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Khryslyn Araño, Driss Mazouzi, Robert Kerr, Bernard Lestriez, Jean Le Bideau, et al.. Understanding the Superior Cycling Performance of Si Anode in Highly Concentrated Phosphonium-Based Ionic Liquid Electrolyte. *Journal of The Electrochemical Society*, 2020, 167 (12), pp.120520. 10.1149/1945-7111/abac84 . hal-03010246

HAL Id: hal-03010246

<https://hal.science/hal-03010246>

Submitted on 25 Nov 2020

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Understanding the Superior Cycling Performance of Si Anode in Highly Concentrated Phosphonium-based Ionic Liquid Electrolyte

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ABSTRACT

Considerable effort has been devoted to improving the cyclability of silicon (Si) negative electrodes for lithium-ion batteries because it is a promising high specific capacity alternative to graphite. In this work, the electrochemical behaviour of Si in two ionic liquid (IL) electrolytes, triethyl(methyl)phosphonium bis(fluorosulfonyl)imide (P₁₂₂₂FSI) and *N*-propyl-*N*-methylpyrrolidinium-FSI (C₃mpyrFSI) with high and low lithium (Li) salt content is investigated at 50 °C. Results highlight that higher capacity and better cycling stability are achieved over 50

cycles with high salt concentration, the first time for a pyrrolidinium-based electrolyte in the area of Si negative electrodes. However, the Si cycling performance was far superior in the P₁₂₂₂FSI-based high salt content electrolyte compared to that of the C₃mpyrFSI. To understand this unexpected result, diffusivity measurements of the IL-based electrolytes were performed using PFG-NMR, while their stability was probed using MAS-NMR and XPS after long-term cycling. A higher apparent transport number for Li ions in highly concentrated ILs, combined with a significantly lower extent of electrolyte degradation explains the superior cycle life of the highly concentrated phosphonium-based system. Si/concentrated P₁₂₂₂FSI-LiFSI/lithium nickel cobalt aluminum oxide (NCA) full cells with more than 3 mAh cm⁻² nominal capacity deliver a promising cycle life and good rate capability.

Keywords:

Lithium-ion battery

Silicon anode

Ionic liquid electrolytes

Highly concentrated electrolytes

Introduction

Lithium-ion batteries (LiBs) are considered the technology of choice for a wide range of applications from portable electronic devices to electric vehicles owing to their favorable properties such as long cycle life, high energy density, and efficiency. The continuous demand for the improvement of these applications comes with the need to also improve the materials behind the technology that make such devices work. The market for LiBs is currently dominated

by graphite as the negative electrode. However, graphite has already reached its full promise and many new devices require materials that can deliver higher energy density to meet the demand of these ever-improving applications. Silicon (Si) is a promising alternative because of its large theoretical gravimetric capacity (3579 mAh g^{-1}) at ambient temperature [1], approximately ten times compared to that of graphite (372 mAh g^{-1}). In terms of volumetric capacity, Si can deliver 2194 mAh cm^{-3} vs. 818 mAh cm^{-3} for graphite.[2]

The major challenge faced by the Si community is the continuous electrolyte decomposition that occurs on the surface of Si particles upon cycling of the battery.[3,4] This is attributed to the huge volumetric changes (280%) taking place during Li insertion and extraction that ultimately leads to cracking and pulverization of the electrode. This phenomenon incessantly exposes new Si surfaces that react with the electrolyte, leading to the uncontrolled formation of solid electrolyte interphase (SEI) products.[5] While incorporating additives such as vinylene carbonate (VC)[2,6] or fluoroethylene carbonate (FEC)[2,7,8] to conventional carbonate-based electrolytes is an established approach to improve the SEI, this does not completely eliminate the continuous parasitic reactions consuming electrolyte that build up the SEI. Combining MAS NMR, STEM-EELS and XPS, Dupré et al.[9] demonstrated that the performance degradation of Si vs. NMC full Li-ion cells using carbonate-FEC electrolyte is mainly due to the irreversible consumption of cyclable Li coupled with endless decomposition of organic electrolyte solvent in the Si SEI. As a result, there is more than ever a need to efficiently control the parasitic reactions degrading the salt and the solvents of the electrolyte at the interface between the Si electrode and the electrolyte. In order to avoid the decomposition-prone carbonate solvents, it appears necessary to switch from these conventional electrolytes to others that exhibit better stability with respect to the highly reducing surface of the Si material.

The use of ionic liquid (IL) electrolytes is an appealing approach because of their interesting properties that are considered key performance indicators in batteries such as good electrochemical stability, high ionic conductivity, low volatility, and low flammability. Anions such as bis(fluorosulfonyl)imide (FSI) and bis(trifluoromethanesulfonyl)imide (TFSI) have been explored for many years and are currently among the most studied in the field of Li-ion batteries. Between the two anions, FSI⁻ is able to form a SEI without the need for electrolyte additives [10] and also allows operation at the high voltage plateaus of high voltage positive electrodes such as LiNi_{0.5}Mn_{1.5}O₂ and LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂. [11–13] These anions, usually combined with pyrrolidinium [10,14–16] or phosphonium [17,18] cations, have demonstrated promising electrochemical behaviour in graphite and Li metal negative electrodes, as well as with Si-based negative electrodes [19–22].

Recently, highly concentrated (>50 mol %) Li salt pyrrolidinium-based and phosphonium-based IL electrolytes have been shown to allow high rate cycling with Li metal [23–25]. The exceptional cycling behaviour with highly concentrated electrolytes is commonly attributed to the lowering of mass transport limitations at the electrode due to the higher Li ion transport number and to a stable SEI. [23,24,26–28] To this date, only a few studies deal with Si electrodes in such highly concentrated pyrrolidinium and phosphonium-based ILs [27,29]. We have previously shown in a short communication [27] the promising electrochemical performance of Si electrode in highly concentrated trimethyl isobutyl phosphonium (P_{11i4}FSI)-LiFSI electrolyte, but a deeper understanding of such behaviour was not carried out. This previous work prompted us to study Si electrode in other concentrated LiFSI-based IL electrolytes with N-propyl-N-methylpyrrolidinium cation (C₃mpyrFSI-LiFSI) and triethyl(methyl)phosphonium cation (P₁₂₂₂FSI-LiFSI) to investigate the possible influence of the IL cation.

In the present work, we show that our chosen IL electrolytes provide much superior performance to the Si electrode than classical carbonate-based electrolytes, that their performance depends strongly on their composition, and that the highly concentrated P₁₂₂₂FSI-LiFSI electrolyte cycles much better than its pyrrolidinium C₃mpyr equivalent over long term cycling. Our main purpose is to understand the difference in cycling performance of Si electrode in the two IL systems P₁₂₂₂FSI and C₃mpyrFSI at extreme Li salt concentrations, and more generally to shed some light on how the composition of IL electrolytes affects Si electrochemical behaviour. To achieve this goal, we decided to focus on 3.2 m high (near saturation) and 0.8 m low LiFSI salt concentrations for comparison, and to operate the measurements in half cells at 50 °C, a temperature at which ILs present no more viscosity and conductivity limitations. Our results indicate that both transport properties of bulk electrolytes measured via PFG-NMR, and electrochemical interfacial reactivity at Si surface measured via MAS-NMR and XPS, strongly influence the cycling performance of the Si anode and explain the differences observed. The best electrolyte, the high Li content P₁₂₂₂FSI-LiFSI IL, was evaluated in a full cell configuration versus a lithium nickel cobalt aluminum oxide (NCA) cathode.

Experimental Section

Electrode Preparation

Si nanoparticles (S'Tile) with a diameter of approximately 150 nm were used as the active material for electrode preparation.[30] Sodium carboxymethyl cellulose (Na-CMC, DS = 0.9, M_w = 700, 000, Sigma Aldrich) was used as binder, graphene nanoplatelets (GM15, length ~15 μm, width ~5-10 μm, S_{BET}: 74 m²g⁻¹, XGSciences) as a conductive additive, pH 3 buffer solution consisting of citric acid and potassium hydroxide (KOH), and polyacrylic co-maleic acid (Sigma Aldrich) as a dispersant. These components are present in 71:7:11:9:2 wt% ratio,

respectively.[31,32] Preparation of the electrode slurry was carried out by adding 1 ml H₂O as solvent to 200 mg of the previous mix. A silicon nitride jar was used as a mixing medium with three silicon nitride balls. The slurries were mixed with a planetary ball mill using a Fritsch Pulverisette 7 classic line mixer for 1 hr at 500 rpm and deposited onto a 25 μm thick copper foil by tapecasting. The electrodes were dried at ambient conditions followed by drying at 100°C for 2 hours prior to cell assembly. Calendaring was not performed on the electrodes. The reported percentage of the different components takes into account the citric acid and KOH which do not evaporate during the drying procedures. The active mass loading of the electrodes was controlled around 1.0 mg/cm² to avoid accentuating the huge volumetric expansion associated with Si during lithiation and delithiation.

