

Impact of the Si Electrode Morphology and of the Added Li-Salt on the SEI Formed Using EMIFSI-Based Ionic-Liquid Electrolytes

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This work presents an in-depth chemical and morphological investigation of the solid electrolyte interphase (SEI) formed on binder-free silicon electrodes, which include both nanowire (Si-NW) and amorphous (a-Si) configurations, for next-generation lithium-ion battery systems. The study focuses on the first five galvanostatic cycles to capture the critical early-stage SEI consolidation process, essential for understanding the interfacial phenomena that dictate long-term performance. By employing innovative electrode fabrication techniques such as plasma-enhanced chemical vapor deposition and utilizing ionic liquid (IL)-based electrolytes—specifically 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIFSI) formulations known for their low viscosity and high conductivity—this work addresses the challenges posed by the significant volume changes inherent to Si-based materials. Advanced characterization methodologies, notably Optical-Photothermal Infrared Spectroscopy (O-PTIR) and Raman spectroscopy are utilized to probe the chemical and structural evolution of the SEI with high spatial resolution. This multifaceted approach reveals the interplay between electrode morphology and electrolyte composition on SEI formation and provides valuable insights into the fundamental processes governing irreversible capacity losses and electrode degradation. The findings demonstrate clear material- and electrolyte-dependent differences in SEI characteristics, thereby establishing new avenues for optimizing interfacial stability and battery performance. Overall, the study contributes innovative perspectives on early SEI formation mechanisms critical for the design of safer and more durable high-capacity battery electrodes.

1. Introduction

Rechargeable batteries with high energy density, good cyclability, and minimum capacity fading in extended charge/discharge cycles are key enabling technology to tackle modern societal needs such as large-scale/long-term energy storage, power supplies for portable electronics, and electric vehicles.^[1] Lithium-ion batteries (LIBs) dominate the current secondary battery market due to their excellent performance. Figures and the flexibility of their formulation that allows incremental enhancements by incorporating higher-performance components.

Due to the high theoretical energy density, the earth-abundance, and environmental benignity, Si has attracted significant attention as one of the most promising next-generation negative electrode materials for LIBs.^[2,3] Si anodes can store ≈ 10 times more lithium than graphite anodes, with a theoretical specific capacity of $\approx 3579 \text{ mAh g}^{-1}$, compared to 372 mAh g^{-1} for graphite.^[4,5] Si electrodes operate at a relatively low discharge potential plateau ($\approx 0.4 \text{ V}$ vs

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Li⁺/Li), which enables a large voltage difference by matching with an intercalation cathode, like cobalt-poor layered oxides. Such combinations can deliver high energy density for full LIBs. However, Si-based anode materials usually suffer large volume changes during the charge and discharge process, leading to pulverization of particles, loss of electric contact, and continuous side reactions.^[6–8] In addition, the Coulombic efficiency is typically poor in the first cycle and the capacity performance fades during extended cycling.^[9]

Generally speaking, capacity fading in Si electrodes originates from the electrolyte degradation at low potentials. Unfortunately, the formation of a stable and resistant passivation layer on the Si surface, known as the solid electrolyte interphase (SEI), is hindered by volume changes. In fact, the volume expansion–contraction of the electrodes promote SEI cracking and further reduction of the electrolyte on freshly exposed electrode material. This process increases the interphase resistance, consumes electrolytes, and eventually leads to cell failure.^[10,11] Therefore, a chemically and mechanically stable SEI is necessary to deliver durable Si anodes, and the study of its chemical and morphological properties is crucial to understanding its evolution and optimizing its features.

The formation of stable SEI over Si is closely linked to the electrolyte composition. This critical component of LIBs requires further innovation to meet the need for improved safety. As an example, the substitution of flammable carbonate electrolytes with ionic liquids (ILs) can improve the overall safety and performance of the battery due to ILs inherent non-volatility, high conductivity, high dielectric constants, and wide electrochemical windows. Among all others, 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMISFI) based ILs have one of the lowest viscosities and highest conductivities of the ILs considered for LIBs^[12] and have shown very good performance with Si composite anodes^[13] and micrometer-sized Si.^[14]

Here we present a comprehensive chemical and morphological analysis of the solid-electrolyte interphase (SEI) formed on nanostructured silicon electrodes—specifically, silicon nanowires (Si-NW)^[15] and amorphous silicon (a-Si)—cycled in ionic liquid (IL)-based electrolytes.^[16] To elucidate the early-stage formation and consolidation of the passivation layer, galvanostatic tests have been deliberately limited to the first five cycles, a strategy that has been previously validated as an effective means to focus on SEI evolution rather than long-term electrochemical performance (“Impact of the Si electrode morphology and of the added Li-salt on the SEI formed using EMISFI based

ionic-liquid electrolytes”, n.d.). The Si electrodes were synthesized using binder-free approaches, where Si-NW samples were grown on pre-cut stainless-steel substrates and a-Si was deposited via Plasma-Enhanced Chemical Vapor Deposition onto copper foils, ensuring that the intrinsic morphological and crystallinity differences were maintained without interference from binders or conductive additives (“Impact of the Si electrode morphology and of the added Li-salt on the SEI formed using EMISFI based ionic-liquid electrolytes”, n.d.).

This approach enables a targeted investigation into how the electrode’s crystallinity and morphology influence the composition and thickness of the SEI layer, an aspect critical to addressing the mechanical strains and electrolyte side reactions characteristic of silicon anodes (“Impact of the Si electrode morphology and of the added Li-salt on the SEI formed using EMISFI based ionic-liquid electrolytes”, n.d.). In addition, state-of-the-art characterization techniques have been employed to achieve a comprehensive understanding of the interface: Optical-Photothermal Infrared Spectroscopy (O-PTIR) was applied to obtain high spatial resolution chemical maps of the interphase (“Impact of the Si electrode morphology and of the added Li-salt on the SEI formed using EMISFI based ionic-liquid electrolytes”, n.d.), while Raman spectroscopy was used to discern the crystalline evolution of the electrodes. Complementary to these methods, Scanning Electron Microscopy (SEM) was utilized to examine the surface morphological changes, thereby establishing a robust multi-technique platform for correlating the interphase characteristics with electrode morphology. This study exploits an experimental protocol already validated by us in a previous publication^[17] concerning the SEI growth on Si electrodes cycled in carbonate-based electrolytes, and therefore extends and applies our successful approach to novel electrolyte/electrode interfaces.

2. Experimental Section

2.1. Electrode and Cell Preparation

The a-Si and Si-NW electrodes were synthesized following the routes reported^[15,16] and did not contain binders or conductive additives. The Si-NW samples were thin Si films grown on pre-cut stainless-steel disks with known Si mass loading, whereas a-Si was deposited onto copper foils by means of Plasma-Enhanced CVD (Smit Thermal Solutions DEP2400) and then cut in electrodes of $\approx 1 \text{ cm}^2$. In this second case, the Si mass loading was estimated by an accurate evaluation of the exact area of each electrode thanks to ImageJ-embedded routines^[18] to estimate the surface area and therefore the corresponding Si loading.

