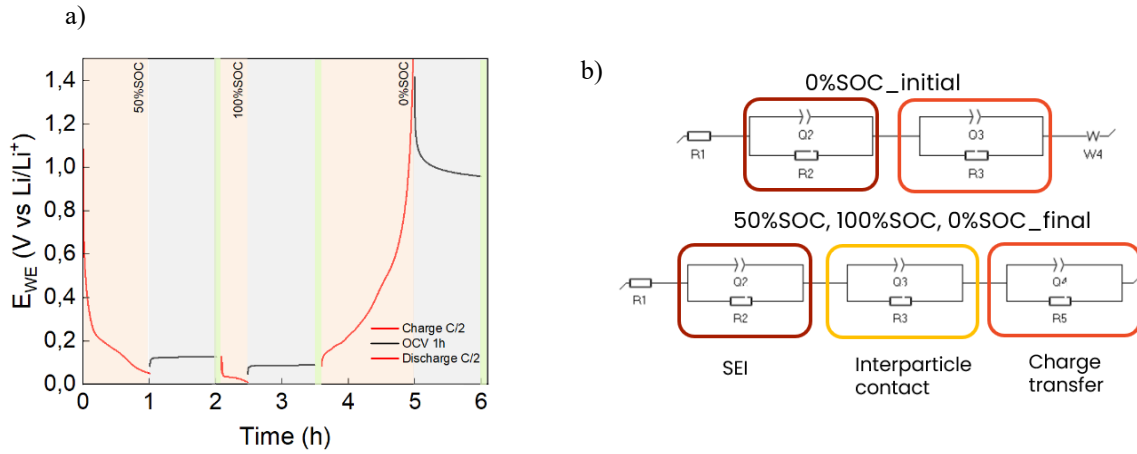


Figure 48. a) Charge-discharge cycle at C/2, reporting both charge-discharge cycle (in red), 1h OCV (in black) and EIS measurements (in green); b) equivalent circuit models used for fitting EIS tests at 0% SOC initial, 50% SOC, 100% SOC and 0% SOC final.

The evolution of the circuit parameters as a function of the SOC provides insights into the interfacial kinetics and transport properties of the electrodes under operating conditions. Indeed, since the interpretation of the fitted parameters relies on the specific role of each circuit element, the following section outlines the equivalent circuit models adopted for fitting the spectra at different SOC.

The high-frequency resistive intercept is an ohmic term, R_{ohm} , depends on electrolyte conductivity, separator thickness/porosity/tortuosity, and cell geometry. The first resolved semicircle in the high-to-mid frequency range is assigned to transport through the solid–electrolyte interphase (SEI). It is modelled with a resistive element, R_{SEI} , in parallel with a

constant-phase element (CPE_{SEI}); CPE was used instead of a capacitor element, due to electrode roughness, porosity and chemical heterogeneity.

A second semicircle appears at 0% SOC (initial, post-formation) and is assigned to interfacial charge transfer at the electrolyte/Si (Li_xSi) interface. In the equivalent circuit this process is modelled by a charge-transfer resistance (R_{ct}) in parallel with a constant-phase element (CPE_{ct}), which captures the non-ideal double-layer response due to surface roughness and heterogeneity. The semicircle amplitude reflects the local exchange kinetics and the effectively connected active area.

At intermediate and high lithiation (50% and 100% SOC), an additional mid-frequency arc must be introduced after the SEI arc: the interparticle-contact (IPC) element ($R_{IPC} || CPE_{IPC}$). As lithiation proceeds, the substantial volume expansion of silicon may lead to progressive particle cracking and debonding from both neighbouring particles and the conductive matrix. These mechanical disruptions progressively reduce the effective contact area and disrupt the electronic percolation pathways. Consequently, a distinct impedance contribution emerges, reflecting the increasing resistance at interparticle junctions, which becomes more pronounced at higher SOC where the degree of expansion and interfacial stress is maximal.

However, upon returning to full delithiation (0% SOC, final), the impedance spectrum does not revert to its initial state ($R_{ct} || CPE_{ct}$). The structural damage accumulated during lithiation is only partly reversible: fractured contacts cannot be fully restored, the SEI thickens and becomes chemically heterogeneous, some active domains are electronically disconnected. As a result, both IPC and SEI arcs remain enlarged and the charge-transfer resistance fails to recover its pristine value, reflecting permanent microstructural and interfacial degradation.

Swagelok cells were assembled with these anodes, and the impedance measurements were carried out at 25 °C. Figure 49 reports the resulting EIS plots at different SOC values for the two systems.

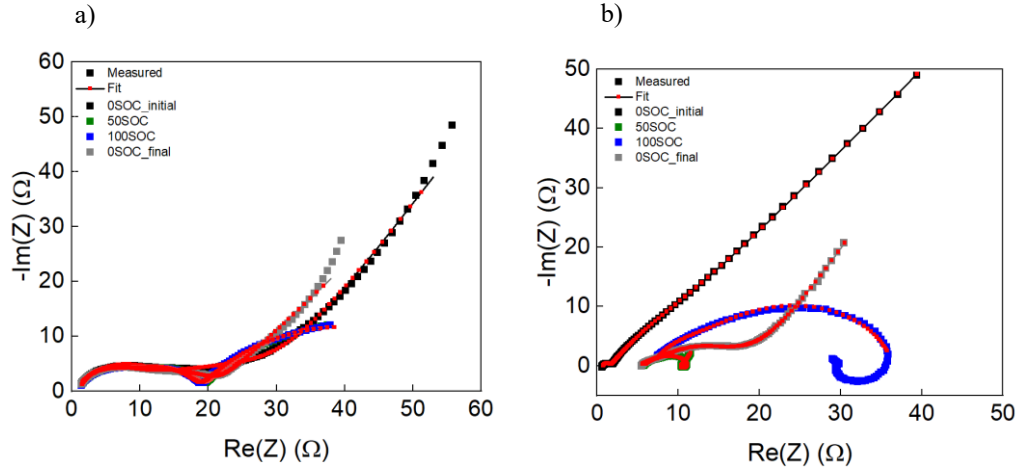


Figure 49. EIS measured at different % SOC for half-cells assembled with Generation 3 acidic binder; Solid symbols represent experimental data, while symbol + line curves correspond to the fitted results obtained using equivalent circuit modelling; a) anode containing Li-SiO_x@C and (b) anode containing Si/C as active material.

Table 13. Resistance values obtained from EIS data fitting using Boukamp for Generation 3 acidic+ Li-SiO_x@C anode and Generation 3 acidic + Si/C anode.

