



Inorganic–Organic Ionic Liquid Electrolytes Enabling High Energy-Density Metal Electrodes for Energy Storage



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ABSTRACT

It has recently been shown, in the case of the bis(fluorosulfonyl)amide (FSI) based ionic liquids, that as the concentration of the alkali metal salt (LiFSI or NaFSI) is increased, the alkali metal cation transference number increases, despite an increase in viscosity and decrease in conductivity. At the same time significant enhancements in electrochemical stability and rate performance of devices are also observed. Here we overview some of the recent findings already in the literature and in addition demonstrate the feasibility of stable, high rate room temperature lithium battery cycling in an electrolyte comprised of 60 mol% LiFSI in a trimethyl, isobutyl phosphonium FSI ionic liquid using a high voltage NMC cathode. We also demonstrate that the high rate cycling of lithium and sodium metal in these phosphonium FSI electrolytes leads to a nanostructured anode deposit and a lowering of the interfacial impedance, suggesting a stable SEI layer formation. Finally, we propose a hypothesis that may explain some of the observations thus made, by which the high alkali ion concentration in these mixed electrolyte systems leads to the effective elimination of the mass transport limitations that are chiefly responsible for the formation of dendrites in traditional electrolytes. This work suggests that a new type of ionic liquid consisting of a mixture of metal cations with organic cations can provide a solution to the instability of the reactive alkali metal anodes and hence enable higher energy density technologies.

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1. Introduction

With our ever-increasing push to move away from fossil fuels to cleaner energy sources, there is a need to improve energy storage technologies. In particular, with respect to electrochemical energy storage, safer, longer cycle-life and cost effective technologies need to be developed. In some applications, such as transportation, improved energy density and higher capacity is also critical if EVs are to be a realistic alternative. Higher capacity can be achieved by moving from intercalation electrodes, such as graphite, towards metal electrodes, eg. lithium or sodium and these can be coupled with higher capacity cathodes such as sulphur or air systems.

The use of metal anodes with traditional organic electrolytes, however, is not feasible from the point of view of safety, and also stable, long term cycling is not possible [1–4]. Room Temperature Ionic Liquids (RTILs) based on the bis(trifluoromethanesulfonyl)amide (TFSI) or the bis(fluorosulfonyl)amide (FSI) anions have

recently been of particular interest as alternative electrolytes for lithium rechargeable batteries due to their superior safety properties in opposition to commonly used organic carbonate electrolytes [5–10]. While such ILs have been shown to facilitate efficient cycling of lithium metal, poor cycling performance at higher rates, related to poor transport properties (high viscosity, low ionic conductivity) has mainly prevented them from being used as electrolytes in commercial devices. Thus, the search for lower viscosity, higher conductivity electrolytes has led to the investigation of new ionic liquids [11]. Novel FSI ionic liquids (ILs) based on a phosphonium cation have been reported with promising properties that make them candidates for alternative electrolytes [9,11–13]. These features include improved transport properties and wider electrochemical windows in comparison to the more commonly studied cyclic ammonium-based (eg pyrrolidinium) ILs.

One of the critical factors dictating the cycling performance of a lithium battery is the lithium salt concentration present in the electrolyte. In general an increase in salt concentration leads to an increase in viscosity and decrease in conductivity, but it also

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greatly increases the amount of lithium cations available in the electrolyte. Indeed, highly concentrated electrolytes (>1 M salt concentration in solvent) have only been studied in the last few years [11,14–16]. In 2013, Yoon et al. reported for the first time the cycling performance at room temperature of a Li | LiCoO₂ cell with a solution of up to 3.2 mol kg⁻¹ of lithium salt in an IL electrolyte. The IL used was an ammonium-based IL, *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (C₃mpyrFSI). The cells with the highest salt content IL electrolyte showed better rate capability, even at high C rates (3C and 5C), than that of a cell with an organic electrolyte.