Electrodes were dried under vacuum at 100 °C and then transferred into an Ar-filled glove box (Itco Eng. SGS30, ppm H₂O <0.1). Electrodes were assembled in half cells versus lithium counter-electrodes using the two different EMISFI-based electrolytes. El-Cell ECC-Std cells were assembled using Whatman separators and 50 μL of electrolyte. The two electrolyte formulations in weight are 0.2 LiTFSI:0.8 EMISFI and 0.2 LIFSI:0.8 EMISFI. Galvanostatic cycling was performed using an MTI 8-channel Battery Analyzer. Cells were kept at a constant temperature (30 °C) using a static oven (Mettmert SG30). Each cell was discharged and charged in the 10 mV – 1 V voltage range at constant current (galvanostatic conditions) five times: the first

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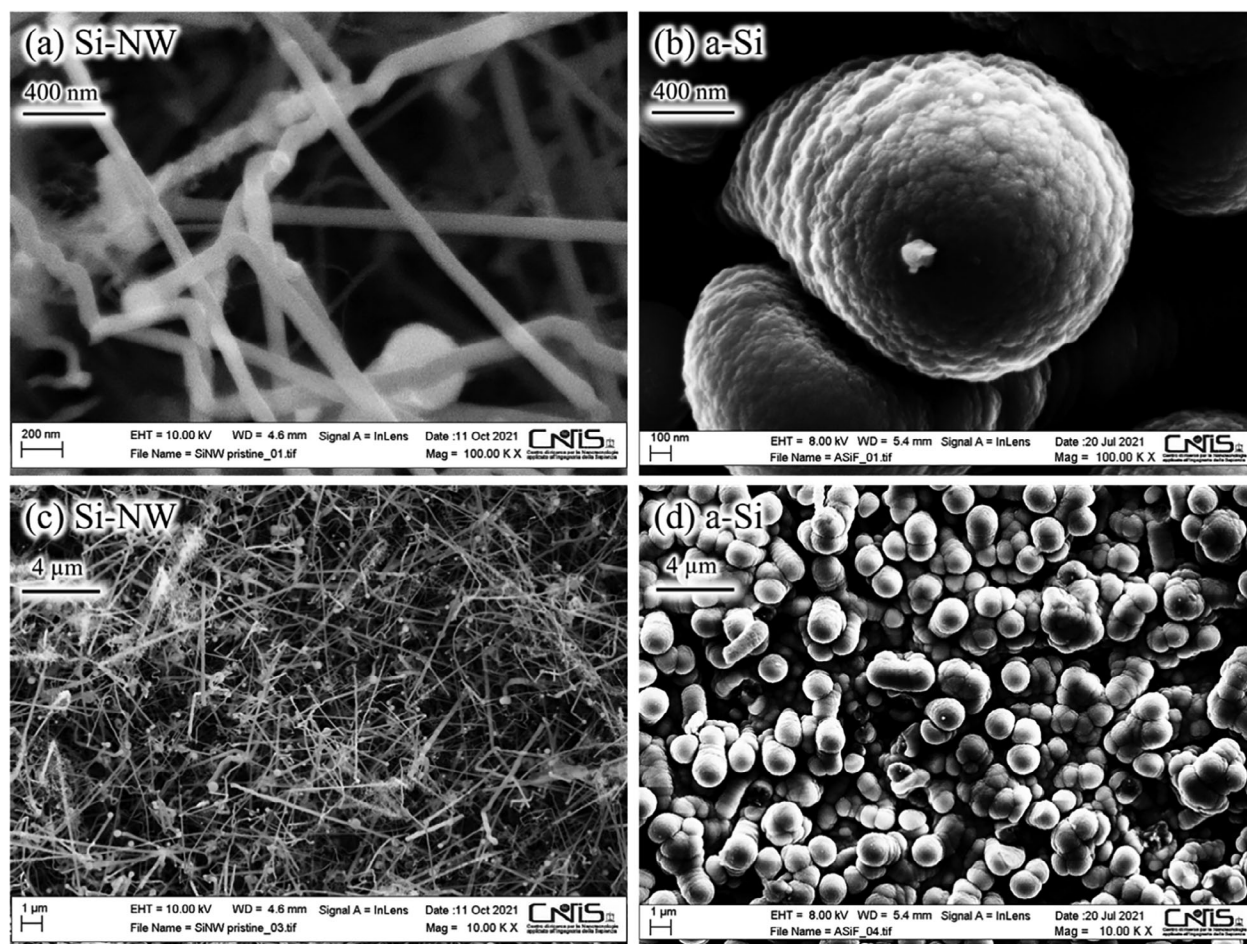


Figure 1. SEM micrographs of the surface of Si-NW and a-Si at 100k X magnification (a,b) and 10k X magnification (c,d).

cycle at C/20 (activation cycle) and the next four at C/5. The C rates were calculated using 3500 mAh g⁻¹ as theoretical capacity (1C = 3500 mA g⁻¹). After the cycling the electrochemical cells were disassembled and post-mortem electrodes were washed in tetrahydrofuran (THF, Merck, dried for two weeks on molecular sieves 3A, Merck) to remove traces of the lithium salts and ILs. THF was removed by gentle evaporation in a dynamic vacuum at room temperature: the final dried samples were stored in an Ar-filled glove box before further characterization.

All samples were characterized using different ex-situ techniques: Scanning Electron Microscopy (SEM), Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, Raman spectroscopy, Optical Photothermal IR (O-PTIR) spectroscopy. The Coulombic Efficiency (CE), the Capacity Retention (Cap.Ret.), and the Cumulative Irreversible Capacity (CIC) at the cycle *N* were calculated using the following equations:

$$CE_{cyN} = \frac{Q_{ch,cyN}}{Q_{disch,cyN}} \times 100 \quad (1)$$

$$Cap.Ret._{cyN} = \frac{Q_{ch,cyN}}{Q_{1st,ch}} \times 100 \quad (2)$$

$$CIC_{cyN} = \sum_{i=1}^N (Q_{disch,cyN} - Q_{ch,cyN}) \quad (3)$$

2.2. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used for the morphological characterization of Si anodes before and after cycling. Micrographs were recorded using a Field Emission Scanning Electron Microscope (FESEM) Zeiss Auriga 405 (Zeiss, Oberkochen - Germany). SEM measurements were performed at the Research Center on Nanotechnology Applied to Engineering (CNIS) of Sapienza University.

2.3. Raman Micro-Spectroscopy

Raman measurements were performed with a Thermo Fisher DXR2 Raman micro-spectrometer, equipped with a solid-state green laser (532 nm of wavelength), and a 900 line/mm grating, that allows an estimated spectral resolution of ≈ 5 cm⁻¹, in a spectral range between 50 and 2500 cm⁻¹. Rayleigh scattered light was rejected by an edge filter and Raman scattering was collected by a Peltier-cooled CCD camera. The spectrometer was coupled with a confocal microscope supplied with a set of objectives (reported

spectra were all acquired with an Olympus Mplan50X/0.75NA) and a motorized mapping stage with a spatial resolution of 0.1 μm . All the spectra that build the maps, result from averaging 2 scans of 5 s of acquisition, with a laser power on the sample of ≈ 6 mW.