Gen3acidic+ Li-SiO _x @C	0%SOC_initial	50%SOC	100%SOC	0%SOC_final
R_{SEI}	25.65 Ω ± 0.22	14.32 Ω ± 0.14	7.13 Ω ± 0.11	9.75 Ω ± 0.021
R_{IPC}	/	19.32 Ω ± 0.19	50.29 Ω ± 0.76	21.76 Ω ± 0.029
R_{ct}	34.39 Ω ± 0.33	60.78 Ω ± 0.83	61.64 Ω ± 0.77	103.99 Ω ± 2.16
Gen3acidic+ Si/C	0%SOC_initial	50%SOC	100%SOC	0%SOC_final
R_{SEI}	1.57 Ω ± 0.0011	7.751 Ω ± 0.030	15.37 Ω ± 0.34	6.857 Ω ± 0.022
R_{pol}	4.264 Ω ± 0.038	11.261 Ω ± 0.043	36.44 Ω ± 0.48	22.07 Ω ± 0.053

Table 13 reports the corresponding fitted parameters for each EIS measurement performed at different states of charge (SOC). For Generation 3 acidic with Li-SiO_x@C anode, the initial behaviour at 0 % SOC, after formation protocol, shows a total resistance composed of an electrolyte/SEI component of $\approx 25.65 \Omega$; the electrode is in its fully delithiated state, so no significant volumetric expansion or particle rearrangement has yet occurred within the silicon-based composite. The active material particles, Li-SiO_x@C or Si/C, are still mechanically intact and well-connected through the binder-carbon conductive network. Since R_{IPC} originates from loss or modulation of electrical pathways between adjacent

particles caused by expansion, contraction, or cracking during lithiation, it is yet negligible because the electrode structure has not yet experienced mechanical stress or interfacial disruption.[255] Therefore, at this early stage, the impedance response is dominated only by the electrolyte/SEI resistance and the charge-transfer process at the electrode/electrolyte interface, R_{ct} of 34.39 Ω .

At 50 % SOC, R_{SEI} decreases to 14.32 Ω due to SEI compaction and improved ionic conduction, while an additional mid-frequency arc appears, corresponding to R_{IPC} of 19.32 Ω , originating from local particle rearrangements caused by the onset of Li-SiO_x@C expansion. R_{ct} increases to 60.78 Ω , indicating a partial reduction in active interfacial area. At 100 % SOC, lithiation induces further mechanical strain, raising R_{IPC} to 50.29 Ω , while R_{SEI} drops further (7.13 Ω) as the SEI becomes thinner and more conductive, and R_{ct} stabilizes around 61.64 Ω . Upon full delithiation (0 % SOC final), the impedance does not return to its initial state: R_{SEI} increases to 9.75 Ω , R_{IPC} decreases but remains significant ($\approx$ 21.76 Ω), and R_{ct} rises sharply to 103.99 Ω . This irreversible evolution indicates partial loss of percolation within the electrode network and accumulation of thicker, chemically inhomogeneous SEI layers, consistent with reported hysteresis in SiO_x/graphite composites where internal buffering confines most deformation within the particle and mitigates large contact losses. [256]

In contrast, Generation 3 acidic with Si/C anode exhibits a distinct evolution.[257]

For the Si/C electrode, the mid-frequency response attributed to interparticle contact resistance and charge-transfer kinetics was not fully resolved, and the corresponding arcs overlapped across the examined SOC window (Figure X). To avoid over-parameterization and ensure comparability, we therefore report a single metric termed the electrode polarization resistance, R_{pol} , defined as the sum of the contact-related and charge-transfer contributions: $R_{pol} = R_{ipc} + R_{ct}$. Since charge-transfer processes are expected to remain operative at all SOC, this approach provides a robust descriptor of the overall mid-frequency polarization while minimizing ambiguity associated with deconvoluting partially overlapping semicircles.

At 0 % SOC initial, the impedance response is dominated by a small R_{SEI} 1.57 Ω and a R_{pol} of 4.64 Ω . As lithiation progresses to 50 % SOC, R_{SEI} increases to 7.75 Ω , R_{pol} emerges (11.26 Ω), reflecting the onset of particle-to-particle detachment and surface SEI thickening caused by silicon core expansion. At 100 % SOC, these effects become pronounced: R_{SEI}

of 15.37 Ω , R_{pol} of 36.44 Ω , consistent with progressive microcracking of the carbon shell and loss of conductive contact across the electrode. After full delithiation (0 % SOC final), resistances only partially recover ($R_{\text{SEI}} \approx 6.85 \Omega$, $R_{\text{pol}} \approx 22.07 \Omega$), confirming irreversible microstructural degradation and thick SEI reconstruction.

As observed in Table 13, at intermediate and high SOC, the impedance features associated with the SEI, IPC, and charge-transfer processes become indistinguishable, overlapping into a single broad and depressed semicircle in the Nyquist plot (Figure 49b). This behaviour may arise from several factors, including possible micro-scale heterogeneities in the electrode coating after punching, as well as the convergence of characteristic time constants for the interfacial and mechanical processes involved. Such overlapping responses are frequently reported for Si/C composite electrodes, where lithiation induces heterogeneous surface stress and concurrent SEI rupture and reformation, resulting in coupled electrochemical and mechanical impedance features. [258]

By comparison, Li-SiO_x@C electrode exhibits a more defined three-arc behaviour and limited resistance evolution, confirming that the oxide-derived matrix and carbon coating effectively localize deformation and maintain contact homogeneity. [259] Conversely, the Si/C system shows higher and more SOC-sensitive impedance evolution, governed by severe surface-directed swelling and progressive contact loss. These distinct EIS signatures align with literature reports demonstrating that SiO_x@C composites exhibit confined, reversible impedance changes, while Si/C systems display overlapping polarization features linked to uncontrolled volume expansion.

3.3. Pilot-scale production: Mg-SiO_x@C

This section introduces the pilot-scale evaluation of the optimized anode system, representing the natural continuation of the laboratory-scale studies toward industrially relevant validation. The transition from lab to pilot scale was designed to reproduce, under real manufacturing conditions, the optimized electrode formulations and binder chemistries previously identified through systematic screening at laboratory scale.

At the laboratory scale, a detailed binder screening campaign was conducted to assess the physicochemical performance of multiple polymer candidates for silicon-based anodes. These binders were tested in slurry formulations containing Li-SiO_x@C and Si/C as active materials, where viscosity and adhesion measurements provided key indicators of their processability and coating quality. The most promising formulations were further evaluated through electrochemical testing in CR2032 coin cells, allowing the correlation between binder properties, electrode integrity, and cycling behaviour.

Based on these findings, two binder systems: Syensqo Generation 1 and Generation 3 terpolymers, were selected for pilot-scale testing, alongside the industrial benchmark SBR/CMC. The objective of this next phase is to assess how the optimized binders perform under larger-scale conditions, where processing parameters such as slurry homogeneity, coating uniformity, drying efficiency, and mechanical integrity become increasingly critical.

