



Article

Exploring Binder–Ionic Liquid Electrolyte Systems in Silicon Oxycarbide Negative Electrodes for Lithium-Ion Batteries

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Abstract

Enhancing the safety of lithium-ion batteries (LIBs) by replacing flammable electrolytes is a key challenge. Ionic liquid (IL)-based electrolytes are considered an interesting alternative due to their thermal and chemical stability, high voltage stability window, and tunable properties. This study investigates the electrochemical behavior of two newly synthesized ILs, comparing them to conventional alkyl carbonate-based electrolytes. Nitrogen-doped carbon silicon oxycarbide (NC-SiOC), used as the active material in negative electrodes, was combined with two polymeric binders: poly(acrylic acid) (PAA) and poly(acrylonitrile) (PAN). NC-SiOC/PAN electrodes exhibited a significantly higher initial charge capacity—approximately 25–30% greater than their PAA-based counterparts in the first cycle at 0.1 A g^{−1} (850–990 mAh g^{−1} vs. 600–700 mAh g^{−1}), and demonstrated an improved initial Coulombic efficiency (67% vs. 62%). Long-term cycling stability over 1000 cycles at 1.6 A g^{−1} retained 75–80% of the initial 0.1 A g^{−1} capacity. This outstanding performance is attributed to the synergistic effects of nitrogen-rich carbonaceous phases within the NC-SiOC material and the cyclized-PAN binder, which facilitate structural stability by accommodating volumetric changes and enhancing solid electrolyte interphase (SEI) stability. Notably, despite the lower ionic transport properties of the IL electrolytes, their incorporation did not compromise performance, supporting their feasibility as safer electrolyte alternatives. These findings offer one of the most promising electrochemical performances reported for SiOC materials to date.

Keywords: lithium-ion batteries; ionic liquids; silicon oxycarbide; polymeric binders



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1. Introduction

The development of non-flammable electrolytes is a crucial step in addressing the safety concerns associated with lithium-ion batteries (LIBs). Currently, highly flammable and volatile solvent-based organic electrolytes are widely posing significant fire hazards [1–5]. Ionic liquids (ILs) are quite promising as electrolytes in LIBs due to their advantages, including high thermal stability, low vapor pressure reflected in non-inflammability, a high voltage stability window, and tunable properties by a suitable selection of cation, anion, or both [4,6]. However, any alternative electrolyte must achieve enhanced safety requirements without compromising battery performance. In this context, understanding the influence of key transport properties

of ILs compared to conventional/commercial organic electrolytes on the electrochemical performance of LIBs is essential.

In previous studies, we reported outstanding battery performance using ILs formed from nitrogen and phosphorus-based cations, such as pyrrolidinium and small asymmetric phosphonium cations, paired with bis(fluoromethylsulfonyl) imide [FSI] anions as electrolytes with silicon nanoparticle (NP) composites [7–9]. Si NPs have gained significant attention as a negative electrode material due to their exceptionally high theoretical gravimetric capacity (up to 3579 mAhg^{-1} considering $\text{Li}_{15}\text{Si}_4$ formation), which is nearly ten times greater than that of graphite, the current state-of-the-art anode material (372 mAhg^{-1} for Li_6C) [10–12]. Despite their promising delithiation properties, Si NPs face critical changes associated with the incorporation of up to 4.4 Li^+ ions per Si atom. These changes lead to instability in the solid-electrolyte interface, particle cracking, loss of electrical contact between particles and the current collector, and consequently, poor cycle life [10–12]. To address these limitations, alternative materials such as silicon oxycarbide (SiOC , $\text{SiO}_{(4-x)}\text{C}_x$, where $x = 0\text{--}4$, i.e., SiO_4 , SiO_3C , SiO_2C_2 , SiOC_3 , and SiC_4), a member of the silicon oxide family, have garnered significant attention [13–16].

Among their key advantages, SiOC materials offer multiple sites for Li insertion/extraction and relatively straightforward synthesis [13–17]. Experimentally, the initial delithiation capacity of SiOC particles at current densities below 0.1 A/g typically ranged from 300 to 900 mAh/g [13–18]. These values are influenced by several factors, including precursors, synthesis conditions, morphology, chemical surface treatment, and composition (i.e., presence of either mixed-bond units or carbonaceous hybrid materials) [13,16–25]. While significant effort has been devoted to understanding and improving the charge capacity of SiOC, little attention has been given to studying the effects of electrolyte–binder combinations on their electrochemical performance. Commonly used binders, such as polyvinylidene fluoride (PVDF) [23,24,26–29], sodium carboxymethyl cellulose (CMC) [22,30], and polyacrylic acid (PAA) [31,32] are typically paired with commercial $1 \text{ molL}^{-1} \text{ LiPF}_6$ carbonate-based electrolyte for SiOC electrodes. In contrast, polyacrylonitrile (PAN), which has demonstrated success as a binder in Si NPs [7–9,33,34], has been rarely reported at all for use with SiOC materials. Cyclized-PAN offers a notable advantage, as it eliminates the need for additional conductive components, such as carbon black, by serving a dual role, acting as both a binder and a conductive additive [33].

In this study, we present a comparative analysis of NC-SiOC/PAN or NC-SiOC/PAA electrodes using three different electrolytes: a commercial ethylene carbonate (EC)/diethyl carbonate (DEC) (50:50 *v/v*) $1 \text{ molL}^{-1} \text{ LiPF}_6$, and two home-made ILs [7,9,34]: N-propyl-N-methylpyrrolidinium bis(fluoromethylsulfonyl)imide [BMPYR][FSI] and triethyl-n-butylphosphonium bis(fluoromethylsulfonyl)imide [P_{2224}][FSI], both using LiFSI as the lithium salt.

To characterize these electrolytes, we measured their viscosity, Li^+ diffusion coefficient by NMR spectroscopy. The primary objective of this study is to evaluate the potential of replacing conventional flammable EC/DEC with ILs in Li-ion batteries featuring nitrogen-doped SiOC composite electrodes, using PAA and PAN as binders.

Our findings reveal that the initial delithiation capacity can be enhanced by approximately 25% through the appropriate combination of binder and electrolyte. Importantly, non-flammable ILs demonstrate excellent performance as electrolytes, offering a safer alternative to conventional organic solvents. Remarkably, despite the ILs' inferior transport properties, they do not negatively affect battery performance, further highlighting their viability for high-performance LIBs.

2. Materials and Methods

2.1. Synthesis of the Active Material and Electrode Preparation

The synthesis of NC/SiOC was carried out as described elsewhere [32]. Briefly, nitrogen gas was bubbled through 32 mL of glycerol (1,2,3-propanetriol, 99% ACS) under magnetic stirring. Subsequently, 2.16 mmol of sodium citrate tribasic dehydrate (99% ACS) and 17.30 mmol of APTES (3-aminopropyltriethoxysilane purity > 98% *v/v*, Sigma-Aldrich, Oakville, ON, Canada) were slowly added to the glycerol. The polymers were cross-linked at 100 °C for 1 h and then cooled to room temperature. After 24 h, the reaction mixture was heated to 180 °C for 1 h under continuous nitrogen flow and magnetic stirring. Residual reagents were removed by dialysis using a 14 kDa membrane (Sigma Aldrich). The purified particles were dried under vacuum at room temperature, and the pyrolysis was conducted by heating at a rate of 5 °C/min up to 1000 °C, which was maintained for 1 h.

The composite electrodes using PAN (Polyacrylonitrile, Sigma-Aldrich, average MW 150,000) as a binder were fabricated following the procedure described elsewhere [7,33]. The active material and PAN were mixed in a 70:30 wt.% ratio (160 mg SiOC, 68.6 mg PAN), and the mixture was pre-ground in an agate mortar before being transferred to a 5 mL beaker. The mixture was then dispersed in 0.8 mL of *N,N*-dimethylformamide (DMF, 99%). The resulting solution/suspension was stirred magnetically for approximately 18 h to produce a viscous slurry, which was cast on a Cu foil current (9 µm) collector using a 120 µm doctor-blade. The coated electrodes were dried at 80 °C for about 3 h. The electrode disks were then punched out using an MSK-T-10 precision disk cutter with a standard 15 mm diameter cutting die. These electrodes had a mass loading of 1.4–1.6 mg (0.7–0.8 mg/cm²) and 0.6–0.8 mg (~0.3–0.4 mg/cm²), see Table A1 for details of each electrode mass loading and thickness. The electrodes were subsequently heat-treated at 300 °C in a tubular furnace under an argon atmosphere to cyclize PAN [33]. The electrodes prepared with PAA as binder (Sigma-Aldrich, 36 mg) contain the active material (108 mg) and a conducting additive (acetylene black carbon, 36 mg) in a 60:20:20 weight ratio. The mixture was ground in a mortar and then transferred to a 5 mL beaker containing 0.7 mL of anhydrous ethanol. The slurry was mechanically stirred at 600 rpm for approximately 8 h. The resulting mixture was coated onto Cu foil using the same method described above and dried under vacuum at 80 °C for 3 h. Electrode disks were subsequently punched out, as described earlier, with a mass loading of 0.6–0.8 mg (~0.3–0.4 mg/cm²), and the thickness of each electrode was measured using a Mitutoyo® digital micrometer.

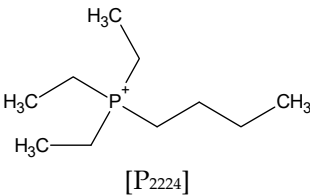
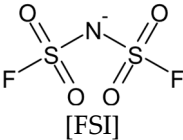
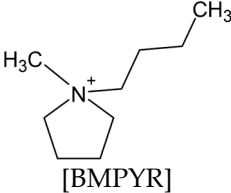
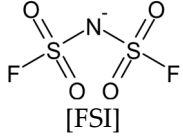
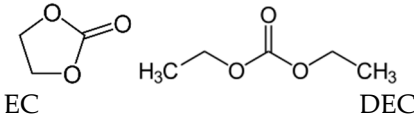
All electrodes were stored in an argon-filled glovebox and were not exposed to air before assembling the test cells. It is worth noting that PAN-based electrodes do not require acetylene black carbon, since cyclized PAN acts as both binder and conductive additive, as discussed earlier.