Raman spectroscopy measurements were used mainly to evaluate the degree of amorphization of Si-NW. Indeed, elemental Si bands at $480\text{--}520\text{ cm}^{-1}$ result from the contribution of amorphous and crystalline Transverse Optical (TO) phonons. By deconvoluting this spectral region into the various active modes, it was possible to estimate the amorphous fraction ($A-F$) as the ratio between the a-TO and the c-TO peak areas, weighed for the cross-section ratio $\frac{\sigma(c\text{-Si})}{\sigma(a\text{-Si})} \cong 0.8$, using the following relation:^[19]

$$A - F = \frac{a - TO_{\text{area}}}{a - TO_{\text{area}} + 1.25c - a - TO_{\text{area}}} \quad (4)$$

Measurements were performed on the SMIS beamline of the Synchrotron SOLEIL (Saint-Aubin, France). The Thermo-Fisher OMNIC software was used for spectral treatment and analysis.^[20]

2.4. ATR-FTIR Spectroscopy

ATR-FTIR spectra were collected by a Thermo Nicolet 8700 FTIR spectrometer coupled to a Continuum microscope, equipped with a $15\times$ Schwarzschild ATR objective, that employs a ZnSe crystal with a refractive index of $n = 2.4$ (ISP Optics Corp., Latvia). All spectra were recorded in the mid-infrared spectral range (from 600 to 1800 cm^{-1}) using a KBr beam-splitter and a liquid nitrogen-cooled MCT detector. Measurements were performed on the SMIS beamline of the Synchrotron SOLEIL (Saint-Aubin, France). The Thermo-Fisher OMNIC software was used for spectral treatment and analysis.^[20]

2.5. Optical-Photothermal Infrared Spectroscopy

Optical-Photothermal Infrared Spectroscopy (O-PTIR) was an innovative technique that retrieves the IR absorption of the sample by measuring its photothermal response induced by a pulsed infrared laser beam in a visible probe reflected by the sample.^[21] O-PTIR measurements on Si anodes were performed through a “mIRage” Infrared Microscope (Photothermal Spectroscopy Corp., Santa Barbara, CA - USA), equipped with an IR pulsed quantum cascade laser from Daylight Solutions, tuneable between 950 and 1700 cm^{-1} , and a visible (532 nm) continuous wave laser probe. All spectra were recorded by a $40\times$ Schwarzschild objective (0.78 NA , 8 mm WD), with a spectral resolution of 2 cm^{-1} . Measurements were performed on the SMIS beamline of the Synchrotron SOLEIL (Saint-Aubin, France). The OMNIC code was used for the manipulation and analysis of the spectra.^[20] Samples were observed using a 3D Printed Air-Tight Cell Adaptable for Far-Infrared Reflectance, Optical Photothermal Infrared Spectroscopy, and Raman Spectroscopy Measurements.^[22]

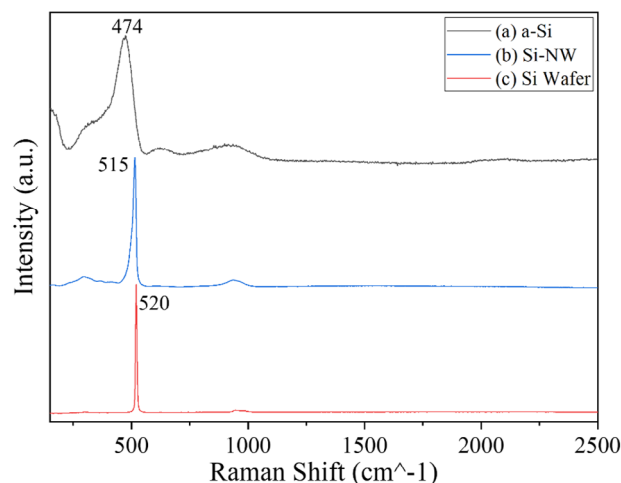


Figure 2. Raman spectra of a) amorphous Si electrode, b) Si Nanowires electrode, and c) Si wafer.

3. Results

3.1. Preliminary Characterization of Si nanomaterials

The SEM micrographs of the surface of the two different Si electrodes at various magnifications are shown in **Figure 1**.

The morphological differences between the two samples are clearly visible: Si-NW (**Figure 1a**) is constituted by few-micrometer-long nanowires with a mean diameter of $\approx 50\text{--}100\text{ nm}$, while the a-Si (**Figure 1b**) is composed of columnar microparticles, with larger semi-spherical tips with diameters in the range $1\text{--}3\text{ }\mu\text{m}$. All particle sizes have been estimated using the software ImageJ.^[18] Overall, both samples display a very homogeneous coverage and morphology across the electrode as shown at low magnifications in **Figure 1c,d**.

The Raman spectra of both samples, benchmarked with a Si wafer reference, are shown in **Figure 2**. As expected two partially overlapped Raman bands are observed: the peak $\approx 474\text{ cm}^{-1}$ is associated with the TO phonon in the amorphous phase (a-TO) and the peak $\approx 520\text{ cm}^{-1}$ is associated with the TO phonon in crystalline Si (c-TO).^[23] The high intensity of the peak at 515 cm^{-1} in the spectrum of Si-NW confirms its extended crystallinity, while a-Si electrode shows a larger amorphous Si content. The two peaks at ≈ 300 and $\approx 1000\text{ cm}^{-1}$ can be assigned to the scattering of overtones of the transverse acoustic (2TA) phonons and of the transverse optical (2TO) phonons.^[24]

Quantitatively, the amorphous fraction (in %), calculated by Equation 1 using the methodology described in the experimental section, is 49% for Si-NW and 100% for a-Si.

3.2. Electrochemical Performance in Lithium Metal Half Cells

The electrochemical performances of the two Si-NW and a-Si electrodes measured during the first five cycles in batteries are shown for the two electrolyte formulations, $0.2\text{ LiFSI} : 0.8\text{ EMISF}$ (**Figure 3**) and $0.2\text{ LiTFSI} : 0.8\text{ EMISF}$ (**Figure 4**). As expected for materials in both electrolytes, the first cycle shows a potential profile, both in discharge and charge, remarkably different

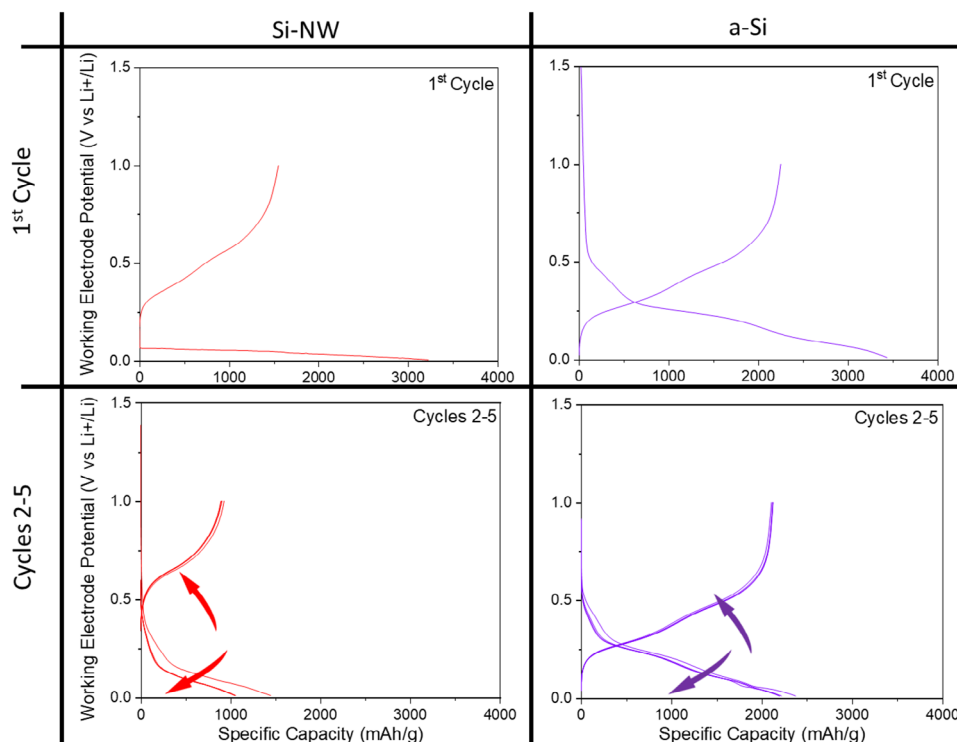


Figure 3. Galvanostatic discharge/charge potential profiles for Si-NW (left panels) and a-Si active material (AM) (right panels) in a galvanic cell: (–) Li/EMIFS: LiFSI 0.8:0.2 / AM(+).