The pilot-scale work thus involves the formulation and processing of multi-kilogram slurry batches to produce electrodes with controlled thickness, areal capacity, and density. At this stage, Mg-doped SiO_x@C is employed as the active material to ensure slurry stability and reproducibility under large-scale processing conditions.

Finally, the results obtained from the pilot-scale electrochemical testing are presented in the following section, where 1 Ah pouch cells, assembled with NCM811 cathodes and the optimized anode formulations, are evaluated. In this analysis, the cathode contribution was considered constant, allowing the observed electrochemical behaviour to be attributed primarily to the binder design and its influence on the anode performance.

This pilot-scale campaign aims to validate the transferability and robustness of the binder formulations optimized at laboratory scale, while identifying possible process-related deviations and their implications for large-scale electrode production.

3.3.1. TEM characterization

A cross-sectional TEM investigation was performed on a representative junction region of the composite anode formulated with the Generation 3 binder, which integrates graphite and Mg-doped $\text{SiO}_x\text{@C}$ particles within its polymeric network. This analysis was conducted exclusively on the Generation 3 system, as laboratory-scale studies had demonstrated its superior performance, both in terms of physicochemical properties and electrochemical stability of the assembled cells, compared to the industrial SBR/CMC reference and the Generation 1 binder.

Figure 50a presents the schematic of the sampling area selected for focused ion beam (FIB) cross-sectioning and platinum (Pt) deposition, the latter applied to protect the electrode surface from ion-beam-induced damage during lamella extraction. This preparation method enabled the acquisition of high-resolution TEM images of the interfacial regions, allowing detailed visualization of the binder–particle interactions, junction morphology, and microstructural continuity achieved during pilot-scale electrode fabrication. The results provide valuable insight into how the optimized binder architecture promotes strong interfacial cohesion and homogeneous dispersion within the composite matrix, crucial for maintaining mechanical and electrochemical integrity during operation.

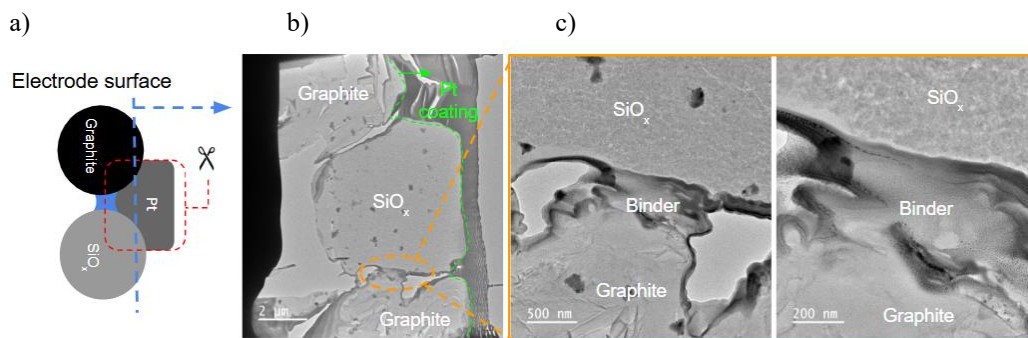


Figure 50. Schematic representation and TEM cross-sectional analysis: a) region selected for FIB lamella extraction and Pt protection, highlighting the junction between graphite and SiO_x particles; b) interfacial morphology reveals uniform Generation 3 binder layer connecting graphite and SiO_x (carbon-coated, Mg-doped) particles, ensuring strong adhesion and preserving structural integrity across the electrode; c) junction area of interest examined at higher magnifications (500 nm and 200 nm), allowing detailed visualization of the binder distribution between the SiO_x and graphite particles.

Figure 50 depicts the interfacial configuration and morphological integration between the Generation 3 binder and the active material particles within the composite anode. The low-magnification image (Figure 50b) reveals a coherent junction in which the binder forms a uniform interphase bridging the graphite and Mg-SiO_x@C particles, demonstrating strong adhesion across both surfaces.

At higher magnifications (500 nm and 200 nm, Fig. 50c), the junction region displays a continuous binder layer coating the active material surfaces, without detectable voids or interfacial gaps. The morphological continuity observed suggests chemical affinity between the binder functional groups (carboxyl, amide) and the SiO_x surface, while also maintaining adhesion with the carbonaceous regions of graphite through secondary interactions such as π - π stacking and van der Waals forces.

This interfacial architecture could improve stress distribution within the active material phase, maintaining intimate particle-to-particle contact and reducing the possibility of interfacial debonding during cycling. Such a structure likely contributes to the enhanced electrode integrity and durability, as further supported by the electrochemical results discussed in the following sections.

To confirm the binder uniform distribution across the active material interfaces, an energy-dispersive X-ray spectroscopy (EDS) analysis was subsequently performed on the same region to evaluate the spatial distribution of the key elements within the composite structure (Figure 51).

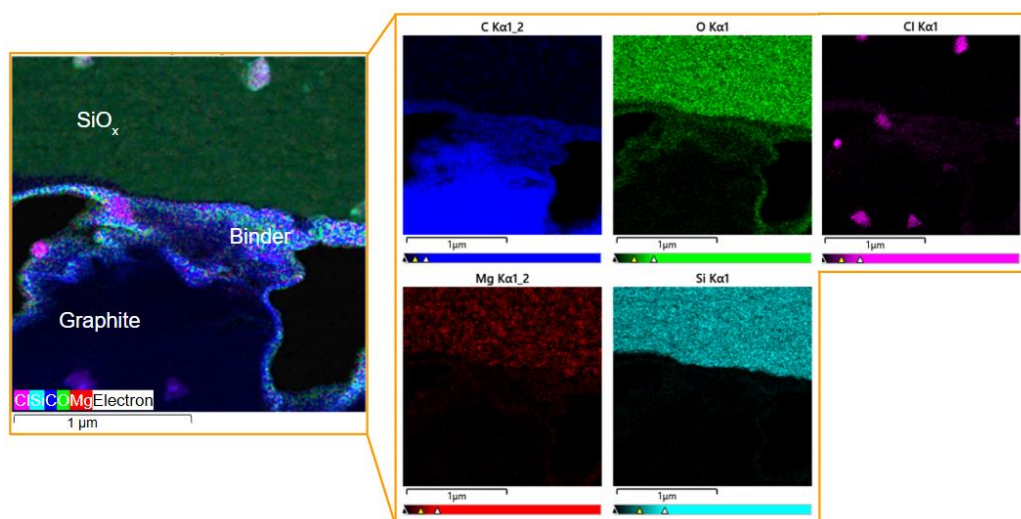


Figure 51. EDS elemental mapping of the SiO_x –graphite interface within the pilot-scale composite anode. The distribution of C, O, Si, Mg, and Cl reveals clear phase separation between graphite and SiO_x domains, while confirming the homogeneous coverage of the Generation 3 binder across both surfaces.