Electrochemical Measurements

The IL electrolytes were composed of P₁₂₂₂FSI (Boron Molecular) and C₃mpyrFSI (Solvionic) with 3.2 and 0.8 mol kg⁻¹ (m) LiFSI (Nippon Shokubai, Japan) salt added to each IL.[23] The IL and the salt were dried separately at 50°C under vacuum for 48 hours prior to mixing. In this work, the electrolytes containing 3.2 m and 0.8 m are referred to as high salt concentration and low salt concentration electrolyte, respectively. Commercial carbonate-based electrolytes such as LP 30 (1.0 M LiPF₆ in ethylene carbonate (EC):dimethyl carbonate (DMC) 50-50 by volume from Sigma Aldrich) and LP30 + 10 wt% fluoroethylene carbonate (FEC)[27,33] were also used for comparison. Prior to cell assembly, the Si electrodes (0.785 cm² disc) were pre-wetted with the IL electrolytes at 50°C for 18 hours under vacuum.

Li|Si Swagelok-type half cells were assembled from the pre-wetted Si electrodes using a 25 μm thick microporous polypropylene membrane (Celgard 3501, Celgard Inc.) and a borosilicate glass-fiber (Whatman GF/A) as separators. Six drops of the electrolyte were added in addition to

the amount used in the pre-wetting step. All the cells were assembled inside an Argon-filled glovebox. After assembly, the cells were transferred to a 50°C oven and allowed to rest for 24 hours prior to cycling. The electrochemical measurements were performed in galvanostatic mode at 50°C at a rate of C/10 (with the following convention: C/n rate corresponding to a full lithiation in n hours i.e. 4Si + 15Li in n hours) with voltage cutoffs at 1 and 0.01 V using a VMP multichannel potentiostat (Bio-Logic). Formation steps were performed at C/40 and C/20 prior to long-term cycling. The rate capability of the Si electrodes in the high salt concentration electrolytes was also tested from C/10 to C. All the capacities reported are normalized by the mass of the active material, i.e. Si.

Full cells in coin cell setup were assembled in an argon-filled glovebox using Si negative electrode and lithium nickel cobalt aluminum oxide (NCA), 90 wt.% Ni, as positive electrode. The size of both negative and positive electrodes were 0.503 cm² in the form of discs. Cells were balanced with a capacity excess of 14% for the silicon negative electrode, to avoid Li plating. A 24-hour rest period was performed at 50°C prior to cycling. Formation steps were performed at C/40 and C/20 prior to long-term cycling at C/5 with voltage cutoffs at 2.8 and 4.1 V, considering that cathode is the limiting electrode.

All data presented herein have been reproduced at least three times.

Diffusivity of the Electrolyte Ions

Pulse-field gradient stimulated echo (PFG-STE) Nuclear Magnetic Resonance (NMR) was used to measure the diffusivity of the individual ions in the electrolytes using Bruker Avance III 300 MHz Ultrashield wide bore spectrometer with a 5 mm PFG probe. The diffusivities of ¹H, ¹⁹F, and ⁷Li nuclei were measured which correspond to the IL cation, FSI anion, and Li ion,

respectively. The samples were prepared by filling a 3 mm Schott E NMR tube inside an Argon-filled glovebox. The tube was sealed and placed in a 5 mm Duran type-E tube where a deuterium oxide (D_2O) was added to prevent the effect of convection during the measurements at higher temperatures. The 5 mm tube was sealed with a high-temperature Teflon cap and Teflon tape.[34,35] All measurements were performed from 20 to 80°C with an error of 5%. Please note that PFG-NMR method underestimates the self-diffusion coefficient [36] because it considers all the species in the system, including ion aggregates.

Electrolyte Stability

The stability of the electrolytes with respect to the Si electrode was monitored *ex-situ* upon cycling of the cells. The cells were disassembled inside an Ar-filled glovebox and the Si electrodes were recovered for analysis. The electrodes were not washed with any solvent. ^{31}P Magic Angle Spinning (MAS) – NMR (Bruker 500 MHz Ultrashield spectrometer) technique was used to investigate the stability of the $P_{1222}FSI$ -based electrolyte by checking for the presence of decomposition species from the phosphonium cation. Fourier Transform Infrared (FTIR) spectroscopy (PerkinElmer IR 101820 series) was also used as a complementary technique to investigate the effect of the salt concentration. For the $C_3mpyrFSI$ -based electrolyte, the stability of the pyrrolidinium cation upon cycling was investigated using N 1s edge *ex situ* X-ray Photoelectron Spectroscopy (NOVA XPS spectrometer, Kratos Analytical Ltd.). The stability of the FSI anion was also assessed from F 1s and S 2p edges *ex situ* XPS.

Results and Discussion

Electrochemical Performance in Half Cells

Fig. 1a displays a comparison of the electrochemical behaviour of the two studied highly concentrated IL electrolytes and traditional carbonate electrolytes, LP 30 and LP 30 + 10 wt.% FEC at 50°C. For all electrolytes, the first discharge capacity exceeds the theoretical capacity (3579 mAh.g⁻¹). The extra capacity in addition to the reversible one is ascribed to parasitic reactions involving electrolyte salt and solvents degradation due to electrons and lithium ions consumption. Corresponding values for irreversible capacities are given in Table 2 and discussed below. The phosphonium and pyrrolidinium-based electrolytes show remarkable performance compared to the organic carbonates both in terms of specific capacities and in terms of cycle life. As expected[27], the carbonates demonstrate very poor electrochemical behaviour as the capacity drops almost immediately upon cycling particularly for LP 30. Addition of FEC is expected to improve the performance of the electrode to some extent but the performance is nonetheless inferior compared to those of the ILs. The poor performance of the carbonates is a well known result of electrolyte decomposition that is aggravated at the cycling conditions used, i.e. 50°C, as observed previously by Kerr et al. and supported by FTIR analysis of the electrolytes[27]. Previous studies [37] investigating the behavior of carbonate-based electrolyte with LiFSI concentration up to 5.5M in the case of lithium metal and graphite electrodes at room temperature evidenced an enhanced rate capability. In the case of positive electrode materials, Shakourian-Fard et al.[38] found a stabilization of the solvent through Li⁺ coordination (by increasing the salt concentration). These studies show that stabilizing the solvent's electron lone-pairs leads to a decrease in the electron energy level at the highest occupied molecular orbital (HOMO) states and increases the oxidative stability of the solvents (e.g. stability at high potentials). Very limited studies on Si-based electrodes cycled in concentrated carbonate electrolytes have been performed to this date. Chang et al.[39] demonstrated a capacity retention

of 63.5% after 100 cycles of Si nanoparticles in concentrated LiFSI-polycarbonate (PC) electrolyte with a molar ratio of PC to LiFSI equal to 2 at room temperature. The same group demonstrated a capacity of 2000 mAhg^{-1} after 100 cycles with an initial capacity of 3300 mAhg^{-1} , in a concentrated dual salt electrolyte composed of LiFSI and LiDFOB (lithium difluoro(oxalato)borate) in PC, also at room temperature.[40] Even though these various electrolytes cannot be compared directly to those investigated here, we can expect the continuous degradation of carbonate –based electrolytes in contact with the silicon surface to still occur and to be exacerbated at 50°C . It is then possible that a slightly longer cycle life could be obtained with highly concentrated LiPF_6 in EC:DMC electrolyte compared to state of the art LP30. The Nyquist plots in Fig. S1 indicate a more blocking interphase in carbonate electrolytes compared to the ILs, in agreement with an extensive degradation of the former leading to a thicker passivating film.