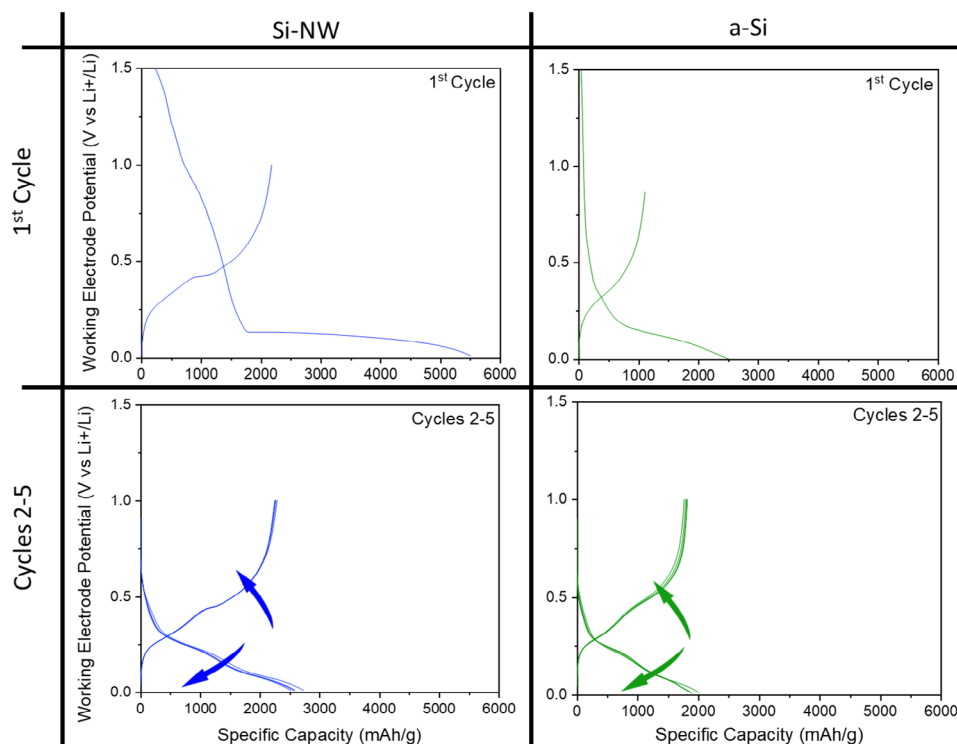


Figure 4. Galvanostatic discharge/charge potential profiles for the two Si-NW and a-Si active materials (AM) in a galvanic cell: (–) Li/EMIFS: LiFSI 0.8:0.2/AM(+).

Table 1. Summary of the galvanostatic performance of the two Si-NW and a-Si active materials (AM) in the two different ILs-based electrolytes.

	EMIFSI: LiFSI 0.8:0.2 electrolyte		EMIFSI: LiTFSI 0.8:0.2 electrolyte	
	Si-NW	a-Si	Si-NW	a-Si
$Q_{1st,disch} [mAhg^{-1}]$	3100	3480	5500	2500
$Q_{1st,ch} [mAhg^{-1}]$	1510	2260	2100	1100
CE_{1st}	49%	65%	38%	44%
$Q_{rev, cy 5} [mAhg^{-1}]$	890	2100	2230	1780
Cap.Ret. _{cy5}	59%	93%	106%	162%
CE_{cy5}	85%	96%	89%	94%
$CIC_{cy5} [mAhg^{-1}]$	2572	1730	4750	1793
$Q_{tot} [mAhg^{-1}]$	12 844	23 194	27 087	18 503
CIC_{cy5}/Q_{tot}	0,200	0,075	0,175	0,097

compared to the following. On the other hand, cycles 2 to 5 show excellent stability in terms of delivered capacity as well as potential profile shape and voltage hysteresis in all four cases. A summary of the performance Figures in the first five cycles of the galvanostatic tests are reported in **Table 1**.

Galvanostatic tests were performed only for the first five cycles to allow the consolidation of the SEI layers over both materials. Here, our goal is not to demonstrate the electrochemical performance in batteries which has been previously reported in^[15,16] but to evaluate the composition and thickness of the passivation film and to outline how the SEI properties are modified by the crystallinity/morphology of the Si active material and/or by the formulation of the IL-based electrolyte.

Starting from the LiFSI-based electrolyte, a-Si shows larger specific capacity values than the Si-NW with a better coulombic efficiency in the first cycle. The performance in the following cycles confirms the superior electrochemical activity of a-Si with respect to Si-NWs with capacity retention of 93% and 59% for a-Si and Si-NW, respectively. On the contrary, in the LiTFSI-based electrolyte, Si-NW electrodes outperform the a-Si in terms of specific capacity in the first as well as in the following cycles. a-Si has a higher CE in the first cycle (44%) compared to the Si-NWs (38%). Generally speaking, the electrodes show non-ideal CE values in the two electrolytes, which is a well-established feature for Si anodes.^[25–27]

The growth of the SEI layer over the surface of the two Si materials impacts the morphology of the electrode surfaces. The SEM micrographs of the post-mortem samples are shown in **Figure 5**.

In both electrolytes, the morphology of Si-NW electrodes is better preserved compared to the a-Si ones. Noticeably, the a-Si are in both cases embedded in a smooth matrix, likely constituted by organic/polymeric byproducts of the electrolyte degradation. This outer film is visibly thicker in the case of a-Si electrodes collected after cycling in LiFSI-based electrolyte. On the other hand, Si-NW electrodes show a smaller morphological degradation after cycling. In electrodes collected from LiTFSI-based electrolytes, some larger particles composed of multiple embedded Si nanowires, as large as a few micrometers were also found.

The atomic compositions by the EDX probe analysis of the electrodes after cycling are summarized in **Table 2**.

For the Si-NW samples, it is possible to notice that fluorine and sulfur are more abundant in the SEI compared to the a-Si samples. This suggests that the anions in the electrolyte are more prone to degrade on Si-NWs than on a-Si. Moreover, one can note from **Table 2** that FSI and TFSI affect the composition of the SEI differently. On Si-NW cycled in the presence of LiTFSI more degradation products can be observed, in particular F, N, and carbonate species are more abundant, indicating a thicker SEI. The opposite trend is observed in the case of a-Si where LiFSI shows a thicker SEI rich in carbon species. Those observations are in good agreement with the SEM micrographs reported in **Figure 5**.

The Raman spectroscopy characterization of the electrode surfaces after cycling in the two electrolytes is shown in **Figure 6**.

The Raman spectra of Si-NW after cycling show an enlargement of the Si band at $\approx 500\text{ cm}^{-1}$ and a shift toward lower wavenumbers, likely due to the amorphization of the Si nanowires. Remarkably in the sample cycled in the LiTFSI-based electrolyte, a broad band in the $1000\text{--}1800\text{ cm}^{-1}$ range is observed: these vibrational modes are assigned to the G and D bands of amorphous carbons^[28,29] and are a direct indication of the degradation of the electrolyte constituents. In fact, in pristine Si-NW samples, that are constituted of Si grown on a metallic substrate, the D and G bands of carbon are not present. In the LiFSI-based electrolyte apparently, no evidence for precipitation of carbonaceous degradation byproducts is observed in Si-NW post-mortem samples. This finding is in agreement with the SEM and EDX results where a larger accumulation of carbon-based degradation byproducts has been highlighted for the Si-NW cycled in the LiTFSI-based electrolyte.

The impact of the electrolyte composition on the amorphization degree of Si after cycling was more quantitatively examined over a larger sample area than a single point (**Figure 7**). This was done using a previously optimized^[26] statistical averaging of the fitting outputs performed on the Raman spectra recorded in the mapping spectral analysis.