The elemental maps (Figure 51) shows the individual distributions of carbon (C), silicon (Si), oxygen (O), and magnesium (Mg). The carbon (C K α) and oxygen (O K α) signals are primarily localized in the binder region, consistent with the polymeric nature of the Generation 3 binder, which contains oxygen-rich functional groups (e.g., carboxyl and amide moieties). This observation validates the binder uniform coverage over both active material surfaces. The silicon (Si K α) signal is concentrated in the lower region, corresponding to the SiO_x particles, while magnesium (Mg K α) is distributed within the same zone, indicating effective Mg-doping within the oxide matrix. The graphite region exhibits a strong carbon signal and a negligible oxygen contribution, consistent with its graphitic structure. Moreover, minor chlorine (Cl K α) traces are present, likely originate from residual chloride-containing reagents or solvents used during binder or precursor synthesis (e.g., acyl chlorides, chlorinated solvents), which can remain weakly bound or adsorbed onto the surface even after purification.

In this analysed junction, these EDS findings confirm that the Generation 3 binder effectively bridges and anchors both Mg doped- SiO_x @C and graphite particles, ensuring a continuous interfacial connection across the composite microstructure. This active binding mechanism is crucial, as it promotes uniform dispersion and homogeneity within the slurry, leading to enhanced mechanical integrity and improved electrode cohesion. Such interfacial uniformity is expected to positively influence the electrochemical behaviour of the anode,

particularly in terms of stability and capacity retention, as discussed in the subsequent section.

3.3.2. Electrochemical stability at 25°C and 45°C

Following the electrode assembly and pouch cell packaging described in Section 2.2, the cells underwent a standardized formation protocol to stabilize the electrode–electrolyte interfaces and ensure consistent initial conditioning. After completing the capacity validation phase, the cells were divided into two thermal environments to evaluate their electrochemical response under different operating conditions.

One batch was cycled at 25 °C, representing standard room-temperature operation, while another was tested at 45 °C, simulating the elevated thermal conditions that can occur during fast charging or prolonged use. Testing at both temperatures enables a direct comparison of the effects of heat on ion transport, SEI stability, and mechanical integrity of the electrode–binder system.

This tests provides valuable insight into the thermal sensitivity and durability of the selected binders, highlighting their ability to maintain capacity retention, coulombic efficiency, and structural stability under conditions relevant to both laboratory testing and industrial operation.

Figure 52 presents the electrochemical stability of pouch cells assembled with Generation 1 and Generation 3 binders, evaluated under two thermal conditions: 25 °C (RT) and 45 °C (HT) at a constant current rate of 1 C (~1 A). The evolution of both capacity retention and coulombic efficiency provides insight into how temperature influences long-term cell performance and binder stability within the anode composite structure.

At 25 °C, both binder systems display a highly stable cycling response, maintaining over 80 % of their initial capacity beyond 300 cycles and achieving a nearly constant coulombic efficiency close to 100 %. This behaviour indicates the formation of stable electrode–electrolyte interfaces and minimal parasitic degradation under mild thermal conditions. This behaviour confirms that under mild thermal conditions, both binders effectively maintain electrode integrity, preventing significant SEI growth or mechanical degradation. Notably, the two binders show comparable performances in terms of long-term stability;

however, electrodes formulated with Generation 3 exhibit a slightly higher initial capacity retention, likely due to improved dispersion and more homogeneous coating provided by its optimized polymeric structure.

When the temperature increases to 45 °C, the electrochemical behaviour changes markedly. Both systems experience accelerated capacity fading, reaching the 80 % retention threshold after approximately 50–60 cycles. This rapid decline reflects the higher reactivity of the electrolyte and reduced stability of the SEI at elevated temperature, leading to repetitive SEI rupture and regrowth, gas evolution, and progressive impedance rise.

The loss of mechanical cohesion within the electrode, especially at binder–active material interfaces, further amplifies this degradation. Despite the overall decline, Generation 3 maintains slightly superior performance, suggesting that its higher acid functionality and denser hydrogen-bonding network confer stronger interfacial cohesion and resistance to thermally induced degradation, thereby partially mitigating the detrimental effects of high-temperature cycling.

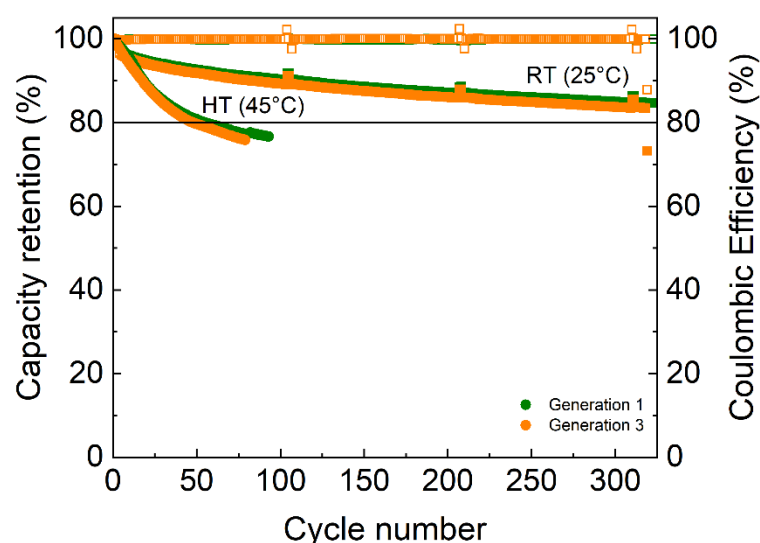


Figure 52. Electrochemical cycling performance of pouch cells, evaluated under controlled temperature conditions (25 °C and 45 °C) at 1C.

Overall, these results clearly demonstrate that thermal stress profoundly affects cell stability, mainly by accelerating interfacial degradation processes. The Generation 3 binder mitigates these effects more effectively than Generation 1, validating its suitability for high-performance silicon–graphite composite anodes intended for next-generation Li-ion cells operating under demanding thermal conditions.

3.3.3. Rate capability at charge-discharge cycles

To further assess the electrochemical resilience and rate-dependent behaviour of different binder systems, selected pouch cells were subjected to rate capability testing at 25°C, conducted after completing the initial formation protocol. In this context, rate capability test was employed as an alternative to long-term cycling, with the aim of quickly screening the charge transport properties and dynamic response of each anode formulation. Two distinct testing strategies were adopted: a *charge rate capability protocol*, where the discharge current (at 1C) was held constant while the charge current was progressively increased, and a *discharge rate capability protocol*, in which the charge current remained constant (at 1C) and the discharge current was varied. These complementary tests provided insights into both lithium-ion insertion (charge) and extraction (discharge) kinetics, interfacial stability, and the mechanical–electrochemical interplay dictated by the binder chemistry.