2.2. Synthesis of Ionic Liquids

The [BMPYR][FSI] and [P₂₂₂₄][FSI] ILs were synthesized following a procedure described elsewhere [35–37]. Briefly, 26 mmol of *N*-propyl-*N*-methylpyrrolidinium bromide (BMPYRBr, Sigma-Aldrich, purity > 99.9%) was dissolved in 50 mL of water and mixed with 26 mmol lithium bis(fluorosulfonyl)imide (LiFSI, TCI America, Portland, OR, USA, purity > 98.0%), which had been previously dissolved in 50 mL of water. The mixture was stirred for two hours. The resulting IL, which formed in the immiscible water phase, was separated using dichloromethane, and the same phase was washed five times with water and stirred vigorously with activated carbon for two hours. Subsequently, the solution was purified in a chromatography column (alumina, dichloromethane), and the IL obtained was dried with a rotary evaporator.

For the synthesis of $[P_{2224}][FSI]$, the triethyl-n-butylphosphonium bromide was obtained through the reaction of triethylphosphine (Sigma-Aldrich, P_{222} , purity > 99.9%) with 2-bromobutane. The ILs were dried under vacuum for 48 h at 80 °C until the water content was reduced to below 10 ppm, as determined via Karl Fischer titration (Metrohm, São Paulo, Brazil). To obtain a lithium salt concentration of 1 mol L⁻¹, an appropriate amount of lithium bis(fluorosulfonyl)imide (LiFSI, TCI America, purity > 98.0%) was added to each IL. The schematic chemical structure of the ions of the ILs, as well as those of commercial organic electrolytes, is provided in Table 1.

Table 1. Chemical structure of anions and cations of the synthesized ILs and the commercial organic solvent used as electrolytes in this study.

Ionic Liquid	Cation	Anion	Lithium Salt (1 mol L ⁻¹)
$[P_{2224}][FSI]$ Triethyl-n-butylphosphonium bis(fluoromethylsulfonyl)imide	 $[P_{2224}]$	 [FSI]	LiFSI
$[BMPYR][FSI]$ N-propyl-N-methylpyrrolidinium bis(fluoromethylsulfonyl)imide	 [BMPYR]	 [FSI]	LiFSI
Alkyl carbonate EC/DEC 50:50 Ethylene carbonate/ Diethyl carbonate	 EC DEC		LiPF ₆

2.3. Electrolyte and Material Characterization

Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) ⁷Li diffusion measurements were performed in a 600 MHz NMR Bruker Avance III HD spectrometer, with a temperature fluctuation less than 1 °C. Deuterated water was used to calibrate the field gradient diffusion method. The ILs were dried under vacuum at an optimal temperature and then transferred to an argon-filled dry box. Samples were analyzed in duplicate using a standard NMR tube, which was filled and sealed inside the dry box. The water content in the same IL batch measured by the Karl Fischer technique was found to be <10 ppm. ⁷Li was probed from a variable field gradient using a Larmor frequency of 233.144 MHz with a 90° pulse of 400 μs. The number of scans was eight, the gradient strengths were incremented in eight steps up to 43.3 G/cm, and the diffusion time was 750 ms. The data were analyzed via a fitted function from the Stejskal–Tanner equation to extract the Li diffusion coefficient [38].

Viscosity was measured using an SVM 3000 viscometer–densimeter (Anton Paar, São Paulo, Brazil) at 25 °C and atmospheric pressure, and it was calibrated using certified reference standards following the manufacturer’s guidelines. Ionic conductivity was determined using an Autolab PGSTAT30 potentiostat (Metrohm Autolab, São Paulo, Brazil) via electrochemical impedance spectroscopy (EIS) with two parallel Pt electrodes (3 mm) connected to an Autolab MAC80132 system, operating within the frequency range of 0.1 to

100,000 Hz. The cell constant (A/l), where A represents the electrode surface area and l the separation distance, was determined using a standard KCl solution at 25 °C.

Microstructural analyses of the powders were conducted using a JEOL Model 2100F (JEOL Ltd., Tokyo, Japan) field-emission gun transmission electron microscope (FEG-TEM) operating at an accelerating voltage of 200 kV. The SEM analyses were performed using a JEOL JSM-7600F (JEOL Ltd., Tokyo, Japan) microscope equipped with a field emission gun (FEG), providing a resolution of 1.0 nm at an accelerating voltage of 15 kV. The electrochemical performance of the cells was evaluated by galvanostatic charging (delithiation) and discharging (lithiation) at 25 °C over a voltage range of 0.05 and 2.5 V (cut-off potentials) vs. Li/Li^+ , using a VMP3 Bio-Logic potentiostat with a two-electrode configuration.

CR2032 (MTI corporation, Richmond, CA, USA) coin cells were assembled in an argon-filled glovebox using a Celgard 2320 and microfiber disk (Whatman GF/F) as separators for EC/DEC and ILs, respectively. Electrolytes were composed as shown in Table 1. Electrochemical measurements of half-cells were normalized based on the mass of the SiOC active material. The rate capabilities of the composite electrodes were evaluated at various current densities ranging from 0.1 to 2.4 A/g. Coulombic efficiency was also calculated with $((C^{\text{dealloy}})/(C^{\text{alloy}})) \times 100$, where C^{alloy} and C^{dealloy} represent the lithiation and delithiation capacities of the negative electrode, respectively.

3. Results

3.1. Composite Electrodes and Electrolyte Characterization

The morphological features observed in the bare particles (Figure 1a,c,d) are consistent with those previously reported for NC/SiOC [32], where spherical-like particles are obtained. A TEM-EDS analysis (Figure 1b) revealed peaks corresponding to oxygen ($K_{\alpha} = 0.533$ keV), silicon ($K_{\alpha} = 1.84$ keV), carbon ($K_{\alpha} = 0.282$ keV), nitrogen ($K_{\alpha} = 0.392$ keV), and Cu ($L_{\alpha} = 0.851$ keV), the latter originating from the Lacey grid used as a substrate for sample deposition.

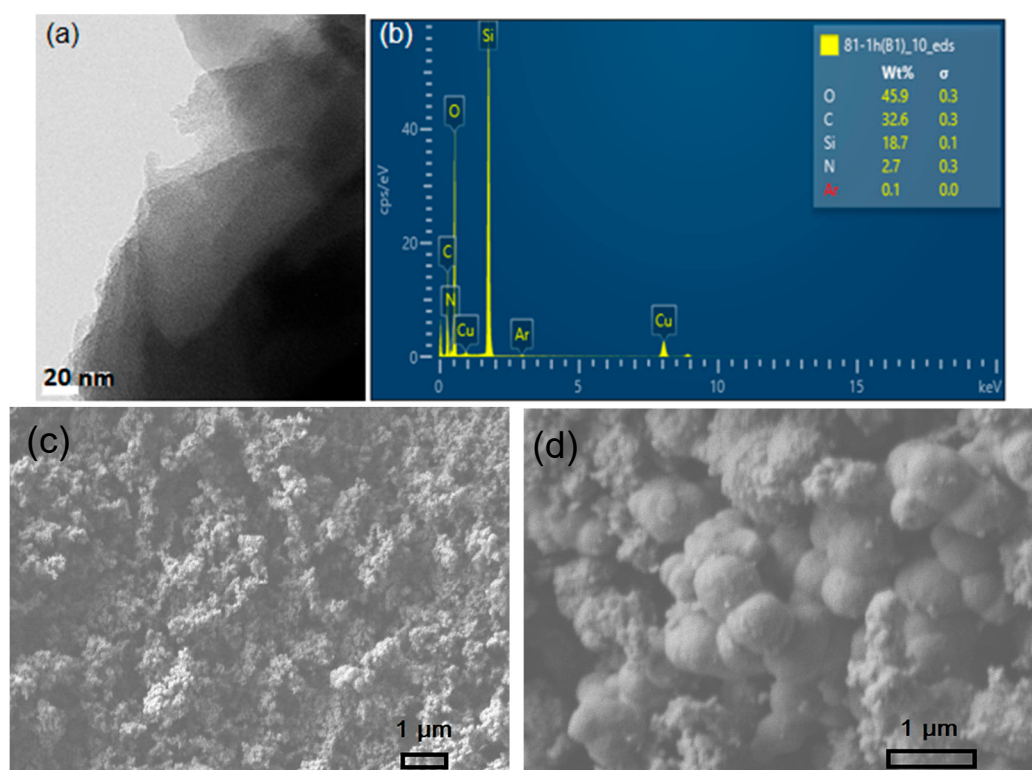


Figure 1. TEM image of the bare N-doped C/SiOC sample (a) with its EDS spectrum (b) and SEM micrographs (c,d).

The semi-quantitative analysis confirmed that oxygen, carbon, and silicon are the main components (45.9, 32.6, and 18.7 wt.%, respectively), while nitrogen represents only around 3 wt.% of the sample. The elemental composition was previously determined by inert gas fusion technique [32], and the same sample batch was used in both studies; the results showed a composition of C = 19.5 at% (14.8 wt.%), O = 52.5 at% (53 wt.%), N = 0.97 at% (0.86 wt.%), and Si = 17.3 at% (30.7 wt.%).

To gain insights into the interactions between different electrode components, TEM analysis was performed on bare NC/SiOC active material as well as SiOC/PAA (Figure 2b) and SiOC/PAN (Figure 2c,d) composite anodes. Both electrodes were ultrasonically dispersed in methanol to detach the composite material from the collector, allowing a direct comparison with bare NC-SiOC particles (Figure 2a), in which a certain degree of sintering was observed, likely resulting from the pyrolysis process at 1000 °C used to obtain the active material.