Nevertheless, significant differences in electrochemical behaviour and performance can also be noticed between the two IL-based systems even though they exhibit very similar ionic conductivities, in particular at 50°C (Table S1). The $\text{P}_{1222}\text{FSI}$ -based highly concentrated electrolyte presents excellent capacity retention, i.e. 80%, with a specific capacity of 2830 mAhg^{-1} after 100 cycles, whereas the $\text{C}_3\text{mpyrFSI}$ -based highly concentrated electrolyte exhibits a slightly lower capacity retention until about 60 cycles before a rapid fading of the capacity down to 1160 mAhg^{-1} after 100 cycles. The behaviour of the pyrrolidinium system indicates that highly concentrated electrolytes are not necessarily entirely beneficial for Si-based electrodes for long-term cycling. In particular, the nature of the IL cation seems to play an important role since the other parameters (salt nature, salt concentration, temperature and cycling conditions) are strictly identical. Moreover, the differential capacity profile of the Si electrodes after the first

cycle in the IL and carbonate electrolytes (Fig. S2) confirm the expected phase transformation of Si during lithiation/delithiation in all cases. A similar behaviour of the two IL electrolytes is also observed in the beginning of cycling (Fig. 1 and S3). This suggests that the rapid loss of capacity of Si electrodes cycled in the pyrrolidinium system may be linked to its degradation which could have an effect on its intrinsic transport properties, or on the formation of a more blocking SEI, or both, after extended cycling. The impedance analysis in Fig. S1 gives a hint on the SEI characteristic wherein a slight difference in the Nyquist plot of the electrodes cycled in the two IL electrolytes is noticeable after 100 cycles. It shows that the interphase of the Si electrode cycled in pyrrolidinium electrolyte may include an additional component, stemming from IL degradation, compared to the phosphonium one, as indicated by the presence of a more pronounced second semi-circle appearing at low frequencies in the Nyquist plot of the former after an extended cycling.

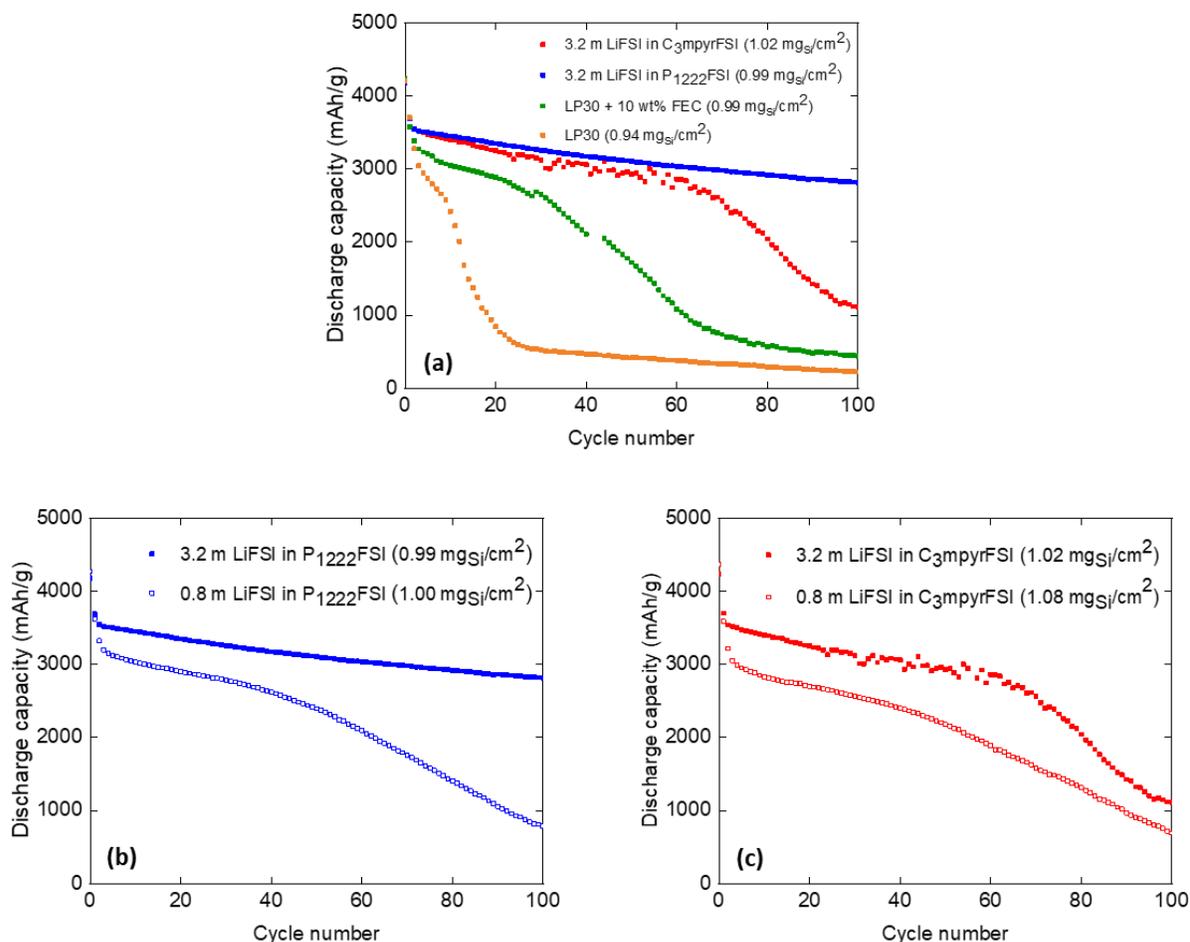


Figure 1. a) Comparison of the electrochemical behaviour of Si negative electrode at 50°C in high-salt concentration ionic liquid electrolytes vs. state-of-the-art organic carbonate electrolytes and effect of salt concentration on the electrochemical performance of Si negative electrode in b) phosphonium system and c) pyrrolidinium system. Voltage profiles corresponding to the 1st and 10th lithiation for the phosphonium and pyrrolidinium system at both concentration are given in

Figure S3.

In the following, we investigate the behaviour and properties of bulk pyrrolidinium and phosphonium-based electrolytes in order to determine the factors ruling intrinsic properties such as transport properties and stability upon cycling. Exploring the concentration of salt in the IL-based electrolytes, it appears that regardless of the nature of the IL cation, Figs. 1b and 1c show

that higher capacity and better capacity retention are obtained for Si electrodes cycled using an IL electrolyte at 3.2 m LiFSI compared to 0.8 m LiFSI. Such a difference cannot be explained by differences in conductivities (for instance, 0.82 mScm⁻¹ and 3.40 mScm⁻¹ for C₃mpyrFSI for 3.2 m LiFSI and 0.8 m LiFSI, respectively). The lower salt concentration electrolytes give a capacity retention of 79% and 75% after 40 cycles and begin to suffer from huge capacity loss reaching about 800 mAhg⁻¹ and 720 mAh g⁻¹ after 100 cycles for P₁₂₂₂FSI and C₃mpyrFSI, respectively. Si electrodes cycled in phosphonium- and pyrrolidinium-based electrolytes have similar behaviour at low salt concentration, suggesting the same failure mechanism whereas at high salt content, the cells cycled with the two different IL electrolytes exhibit clearly different behaviours with an enhanced cycle life and long-term capacity retention for the one using the phosphonium system. The first irreversible capacity loss for Si electrodes cycled in the studied electrolytes are also presented in Table 1 for comparison. It suggests that more electrolyte is consumed in parasitic reaction leading to the formation of more SEI for C₃mpyrFSI compared to P₁₂₂₂FSI, and for the low salt-content systems in both electrolytes. It appears at this point that both salt content and nature of the IL influence the specific capacity and cycle life. Previous efforts to understand the electrochemical performance of IL electrolytes linked the observed enhanced cycling stability to the formation of a SEI, possessing good mechanical robustness while also allowing fast Li⁺ diffusion.[41] Moreover, in an earlier study on Si negative electrode with 3.2 m LiFSI in P₁₁₁₄FSI, Kerr et al. [27] suggested the formation of a stable SEI based on SEM images which keeps the Si electrode intact upon cycling, resulting in excellent cycling stability at 50°C. With the same IL electrolyte cycled in symmetric cells using Li metal electrodes, Girard et al.[42] also found that more concentrated systems promote a more stable and uniform SEI based on SEM and spectroscopic analysis, allowing prolonged and efficient Li metal cycling. Nevertheless,

intrinsic transport properties and IL stability, influenced by the salt content and the nature of the IL, are two factors that could also yield such behaviour. In particular, the formation of a different SEI, depending on either the nature or the salt content of the IL electrolyte, implies also a different degradation process of the IL electrolyte itself. This is expected to lead to significant differences in the bulk properties of the electrolyte. The results obtained in the present work suggest therefore a more complex interplay of factors such as electrolyte stability and electrolyte transport properties, beyond the simple formation of an enhanced SEI inherent to the IL nature of the electrolyte solvents.