Among the investigated cells, three different batches were tested under *charge rate capability* conditions, all based on the same Mg-SiO_x@C - graphite electrode composition, but incorporating different binders: SBR/CMC (industrial reference), Syensqo Generation 1, and Syensqo Generation 3.

The applied protocol consisted of sequential current steps: 3 cycles each at 0.33C, 0.1C, 0.2C, 0.33C, 0.5C, 1C, 2C, and a final return to 0.33C. As illustrated in Figure 53, the SBR/CMC-based cells showed significantly reduced capacity as the rate increased and only partial recovery during the final 0.33C stage. In contrast, the Generation 1 and Generation 3 binder-based cells demonstrated markedly improved capacity retention and reversibility throughout the protocol.

The irreversible capacity loss (Q_{irr}) was calculated using the following equation (15):

$$Q_{irr}(\%) = \frac{Q_{initial} - Q_{final}}{Q_{initial}} \times 100 \quad (15)$$

where $Q_{initial}$ is the average capacity measured during the first 0.33C step, Q_{final} is the average capacity measured during the final 0.33C step after cycling at higher discharge rates.

Notably, despite being exposed to high-rate cycling at 2C, both Syensqo binders maintained structural coherence and regained most of their initial capacity during the final low-rate steps, highlighting the mechanical robustness and electrochemical compatibility of the advanced binders.

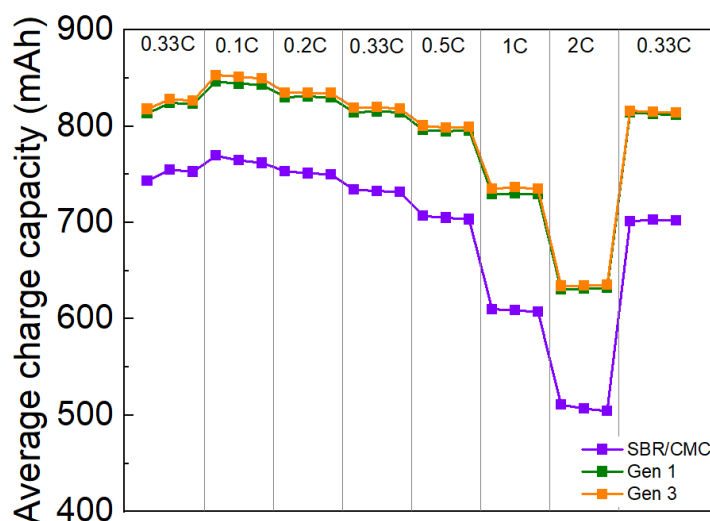


Figure 53. Charge rate capability performance of pouch cells cycled at increasing current densities, highlighting the influence of different binder chemistries in the anode formulation. The tested binders include SBR/CMC, Generation 1, and Generation 3. Each step consists of three charge–discharge cycles, while the discharge rate is held constant.

The results of the *discharge rate capability tests* are presented in Figure 54. The applied protocol consisted of three charge–discharge cycles (charge current constant) at each current density in the following order: 0.5C, 0.2C, 0.33C, 0.5C, 1C, 2C, 3C, and again 0.5C. This cycling scheme was intentionally designed to evaluate not only rate performance under stress, but also the recovery behaviour of the electrodes when returning to moderate discharge conditions.

From the average results, it is evident that SBR/CMC-based cells exhibit a significant drop in specific capacity at higher discharge rates, with a noticeable irreversible loss of capacity when returning to the final 0.5C step. In contrast, pouch cells with Generation 1 and Generation 3 anode formulations maintain much more stable profiles, with only minimal deviations between the initial and final 0.5C capacity values. This suggests that the enhanced mechanical integrity and ionic/electronic conductivity imparted by the modified

binder architectures contribute to a more resilient interfacial behaviour under high-rate conditions.

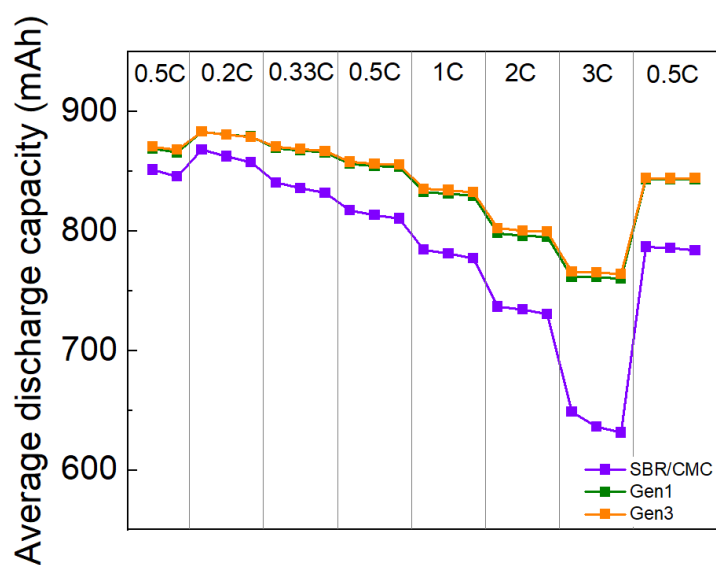


Figure 54. Discharge rate capability performances of pouch cells cycled at increasing current densities,. Each step consists of three charge–discharge cycles, while the charge rate is held constant.

Table 14. Irreversible charge (at 0.33C) and discharge (at 0.5C) capacities tested for pouch cells

	Pouch cells tested		
	Batch 1 (NCM811 Anode SBR/CMC)	Batch 2 (NCM811 Anode Generation 1)	Batch 3 (NCM811 Anode Generation 3)
Avg $Q_{\text{initial,charge, 0.33C}}$ (mAh)	96.15	96.54	96.60
Avg $Q_{\text{final,charge, 0.33C}}$ (mAh)	89.5	95.31	95.19
$Q_{\text{irr,charge,0.33C}}$ (%)	6.92	1.28	1.46
Avg $Q_{\text{initial,discharge, 0.5C}}$ (mAh)	848.44	867.48	869.29
Avg $Q_{\text{final,discharge, 0.5C}}$ (mAh)	785.49	843.35	844.28
$Q_{\text{irr,discharge,0.5C}}$ (%)	7.42	2.78	2.88

Table 14 summarizes both irreversible charge (at 0.33C) and discharge (at 0.5C) capacities value after rate capability protocols. The results reported show that, for each batch, the percentage of irreversible capacity loss at the reference current is consistently lower for pouch cells batch using an anode formulation with Generation 1 and Generation 3 binders than for the conventional SBR/CMC system, confirming their superior electrochemical resilience. However, a closer comparison between the two protocols also provides insights into the charge–discharge asymmetry of the Mg-SiO_x@C-based anodes.