Si-NW cycled in the LiTFSI-based electrolyte undergo a deeper amorphization compared to those collected from the LiFSI-based cells as seen from the amorphous content of 92 and 69%, respectively, to be compared to the 47% for the pristine Si-NW. These findings can be explained in the context of the electrochemical performance data shown in **Table 1**. In the TFSI-based electrolyte, Q_{tot} is higher and CIC/Q_{tot} is lower than in the FSI-based electrolyte, indicating more reversible lithium alloying/dealloying and reduced capacity wasted in parasitic reactions. Thus, when cycled in the presence of the TFSI, the Si-NW anode is more effectively lithiated–delithiated and is more prone to undergo amorphization. A different picture is found in the case of a-Si samples where, as expected, all bands of amorphous Si are almost unaltered after cycling (**Figure S1**). Furthermore, in both electrolytes, the vibrational fingerprints of deposition of an amorphous carbon component of the SEI are observed, similar to the Si-NW cycled in the LiTFSI-based electrolyte. Again, this evidence matches very well the morphological evidence of the accumulation of byproducts over the surface of the a-Si electrodes after cycling.

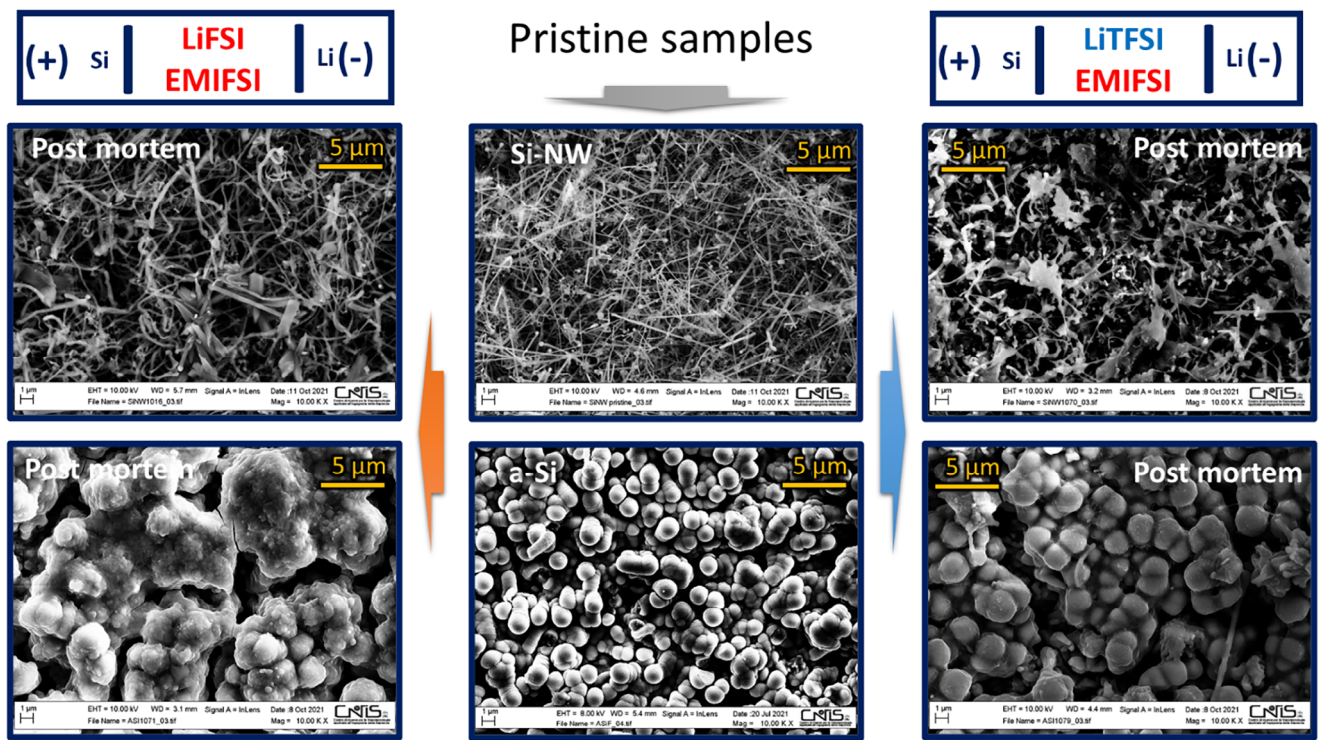


Figure 5. Scanning electron micrographs of the electrodes before (pristine Si-NW and a-Si) and after cycling (post-mortem) in the two different ILs-based electrolytes.

Table 2. EDX surface relative composition of samples before and after cycling in ILs-based electrolytes.

	Si-NW			a-Si		
	Pristine	EMIFSI:LiFSI	EMIFSI:LiTFSI	Pristine	EMIFSI:LiFSI	EMIFSI:LiTFSI
C/Si	0.24	0.86	1.40	0.14	1.02	0.30
O/Si	0.09	1.96	2.01	0.27	2.46	0.83
S/Si	–	0.40	0.62	–	0.10	0.01
F/Si	–	0.19	1.09	–	0.09	0.02
N/Si	–	0.01	0.58	–	0.14	0.03

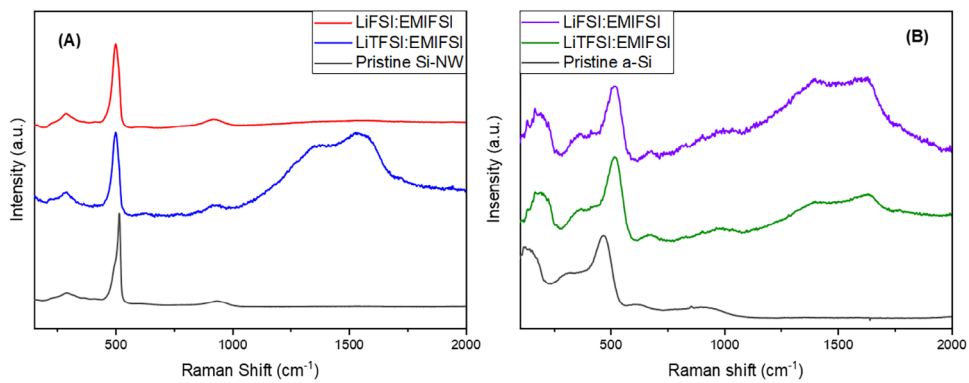


Figure 6. Raman spectra of the electrode surfaces before and after cycling: a) SiNW; B) a-Si.