Table 1. First total and irreversible capacities in each electrolyte system at 50°C with corresponding coulombic efficiencies

Salt Content	IL/Solvent	1 st Total Capacity (mAhg ⁻¹)	1 st Irreversible Capacity (mAhg ⁻¹)	1 st Cycle Coulombic Efficiency (%)
3.2 m	C ₃ mpyrFSI	4240	610	86
LiFSI	P ₁₂₂₂ FSI	4180	535	87
0.8 m	C ₃ mpyrFSI	4370	750	83
LiFSI	P ₁₂₂₂ FSI	4275	655	85

In a first step, in order to better grasp the influence of electrolyte intrinsic properties on the resulting electrochemical performance and behaviour of Si electrodes as a function of the nature of the IL cation, rate capability tests are performed as a way of investigating the ease of ion transport towards the electrode. Tests were performed both at 50°C, which is the temperature of interest for the present study and at 25°C to exacerbate possible differences between the pyrrolidinium- and phosphonium-based electrolytes. As shown in Figs. 2a and 2b, the behaviour of the phosphonium and the pyrrolidinium highly concentrated electrolytes is closely related, in agreement with comparable pristine ionic conductivities both at 25°C and 50°C (Table S1). At

50°C, excellent rate performance is achieved in both systems. The gradual decrease in the capacity appears to be the result of the effects of Si volume expansion, identified by the Si anode research community as the primary cause of capacity fading in Si-based negative electrodes, and not a consequence of kinetic limitations as one would expect with the inherently viscous ILs. However, poor rate capabilities are observed at 25°C for the Si electrodes cycled in the two different IL systems as the C-rate is increased from C/10 to C. It seems reasonable to see this overall behaviour as a consequence of higher viscosity especially of high salt concentration systems at this temperature, resulting in the slower diffusion of ions.

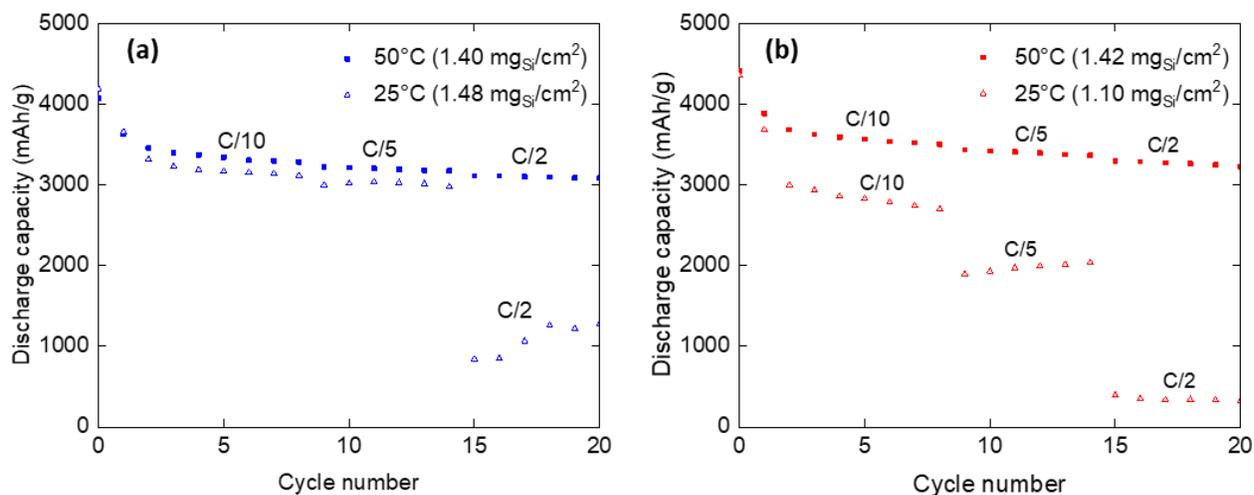


Figure 2. Rate capability of Si electrodes at 25°C and 50°C in a) P₁₂₂₂FSI with 3.2 m LiFSI and b) C₃mpyrFSI with 3.2 m LiFSI

Nevertheless, a closer look at Figs. 2a and 2b suggests that the phosphonium-based IL may be able to sustain higher cycling rate than the pyrrolidinium system. This is particularly exacerbated and thus visible at 25°C; significant capacity drops are indeed observed from the C/10 to C/5 rate as well as from C/5 to C/2 rate in the case of the pyrrolidinium system. Such a capacity drop is only observed from C/5 to C/2 rate in the case of the phosphonium system. Recently, an

increasing number of studies reported promising behaviour of phosphonium-based ILs[24,27,34,43] in highly concentrated systems, in part due to improved transport properties compared to the analogous ammonium derivatives. The difference in the performance of the phosphonium and pyrrolidinium-based electrolytes may also be a consequence of the enhanced transport properties of the former.[24,44] The transport of the ions in these electrolytes is therefore investigated, by PFG-NMR, in the following section.

Diffusivity of Ions by PFG-NMR

Self-diffusion coefficients

Good transport properties, and in particular high Li ion diffusivity, are key to good device performance. The diffusivity of the ions in P₁₂₂₂FSI and C₃mpyrFSI-based electrolytes were measured from 20°C to 80°C and are displayed in Fig. S4, [Table S2](#) and [Table S3](#). The diffusivity of the ions at 50°C in the pyrrolidinium and phosphonium-based IL electrolytes for the two different LiFSI salt concentrations (0.8 and 3.2 m) are presented in Fig. 3. As expected, ion diffusivities are much lower at high salt concentration compared to their low concentration counterparts. This behaviour is attributed to the higher viscosity inherent to the drastic increase of salt content in the IL.[34] An interesting behaviour of Li⁺ diffusivity as a function of the nature of the IL cation as well as the salt content can be noticed. For the phosphonium electrolyte, the self-diffusion coefficient (D) of Li⁺ exceeds that of the IL cation at 3.2 m LiFSI at 50°C. This inversion of the diffusivity of the ions has been previously reported by Girard et al.[34] where $D_{\text{Li}^+} > D_{\text{H}}^1$ or D_{IL}^+ was observed above 2.0 m LiFSI in P₁₁₁₄FSI at 22°C. The faster diffusion of the Li ions relative to the IL cation was claimed to be a result of structural rearrangement as the salt content is increased[45], ultimately leading to a change in the transport mechanism of the Li ions, going from a vehicular transport mechanism to an alkali metal (here

Li^+) cation hopping mechanism. In this case, the transport of Li ions occurs through ion-exchange or rearrangement of the Li coordination environment which assists Li ion hopping across the more interconnected network. This is in contrast to a vehicular-type mechanism that is commonly observed at low salt concentration systems where smaller, unconnected ion aggregates are more likely present along with pairs and triplets. It is also worth mentioning that the size and coordination shell of Li^+ are known to have a major influence on the transport properties of Li^+ in LiX-IL systems, X referring to the anion.[46] In Fig. 3b at low salt content, D_{Li^+} is significantly lower than that of the IL cation for both the phosphonium and the pyrrolidinium. The lower diffusivity of Li^+ compared to the IL cation is often linked to a strong association between the Li^+ cations and the IL anions in many IL electrolyte systems, in agreement with a vehicular mechanism[47]. In this case, IL cations diffuse faster than Li ions. This somewhat less efficient, vehicular Li^+ ion diffusivity is in agreement with the lower corresponding electrochemical performance at low salt content for both phosphonium and pyrrolidinium-based electrolytes (Fig. 1b and c).

The case of pyrrolidinium electrolyte with high Li salt content appears more complex to interpret and somehow intermediate between the cases of low salt content electrolytes on the one hand and phosphonium-based electrolyte at high salt content on the other hand. This intermediate behaviour might nevertheless be linked to the electrochemical performance, which also appears to be intermediate, both in terms of cycle life and in terms of specific capacity. Although D_{Li^+} remains slightly lower than that of the IL cation at 50°C , the values obtained for D_{Li^+} , D_{H}^1 and D_{F}^{19} are all lower than those measured in the case of the low salt content electrolytes and of the same order of magnitude as those measured for the phosphonium-based electrolyte at high salt content (Fig. 3). In this case it is also likely that a hopping/exchange mechanism contributes to

the overall Li^+ ion diffusivity. Moreover, the self-diffusion coefficient of the Li^+ and FSI at 50°C is identical and equal to $1.3 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ and $1.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ for $\text{P}_{1222}\text{FSI}$ and $\text{C}_3\text{mpyrFSI}$ containing 3.2 m LiFSI , respectively. These identical diffusivity values for Li^+ and FSI anion at high salt concentration, strongly suggest the presence of an interconnected network in both cases. We confirm this hopping mechanism in the next paragraph dealing with diffusivity ratio analyses.