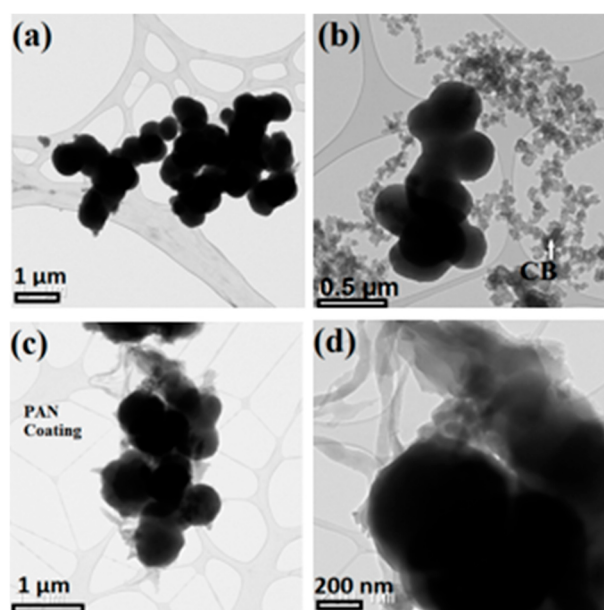


Figure 2. TEM micrographs of NC/SiOC bare particles used as active material (a) and from composite electrodes: SiOC/PAA (b); SiOC/PAN (c), enlarged in (d).

Figure 2b shows dispersed carbon black conducting additive and SiOC particles. The image provides evidence that, once the PAA is dissolved in methanol, carbon black and SiOC particles are no longer aggregated. This is expected since hydrogen bonding between the carboxyl groups of PAA and the hydroxyl groups of carbon black and SiOC particles holds them together [39]. Conversely, in PAN composites (Figure 2c,d), a carbonaceous layer formed from cyclized PAN [33] is observed on the surface of the active material.

Turning to the electrolyte, for ILs to be considered a viable alternative to organic solvents, it is essential to compare physicochemical properties [40]. Viscosity is one of the most critical parameters in electrochemical studies, as it strongly influences the rate of mass transport within the solution. High viscosities can negatively affect both ionic conductivity and lithium-ion diffusion in the electrolyte [41,42]. In fact, in some cases, excessive viscosity has rendered certain ILs unsuitable for use as Li-ion battery electrolytes, as observed with imidazolium-based ILs [35].

Table 2 summarizes key transport properties measured for [P₂₂₂₄][FSI] with 1 molL^{−1} LiFSI, alongside previously reported values for EC/DEC 1 molL^{−1} LiFP₆ and [BMPYR][FSI] with 1 molL^{−1} LiFSI. The measured D_{Li⁺} values for [P₂₂₂₄][FSI] and [BMPYR][FSI] are consistent with previous reports on ILs containing small phosphonium

cations [35] and N-butyl-N-methylpyrrolidinium cations [43]. These results demonstrate that Li^+ ions diffuse more freely in EC/DEC, as the Li^+ diffusion coefficient in this solvent is at least 100 times higher than in the ILs used in this study.

Table 2. Li^+ diffusion coefficient of IL-based electrolytes obtained by NMR, compared with data for EC/DEC from ref. [44]. Measurements at 30 °C in an EC/DEC 4:6 ratio. Viscosity (η) and ionic conductivity (σ) for all electrolytes were measured at 25 °C. A concentration of 1 molL^{−1} LiFP₆ was used as the salt for EC/DEC, while 1 molL^{−1} LiFSI was used for both ILs.

Electrolyte	D_{Li^+} NMR (10 ^{−7} cm ² s ^{−1})	η (mPa.s)	σ (mS.cm ^{−1})
EC/DEC	17.0 [44]	4.7 [45]	7.8 [45]
[BMPYR][FSI]	0.18 ± 0.01	87 [7]	3.3 [7]
[P ₂₂₂₄][FSI]	0.16 ± 0.01	97.3	2.5

Similarly, both ILs are at least eighteen times more viscous than the commercial organic electrolyte, in accordance with the Stokes–Einstein equation [46]. Likewise, the observed trend $\sigma_{\text{EC/DEC}} > \sigma_{[\text{BMPYR}][\text{FSI}]} > \sigma_{[\text{P}_{2224}][\text{FSI}]}$ is predicted by the Nernst–Einstein equation [47], as conductivity is proportional to the diffusion coefficient. It is worth noting that ionic conductivity measurements were performed using electrochemical impedance spectroscopy; therefore, the reported values represent the contribution of all ionic species in solution. At first glance, the values presented in Table 2 may suggest a disadvantage for ILs in terms of transport properties. However, some ILs, such as those based on FSI, can form a more stable SEI layer compared to conventional organic solvent EC/DEC, as demonstrated in Si anode electrodes tested over 1000 cycles at 1 A g^{−1}. Hence, the lower electrical conductivity of ILs may be compensated, to some extent, by the improved electrochemical performance of the electrodes during cycling [7,34].

On the other hand, marked differences in the thermal stability of the commercial EC/DEC mixture and the ionic liquids have been documented. DEC exhibits a relatively low boiling point (126 °C), an enthalpy of vaporization of 43.6 kJ mol^{−1} (at 25 °C), and a flash point of just 33 °C, indicating its tendency to form flammable mixtures with air under ambient conditions [48]. In contrast, EC is more thermally robust—boiling point of 248 °C, heat of vaporization of 60.3 kJ mol^{−1} (at 25 °C)—yet its flash point of 145.5 °C still poses a risk of an explosive atmosphere formation when battery temperature rises during overcharge or short-circuit events [49].

Similarly, our previous thermogravimetric analyses [7,9] revealed that the EC/DEC electrolyte undergoes two abrupt weight-loss events at approximately 39 °C and 118 °C, corresponding to the rapid evaporation of its more volatile components and indicating an inherent fire risk, particularly given its low flash point. By contrast, both [BMPYR][FSI] and [P₂₂₂₄][FSI] ionic liquids exhibit no appreciable weight loss until temperatures exceed ~300 °C. This outstanding thermal resistance, stemming from their negligible vapor pressure, renders these ILs considerably safer as electrolytes for lithium-ion batteries.

Despite the structural contrast between their cations (cyclic pyrrolidinium vs. linear phosphonium) [7,9], both [BMPYR][FSI] and [P₂₂₂₄][FSI] decompose at nearly the same temperature (~342 °C), underscoring the dominant role of the FSI[−] anion in governing overall thermal stability [50].

3.2. Electrochemical Performance

Typical discharge/charge voltage profiles for the first three cycles of SiOC/PAN electrodes are shown in Figure 3. In all three cases, the discharge profile exhibits a plateau at approximately 0.25 V vs. Li/Li⁺ for the first cycle, whereas in the second and subsequent insertion cycles, no clear plateaus are observed. At potential values below 0.5 V, several

lithiation processes can occur, including SiOC/SiO_x reduction [51], lithium absorption into turbostratic nitrogen-doped carbon structure [52,53], and SEI layer formation on the anode surface due to the reductive decomposition of the electrolyte and salt [34,54].

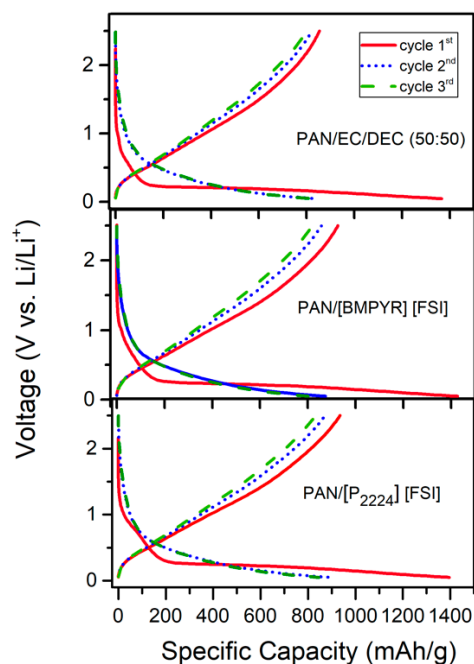
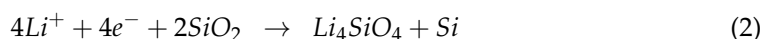
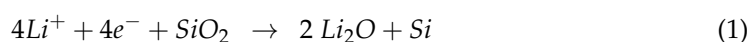


Figure 3. Charge/discharge voltage profiles for the first three cycles at a current density of 0.1 A/g for NC/SiOC-PAN composite electrodes with a mass loading of 1.4–1.6 mg with different electrolytes. (Top) commercial organic solvent EC/DEC with 1 molL^{−1} LiPF₆; (middle): [BMPYR][FSI]; and (Bottom): [P₂₂₂₄][FSI]. For both ionic liquid-based electrolytes, 1 molL^{−1} LiFSI was used as the lithium salt.

The initial delithiation capacities obtained at the lowest rate (0.1 A/g) were 926, 936, and 854 mAh/g for coin cells with [BMPYR][FSI], [P₂₂₂₄][FSI], and EC/DEC, respectively. Notably, IL-based electrolytes exhibited a slightly higher discharge capacity (~9.6%) than EC/DEC. However, this difference is significantly smaller than expected, considering the variation in transport properties between the electrolytes. A similar trend was observed in Si/PAN composites with ILs and EC/DEC [7]. Nonetheless, these values are among the highest reported for SiOC particles (see Appendix A, Table A2).