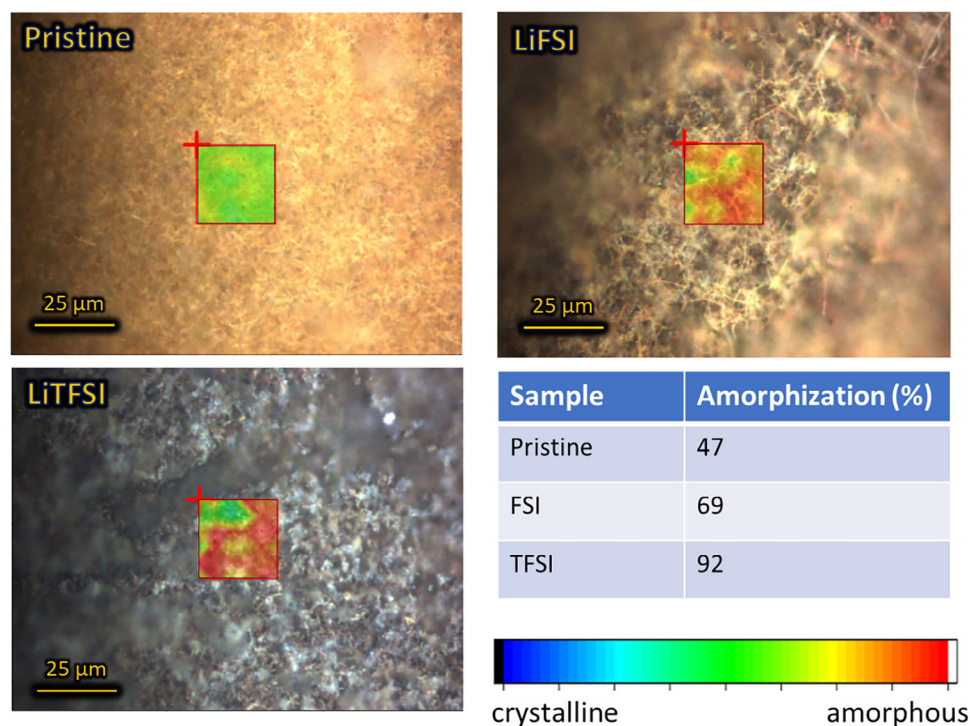


Figure 7. Raman maps obtained from the ratio between the intensity of amorphous Si and crystalline Si peaks, for spectra collected on Si-NW electrodes, pristine, and after 5 galvanostatic cycles in LiFSI: EMIFSI or LiTFSI: EMIFSI electrolytes. (colour palette: blue-green-yellow-red passing from small to large (0–100%) amorphous-to-crystalline ratio).

3.3. SEI Precipitation and Electrode Evolution

To gain insight into the composition of the SEI, ATR, and O-PTIR measurements were performed on pristine and cycled electrodes, as shown in **Figure 8**. From a semiquantitative analysis of these infrared spectroscopy data, it is possible to obtain information about the relative content of inorganic (Li_2CO_3) and organic carbonates developed on the electrode surfaces, similar to the case of Si-NW cycled in organic carbonates.^[17]

The ATR spectra of the pristine materials display a smooth decrease of the absorption with increasing wavenumber due to the tail of the Si TO phonon, which should be present $\approx 600\text{ cm}^{-1}$ (at the edge of the spectral range attainable with the ZnSe ATR crystal), and the combination bands of the Si phonons and the Si–O–Si stretching vibrations.^[30] After the galvanostatic tests in IL-based electrolytes, several bands appear in the ATR spectra. In general, they are better defined in the Si-NW electrodes than for a-Si; in these last samples, all absorption bands are extremely broad. Despite being almost impossible to attribute the single bands to specific vibrations, a division in several interesting regions can be roughly proposed. Between 800 and 1100 cm^{-1} one could find the Si–F, SiOH, SiO, SiH, and LiOC bending vibrations.^[31] In this region, the Si-NW sample cycled in the LiTFSI-based electrolyte displays intense and defined bands, while broader absorption bands can be identified in the specimen for which FSI-based electrolytes were used. In the region between 1100 and 1400 cm^{-1} , stretching bands of SO and SO_2 species can be detected in all samples. Moreover, well-defined bands at 1450 and 1520 cm^{-1} , present in all samples, can be attributed to the

vibrations of Li_2CO_3 . At higher frequencies, some small features can be ascribed to the presence of polyesters and polyamides.

The O-PTIR spectra of the samples are reported in **Figure 8c,d**. In the spectra of the pristine samples, a clear band centered $\approx 1100\text{ cm}^{-1}$ due to the vibrations of terminal Si–O, Si–C or Si–H groups is present. After cycling, new bands develop in the same spectral regions where new spectral features were measured by ATR. Between 950 (the lower limit of the O-PTIR measures) and 1130 cm^{-1} , several vibrations due to Si–F, SiOH, SiO, SiH, and LiOC bending can be identified. Between 1130 and 1400 cm^{-1} the stretching of S–O_n bonds are seen and at 1430 and 1500 cm^{-1} the vibrations of Li_2CO_3 are clearly visible. In a-Si, all bands are extremely broad with a visible red shift of the absorption $\approx 1000\text{ cm}^{-1}$, possibly due to the formation of inorganic carbonates and the development of the broad peak between 1400 and 1500 cm^{-1} , assigned to Li_2CO_3 . The IR evaluation is in general in line with the SEM and EDX analysis; the higher absorption signals for the Si-NW compared to the a-Si in the region of 800–1400 cm^{-1} suggests a stronger degradation of the electrolyte anions, especially when cycling in LiTFSI: EMIFSI electrolyte, while the a-Si IR spectroscopy reveals essentially only the presence of carbonate species.

3.4. Morphological and Phase Evolution of the Si Nanomaterials

Combining Raman analysis with the electrochemical data and following the model described in our previous work,^[17] the

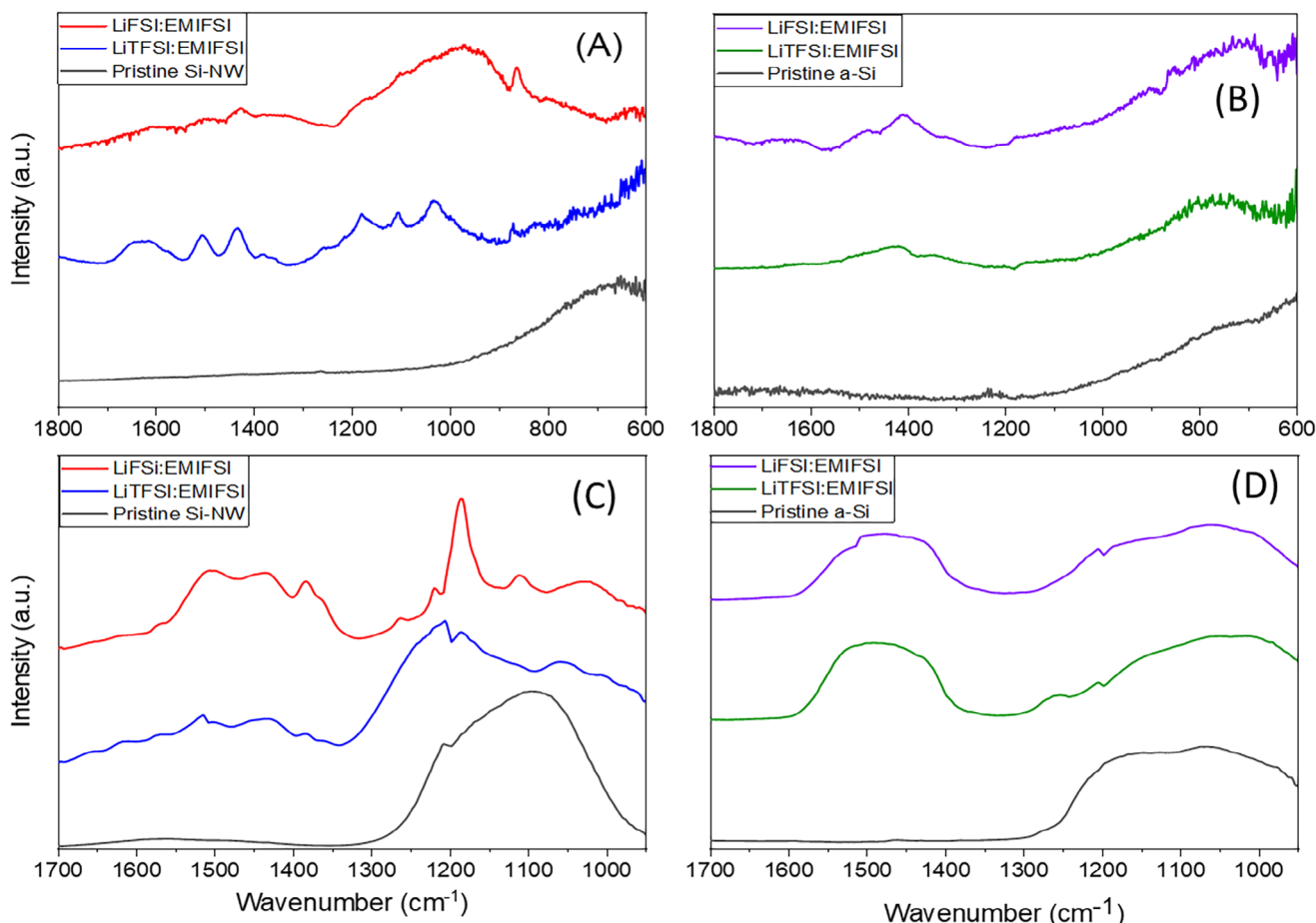


Figure 8. Infrared spectroscopic investigation of the electrode surfaces before and after cycling: a) ATR-FTIR of the Si-NW; b) ATR-FTIR of the a-Si; c) O-PTIR of the Si-NW; d) O-PTIR of the a-Si.