The average irreversible capacity loss observed under charge rate capability testing was consistently lower for all binder types compared to that measured under discharge rate capability testing. Specifically, pouch cells employing the SBR/CMC-based anode formulation showed a loss of 6.92% during charge cycling at 0.33C, slightly lower than the 7.42% observed during discharge cycling at 0.5C. This difference becomes even more significant for the Generation 1 and Generation 3 binders: Generation 1 exhibits only 1.28% capacity loss during the charge protocol versus 2.78% during discharge, while Generation 3 shows 1.46% versus 2.88%, respectively.

These differences can be primarily attributed to the different configurations of the charge and discharge rate capability protocols. In the charge rate protocol, the C-rate is varied only during the charging steps (0.1C, 0.2C, 0.33C, up to 2C), while the discharge rate is kept constant at 1C. The presence of slower charging steps at low C-rates favours lithium-ion kinetics and minimizes overpotential effects, enabling more complete lithiation of the active material and thus reducing the extent of irreversible capacity loss.

Conversely, in the discharge rate capability protocol, the charging step is performed at a constant 1C, while the discharge rate is varied (from 0.2C to 3C). Although slower discharge rates such as 0.2C and 0.5C are included, they are generally faster than the slowest steps used in the charge protocol, and the high current applied during charging may lead to incomplete lithiation and more pronounced interfacial or kinetic limitations. These factors collectively contribute to a higher irreversible capacity loss observed in the discharge rate tests.

3.3.4. DC-IR measurements

To further assess the internal resistance evolution of the pouch cells, DC-IR (Direct Current Internal Resistance) measurements were periodically performed. This diagnostic technique provides an estimate of the overall cell impedance by analysing the voltage drop (ΔV) observed in response to a controlled current pulse, typically measured after 10 seconds from the application of the current. The DC-IR thus reflects the cumulative resistance contributions from the electrolyte, electrode interfaces, active materials, and current collectors, and is especially sensitive to changes induced by cycling degradation or thermal effects.

In this study, DC-IR measurements were conducted on pouch cells assembled with different silicon-based anodes and binder formulations. After the initial formation step and capacity validation, a standardized procedure was applied to ensure consistency across batches. Specifically, each pouch cell underwent two stabilization cycles at 0.5C at 25 °C in the potential window of 4.2 V–3.0 V, in order to reach a state of charge (SOC) of 50%. Subsequently, the DC-IR was evaluated through a dual-pulse protocol, involving a low current pulse at 0.2C at $t = 0$ s, followed by a higher current pulse at 2C at $t = 10$ s. This approach enables the capture of both the instantaneous and delayed resistance contributions and allows the monitoring of impedance evolution over time. The analysis covered three distinct test conditions:

- Room temperature cycling (25 °C),
- Elevated temperature cycling (45 °C),
- High-temperature storage test (60 °C), in which cells were aged statically, after formation protocol and no cycling occurred.
-

The DC-IR was calculated by applying a constant current pulse (usually 1C) and measuring the instantaneous voltage drop after 10 seconds, as reported in equation (16):

$$DC - IR = \frac{V_{t=10s} - V_{t=0s}}{I} \quad (16)$$

where $V_{t=10s}$ is the cell voltage 10 seconds after the current is applied, $V_{t=0s}$ is the initial voltage at the start of the pulse, and I is the applied current.

In Figure 55, the DC-IR values are presented for each testing condition, specifically during cycling at 25 °C, at 45 °C, and during high-temperature storage at 60°C over 4 weeks. For each condition, data from three independent batches are reported, ensuring statistical reproducibility.

The comparative trends highlight the distinct impact of binder formulation and temperature on the internal resistance evolution of the cells over time.

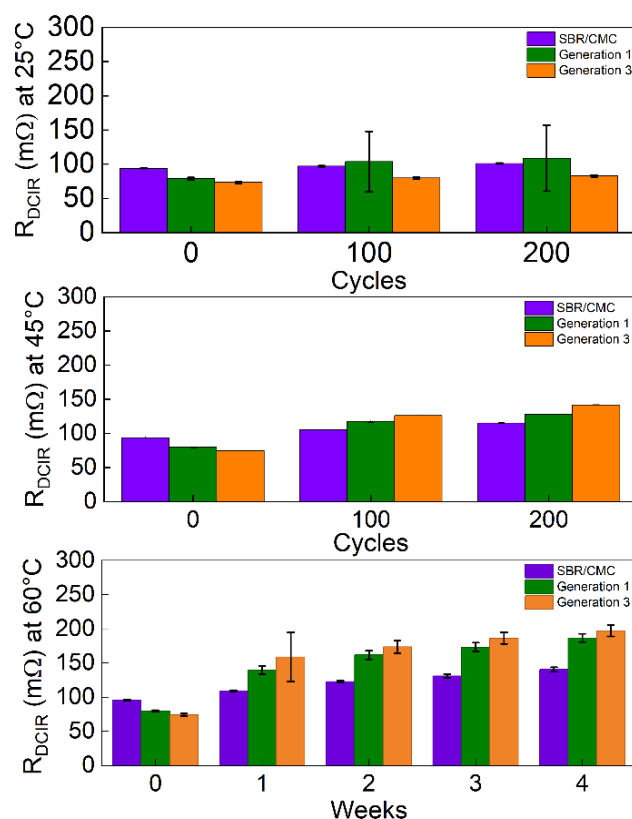


Figure 55. DC-IR values measured on full pouch cells after formation and during cycling for: (a) 25 °C, (b) 45 °C, and (c) 60 °C storage conditions.

A clear temperature-dependent trend emerges in the DC-IR evolution across all tested binder systems. At room temperature (25 °C), the internal resistance values remain relatively low and stable, indicating limited interfacial degradation. The SBR/CMC-based cells begin with a DC-IR of 93.7 mΩ and show only a modest increase to 100.98 mΩ after 200 cycles, reflecting a moderate resistance build-up. Generation 1 starts at a lower value (78.6 mΩ) but increases more noticeably to 108.7 mΩ, suggesting greater reactivity at the interface, possibly due to binder-related structural evolution or gradual SEI thickening. Generation 3 displays the most stable resistance profile at RT, increasing from 73.4 mΩ to 85.7 mΩ over 200 cycles. This limited growth highlights its superior ability to preserve

interfacial integrity under mild conditions, likely due to its more cross-linked, branched architecture which better accommodates volume changes and suppresses contact loss.