In SiOC, lithium storage mechanisms involve complex and intriguing processes due to the multiple possible sites for Li⁺ insertion/extraction [17,32,55]. These sites include SiO₃C/SiO₄ tetrahedral units, carbonaceous and/or nitrogen-doped carbon species, and voids, among others. Regarding silicon-based components, the synthesis conditions followed for NC/SiOC suggest a predominant formation of SiO₃C units over other tetrahedral structures [32]. Since experimental evidence on the reaction products formed through the interaction of the SiO₃C unit with Li⁺ remains limited, studies often rely on the well-documented reaction of SiO₂ with Li⁺. Three possible reaction pathways involve the formation of Li_xSi alloys, lithium silicates (e.g., Li₄SiO₄, Li₆Si₂O₇, Li₂SiO₃), and Li₂O [13,56].



From the semi-quantitative elemental analysis obtained by EDS, the nitrogen-carbonaceous phase accounts for approximately 33 wt.% of the material. Previous studies in NC/SiOC have demonstrated the presence mainly of pyrrolic and pyridinic nitrogen species [32].

Nitrogen atoms have one additional valence electron compared to carbon atoms and may easily replace carbon atoms in a graphene-like structure, forming graphitic, pyridinic or pyrrolic nitrogen species. Consequently, nitrogen may induce polarization in the sp^2 C network and modify the local charge and introduce greater structural disorder [57]. Although there is still ambiguous information regarding the role of the nitrogen species in Li-ion storage, it is widely accepted that pyridinic N promotes attaining higher reversible capacities, while pyrrolic N is responsible for the diffusion of Li-ions [57–59]. Therefore, the disordered carbon phase is expected to generate additional structural defects, leading to an increased number of lithium insertion sites [53,60,61].

The initial Coulombic efficiency (ICE), which is estimated by dividing the initial delithiation capacity by the initial lithiation capacity, is a key indicator of the electrochemical reaction's reversibility [62]. The obtained ICE value followed the same trend observed for the first delithiation capacity (Table 3), with $EC/DEC < [BMPYR][FSI] < [P_{2224}][FSI]$, yielding 62.5, 64.9, and 67%, respectively. In general, these values are in the range of 40–70% commonly reported for silicon oxycarbide (see Table A2). The consumption of Li^+ due to the formation of irreversible side products, such as Li_2O and lithium silicates [63], is often cited as the primary cause of low ICE. However, electrolyte decomposition also plays a contributing role [64].

Table 3. Electrode characterization and electrochemical performance values corresponding to Figure 3. In the EC/DEC-based organic solvent, 1 M $LiPF_6$ was used as the lithium salt, whereas the ILs electrolytes contained 1 M LiFSI.

NC-SiOC/PAN	Active Material Mass (mg)	Thickness (μm)	1st Discharge mAh/g	1st Charge mAh/g	ICE (%)
EC/DEC	1.58	38	1367	854	62.5
[BMPYR][FSI]	1.52	35	1427	926	64.9
[P ₂₂₂₄][FSI]	1.4	33	1395	934	67

Both the active material and PAN binder were the same for all composites; therefore, it can be assumed that the irreversible phases formed within the NC/SiOC particles are identical in all three cases. Consequently, the slight difference in ICE (62 vs. 67%) may be attributed to variations occurring at the binder–electrolyte interface. Since both lithium salts and electrolytes differ in composition (see Table 1), distinct decomposition products are expected to form [17,34].

Regarding FSI-based electrolytes, electrodes made with Si/PAN composites have demonstrated improved electrochemical performance when ILs are used [7,34]. Differences in the formation rate of decomposition products, such as LiF , are closely associated with the development of a more stable SEI layer. In the presence of [FSI] anions, the S-F bonds rapidly break, releasing F^- , which reacts with lithium to form small inorganic compounds, such as LiF and SO_2 , which may undergo reactions with the anode surface [7,34]. These compounds may play an “additive role”, contributing to the formation of a robust protective film [7,34]. On the other hand, in EC/DEC-based electrolytes, the primary decomposition products are organic species, such as Li_2CO_3 and oligomers [65]. The formation of LiF is expected to be minimal since F^- ions, derived from the slow decomposition of $LiPF_6$ salt, are released gradually [34,66].

Indeed, a comparison between SiOC and silicon-based systems requires caution due to differences in composition and volume expansion during lithium insertion/extraction. However, in the first cycle, both silicon nanoparticles (NPs) and SiOC have PAN-cyclized surfaces, as the SEI layer is still forming, making this comparison feasible.

In the first cycle, the SEI layer formed in PAN-ILs is more favorable for achieving higher delithiation capacities. However, in subsequent cycles (from the 1st to 5th cycle), a gradual decrease in delithiation capacity (<4% per cycle) is observed, as shown in the rate capability analysis presented in Figure 4. At high current densities (0.8–2.4 A/g), EC/DEC exhibits slightly better performance. The observed capacity correlates with the previously reported Li^+ diffusion coefficients: $D \text{Li}^+_{\text{EC/DEC}} > D \text{Li}^+_{[\text{BMPYR}][\text{FSI}]} > D \text{Li}^+_{[\text{P2224}][\text{FSI}]}$, as well as with the viscosities (η): $\eta_{\text{EC/DEC}} < \eta_{[\text{BMPYR}][\text{FSI}]} < \eta_{[\text{P2224}][\text{FSI}]}$. This suggests that at high rates, the differences in Li^+ transport properties become more relevant.

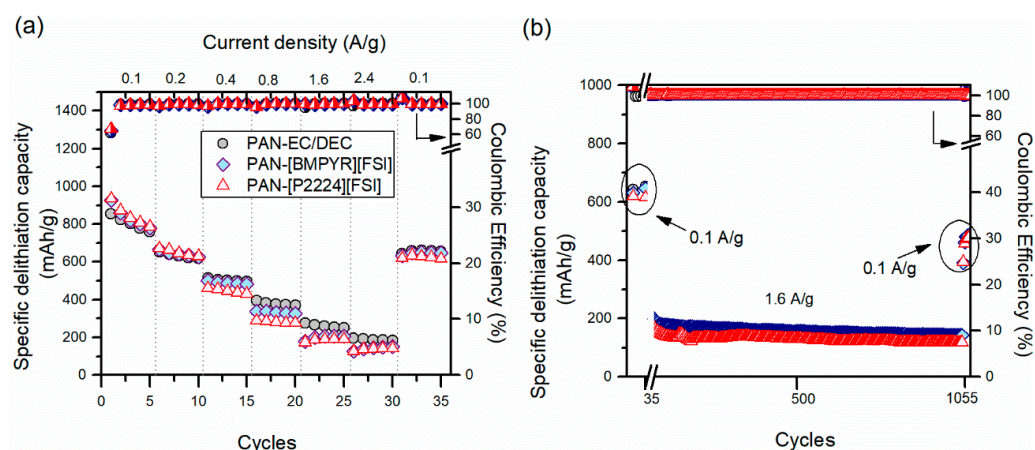


Figure 4. Electrochemical characteristics of NC/SiOC-PAN electrodes containing different electrolytes. (a) Delithiation capacity (shaded symbols) and Coulombic efficiency (semi-shaded symbols) as a function of the cycle number. (b) Capacity retention vs. cycles. EC/DEC (gray circles) and ionic liquids [BMPYR][FSI] (blue diamonds) and [P₂₂₂₄][FSI] (red triangles). A concentration of 1 molL^{−1} LiPF₆ was used as the lithium salt for the organic solvent EC/DEC, while 1 molL^{−1} LiFSI was used for both ILs. Cut-off: 0.05–2.5 V.

As mentioned earlier, EC/DEC is less viscous and approximately twice as conductive as both ILs. However, at low current rates, this difference in electrochemical performance is not significant. This suggests that the Li^+ concentration available near the PAN-electrolyte interface is sufficient to support the alloying/dealloying processes, that is, the Li^+ transport from the bulk solution to the interface is not the limiting step. Conversely, in materials with higher capacities, such as silicon NPs, Li^+ transport properties become more critical at high C-rates, as significantly more lithium is required for the alloying/dealloying reaction.

After 30 cycles, the charge capacity retention was 70%, with approximately 650 mAh/g obtained in all three cases. To gain further insights into the role of the electrolyte in electrochemical performance, after 35 cycles, the half-cell batteries were tested at 1.6 A/g during 1000 cycles to assess their long-term cycling stability. Similarly, as observed in Figure 4a, the delithiation capacity for ILs is slightly lower at high rates.

From the 1035th to the 1055th cycles (Figure 4b), the electrodes were returned to the initial rate (0.1 A/g). All three cells exhibited delithiation capacities of approximately 470–500 mAh/g. A recovery capacity of 75–76% suggests that, even after prolonged cycling at high rates, the electrodes remain attached to the current collector. This also indicates that most Li^+ insertion/extraction sites are still active, which can be correlated with the formation of a stable SEI, regardless of the electrolyte composition and/or transport properties.

3.3. Effect of Binder

To gain further insights into the binder–electrolyte effect on the electrochemical performance, SiOC/PAA electrodes with [BMPYR][FSI] and [P₂₂₂₄][FSI] (1 molL^{−1} LiFSI) electrolytes were compared with previously reported SiOC/PAA composites in EC/DEC [32]. To ensure a valid comparison, PAA electrodes containing approximately 0.65–0.85 mg of active material were used, similar to the active material mass reported by Monje et al. [32].