decoupling of the various sources of capacity for the Si-NW sample was developed using the following equations:

$$Q_{\text{discharge}} = Q_{\text{a-Si,red}} + Q_{\text{c-Si,red}} + Q_{\text{SEI,red}}/\text{mAhg}^{-1} \quad (5)$$

where:

$$Q_{\text{a-Si,red}} = (\%_{\text{a-Si}}/100) \cdot Q_{\text{th,Si}}/\text{mAhg}^{-1} \quad (6)$$

$$Q_{\text{c-Si,red}} = \Delta Q_{\text{amorphization}} \quad (7)$$

$$Q_{\text{charge}} = Q_{\text{a-Si,ox}} + Q_{\text{SEI,ox}} - Q_{\text{Li-trapping}}/\text{mAhg}^{-1} \quad (8)$$

where:

$$Q_{\text{a-Si,ox}} = \%_{\text{a-Si}} \cdot Q_{\text{th,Si}}/\text{mAhg}^{-1} \quad (9)$$

Being $Q_{\text{discharge}}$ and Q_{charge} the experimental capacities obtained by the galvanostatic discharge-charge, $Q_{\text{a-Si}}$ the capacity delivered by the lithium insertion-de-insertion into/from a-Si, $Q_{\text{c-Si,red}}$ the capacity originated from the lithium insertion into the c-Si that leads to its amorphization, Q_{SEI} the capacity exchanged in the parasitic reactions involving the SEI and $Q_{\text{Li-trapping}}(n)$ the capacity eventually trapped in the electrode due to kinetics constraints in the charge step. Cumulated results for the first five cycles are shown in Table 3.

Table 3. Decoupling of the various sources of capacity during the first 5 cycles for the two different electrolytes (% of the total cumulative capacities in cycles 1–5).

Electrolyte	Lithiation Reactions (Reductions, Discharges)			De-lithiation Reactions (Oxidations, Charges)		
	$Q_{\text{a-Si, red}}$	$Q_{\text{c-Si, red}}$	$Q_{\text{SEI, red}}$	$Q_{\text{a-Si, red, net}}$	$Q_{\text{Li-trapping}}$	$Q_{\text{SEI, OX}}$
EMFSI UFSI 0.8:0.2	69%	5%	26%	78%	0%	22%
EMFSI UTSI 0.8:0.2	68%	7%	25%	97%	3%	0%

Table 4. Summary of the most relevant experimental features obtained from the multi-technique analysis on the Si-NW electrodes.

Samples		Morphological changes	Si amorphization	Carbon content	Li ₂ CO ₃	Organic carbonates
Pristine		-	Medium	None	None	None
Post mortem	LiFSI: EMIFSI	Small	Medium	Negligible	Large	Small
	LiTFSI: EMIFSI	Medium	High	Large	Large	Large

The use of LiFSI promotes a more reversible SEI reduction/oxidation, while with LiTFSI the amorphization is larger and lithium becomes trapped in the electrode due to kinetics constraints in the charge step. Those evaluations are in good agreement with the other characterization reported above. In fact, SEM-EDX and infrared data suggest that LiTFSI induced the accumulation of degradation by-products on the surface of Si-NW electrodes after the cycling, thus leading to a thicker SEI.

The analysis of the surface modifications of two different nano-morphologies of Si-based electrodes collected post-mortem after cycling in a lithium cell with two different ILs-based electrolytes outlines some similarities and differences. A qualitative summary of the experimental evidence is reported in Table 4 and Table 5 for the Si-NW and a-Si samples, respectively.

The primary consideration is the intricate interplay between electrolyte formulation and silicon morphology in governing both electrochemical behavior and surface reactivity. Specifically, the reversible and irreversible aspects of electrochemical performance are significantly influenced by the silicon morphology—whether characterized by extended crystallinity or a higher amorphous content—and by the chemical nature of the lithium salt incorporated into the ionic liquids-based electrolyte. This synergy affects key performance indicators such as capacity retention, Coulombic efficiency, and the development and stability of the solid electrolyte interphase, underscoring the need for a carefully balanced formulation that addresses both the physical characteristics of the active material and the inherent properties of the electrolyte.

LiFSI and LiTFSI give rise to different SEI compositions and morphologies on the Si-NWs. The former induces an SEI mostly composed of lithium carbonate and a small organic component, while in the latter the SEI layer is rich in organic carbonates, lithium carbonate, and carbon. Furthermore, FSI induces reduced morphological changes and amorphization of the Si-NW anode than TFSI. In the case of the a-Si anodes, the two ILs formulations give rise to similar chemical compositions of the SEI. In a-Si, the Li₂CO₃ content in the SEI is higher than FSI but it is composed also of organic carbonates and small carbon content. Differently from Si-NW, with a-Si, the FSI-containing electrolyte induces more morphological changes than TFSI.

The comparative analysis of the SEI layers formed using LiTFSI and LiFSI salts reveals that, despite minor differences in the electrode amorphization degree and specific spectroscopic details, both salts result in passivating interphases with comparable chemical constituents and morphological characteristics. In particular, the SEIs formed in both electrolytes exhibit a combination of inorganic and organic species—such as LiF and other typical decomposition products from the ionic liquid matrix—indicating that the underlying chemical reactions are analogous regardless of the specific Li-salt employed. Our vibrational spectroscopy data, for instance, reveals that characteristic absorption bands associated with Si–F, Si–O, and other functional groups are present in both cases, suggesting similar decomposition pathways of the electrolyte components under reductive conditions. One may speculate that these decomposition pathways likely originate from the IL solvent anion hydrolysis (i.e. FSI[−]) in line with a previous finding from us on pyrrolidinium-based electrolytes.^[29] In fact, the FSI[−]-degradation path, being this anion present in both electrolyte formulations, surely contributes to all SEI chemistries.^[32] Furthermore, while quantitative differences have been reported—such as a deeper amorphization of silicon in LiTFSI-based electrolytes compared to LiFSI-based ones—the overall SEI morphology, including factors like film continuity and the distribution of chemical species, remains largely consistent. This consistency implies that the choice of LiTFSI or LiFSI mainly influences the degree of amorphization and perhaps the kinetics of SEI formation, rather than the fundamental chemical nature of the passivation layer itself. In conclusion, our results enlarge the comprehension of the impact of the use of IL as solvents using advanced electrode active materials and the relevant differences while comparing SEI layers formed starting from different electrolyte formulations.^[33,34]

4. Conclusion

In summary, the present study provides a detailed chemical and morphological evaluation of the solid electrolyte interphase (SEI) layer formed on nanostructured silicon electrodes when cycled in ionic liquid-based electrolytes. Our findings confirm that the early-stage consolidation of the SEI—achieved through galvanostatic testing limited to the first five cycles—is critical to

Table 5. Summary of the most relevant experimental features obtained from the multi-technique analysis on the a-Si electrodes.