At elevated temperature (45 °C), all systems exhibit a significantly steeper increase in DC-IR. This behaviour can be attributed to accelerated side reactions, faster SEI reformation, and thermal softening or decomposition of binder–electrode interfaces. Generation 3, despite its best-in-class performance at 25 °C, undergoes a marked increase from 74.6 mΩ to 164.7 mΩ at 200 cycles. Generation 1 follows a similar trend, rising from 79.9 mΩ to 127.6 mΩ. SBR/CMC, though starting from a higher value (93.7 mΩ), reaches 115 mΩ, showing comparatively slower resistance growth. These results imply that while Gen1 and Gen3 maintain superior mechanical and electrochemical properties at RT, their structures may be more susceptible to thermal-induced interfacial degradation, such as excessive SEI layering or binder relaxation at higher temperatures.

The most pronounced increases are observed under thermal storage at 60 °C, even in the absence of electrochemical cycling. Here, pouch cells with Generation 3 exhibit the sharpest rise, from 75.5 mΩ to 197.2 mΩ over four weeks, indicating a strong sensitivity to sustained thermal exposure. Generation 1 also shows significant resistance growth (from 79.8 mΩ to 178.6 mΩ), while SBR/CMC increases from 95.5 mΩ to 140.4 mΩ. The absence of lithiation/delithiation in these tests confirms that resistance rise is primarily due to electrolyte decomposition and subsequent gas formation, resulting in SEI instability and local contact loss. Generation 3 steeper DC-IR evolution may reflect a higher reactivity of the interface or insufficient suppression of parasitic reactions under static thermal stress, despite its good performance in cycling.

Overall, DC-IR measurements confirm the strong temperature dependence of internal resistance. At 25 °C, both Generation 1 and Generation 3 maintain low, stable values, while higher temperatures (45–60 °C) accelerate interfacial degradation and resistance growth. Nevertheless, Syensqo binders consistently outperform SBR/CMC, demonstrating enhanced interfacial stability and resilience under thermal stress—key factors for durable electrode performance in high-temperature conditions.

3.3.5. Evaluation of cell swelling during thermal storage

A dedicated set of pouch cells was assembled to investigate the effects of thermal storage on dimensional stability. [254]

As described in Section 2.2, each test involved a 1 Ah pouch cell assembled by pairing an NCM811 cathode with a silicon–composite anode formulated with one of the three binder systems: SBR/CMC, Generation 1, or Generation 3.

After completing the standard formation and capacity validation steps, the pouch cells were positioned between rigid compression plates applying a constant mechanical constraint and subsequently stored in an oven at 60 °C to induce accelerated aging.

This configuration ensures uniform mechanical confinement, preventing uncontrolled swelling and enabling accurate monitoring of the total cell thickness variation during storage. Measuring this dimensional change provides direct insight into gas evolution, SEI thickening, and electrode expansion phenomena, which are thermally activated at elevated temperature and directly correlated with the binder’s mechanical and interfacial stability.

The total cell thickness was measured weekly using a micrometre to evaluate the extent of swelling (Figure 56). The observed increase in thickness was attributed to gas generation within the cell, a known phenomenon under elevated temperature conditions due to electrolyte decomposition and parasitic reactions.

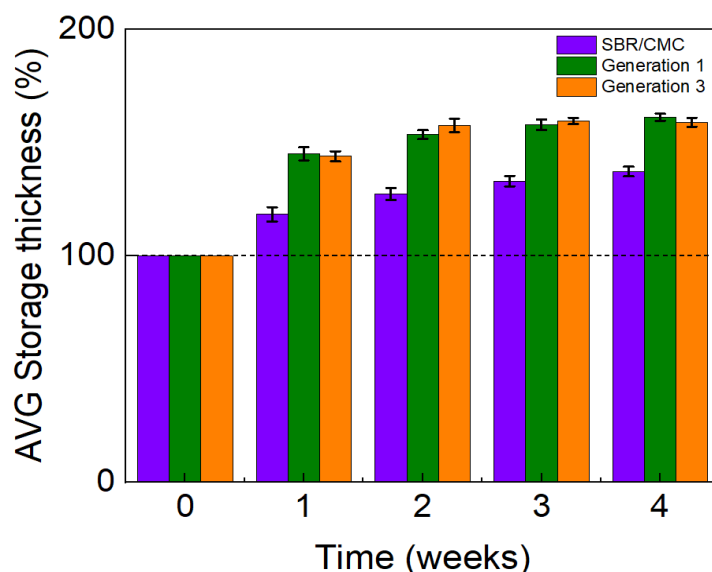


Figure 56. Average cell thickness measurements of pouch cells stored at 60°C

Figure 56 reports the evolution of the total pouch cell thickness during isothermal storage at 60 °C over a four-week period. The thickness measured immediately after formation and capacity check (Week 0) was taken as the reference (100 %) to normalize subsequent values. The observed increase in thickness is primarily associated with gas generation within the cell, arising from electrolyte decomposition and parasitic side reactions accelerated by temperature. Although lithiation does not occur during storage, partial SEI restructuring and electrolyte oxidation at the silicon interface may contribute to internal pressure buildup.

In this context, a clear divergence in behaviour emerges among the different binder systems. Pouch cells employing the conventional SBR/CMC binder exhibit a progressive and nearly linear increase in total thickness over time, reaching approximately +37.3% by the fourth week. This continuous swelling suggests ongoing gas evolution and indicates a lack of effective mechanical buffering, as well as weaker interfacial adhesion, which compromises dimensional stability under thermal stress.

Conversely, pouch cells using Generation 1 and Generation 3 binders show a markedly different trend. Although both exhibit a higher initial swelling during the first week (+45% and +44%, respectively), likely due to rapid early-stage electrolyte decomposition or binder rearrangement, the total thickness quickly stabilizes. By the fourth week, the thickness plateaus at approximately +61% for Generation 1 and +59% for Generation 3, with negligible increases observed beyond the second week. Such stabilization is attributed to the optimized viscoelastic and interfacial properties of the polymer matrix, where the

presence of polar functionalities ($-\text{COOH}$ and $-\text{CONH}_2$) enhances particle adhesion and reduces gas pathways. These results are consistent with literature reports identifying post-formation swelling at 60 °C as a sensitive indicator of interfacial degradation and binder-electrolyte compatibility. [260]

Therefore, the improved dimensional stability achieved with Generation 1 and Generation 3 highlights their potential to ensure safer and more durable performance under thermally demanding conditions.

4. Conclusion

Across laboratory and pilot-scale operation, this work identifies binder architecture as the main determinant, controlling both processability and durability of silicon-based composite anodes.

Indeed, before electrode production, a rigorous design was established to ensure full compatibility with pilot-scale manufacturing and electrochemical balancing requirements. To match those needs, the main goal was to define an integrated electrode design capable of meeting industrial constraints such as post-calendering thickness, density, areal capacity, and adhesion strength, while maintaining a fixed N/P ratio of 1.1–1.2 against the selected cathode (NCM622 or NCM811).