Delithiation capacities over 35 cycles at current densities ranging from 0.1 to 2.4 A/g, along with Coulombic efficiency, are shown in Figure 5. The three electrolytes exhibit similar delithiation behavior, with a slight difference observed at the beginning as both PAA-[BMPYR][FSI] and EC/DEC deliver capacities around 620–630 mAh/g, while PAA-[P₂₂₂₄][FSI] shows a slightly higher capacity of approximately 690 mAh/g. At higher current densities (0.4–2.4 A/g), the performance trends differ. PAA-[BMPYR][FSI] exhibits significantly lower capacities, while PAA-[P₂₂₂₄][FSI] and EC/DEC maintain relatively similar values. As the current increases, the time available for lithium-ion insertion/extraction is reduced. Under these conditions, IL-based electrolytes suffer from higher viscosity and slower ion mobility compared to EC/DEC, leading to more pronounced capacity fading, as has been previously reported [9]. However, the similar electrochemical performance observed for PAA-[P₂₂₂₄][FSI] and EC/DEC has also been reported in silicon-based electrodes, where [P₂₂₂₄][FSI] appears to compensate for its high viscosity by contributing to the stabilization of the SEI [9].

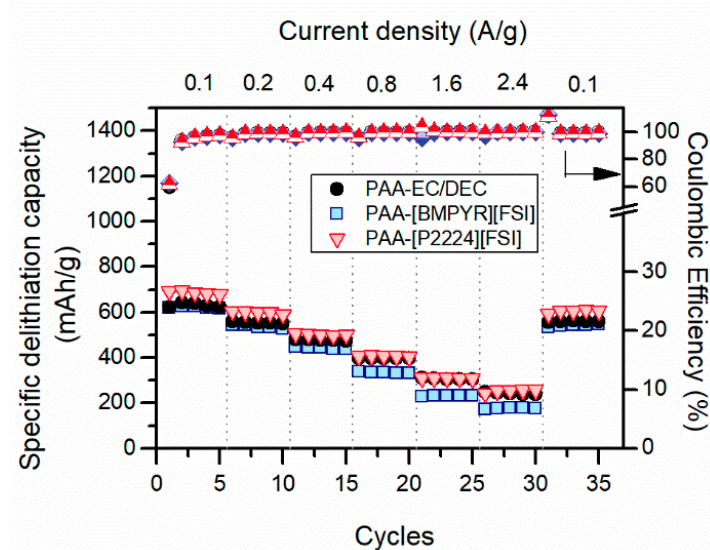


Figure 5. Electrochemical performance (rate capability) and Coulombic efficiency of NC/SiOC fabricated with PAA as binder and different electrolytes. Cut-off voltage: 0.05–2.5 V. A concentration of 1 molL^{−1} LiFSI was used for both ionic liquids: [BMPYR][FSI] (blue squares) and [P₂₂₂₄][FSI] (inverted triangles). Electrode mass loading ~0.8 mg. The rate data for EC/DEC (black circles) were taken from reference [32].

Voltage profiles for the first three cycles (Appendix A, Figure A1a,b) also indicate ICE values of approximately 60–62%. As mentioned for the PAN binder, the commercial electrolyte delivers a slightly lower capacity compared to ILs, with reported values of 614 mAh/g and an ICE of 62.5%.

Overall, Figures 4 and 5 indicate that, for the PAA binder, the initial cycle capacities were 25–30% lower than those of PAN. After 30 cycles at current densities ranging from 0.1 to 2.4 A/g, once the current density returned to the initial value, the capacities were around 545–605 mAh/g, indicating a recovery of 87–90%.

To achieve a more rigorous binder comparison, additional sets of PAN electrodes with a mass loading of 0.84 mg were tested (Figure A1a and Table A1). Similarly to the results shown in Figure 3, the superior performance of PAN was confirmed once again. The PAN electrodes exhibited higher capacity, greater first-cycle Coulombic efficiency, and a rapid increase in cycling efficiency, reaching above 98% by the second cycle (Figure A1c). In contrast, for PAA-ILs, five cycles were required to achieve the same cycling efficiency.

The superior performance of PAN could be attributed to the modified surface chemistry of NC-SiOC due to the PAN coating, which may cover the oxygen-containing groups of the SiOC surface, preventing their direct contact with the electrolyte. Consequently, the formation of irreversible products (e.g., Li_2O) resulting from the reaction of Li^+ with surface oxygen groups could be reduced, which could explain the improvement in the CE.

Additionally, it is well established that the initial PAN structure undergoes cyclization upon heating to approximately 300 °C under an inert atmosphere. During this process, the original cyanic group is transformed into cyclized pyridinic and substitutional graphite-like structure groups featuring delocalized sp^2 π bonds [33]. It could be expected that annealing of sp^2 -hybridized carbon structures (e.g., cyclized PAN and N-doped graphene-like domains from NC-SiOC) under inert conditions promotes π - π cross-coupling and network reorganization, leading to the formation of a continuous conductive framework. Then, enhanced ionic and electronic conductivity can be expected. However, further studies are required to confirm this hypothesis.

An improved interaction between sp^2 π -bonds of the cyclized PAN nitrile groups [33,67] and the sp^2 π -bonds of nitrogen-carbonaceous structures in SiOC [32] may contribute to enhanced ionic and electronic conductivity, similar to what has been reported for Si-PAN composites [33]. However, further studies are required to confirm this hypothesis.

Despite the lower capacities obtained for SiOC/PAA electrodes, it is worth noting that these electrodes not only exhibit similar delithiation capacities regardless of the electrolyte used but also demonstrate superior delithiation capacity and remarkable recovery capacity compared to other SiOC materials, as evidenced in Table A2. The promising performance of PAA reported here could be attributed to its ability to prevent the accumulation of decomposition products from the electrolyte solution, while also acting as an artificial protective layer, similar to what has been reported for graphite-silicon/PAA composites [63,68,69]. Notably, PAA undergoes decarbonylation and cross-linking reactions during the curing process, resulting in the formation of a polyether-based passivation film. This cross-linked structure facilitates Li-ion desolvation and contributes to ionic conductivity [70].

Beyond the intrinsic properties of the active material, binder, and SEI composition, mechanical properties also play a key role in overall electrode performance [71–73]. Previous studies employing the same electrode formulations as those used in this work have reported comparable adhesion strength to the current collector, a key factor in maintaining electrical contact and structural integrity during cycling. While PAN offers greater ductility, it exhibits lower tensile strength compared to PAA [71]. Although such mechanical characteristics are particularly critical in silicon-based electrodes, which can experience volume expansions of up to ~300%, the NC-SiOC materials investigated in this study may exhibit only ~22% expansion [74]. Therefore, it is likely that mechanical properties are not the primary limiting factor governing the performance of these electrodes.

The fact that the electrochemical performance remains similar regardless of the electrolyte suggests that comparison of [BMPYR][FSI] and [P₂₂₂₄][FSI] ILs with EC/DEC is a valuable approach for studying the electrolyte-electrode interface in similar materials. An indirect estimation of the electrolyte degradation contribution to the ICE could be particularly useful for improving battery performance.

Low ICE is a significant concern for full batteries, where the availability of Li^+ ions is limited. Unlike in half-cell batteries, where Li^+ is supplied by metallic lithium, in full batteries, Li^+ ions are supplied by the cathode [64]. Therefore, Li^+ consumption by the formation of any irreversible products, either in the active material or through irreversible electrolyte decomposition, negatively impacts the battery's energy density and cycling stability [64].

4. Conclusions

In summary, the high viscosity, lower Li^+ diffusion coefficient, and lower ionic conductivity of [BMPYR][FSI] and $[\text{P}_{2224}][\text{FSI}]$ compared to EC/DEC do not prevent achieving excellent battery performance. Overall, for all three electrolytes, NC-SiOC/PAN electrodes exhibit better electrochemical performance compared to NC-SiOC/PAA, with about 25–30% higher reversible capacity in the first cycle at 0.1 A/g, relatively higher ICE (67 vs. 62%), and a rapid increase in Coulombic efficiency to 98% after only two cycles. This remarkable performance (850–990 mAh/g for PAN vs. 600–700 mAh/g for PAA) is among the highest reported for SiOC materials, highlighting the importance of exploring alternative binders. At low rates, the ILs contribute to approximately a 10% improvement in the charge capacity.

This result can be attributed to the formation of an improved SEI, the cooperative effect of small decomposition products of FSI, the good ionic and electronic conductivity of cyclized PAN, as well as the modified surface chemistry of NC-SiOC. The PAN coating may prevent direct contact between surface oxygen groups with Li^+ ions, thereby reducing the formation of irreversible products at the interface. After 1000 cycles at 1.6 A/g, the capacity retention evaluated at 0.1 A/g was 75–80% for all three electrolytes. The formation of a highly stable SEI layer over long cycling times is attributed to both N-carbonaceous phases of the active material and the cyclized-PAN structure, which may help buffer potential volume change in the material.

Moreover, these results represent an improvement over previously reported capacities for SiOC particles and demonstrate, for the first time, the effective use of PAN-ionic liquid as a binder-electrolyte system in a SiOC negative electrode. More importantly, this work demonstrates that ILs can be used instead of flammable EC/DEC electrolytes despite having lower transport properties. Hence, [FSI]-based ILs hold great promise as electrolytes for lithium-ion batteries employing silicon oxycarbide anode.

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Abbreviations

The following abbreviations are used in this manuscript:

LIBs	Lithium-ion batteries
ILs	Ionic liquids
NC-SiOC	Nitrogen-doped carbon silicon oxycarbide
PAA	Poly(acrylic acid)
PAN	Poly(acrylonitrile)
SEI	Solid electrolyte interphase
FSI	bis(fluoromethylsulfonyl) imide
NPs	Nanoparticles
PVDF	Polyvinylidene fluoride
CMC	Carboxymethyl cellulose
DEC	Diethyl carbonate
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
P ₂₂₂₄	triethyl-n-butylphosphonium bis(fluoromethylsulfonyl)imide
BMPYR	N-propyl-N-methylpyrrolidinium bis(fluoromethylsulfonyl)imide
PFG-NMR	Pulsed-field gradient nuclear magnetic resonance
FEG-TEM	Field-emission gun transmission electron microscope
APTES	3-aminopropyltriethoxysilane

Appendix A

Table A1. Electrode characterization and electrochemical performance data for NC-SiOC/PAA composites are shown in Figure 4, as well as NC-SiOC/PAN electrodes with 0.65–0.84 mg mass loading used for a binder comparison. A 1 molL^{−1} LiFSI solution was used as the lithium salt in both ILs.