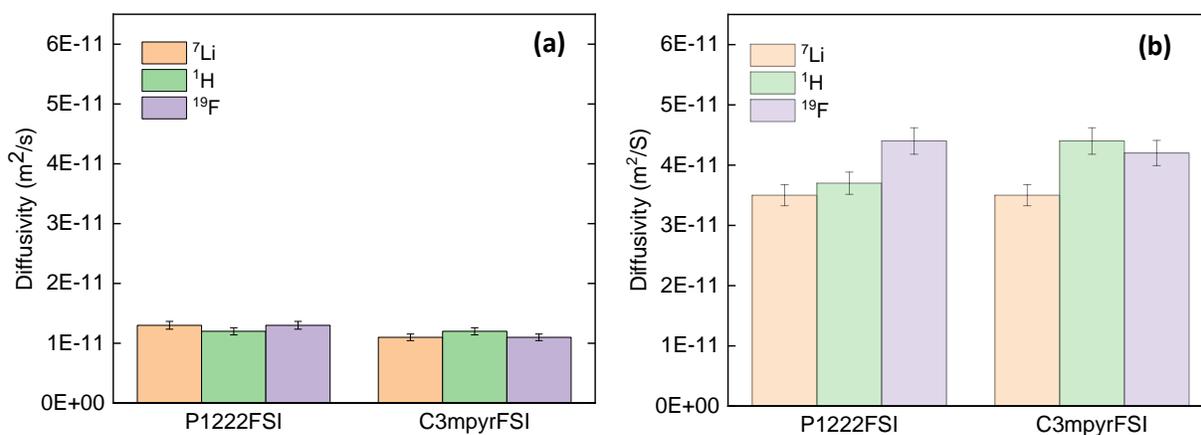


Figure 3. Diffusivity of the ions in $\text{P}_{1222}\text{FSI}$ and $\text{C}_3\text{mpyrFSI}$ with a) 3.2 m LiFSI and b) 0.8 m LiFSI as measured by PFG-NMR at 50°C

Diffusivity ratios

The results discussed above implied a hopping/exchange, and more efficient, transport mechanism for Li^+ in the high salt concentration electrolyte in the phosphonium system but left some uncertainties as to what mechanism controls the transport of Li^+ in the high salt concentration electrolyte in the pyrrolidinium system. PFG-NMR data can also be used to estimate the apparent transport number [36,48], herein referred to as the diffusivity ratio. The diffusivity ratios of the ions are calculated using the equation below.

$$D_{ratio,i} = \frac{x_i D_i}{\sum_i x_i D_i} \quad (1)$$

$D_{ratio,i}$ corresponds to the diffusivity of ion i with respect to all the ions in the electrolyte, x_i the molar fraction of ion i and D the self-diffusion coefficient of ion i in m^2s^{-1} . A summary of the apparent transport number of Li^+ in the electrolytes investigated is presented in Table 2. There is a notable increase in the diffusivity ratio at 3.2 m LiFSI compared to the ILs with 0.8 m Li salt for both ILs. Higher diffusivity ratios have also been previously reported [24] for highly concentrated systems and correlated with a hopping/exchange mechanism. The significantly higher values obtained here at 3.2 m LiFSI support unambiguously a change in the transport mechanism of the Li ions, not only for the phosphonium system but also for the pyrrolidinium one. The differences observed here for highly concentrated electrolytes correlate well with the higher capacities obtained during the early stages (below 60 cycles) of cycling for the phosphonium and pyrrolidinium-based electrolytes with a 3.2 m LiFSI concentration with respect to their lower concentration respective counterparts.

Moreover, while the values may not be significantly different, it is worth mentioning that the diffusivity ratio seems to be slightly higher in the phosphonium system than in the pyrrolidinium one at the two salt concentrations. This is consistent with the better electrochemical performance obtained for the Si electrodes cycled below 60 cycles with phosphonium-based electrolyte at both concentrations.

Table 2. Diffusivity ratio of Li⁺ with respect to all the ions in the electrolyte at 50°C

	0.8 m LiFSI	3.2 m LiFSI
C ₃ mpyrFSI	0.08 ± 0.01	0.25 ± 0.01
P ₁₂₂₂ FSI	0.09 ± 0.01	0.26 ± 0.01

To conclude on the bulk properties of the studied electrolytes, the change in transport mechanism and increased Li ion transport number seems to have an important impact on the observed specific capacities below 60 cycles for the Si electrodes cycled in highly concentrated electrolytes. Moreover, the higher diffusivity of Li⁺ ($5.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 25°C and $1.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 50°C) vs. P₁₂₂₂⁺ ($4.7 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 25°C and $1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at 50°C), as extracted from PFG-NMR self-diffusion coefficients measurements in the case of the highly concentrated phosphonium system seems to be linked to the slightly better specific capacity (Fig. 1a) as well as its better rate capability at 25°C (Fig. 2) compared to its pyrrolidinium counterpart.

In addition, a more efficient transport mechanism for Li⁺ ions seems to be obtained at moderately elevated temperature (50°C) and high salt concentrations for both P_{111i4} (from a previous work [27]) and P₁₂₂₂ (this work) phosphonium-based electrolytes compared to pyrrolidinium-based electrolytes. It suggests that this behaviour may be extended to other phosphonium-based electrolytes and could predict the better performance obtained for Si electrodes cycled with phosphonium-based vs pyrrolidinium-based electrolytes, at least below 60 cycles.

Nevertheless, the bulk properties alone cannot explain the different capacity fadings that are observed for Si electrodes cycled in the electrolytes studied here. What happens to the IL components upon reaching the electrode is equally relevant to understanding the electrochemical

behaviour. Hence, the succeeding sections present an investigation of the electrochemical stability after long-term cycling of the phosphonium and pyrrolidinium-based electrolytes upon contact with a Si negative electrode.

Ionic Liquid Stability

Phosphonium Cation Stability

^{31}P MAS-NMR appears as an appropriate technique to probe the stability of the phosphonium-based IL at the Si surface. Please note here that the electrodes were not rinsed neither with carbonate solvents nor with pure P₁₂₂₂FSI IL as it is typically done in most of the works dealing with *ex situ* characterization of cycled electrodes. First of all, we chose not to rinse the electrodes with carbonates to avoid introducing new chemical species that could alter or modify products formed from the degradation of the IL electrolyte upon cycling. In addition, it is then also possible to detect at the same time degradation species precipitating on the surface of the Si particles as well as soluble species present in the remaining IL electrolytes impregnating the sample. The spectrum in Fig. 4a demonstrates the stability of the phosphonium cation of the IL with 3.2 m LiFSI after 100 cycles, as it shows only the peak for residual electrolyte on the electrode which appears as a strong peak at 35 ppm. The different peaks around 35 ppm correspond to the non-degraded phosphonium cation with different interaction with the electrode or the SEI. The sharp resonance corresponds to a liquid-like environment whereas the broad resonance represents less free or trapped species. The stability of phosphonium cation is confirmed by XPS analysis using P 2p edge spectra wherein no decomposition product of the phosphonium cation is found (not shown). Even with the strongly reducing Li negative electrode, Girard et al.[42] reported no phosphonium cation breakdown products in the SEI as investigated by MAS-NMR, XPS, and FTIR. This result is in agreement with the stability of **the same**

phosphonium cation in high salt concentration electrolyte systems in contact with the very reducing Li metal surface [43]. However, the low salt content system exhibits some signs of degradation. The resonance peaks at 66 ppm and 46 ppm in Fig. 4b correspond to breakdown products of P_{1222}^+ which are tentatively assigned to $S=PR_3$ and $O=PR_3$ -containing groups [49], based on the observed chemical shift. S 2p and O 1s XPS analyses also provide evidence of sulfur and oxygen-containing decomposition products (Fig. S5). These products may then participate in some reactions with the phosphonium cation to form $S=PR_3$ and $O=PR_3$ compounds although the reaction mechanism(s) is not clear at the moment and needs further investigation. This result sheds a new light on understanding the failure mechanism of batteries using this family of IL since it is the first time that the breakdown for any phosphonium cation used in LiBs has been reported. Furthermore, accompanying the breakdown of the IL cation is the degradation of the FSI anion as observed using ^{19}F NMR. The resonance corresponding to LiF, appearing at -205 ppm is clearly visible on ^{19}F MAS NMR spectra (Fig. S7).