This comprehensive approach guided both binder selection and optimization strategy. A fixed electrode formulation, comprising $\text{SiO}_x\text{@C}$ –graphite and Si/C as active materials and carbon black as conductive additive, was maintained across lab and pilot scales, while the binder chemistry was tuned to achieve the desired rheological and mechanical behaviour.

Despite conventional SBR/CMC binder system remains the most widely used industrial binder for silicon–graphite anodes, it suffers from limited mechanical resilience, poor interfacial binding with silicon, and moderate electrochemical stability. Therefore, this project focused on a suitable binder design to overcome those issue; Syensqo terpolymer family was developed as an advanced alternative tailored for anodes to be implemented into next-generation LIB. This is a linear terpolymer, composed of poly(acrylic acid), polyacrylamide, and a third confidential monomer, emerged as a leading candidate. Its molecular architecture enables multifunctional interactions such as hydrogen, ionic coordination, and covalent bonds, with both carbonaceous and silicon active materials surfaces. This structural versatility translates into enhanced slurry homogeneity, optimized rheological behaviour, and robust adhesion to the copper current collector. As a result, compared to SBR/CMC, Syensqo binders not only improve the mechanical and interfacial stability of the electrode, but also sustain electrochemical integrity under high-capacity cycling, making them more suitable for industrial pilot-scale processing of silicon–composite anodes.

These physico-chemical targets enabled the translation from lab slurries to pilot manufacturing, yielding uniform particle wetting, robust carbon–binder domains, and

defect-limited microstructures suitable for scale. The same binder geometry and functionality also supported electrochemical stability, by promoting a conformal, resilient interphase and sustained electronic percolation, manifested as improved cycling stability, capacity retention, and controlled resistance growth. With cathode chemistry and protocols held constant, performance differences are attributable to the anode binder, confirming the centrality of binder architecture to scalable electrode quality and cell performance. The conclusions that follow synthesize scale evidence (lab- and pilot-scale) and outline implications for industrial application and future optimization.

At lab scale, slurries formulated with all four binders displayed shear-thinning rheology with viscosities, quantified at the mixing-relevant setpoint (e.g., η at 10 Hz), falling within the predefined acceptance window adopted as a reference for pilot scale transfer. Electrodes produced by casting and drying were then assessed by 180° peel testing to quantify coating–Cu collector adhesion strength. Anodes formulated with Generation 3 and Generation 3 acidic binders displayed significantly higher peel forces compared to SBR/CMC and Generation 1, confirming stronger interfacial cohesion and enhanced particle–binder interactions, consistent with their optimized molecular weight and pH-driven functionalities.

When comparing the two active materials, Li-SiO_x@C and Si/C, their distinct morphology and structural design significantly influence both physicochemical and electrochemical properties of the resulting anodes. Li-SiO_x@C - graphite composite, consisting of an amorphous silicon oxide core embedded within a carbon matrix and pre-lithiated domains, exhibits a more compact and homogeneous morphology. This architecture promotes uniform slurry dispersion, smoother coating formation, and enhanced binder compatibility, leading to mechanically cohesive and defect-free electrode layers. In contrast, Si/C composite anode, composed of elemental silicon particles encapsulated by a thin carbon shell, presents a more heterogeneous surface. Such structural disparity results in greater viscosity sensitivity during slurry processing and less uniform adhesion, reflecting a weaker interfacial interaction between the binder and the particle surface.

These morphological differences are also present in the electrochemical response. As observed from cycling and impedance analyses, Li-SiO_x@C-based anodes demonstrate superior long-term electrochemical stability compared to Si/C-based systems. During lithiation and delithiation, the oxide matrix in Li-SiO_x@C acts as a mechanical buffer,

confining the volume expansion within the particle and preserving interfacial integrity. On the other hand, in Si/C electrodes, the lithiation-induced expansion predominantly propagates from the silicon core, exerting stress on the carbon shell and causing interfacial cracking, contact loss, and accelerated SEI growth. This leads to progressive impedance rise and capacity fading upon cycling.

Overall, the comparative analysis confirms that the structural design of the active material plays a key role in dictating slurry processability, adhesion behaviour, and electrochemical durability. The combination of Li-SiO_x@C with Generation 3 binders, especially the acidic variant, proved most effective in balancing these aspects, ensuring both manufacturing compatibility and enhanced cell stability over extended cycling.

Based on these laboratory-scale results, Li-SiO_x@C was initially selected as the reference active material for pilot-scale validation, in combination with Generation 1 and Generation 3 binders. The pilot-scale process followed the same key steps as in laboratory-scale preparation, such as slurry mixing, coating, drying, and electrode cutting, while implementing industrially relevant conditions. However, during large-batch processing and coating via reverse comma-roll, both the slurry and coated layers exhibited heterogeneities, including the formation of gas bubbles. These were attributed to hydrogen evolution arising from the use of the pre-lithiated SiO_x@C material, whose reactivity under aqueous processing led to localized gas generation and coating defects.

To overcome these issues, the Mg-doped SiO_x@C active material was introduced for subsequent pilot-scale production, maintaining the same binder systems (Generation 1 and Generation 3) and electrode formulation. The optimized process successfully proceeded through planetary slurry mixing, reverse comma-roll coating, and drying, yielding electrodes that met the targeted post-calendering specifications in terms of thickness, density, and areal capacity.

Following electrode fabrication, multiple batches of 1 Ah pouch cells were assembled using NCM811 cathodes, enabling comprehensive electrochemical testing. These included cycling stability, direct current internal resistance (DC-IR) evolution during cycling, cell swelling assessment under storage at 60 °C, and rate capability evaluation. The results from these tests provided the basis for correlating binder chemistry, electrode microstructure, and large-format cell performance under realistic operating conditions.

In future, additional multi-scale analyses will be carried out on both binders and anodes to deepen the understanding of interfacial and mechanical phenomena governing electrode performance. These will include in-situ dilatometry to monitor electrode expansion during cycling, cross-sectional FIB–SEM and nanoindentation to evaluate structural and mechanical evolution, and differential capacity (dQ/dV) analyses for long-term degradation tracking. Together, these investigations will provide a more comprehensive picture of the binder–active material interactions and their impact on the scalability and durability of next-generation silicon-based anodes.

In summary, this doctoral research has established a systematic framework for binder design, selection, and validation across multiple manufacturing scales, linking the molecular chemistry of polymeric binders to electrode architecture, processing behaviour, and electrochemical stability. By coupling laboratory and pilot-scale experimentation, the work provides both fundamental insights and practical guidelines for the industrial implementation of advanced polymer binders in high-energy silicon-based lithium-ion batteries.

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