Samples		Morphological changes	Si amorphization	Carbon content	Li ₂ CO ₃	Organic carbonates
Pristine		–	Complete	None	None	None
Post mortem	LiFSI: EMIFSI	Large	Complete	Large	Large	Large
	LiTFSI: EMIFSI	Medium	Complete	Medium	Medium	Large

elucidate the fundamental formation mechanisms and morphological evolution of the passivation layer. Through the application of advanced spectroscopic techniques, particularly O-PTIR and Raman spectroscopy, we obtained high-resolution insights into the chemical composition and structural modifications of the SEI, demonstrating that the crystallinity and morphology of the silicon electrodes significantly affect both the thickness and uniformity of the interphase. Moreover, our results underscore the importance of establishing a stable SEI to mitigate the adverse effects of the mechanical stresses associated with silicon's volume changes during cycling. The observed differences in amorphization and organic/inorganic content indicate that the choice of electrolyte formulation plays a decisive role in SEI optimization, which is crucial for enhancing electrode durability and overall battery performance.

Our results allow us to draw possible future working directions by which the performance of Si anodes can be enhanced. First, insights into the formation and evolution of a chemically and mechanically stable SEI underscore the importance of mitigating the detrimental effects of volume expansion and contraction that are inherent to Si anodes. In fact, the cracking and continuous reformation of an unstable SEI consume electrolytes and increase interphase resistance, ultimately leading to cell failure. Therefore, by establishing processing conditions and electrolyte formulations that foster the formation of a robust and uniform SEI, the electrode's durability can be markedly improved, reducing irreversible capacity losses during cycling. Being the chemical composition of the SEI strongly dependent on the electrolyte formulation, the choice of solvent, salts, and additives is critical for fine-tuning the balance between organic carbonates and inorganic compounds such as LiF and Li_2CO_3 within the interphase. By optimizing this balance, it is possible to enhance the protective characteristics of the SEI, thereby reducing continuous electrolyte decomposition and enhancing cycle life.

In conclusion, the applications of our study's findings—ranging from optimizing SEI composition and ensuring its mechanical stability to adopting novel electrolyte formulations and controlled cycling protocols—can significantly improve the performance and longevity of Si anodes. These strategies address both the fundamental limitations associated with Si's intrinsic material properties as well as the practical challenges in achieving stable battery performance, thereby paving the way for the development of durable, high-capacity battery systems.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare that they have no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

aprotic electrolytes, ionic liquids, Li-ion batteries, solid electrolyte interphase (SEI), Si

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- [1] D. Larcher, J. M. Tarascon, *Nat. Chem.* **2015**, 7, 19.
- [2] M. N. Obrovac, V. L. Chevrier, *Chem. Rev.* **2014**, 114, 11444.
- [3] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, Y. Cui, *Nat. Nanotechnol.* **2008**, 3, 31.
- [4] S. Goutam, N. Omar, P. Van Den Bossche, J. Van Mierlo, *Emerging Nanotechnologies In Rechargeable Energy Storage Systems*, Elsevier **2017**, p. 45.
- [5] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, *Sustainable Energy Fuels* **2020**, 4, 5387.
- [6] T. R. Hatchard, J. R. Dahn, *Electrochem. Soc.* **2004**, 151, A838.
- [7] B. Philippe, R. Dedryvère, J. Allouche, F. Lindgren, M. Gorgoi, H. Rensmo, D. Gonbeau, K. Edstrom, *Chem. Mater.* **2012**, 24, 1107.
- [8] F. Shi, Z. Song, P. N. Ross, G. A. Somorjai, R. O. Ritchie, K. Komvopoulos, *Nat. Commun.* **2016**, 7, 11886.
- [9] C. K. Chan, R. Ruffo, S. S. Hong, R. A. Huggins, Y. Cui, *J. Power Sources* **2009**, 189, 34.
- [10] K. Xu, *Chem. Rev.* **2014**, 114, 11503.
- [11] K. Xu, A. von Cresce, *J. Mater. Chem.* **2011**, 21, 9849.
- [12] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources* **2006**, 162, 658.
- [13] H. Shobukawa, J. Shin, J. Alvarado, C. S. Rustomji, Y. S. Meng, *J. Mater. Chem.* **2016**, 4, 15117.
- [14] D. T. Rogstad, M. A. Einarsrud, A. M. Svensson, *J. Electrochem. Soc.* **2021**, 168, 110506.
- [15] E. Mullane, T. Kennedy, H. Geaney, C. Dickinson, K. M. Ryan, *Chem. Mater.* **2013**, 25, 1816.
- [16] K. Stokes, H. Geaney, M. Sheehan, D. Borsa, K. M. Ryan, *Nano Lett.* **2019**, 19, 8829.
- [17] A. Sarra, S. Brutti, O. Palumbo, F. Capitani, F. Borondics, G. B. Appetecchi, N. Carboni, S. Abdul Ahad, H. Geaney, K. Ryan, A. Paolone, *Batteries* **2023**, 9, 148.
- [18] M. D. Abràmoff, P. J. Magalhães, S. J. Ram, *Biophotonics Int.* **2004**, 11, 36.
- [19] C. Smit, *J. Appl. Phys.* **2003**, 94, 3582.

- [20] <https://www.thermofisher.com/order/catalog/product/833-036200> (accessed: May 2025).
- [21] O. Klementieva, C. Sandt, I. Martinsson, M. Kansiz, G. K. Gouras, F. Borondics, *Adv. Sci.* **2020**, *7*, 1903004.
- [22] A. Paolone, A. Celeste, M. Di Pea, S. Brutti, F. Borondics, F. Capitani, *Opt. Photothermal Infrared Spectros. Raman Spectros. Measurement. Instru.* **2024**, *8*, 54.
- [23] B. Li, D. Yu, S. Zhang, *Phys. Rev. B.* **1999**, *59*, 1645.
- [24] J. R. Szczech, S. Jin, *Energy Environ. Sci.* **2011**, *4*, 56.
- [25] X. Zhang, D. Wang, X. Qiu, Y. Ma, D. Kong, K. Müllen, X. Li, L. Zhi, *Nat. Commun.* **2020**, *11*, 3826.
- [26] C. Fu, C. Song, L. Liu, W. Zhao, X. Xie, *Int. J. Electrochem. Sci.* **2016**, *11*, 154.
- [27] A. Sarra, S. Brutti, O. Palumbo, F. Capitani, F. Borondics, G. B. Appetecchi, N. Carboni, S. Abdul Ahad, H. Geaney, K. Ryan, A. Paolone, *Batteries* **2023**, *9*, 148.
- [28] N. Carboni, L. Mazzapioda, A. Capri, I. Gatto, A. Carbone, V. Baglio, M. A. Navarra, *Electrochim. Acta* **2024**, *486*, 144090.
- [29] A. Celeste, L. Silvestri, M. Agostini, M. Sadd, O. Palumbo, J. K. Panda, A. Matic, V. Pellegrini, S. Brutti, *Batteries and Supercaps* **2020**, *3*, 1059.
- [30] F. A. Johnson, *Proc. Phys. Soc.* **1959**, *73*, 265.
- [31] P. J. Linstrom, W. G. Mallard, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg MD, 20899.
- [32] S. Di Muzio, A. Paolone, S. Brutti, *J. Electrochem. Soc.* **2021**, *168*, 100514.
- [33] M. Palluzzi, L. Silvestri, A. Celeste, M. Tuccillo, A. Latini, S. Brutti, *Crystals* **2022**, *12*, 885.
- [34] G. Maresca, M. Ottaviani, K. M. Ryan, S. Brutti, G. B. Appetecchi, *ChemSusChem* **2024**, *17*, 202400514.