In the high salt concentration system, the Li-FSI complexes are more likely to be available at the Si electrode interface and these may be more susceptible to breakdown than the phosphonium cation. Alternatively, the phosphonium cation may be expelled from the inner electrolyte/electrode interface layer to some extent, decreasing the concentration and hence availability for breakdown, as has been recently suggested in the case of high salt concentration IL electrolytes[25,50]. In this case, the SEI is expected to be mostly composed of breakdown products from the FSI anion although the possibility of some non-degraded phosphonium cations trapped in the SEI cannot be ruled out. On the contrary, for the electrolyte with low salt content, the IL cation is more exposed as they may dominate the inner electrolyte/electrode interface layer and hence there are less FSI⁻ and Li⁺ ions available to take part in the formation of

the passivation layer on the Si surface. MD simulations have been initiated to further investigate the presence and interaction of IL ions at the interface between the Si negative electrode and the electrolyte and will be the topic of a forthcoming paper.

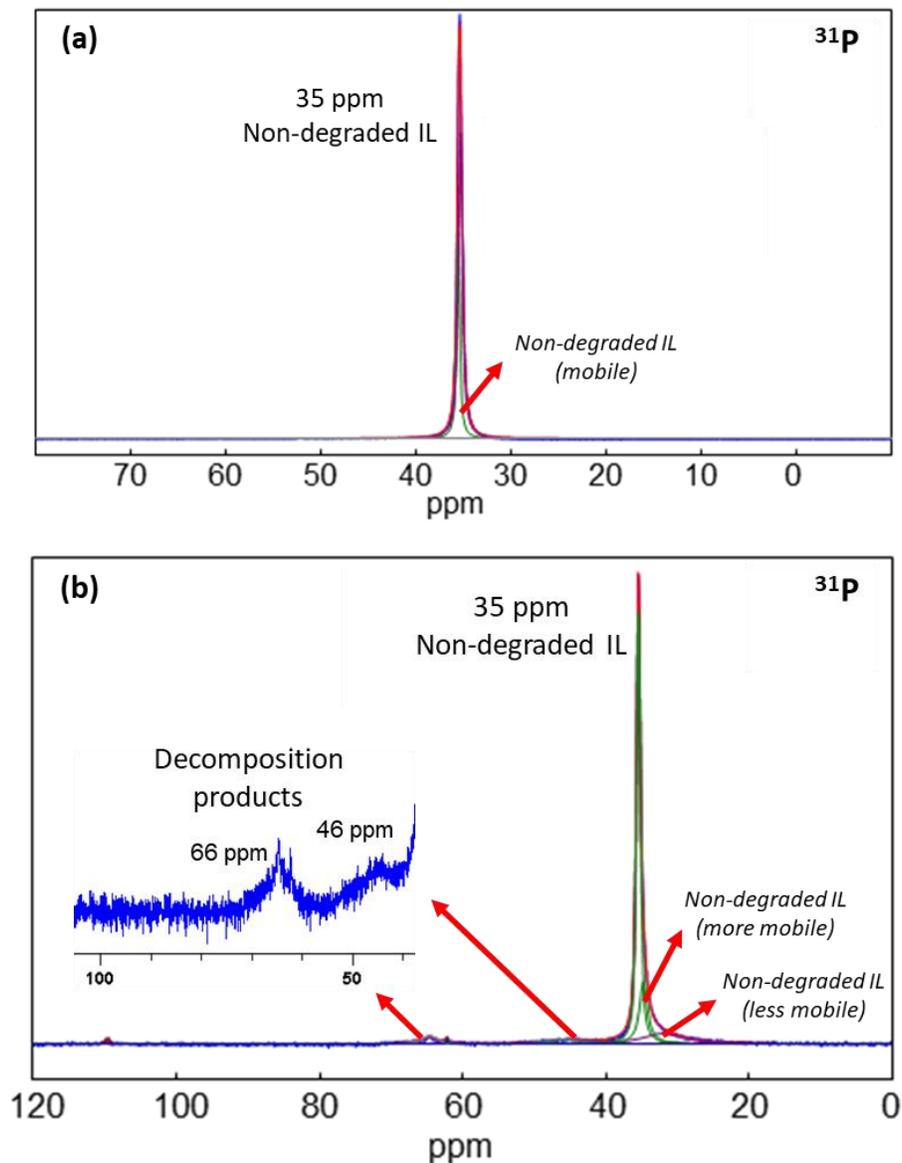


Figure 4. ^{31}P NMR spectra of Si negative electrode after 100 cycles at 50°C in P₁₂₂₂FSI with a) 3.2 m LiFSI and b) 0.8 m LiFSI

Pyrrolidinium Cation Stability

In the case of the pyrrolidinium-based electrolyte, XPS analysis was preferred to MAS NMR to investigate the stability of the $C_3\text{mpyr}^+$ cation since the detection of low level ^{15}N nuclei that may be present can be quite challenging or at least extremely time consuming without ^{15}N -enriched $C_3\text{mpyr}^+$ cations. Fig. 5 displays the XPS N 1s spectra of Si negative electrode after 100 cycles at 50°C in $C_3\text{mpyrFSI}$ with (a) 3.2 m LiFSI and (b) 0.8 m LiFSI. The peaks appearing at binding energies of 403 and 400 eV correspond to non-degraded $C_3\text{mpyr}^+$ cation (N^+) and non-degraded FSI anion (N^-), respectively. FSI and $C_3\text{mpyr}^+$ degradation products appear as minor species at lower binding energies (398 eV and 401 eV, respectively) with respect to the main component. Although it is difficult to determine the precise compounds formed based only on XPS binding energies, previous studies proposed the formation of NS_xO_y species from the breaking of S-C bonds in FSI (NH_2SO_3^-) or in TFSI (NSO_2 , NS_2O_4^-) in the case of cycling using graphite or Si electrodes.[51,52] The breakdown of the pyrrolidinium cation has also been previously reported upon contact and cycling with Li electrode.[53,54]

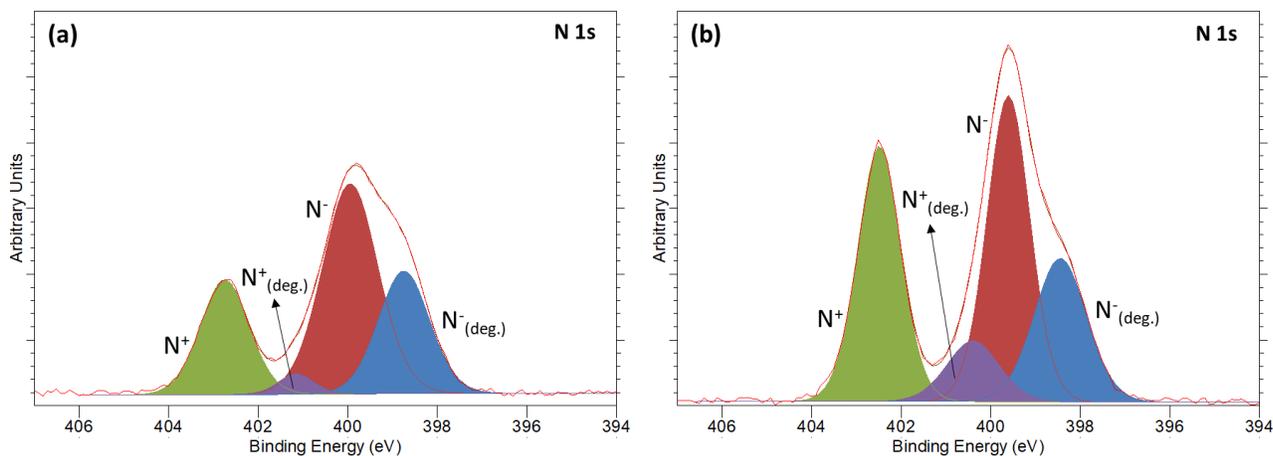


Figure 5. XPS N 1s spectra of the Si electrode after 100 cycles at 50°C in $C_3\text{mpyrFSI}$ with a) 3.2 m LiFSI and b) 0.8 m LiFSI

In this study, the amount of the degraded component of the pyrrolidinium cation is found to be higher for the IL with 0.8 m LiFSI (0.19) compared to that with 3.2 m LiFSI (0.05). However, Basile et al.[54] reports that an increased amount of FSI⁻ promotes the decomposition of the cation to propyl pyrrolidine. To have a closer look at the amount of decomposition products as a function of salt content, an electrolyte containing 1.6 m LiFSI was prepared and used in cycling the negative electrode under the same conditions. Based on N 1s XPS, we found that increasing the amount of LiFSI from 0.8 m to 1.6 m leads to a slight increase in the amount of cation breakdown products from 0.19 to 0.20 arbitrary unit based on the quantity of degraded C₃mpyr⁺ normalized with respect to degraded anion, which then decreases to 0.05 when the salt content is increased to 3.2 m LiFSI. This implies the existence of a concentration threshold beyond which the cation starts to be stabilized. A summary of the breakdown product quantification is presented in Table 3.