	Active Material Mass (mg)	Thickness (μm)	ICE (%)	1st Discharge mAh/g	1st Charge mAh/g
NC-SiOC/PAA					
[BMPYR][FSI]	0.81	27	60	1035.3	619.8
[P ₂₂₂₄][FSI]	0.64	24	61.8	1122.4	693.6
NC-SiOC/PAN					
[BMPYR][FSI]	0.84	28	66.2	1495.6	990.8
[P ₂₂₂₄][FSI]	0.84	24	67.2	1266.1	851.1

Table A2. Summary of experimental results of different SiOC materials.

Active Material	Binder, Electrolyte (Li Salt)	First Delithiation Capacity mAh/g (Current Density)	Initial Coulombic Efficiency %	Ref.
NC/SiOC	PAN, EC/DEC (1 M LiPF ₆)	854 (0.1)	62	This work
	PAN, [BMPYR][FSI] (1 M LiFSI)	926 (0.1)	64	
	PAN, [P ₂₂₂₄][FSI] (1 M LiFSI)	934 (0.1)	67	
NC/SiOC	PAA, EC/DEC (1 M LiPF ₆)	622 (0.1)	63	[32]
		367 (0.1)	55	
SiOC/N-doped C fibers	Free-standing, PC:EC:DMC (1 M LiPF ₆)	518	73	[21]

Table A2. Cont.

Active Material	Binder, Electrolyte (Li Salt)	First Delithiation Capacity mAh/g (Current Density)	Initial Coulombic Efficiency %	Ref.
SiOC/ Graphene (60:40)	Free-standing, DMC:EC (1 M LiPF ₆)	702 (0.1)	70	[20]
SiOC/graphene	CMC, EC:DMC:EMC (1 M LiPF ₆)	608 (0.05)	63	[22]
SiOC/CNT	PAA, EC:DMC (1 M LiPF ₆)	842 (at C/10~0.1)	67	[31]
SiOC-10-HF	PVDF, EC:DMC (1 M LiPF ₆)	272 (0.018)	60	[24]
SiOC/C rich	PVDF, EC:DMC (1 M LiPF ₆)	700 (0.018)	---	[28]
SiOC	PVDF, EC:DMC (1 M LiPF ₆)	562 (0.019)	61.5	[18]

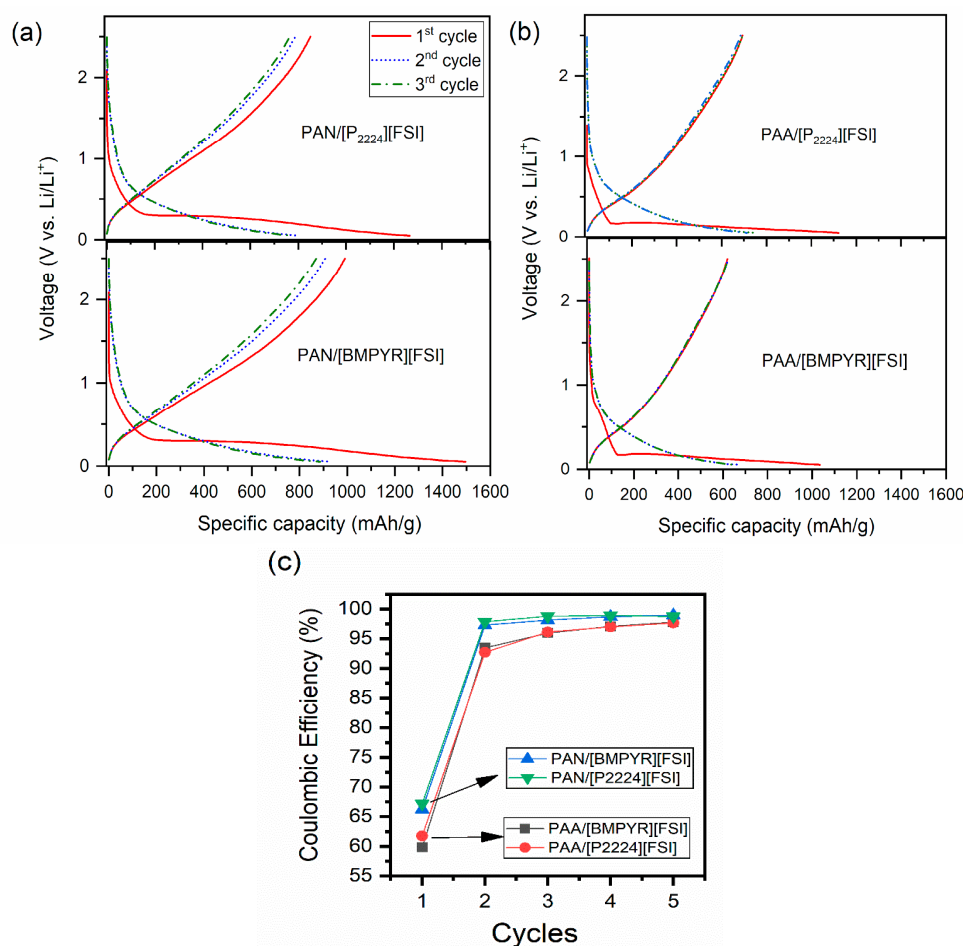


Figure A1. Discharge/charge voltage profiles at a current density of 0.1 A/g for NC/SiOC electrodes (mass loading ~0.65–0.85 mg) containing [BMPYR][FSI] and [P2224][FSI] (1 mol L^{−1} LiFSI) ILs electrolytes with different binders: (a) PAN; (b) PAA. (c) Coulombic efficiency for the first 5 cycles at 0.1 A/g for the half-cells shown in (a,b).

References

- Schmich, R.; Wagner, R.; Höppl, G.; Placke, T.; Winter, M. Performance and cost of materials for lithium-based rechargeable automotive batteries. *Nat. Energy* **2018**, *3*, 267–278. [CrossRef]
- Wang, J.; Yamada, Y.; Sodeyama, K.; Watanabe, E.; Takada, K.; Tateyama, Y.; Yamada, A. Fire-extinguishing organic electrolytes for safe batteries. *Nat. Energy* **2018**, *3*, 22–29. [CrossRef]