More recently Na metal batteries have been considered as an alternative energy storage technology, with FSI based ionic liquids being demonstrated as suitable electrolytes for sodium metal cycling, in particular at higher concentrations of dissolved NaFSI. Indeed, Ding et al. reported 123 mAh g⁻¹ for a NaCrO₂ cathode using a 25 mol% NaFSI in C₃mpyrFSI electrolyte (at 20 mA g⁻¹ and 363 K). Thus, in both Na and Li cases, these high alkali salt concentration ionic liquid electrolytes present unique properties that lead to long term stable and efficient cycling.

High concentration electrolytes such as these can be considered as a new dimension in ionic liquids research whereby the alkali salt concentrations can be more than 50 mol% and lead to speciation and structures which alter the basic ion transport mechanisms and perhaps decouple the alkali ion transport from vehicular transport. These mixed inorganic-organic cation ionic liquid electrolytes may also present a unique interface between the electrolyte and the reactive metal anode which influences its dissolution and deposition processes. In this paper, we summarise some of the transport and physicochemical properties of mixtures of ionic liquids with LiFSI and NaFSI salts and demonstrate effective cycling of alkali metal anodes in these metal cation/phosphonium cation based FSI ionic liquids.

2. Experimental

Given that this article attempts to bring together already published work as well as highlighting some very recent, as yet unpublished data, it was considered appropriate to provide a detailed methodology section in the supplementary information. Here we briefly outline the nature of the experiments discussed. Ionic conductivity of the ionic liquid electrolytes is typically measured using a.c. impedance spectroscopy, as discussed in the references cited herein [11,15]. Vibrational spectroscopy is also used to probe ion speciation as a function of concentration in the LiFSI based ionic liquids using ATR-FTIR techniques. Symmetric cell cycling for both Li and Na cells, to determine the cycling stability in different electrolyte formulations, has been previously described [11,15,17] and is also presented in this paper. The plated and stripped surfaces of both Li and Na are examined using SEM techniques, following careful washing with a dimethyl carbonate (DMC) solvent. Full cell cycling of lithium metal batteries were carried out using a high voltage LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC, L&F Material Co. Ltd) using an Al current collector (Battery use, Hohsen). The charge-discharge tests of the Li cells discussed below were conducted with 4.2–2.75 V cut-off voltages at 0.5C, 1C, 2C and 4C current rates at 25 °C.

3. Results and Discussion

3.1. Conductivity and transport

The effect of LiFSI and NaFSI concentration on the conductivity in FSI ionic liquids is summarised in Fig. 1 from previous literature data [18–20]. This series of electrolytes includes a comparison of the C₃mpyrFSI and trimethylisobutylphosphonium (P₁₁₁₄FSI) ionic

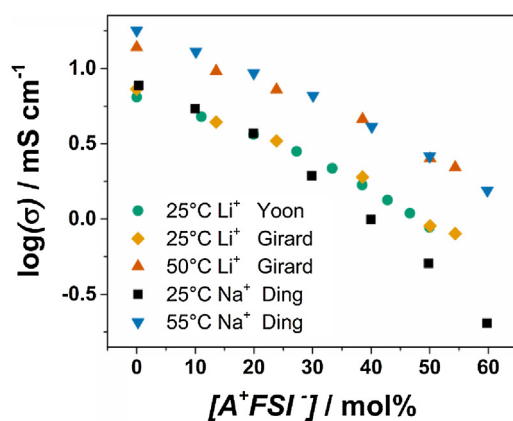


Fig. 1. Comparison of conductivity in LiFSI and NaFSI containing ionic liquid electrolytes as a function of concentration; A⁺ = Li⁺ or Na⁺. Electrolytes include LiFSI in \bullet -C₃mpyrFSI [14], and P₁₁₁₄FSI at \blacklozenge - 25 °C and \blacktriangle - 50 °C. NaFSI in C₃mpyrFSI at \blacksquare - 25 °C and \blacktriangledown - 50 °C [20].