Table 3. Quantity of degraded C₃mpyr⁺ normalized with respect to degraded anion

Salt Content	Amount of degraded C ₃ mpyr ⁺
0.8 m	0.19
1.6 m	0.20
3.2 m	0.05

Quantification of FSI Anion Degradation

As observed in the two previous sections concerning the degradation of IL C₃mpyr⁺ and P₁₂₂₂⁺ cations, the FSI⁻ anions degradation is also detected upon cycling. This has been previously reported, along the major contribution of FSI⁻ anion fragments to various species making up the SEI.[42] FSI⁻ tends to react readily upon contact with a highly reducing negative electrode and several reduction pathways have been proposed concerning the breakdown of FSI and TFSI-

based electrolytes.[53,55] In this last section, we investigate the extent of the FSI⁻ anion degradation as a function of the nature of the IL cation and the Li salt concentration. The relative atomic concentration of the non-degraded FSI⁻ anion and its degradation products were estimated from S 2p and F 1s XPS (Figs. S5 and S6) spectra and are presented in Fig. 6 for comparison. F 1s XPS only shows LiF as a decomposition product of the anion while the S 2p spectra show a mixture of degradation products assigned to oxidized sulfur species such as sulfone, sulfite, -SO₂F groups, and Li₂S [42,53,56]. The results from both F 1s and S 2p analyses highlight the greater stability of the FSI⁻ anion in the phosphonium-based IL electrolyte and particularly at 3.2 m LiFSI. On the other hand, in the case of pyrrolidinium-based IL electrolyte, the extent of FSI⁻ degradation is i) larger compared to the phosphonium system and ii) almost the same regardless of the salt concentration. These results show that the degree of anion degradation is strongly influenced by the nature of the IL cation and the Li salt concentration and does not depend only on the presence of a strongly reducing surface such as that of Si particles.

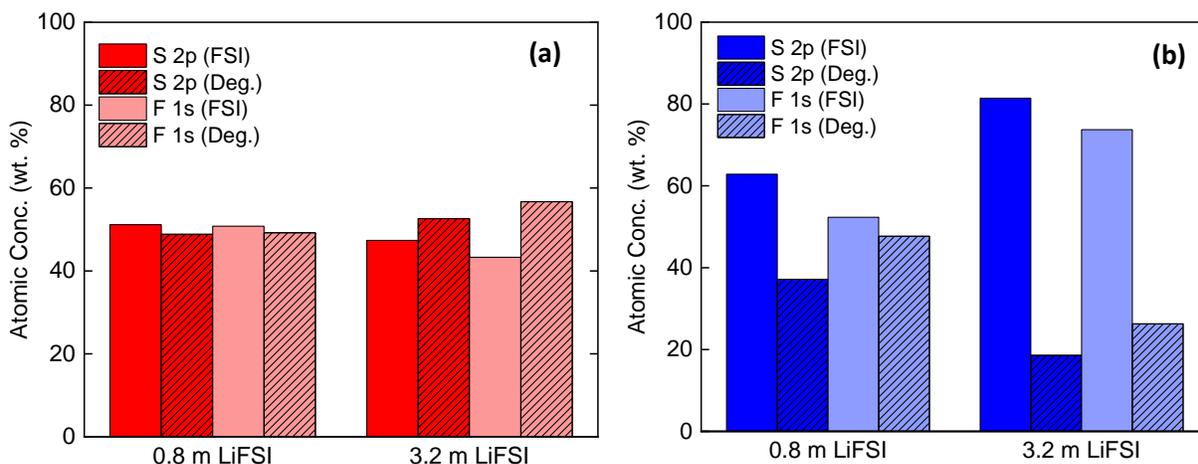


Figure 6. Relative amount of degraded and non-degraded FSI from the electrodes cycled in a) C₃mpyrFSI and b) P₁₂₂₂FSI system as estimated from S 2p and F 1s XPS after 100 cycles at 50°C

Overall, these observations on IL electrolyte components stability support the electrochemical behaviour of the Si electrode cycled as a function of the nature of the IL cation and the Li salt concentration. The good electrochemical stability of Si electrodes cycled in highly concentrated phosphonium-based electrolyte is associated with good electrolyte stability, e.g. limited degradation of FSI⁻ anions compared to all other electrolytes studied here as well as absence of P₁₂₂₂⁺ cations degradation. The phosphonium system starts to suffer from degradation at low salt concentration only. The capacity fading observed in the pyrrolidinium system appears to be related to a significant degradation of the C₃mpyr⁺ cation and an amplified degradation of FSI⁻ anion upon cycling compared to the phosphonium system. At 0.8 m LiFSI concentration, although exhibiting a slightly higher specific capacity due to enhanced transport properties, the overall behaviour of the phosphonium-based electrolyte is very similar to that of the pyrrolidinium-based electrolytes. While for both electrolytes at 0.8 m salt content a significant degradation of FSI⁻ anions is observed, P₁₂₂₂⁺ cations show only traces of degradation products and C₃mpyr⁺ cations are significantly degraded. It indicates that, for low salt concentration, issues linked to the stability of the FSI⁻ anions become dominant regardless of the lower degradation extent of P₁₂₂₂⁺ vs C₃mpyr⁺. It seems that the intermediate behaviour in terms of cycle life, for Si electrodes cycled in the 3.2m LiFSI in C₃mpyrFSI electrolyte is due to a significant degradation of FSI⁻ anions forming a favorable SEI layer balanced by i) a hindered degradation of C₃mpyr⁺ cations compared to the 0.8 m LiFSI concentration electrolyte and ii) an exacerbated degradation of the C₃mpyr⁺ cations compared to P₁₂₂₂⁺ cations at 3.2 m salt content. **Figure 7 summarizes the results obtained in this work with the different factors ruling the electrochemical behaviours of the investigated system as a function of salt concentration, nature of IL cation, and number of cycles.** Further study is nevertheless needed to determine if the

complex electrolyte components degradation is influenced only by the bulk properties of the electrolyte or also the composition and structure of the electrolyte and the resultant SEI at the surface of Si particles.

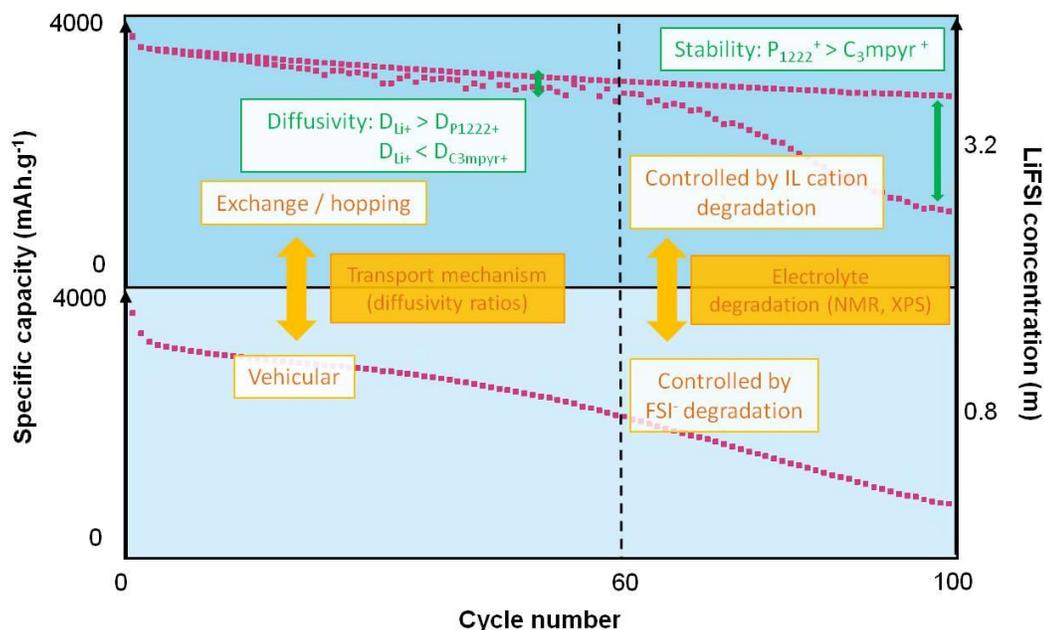


Figure 7. Factors dominating the electrochemical behaviours of silicon electrodes cycled in half-cell configuration with the IL-based electrolytes investigated in this work, as a function of salt content, IL cation nature and number of cycles.