3. Cheng, H.; Ma, Z.; Kumar, P.; Liang, H.; Cao, Z.; Xie, H.; Cavallo, L.; Li, Q.; Ming, J. Non-Flammable Electrolyte Mediated by Solvation Chemistry toward High-Voltage Lithium-Ion Batteries. *ACS Energy Lett.* **2024**, *9*, 1604–1616. [[CrossRef](#)]
4. Chawla, N.; Bharti, N.; Singh, S. Recent advances in non-flammable electrolytes for safer lithium-ion batteries. *Batteries* **2019**, *5*, 19. [[CrossRef](#)]
5. Wang, Y.; Zaghib, K.; Guerfi, A.; Bazito, F.F.C.; Torresi, R.M.; Dahn, J.R. Accelerating rate calorimetry studies of the reactions between ionic liquids and charged lithium ion battery electrode materials. *Electrochim. Acta* **2007**, *52*, 6346–6352. [[CrossRef](#)]
6. Balakrishnan, P.G.; Ramesh, R.; Kumar, T.P. Safety mechanisms in lithium-ion batteries. *J. Power Sources* **2006**, *155*, 401–414. [[CrossRef](#)]
7. Sanchez-Ramirez, N.; Assresahegn, B.D.; Torresi, R.M.; Bélanger, D. Producing high-performing silicon anodes by tailoring ionic liquids as electrolytes. *Energy Storage Mater.* **2020**, *25*, 477–486. [[CrossRef](#)]
8. Sánchez-Ramírez, N.; Monje, I.E.; Bélanger, D.; Camargo, P.H.C.; Torresi, R.M. High rate and long-term cycling of silicon anodes with phosphonium-based ionic liquids as electrolytes for lithium-ion batteries. *Electrochim. Acta* **2023**, *439*, 141680. [[CrossRef](#)]
9. Sánchez-Ramírez, N.; Monje, I.E.; Martins, V.L.; Bélanger, D.; Camargo, P.H.C.; Torresi, R.M. Four Phosphonium-based Ionic Liquids. Synthesis, Characterization and Electrochemical Performance as Electrolytes for Silicon Anodes. *ChemistrySelect* **2022**, *7*, e202104430. [[CrossRef](#)]
10. Pomerantseva, E.; Bonaccorso, F.; Feng, X.; Cui, Y.; Gogotsi, Y. Energy storage: The future enabled by nanomaterials. *Science* **2019**, *366*, eaan8285. [[CrossRef](#)]
11. Piper, D.M.; Evans, T.; Xu, S.; Kim, S.C.; Han, S.S.; Liu, K.L.; Oh, K.H.; Yang, R.; Lee, S. Optimized Silicon Electrode Architecture, Interface, and Microgeometry for Next-Generation Lithium-Ion Batteries. *Adv. Mater.* **2016**, *28*, 188–193. [[CrossRef](#)]
12. Andersen, H.F.; Foss, C.E.L.; Voje, J.; Tronstad, R.; Mokkelbost, T.; Vullum, P.E.; Ulvestad, A.; Kirkengen, M.; Mæhlen, J.P. Silicon-Carbon composite anodes from industrial battery grade silicon. *Sci. Rep.* **2019**, *9*, 14814. [[CrossRef](#)]
13. Liu, Z.; Yu, Q.; Zhao, Y.; He, R.; Xu, M.; Feng, S.; Li, S.; Zhou, L.; Mai, L. Silicon oxides: A promising family of anode materials for lithium-ion batteries. *Chem. Soc. Rev.* **2019**, *48*, 285–309. [[CrossRef](#)]
14. Halim, M.; Hudaya, C.; Kim, A.Y.; Lee, J.K. Phenyl-rich silicone oil as a precursor for SiOC anode materials for long-cycle and high-rate lithium ion batteries. *J. Mater. Chem. A* **2016**, *4*, 2651–2656. [[CrossRef](#)]
15. Stabler, C.; Ionescu, E.; Graczyk-Zajac, M.; Gonzalo-Juan, I.; Riedel, R. Silicon oxycarbide glasses and glass-ceramics: ‘All-Rounder’ materials for advanced structural and functional applications. *J. Am. Ceram. Soc.* **2018**, *101*, 4817–4856. [[CrossRef](#)]
16. Shi, H.; Yuan, A.; Xu, J. Tailored synthesis of monodispersed nano/submicron porous silicon oxycarbide (SiOC) spheres with improved Li-storage performance as an anode material for Li-ion batteries. *J. Power Sources* **2017**, *364*, 288–298. [[CrossRef](#)]
17. Fukui, H.; Harimoto, Y.; Akasaka, M.; Eguchi, K. Lithium species in electrochemically lithiated and delithiated silicon oxycarbides. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12827–12836. [[CrossRef](#)] [[PubMed](#)]
18. Wilamowska-Zawlocka, M.; Puczkarski, P.; Grabowska, Z.; Kaspar, J.; Graczyk-Zajac, M.; Riedel, R.; Sorarù, G.D. Silicon oxycarbide ceramics as anodes for lithium ion batteries: Influence of carbon content on lithium storage capacity. *RSC Adv.* **2016**, *6*, 104597–104607. [[CrossRef](#)]
19. Graczyk-Zajac, M.; Vrankovic, D.; Waleska, P.; Hess, C.; Sasikumar, P.V.; Lauterbach, S.; Kleebe, H.-J.; Sorarù, G.D. The Li-storage capacity of SiOC glasses with and without mixed silicon oxycarbide bonds. *J. Mater. Chem. A* **2017**, *6*, 93–103. [[CrossRef](#)]
20. David, L.; Bhandavat, R.; Barrera, U.; Singh, G. Silicon oxycarbide glass-graphene composite paper electrode for long-cycle lithium-ion batteries. *Nat. Commun.* **2016**, *7*, 10998. [[CrossRef](#)]
21. Ma, M.; Wang, H.; Li, X.; Peng, K.; Xiong, L.; Du, X. Free-standing SiOC/nitrogen-doped carbon fibers with highly capacitive Li storage. *J. Eur. Ceram. Soc.* **2020**, *40*, 5238–5246. [[CrossRef](#)]
22. Ren, Y.; Yang, B.; Huang, X.; Chu, F.; Qiu, J.; Ding, J. Intercalated SiOC/graphene composites as anode material for li-ion batteries. *Solid State Ion.* **2015**, *278*, 198–202. [[CrossRef](#)]
23. Xia, K.; Wu, Z.; Xuan, C.; Xiao, W.; Wang, J.; Wang, D. Effect of KOH etching on the structure and electrochemical performance of SiOC anodes for lithium-ion batteries. *Electrochim. Acta* **2017**, *245*, 287–295. [[CrossRef](#)]
24. Dibandjo, P.; Graczyk-Zajac, M.; Riedel, R.; Pradeep, V.S.; Soraru, G.D. Lithium insertion into dense and porous carbon-rich polymer-derived SiOC ceramics. *J. Eur. Ceram. Soc.* **2012**, *32*, 2495–2503. [[CrossRef](#)]
25. Sujith, R.; Gangadhar, J.; Greenough, M.; Bordia, R.K.; Panda, D.K. A review of silicon oxycarbide ceramics as next generation anode materials for lithium-ion batteries and other electrochemical applications. *J. Mater. Chem. A* **2023**, *11*, 20324–20348. [[CrossRef](#)]
26. Kaspar, J.; Graczyk-Zajac, M.; Riedel, R. Carbon-Rich Silicon Oxycarbide (SiOC) and Silicon Oxycarbide / Element (SiOC/X, X = Si, Sn) Nano-Composites as New Anode Materials for Li-Ion Battery Application. Ph.D. Thesis, Technische Universität Darmstadt, Darmstadt, Germany, 2014; pp. 1–117.
27. Wilamowska, M.; Pradeep, V.S.; Graczyk-Zajac, M.; Riedel, R.; Sorarù, G.D. Tailoring of SiOC composition as a way to better performing anodes for Li-ion batteries. *Solid State Ion.* **2014**, *260*, 94–100. [[CrossRef](#)]

28. Graczyk-Zajac, M.; Toma, L.; Fasel, C.; Riedel, R. Carbon-rich SiOC anodes for lithium-ion batteries: Part I. Influence of material UV-pre-treatment on high power properties. *Solid State Ion.* **2012**, *225*, 522–526. [\[CrossRef\]](#)
29. Tao, A.; Ren, J.; Liu, B.; Yang, M.; Kong, Y.; Zhao, X.; Shen, X. Hierarchical porous silicon oxycarbide as a stable anode material for lithium-ion batteries. *J. Energy Storage* **2024**, *104*, 114617. [\[CrossRef\]](#)
30. Lee, S.H.; Park, C.; Do, K.; Ahn, H. Maximizing the utilization of active sites through the formation of native nanovoids of silicon oxycarbide as anode materials in lithium-ion batteries. *Energy Storage Mater.* **2021**, *35*, 130–141. [\[CrossRef\]](#)
31. Bhandavat, R.; Singh, G. Stable and Efficient Li-Ion Battery Anodes Prepared from Polymer-Derived Silicon Oxycarbide–Carbon Nanotube Shell/Core Composites. *J. Phys. Chem. C* **2013**, *117*, 11899–11905. [\[CrossRef\]](#)
32. Monje, I.; Sanchez-Ramirez, N.; Santagneli, S.H.; Camargo, P.H.; Bélanger, D.; Schougaard, S.B.; Torresi, R.M. In-situ formed Nitrogen-doped carbon/silicon-based materials as negative electrodes for lithium ion batteries. *J. Electroanal. Chem.* **2021**, *901*, 115732. [\[CrossRef\]](#)
33. Piper, D.M.; Yersak, T.A.; Son, S.; Kim, S.C.; Kang, C.S.; Oh, K.H.; Ban, C.; Dillon, A.C.; Lee, S. Conformal coatings of cyclized-PAN for mechanically resilient Si nano-composite anodes. *Adv. Energy Mater.* **2013**, *3*, 697–702. [\[CrossRef\]](#)
34. Piper, D.M.; Evans, T.; Leung, K.; Watkins, T.; Olson, J.; Kim, S.C.; Han, S.S.; Bhat, V.; Oh, K.H.; Buttry, D.A.; et al. Stable silicon-ionic liquid interface for next-generation lithium-ion batteries. *Nat. Commun.* **2015**, *6*, 6230. [\[CrossRef\]](#)
35. Martins, V.L.; Sanchez-Ramirez, N.; Ribeiro, M.C.C.; Torresi, R.M. Two phosphonium ionic liquids with high Li⁺ transport number. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23041–23051. [\[CrossRef\]](#)
36. Sánchez-Ramírez, N.; Assresahegn, B.D.; Bélanger, D.; Torresi, R.M. A Comparison among Viscosity, Density, Conductivity, and Electrochemical Windows of N-n-Butyl-N-methylpyrrolidinium and Triethyl-n-pentylphosphonium Bis(fluorosulfonyl imide) Ionic Liquids and Their Analogues Containing Bis(trifluoromethylsulfonyl) Imide Anion. *J. Chem. Eng. Data* **2017**, *62*, 3437–3444. [\[CrossRef\]](#)
37. Rennie, A.J.R.; Sanchez-Ramirez, N.; Torresi, R.M.; Hall, P.J. Ether-Bond-Containing Ionic Liquids as Supercapacitor Electrolytes. *J. Phys. Chem. Lett.* **2013**, *4*, 2970–2974. [\[CrossRef\]](#)
38. Stejskal, E.O.; Tanner, J.E. Spin diffusion measurements: Spin echoes in the presence of a time-dependent field gradient. *J. Chem. Phys.* **1965**, *42*, 288–292. [\[CrossRef\]](#)
39. Wei, L.; Chen, C.; Hou, Z.; Wei, H. Poly (acrylic acid sodium) grafted carboxymethyl cellulose as a high performance polymer binder for silicon anode in lithium ion batteries. *Sci. Rep.* **2016**, *6*, 19583. [\[CrossRef\]](#)
40. Shekaari, H.; Zafarani-Moattar, M.T.; Golmohammadi, B. Thermodynamic and transport properties of ionic liquids, 1-alkyl-3-methylimidazolium thiocyanate in the aqueous lithium halides solutions. *J. Chem. Thermodyn.* **2020**, *141*, 105953. [\[CrossRef\]](#)
41. Bazito, F.F.C.; Kawano, Y.; Torresi, R.M. Synthesis and characterization of two ionic liquids with emphasis on their chemical stability towards metallic lithium. *Electrochim. Acta* **2007**, *52*, 6427–6437. [\[CrossRef\]](#)
42. Yuan, W.; Yang, X.; He, L.; Xue, Y.; Qin, S.; Tao, G. Viscosity, Conductivity, and Electrochemical Property of Dicyanamide Ionic Liquids. *Front. Chem.* **2018**, *6*, 59. [\[CrossRef\]](#)
43. Sanchez-Ramirez, N.; Martins, V.L.; Ando, R.A.; Camilo, F.F.; Urahata, S.M.; Ribeiro, M.C.C.; Torresi, R.M. Physicochemical Properties of Three Ionic Liquids Containing a Tetracyanoborate Anion and Their Lithium Salt Mixtures. *J. Phys. Chem. B* **2014**, *118*, 8772–8781. [\[CrossRef\]](#)
44. Hayamizu, K. Temperature dependence of self-diffusion coefficients of ions and solvents in ethylene carbonate, propylene carbonate, and diethyl carbonate single solutions and ethylene carbonate + diethyl carbonate binary solutions of LiPF₆ studied by NMR. *J. Chem. Eng. Data* **2012**, *57*, 2012–2017. [\[CrossRef\]](#)
45. Lundgren, H.; Behm, M.; Lindbergh, G. Electrochemical Characterization and Temperature Dependency of Mass-Transport Properties of LiPF₆ in EC:DEC. *J. Electrochem. Soc.* **2015**, *162*, A413–A420. [\[CrossRef\]](#)
46. Tsimpanogiannis, I.N.; Jamali, S.H.; Economou, I.G.; Vlugt, T.J.H.; Moulton, O.A. On the validity of the Stokes–Einstein relation for various water force fields. *Mol. Phys.* **2019**, *118*, e1702729. [\[CrossRef\]](#)
47. Shao, Y.; Shigenobu, K.; Watanabe, M.; Zhang, C. Role of Viscosity in Deviations from the Nernst–Einstein Relation. *J. Phys. Chem. B* **2020**, *124*, 4774–4780. [\[CrossRef\]](#)
48. Hess, S.; Wohlfahrt-Mehrens, M.; Wachtler, M. Flammability of Li-Ion Battery Electrolytes: Flash Point and Self-Extinguishing Time Measurements. *J. Electrochem. Soc.* **2015**, *162*, A3084–A3097. [\[CrossRef\]](#)
49. Dai, Y.; Panahi, A. Thermal runaway process in lithium-ion batteries: A review. *Next Energy* **2025**, *6*, 100186. [\[CrossRef\]](#)
50. Huang, Y.; Chen, Z.; Crosthwaite, J.M.; Aki, S.N.V.K.; Brennecke, J.F. Thermal stability of ionic liquids in nitrogen and air environments. *J. Chem. Thermodyn.* **2021**, *161*, 106560. [\[CrossRef\]](#)
51. Lv, P.; Zhao, H.; Gao, C.; Du, Z.; Wang, J.; Liu, X. SiO_x-C dual-phase glass for lithium ion battery anode with high capacity and stable cycling performance. *J. Power Sources* **2015**, *274*, 542–550. [\[CrossRef\]](#)
52. Kaspar, J.; Graczyk-Zajac, M.; Riedel, R. Determination of the chemical diffusion coefficient of Li-ions in carbon-rich silicon oxycarbide anodes by electro-analytical methods. *Electrochim. Acta* **2014**, *115*, 665–670. [\[CrossRef\]](#)