liquids. In all cases the addition of the alkali metal salt decreases the ionic conductivity, however, at the higher concentrations there appears to be little difference between the pyrrolidinium and phosphonium based systems (comparing the Yoon and Girard data at 25 °C). For the most part, the decrease in conductivity reflects an increase in viscosity with increasing alkali metal ion concentration which results from strong coordination of the Li⁺ or Na⁺ ion to the anions and ultimately strong association and clustering, as has previously been reported and is discussed further below [18–20]. Interestingly, at room temperature the Na⁺ ion has a more dramatic effect on reducing conductivity (increasing viscosity) than the Li⁺ ion, likely due to the higher coordination number demanded by the larger Na⁺ cation [21]. At higher temperatures however, the differences appear less pronounced.

Table 1 summarises the viscosity and alkali cation (Li⁺ or Na⁺) transference number measurement as determined using a modified Bruce-Vincent method [22,23] for a series of ionic liquid electrolytes in comparison with a typical organic electrolyte. Most significantly, t⁺ increases substantially with increasing concentration of the Li⁺ ion and approaches 0.5 at 50 mol% and above. In comparison, t⁺ for the organic electrolyte is 0.26. In the case of NaFSI in C₃mpyrFSI, t_{Na⁺} measured both by Yoon et al. and Hagiwara

Table 1

Viscosity and Li/Na transference number of various electrolytes at 25 °C obtained from various literature sources. The organic electrolyte (1 M LiPF₆ in EC-DMC) values are included for comparison.

Electrolyte	η /mPa s ($\pm 10\%$)	t(Li ⁺ /Na ⁺)	Reference
1 M LiPF ₆ -EC-DMC	5.1 (<10)	0.26 \pm 0.07	[25]
Neat P ₁₁₁₄ FSI	41	-	[18]
0.5 mol kg ⁻¹ LiFSI in P ₁₁₁₄ FSI	55	-	[18]
1.0 mol kg ⁻¹ LiFSI in P ₁₁₁₄ FSI	79	0.28 \pm 0.05	[18]
2.0 mol kg ⁻¹ LiFSI in P ₁₁₁₄ FSI	163	0.30 \pm 0.06	[18]
3.2 mol kg ⁻¹ LiFSI in P ₁₁₁₄ FSI	323	0.40 \pm 0.01	[18]
3.8 mol kg ⁻¹ LiFSI in P ₁₁₁₄ FSI	571	0.46 \pm 0.04	[18]
0.7 mol kg ⁻¹ LiFSI in P ₂₂₂₅ TFSI	-	0.44 \pm 0.05	[12]
0.7 mol kg ⁻¹ LiFSI in P ₂₂₂₍₂₀₁₎ TFSI	-	0.54 \pm 0.04	[12]
Neat C ₃ mpyrFSI	33	-	[26,27]
0.8 mol kg ⁻¹ NaFSI in C ₃ mpyrFSI	96	0.01 \pm 0.001	[17,20]
1.4 mol kg ⁻¹ NaFSI in C ₃ mpyrFSI	163	0.07 \pm 0.005	[17,20]
2.2 mol kg ⁻¹ NaFSI in C ₃ mpyrFSI	299	0.19 \pm 0.03	[17,20]
3.2 mol kg ⁻¹ NaFSI in C ₃ mpyrFSI	780	0.31 \pm 0.01	[17,20]
4.0 mol kg ⁻¹ NaFSI in C ₃ mpyrFSI	-	0.32 \pm 0.01	[17]
0.8 mol kg ⁻¹ LiFSI in C ₃ mpyrFSI	49.4	0.11 \pm 0.01	[15,19]
1.6 mol kg ⁻¹ LiFSI in C ₃ mpyrFSI	85.7	0.14 \pm 0.006	[15,19]
2.4 mol kg ⁻¹ LiFSI in C ₃ mpyrFSI	136	0.185 \pm 0.03	[15,19]
3.2 mol kg ⁻¹ LiFSI in C ₃ mpyrFSI	253	0.183 \pm 0.008	[15,19]

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