Demonstrating Full-cell Performance of Si Negative Electrode in the best IL Electrolyte

The electrochemical behaviour of Si negative electrode was investigated in full cell configuration using the highly concentrated P₁₂₂₂FSI-LiFSI optimum electrolyte and a high voltage NCA cathode at a rate of C/5 at 50°C. Fig. 8 shows that the initial capacity of the Si/NCA cell is more than 3000 mAh/g of Si, not far from full lithiation. The capacity retention after 100 cycles is

excellent for the chosen high temperature of 50°C, with still 1800 mAh/g, almost 60% of the initial value. The capacity decay on cycling is faster than that measured in Si half cells, in agreement with the aging mechanism being different in full cell vs. half-cell [9,57,58]. In short, this difference possibly comes from a depletion of cyclable lithium due to the continuous reduction of the electrolyte components at the Si surface at each cycle, leading to an internal continuous imbalance of the cell. Nevertheless, it is also possible that the oxidation stability of IL cation becomes an issue considering the oxidative surface of the positive electrode material. In this case, the faster capacity decay in Si/NCA full-cell than in Li half-cell could be due to the oxidative decomposition of the phosphonium cations and a chemical oxidation by the oxygen released from NCA at high SOC cannot be ruled out. However, the average capacity decay per cycle is still only double of that measured for Si in the half cell (see Fig. 1) [9,57,58], which suggests well-controlled parasitic reactions at Si surface with low irreversible capacity at each cycle in the concentrated P₁₂₂₂FSI-LiFSI electrolyte. Further characterization of the SEI on both positive and negative electrodes, as well as a thorough study of the stability of IL cations in full cell configuration is needed. Nevertheless, the excellent preliminary cycling results shown here indicate the possible use of Si in commercial batteries with improved IL electrolytes.

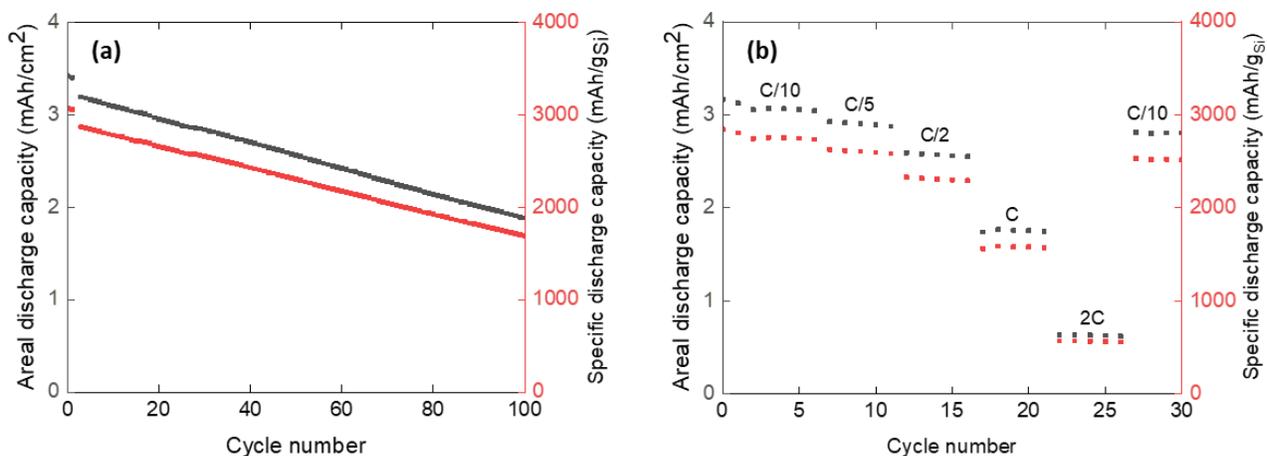


Figure 8. Full cell a) long-term behaviour at C/5 rate and b) rate capability performance of Si negative electrode with NCA cathode at 50°C in P₁₂₂₂FSI with 3.2 m LiFSI

Fig.8b shows the full cell rate capability performance of Si in the chosen IL electrolyte. As expected, the specific capacity is progressively decreasing as the cycling rate is increased, even though approximately 80% of the initial capacity obtained at C/10 is still measured at C/2. The capacity drops more severely at higher rates. Nevertheless, when back at a C/10 rate, a specific capacity comparable to that obtained firstly at C/10 during early stages of cycling is retrieved. This indicates that neither the electrode nor the active materials have suffered from high-rate cycling. The slightly lower capacity compared to the initial C/10 cycles is in agreement with the capacity fading observed in Fig. 8a at a C/5 rate.

Conclusions

The electrochemical behaviour of Si negative electrodes in P₁₂₂₂FSI and C₃mpyrFSI ILs with high and low amount of LiFSI salt was investigated at 50°C. Organic carbonate electrolytes also used for comparison showed very poor performance at this temperature, as expected. Whatever the salt concentration, both IL electrolytes displayed better performance than carbonate analogues, clearly showing the superiority of selected ILs in this temperature range. However, the capacity and cyclability levels depended strongly on the IL composition. Our results show that the difference in performance can be explained from both bulk IL electrolytes transport properties measured from PFG measurements, and electrochemical decomposition of the IL components at the Si surface characterized from NMR and XPS analyses.

We found that high Li content IL electrolytes exhibit much higher capacity and slightly better cyclability than their low content counterpart at first 60 cycles. Such behaviour is consistent with

their much higher transport number by a factor of 3, coming from a change of the Li ion transport mechanism from vehicular to hopping, and leading to more efficient ion transfer in the cell. Phosphonium systems at high salt content present slightly better cyclability than pyrrodiminium ones, in agreement with their slightly higher apparent transport number higher Li cation diffusivity.

While phosphonium and pyrrodiminium systems at high salt content exhibit quite similar capacity retention at low cycle number, a catastrophic capacity loss on cycling is observed for C₃mpyrFSI-based electrolyte above 60 cycles. Since the much better long-term cyclability of P₁₂₂₂FSI system above 60 cycles cannot be explained by the similar transport properties in both high salt content electrolytes, their stability on Si after 100 cycles was carefully investigated. A much lower amount of FSI anion degradation products were found for P₁₂₂₂FSI system. In addition, decomposition products of C₃mpyr⁺ cations were easily detected, while no decomposition of P₁₂₂₂⁺ cations was detected at high concentration (though traces of P₁₂₂₂ cation decomposition products were detected for low concentration), which is a very remarkable result. Such higher electrochemical stability of P₁₂₂₂FSI-based IL components is a likely explanation for the excellent long-term cyclability of this high salt content IL electrolyte. The excellent long-term cycling stability of the Si/concentrated P₁₂₂₂FSI-LiFSI encouraged us to evaluate this system in full cell configuration with NCA as the positive electrode. Preliminary results indicate a very promising cyclability at C/5 over 100 cycles as well as a good rate capability up to a rate of C/2.

This study highlights the significance of IL type and salt concentration selection in designing batteries based on Si negative electrodes. We confirm that a highly concentrated IL electrolyte approach works with Si-based electrodes because of the improved transport properties that can

be obtained for high salt concentration. However, although IL and IL-based electrolytes are often considered to be very stable upon battery cycling, their possible decomposition is still a factor to be taken into account. To this point, it is not clear how the degradation of the IL components affects the SEI layer and consequently the cell performance. Hence, a more detailed investigation of the SEI composition and properties is currently underway to further understand how these IL electrolytes interact with a Si negative electrode and affect their electrochemical behaviour.

In short, these results confirm that increasing the salt concentration is a promising strategy that can be extended to various types of ILs, but also that this research direction may have some limitations due to possible IL electrolyte instability with respect to the electrode surface.

Acknowledgements

The authors would like to thank Agence de l'Environnement et de la Maîtrise de l'Énergie (ADEME) and Deakin University for the financial support. **The authors would also like to acknowledge Deakin Advanced Characterisation Facility for the use of NMR spectrometer at Deakin University.**

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