53. Dahn, J.R.; Zheng, T.; Liu, Y.; Xue, J.S. Mechanisms for lithium insertion in carbonaceous materials. *Science* **1995**, *270*, 590–593. [\[CrossRef\]](#)
54. Gauthier, M.; Carney, T.J.; Grimaud, A.; Giordano, L.; Pour, N.; Chang, H.-H.; Fenning, D.P.; Lux, S.F.; Paschos, O.; Bauer, C.; et al. Electrode–Electrolyte Interface in Li-Ion Batteries: Current Understanding and New Insights. *J. Phys. Chem. Lett.* **2015**, *6*, 4653–4672. [\[CrossRef\]](#)
55. Fukui, H.; Ohsuka, H.; Hino, T.; Kanamura, K. A Si-O-C composite anode: High capability and proposed mechanism of lithium storage associated with microstructural characteristics. *ACS Appl. Mater. Interfaces* **2010**, *2*, 998–1008. [\[CrossRef\]](#)
56. Nita, C.; Fullenwarth, J.; Monconduit, L.; Le Meins, J.-M.; Fioux, P.; Parmentier, J.; Ghimbeu, C.M. Eco-friendly synthesis of SiO₂ nanoparticles confined in hard carbon: A promising material with unexpected mechanism for Li-ion batteries. *Carbon* **2019**, *143*, 598–609. [\[CrossRef\]](#)
57. Kammoun, H.; Ossonon, B.D.; Tavares, A.C. Nitrogen-Doped Graphene Materials with High Electrical Conductivity Produced by Electrochemical Exfoliation of Graphite Foil. *Nanomaterials* **2024**, *14*, 123. [\[CrossRef\]](#)
58. Gomez-Martin, A.; Martinez-Fernandez, J.; Rutttert, M.; Winter, M.; Placke, T.; Ramirez-Rico, J. An electrochemical evaluation of nitrogen-doped carbons as anodes for lithium ion batteries. *Carbon* **2020**, *164*, 261–271. [\[CrossRef\]](#)
59. Naveenkumar, P.; Maniyazagan, M.; Yang, H.W.; Kang, W.S.; Kim, S.J. Nitrogen-doped graphene/silicon-oxycarbide nanosphere as composite anode for high-performance lithium-ion batteries. *J. Energy Storage* **2023**, *59*, 106572. [\[CrossRef\]](#)
60. Bhattacharjya, D.; Park, H.Y.; Kim, M.S.; Choi, H.S.; Inamdar, S.N.; Yu, J.S. Nitrogen-doped carbon nanoparticles by flame synthesis as anode material for rechargeable lithium-ion batteries. *Langmuir* **2014**, *30*, 318–324. [\[CrossRef\]](#)
61. Ou, J.; Zhang, Y.; Chen, L.; Zhao, Q.; Meng, Y.; Guo, Y.; Xiao, D. Nitrogen-rich porous carbon derived from biomass as a high performance anode material for lithium ion batteries. *J. Mater. Chem. A* **2015**, *3*, 6534–6541. [\[CrossRef\]](#)
62. Chae, S.; Ko, M.; Kim, K.; Ahn, K.; Cho, J. Confronting Issues of the Practical Implementation of Si Anode in High-Energy Lithium-Ion Batteries. *Joule* **2017**, *1*, 47–60. [\[CrossRef\]](#)
63. Komaba, S.; Shimomura, K.; Yabuuchi, N.; Ozeki, T.; Yui, H.; Konno, K. Study on polymer binders for high-capacity SiO negative electrode of Li-Ion batteries. *J. Phys. Chem. C* **2011**, *115*, 13487–13495. [\[CrossRef\]](#)
64. He, H.; Sun, D.; Tang, Y.; Wang, H.; Shao, M. Understanding and improving the initial Coulombic efficiency of high-capacity anode materials for practical sodium ion batteries. *Energy Storage Mater.* **2019**, *23*, 233–251. [\[CrossRef\]](#)
65. Leung, K. Electronic structure modeling of electrochemical reactions at electrode/electrolyte interfaces in lithium ion batteries. *J. Phys. Chem. C* **2013**, *117*, 1539–1547. [\[CrossRef\]](#)
66. Lewandowski, A.; Świdarska-Mocek, A. Ionic liquids as electrolytes for Li-ion batteries—An overview of electrochemical studies. *J. Power Sources* **2009**, *194*, 601–609. [\[CrossRef\]](#)
67. Kopeć, M.; Lamson, M.; Yuan, R.; Tang, C.; Kruk, M.; Zhong, M.; Matyjaszewski, K.; Kowalewski, T. Polyacrylonitrile-derived nanostructured carbon materials. *Prog. Polym. Sci.* **2019**, *92*, 89–134. [\[CrossRef\]](#)
68. Komaba, S.; Okushi, K.; Ozeki, T.; Yui, H.; Katayama, Y.; Miura, T.; Saito, T.; Groult, H. Polyacrylate modifier for graphite anode of lithium-ion batteries. *Electrochem. Solid-State Lett.* **2009**, *12*, 107–110. [\[CrossRef\]](#)
69. Komaba, S.; Yabuuchi, N.; Ozeki, T.; Okushi, K.; Yui, H.; Konno, K.; Katayama, Y.; Miura, T. Functional binders for reversible lithium intercalation into graphite in propylene carbonate and ionic liquid media. *J. Power Sources* **2010**, *195*, 6069–6074. [\[CrossRef\]](#)
70. Martin, T.R.; Pekarek, R.T.; Coyle, J.E.; Schulze, M.C.; Neale, N.R. Understanding Why Poly(Acrylic Acid) Works: Decarbonylation and Cross-Linking Provide an Ionically Conductive Passivation Layer in Silicon Anodes. *J. Mater. Chem. A* **2021**, *9*, 21929–21938. [\[CrossRef\]](#)
71. Assresahegn, B.D.; Bélanger, D. Effects of the Formulations of Silicon-Based Composite Anodes on their Mechanical, Storage, and Electrochemical Properties. *ChemSusChem* **2017**, *10*, 4080–4089. [\[CrossRef\]](#)
72. Jin, B.; Dolocan, A.; Liu, C.; Cui, Z.; Manthiram, A. Regulating Anode-Electrolyte Interphasial Reactions by Zwitterionic Binder Chemistry in Lithium-Ion Batteries with High-Nickel Layered Oxide Cathodes and Silicon-Graphite Anodes. *Angew. Chem. Int. Ed.* **2024**, *63*, e202408021. [\[CrossRef\]](#)
73. Jin, B.; Wang, D.; Song, L.; Cai, Y.; Ali, A.; Hou, Y.; Chen, J.; Zhang, Q.; Zhan, X. Biomass-derived fluorinated corn starch emulsion as binder for silicon and silicon oxide based anodes in lithium-ion batteries. *Electrochim. Acta* **2021**, *365*, 137359. [\[CrossRef\]](#)
74. Sun, H.; Zhao, K. Atomistic Origins of High Capacity and High Structural Stability of Polymer-Derived SiOC Anode Materials. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35001–35009. [\[CrossRef\]](#)

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