



## Short communication

## Beneficial effect of added water on sodium metal cycling in super concentrated ionic liquid sodium electrolytes



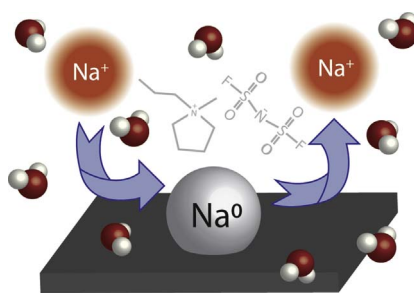
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## HIGHLIGHTS

- Controlled [H<sub>2</sub>O] benefits ionic liquid electrolyte's physicochemical properties.
- Demonstrated Na<sup>0/+</sup> plating/stripping containing large amounts of H<sub>2</sub>O up to 500 ppm.
- H<sub>2</sub>O promotes [FSI]<sup>-</sup> breakdown forming a beneficial Solid-electrolyte interphase.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Keywords:

Room temperature ionic liquid  
Additives  
Sodium metal  
Superconcentrated  
Solid-electrolyte interphase

## ABSTRACT

The plating and stripping performance of sodium metal in an ionic liquid electrolyte is improved when including water as an additive. Herein we report for the first time the trend of improved cycling behavior of Na<sup>0/+</sup> in *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide with 500 ppm H<sub>2</sub>O. The addition of water to this ionic liquid electrolyte promotes the breakdown of the [FSI]<sup>-</sup> anion towards beneficial SEI formation. The benefits during plating and stripping of sodium is observed as lower total polarization during symmetrical cell cycling and decreased electrode/electrolyte interface impedance. Sodium metal surfaces after cycling with 500 ppm H<sub>2</sub>O are shown to be smooth in morphology in comparison to lower additive concentrations. The outcome of adventitious moisture benefiting Na<sup>0/+</sup> cycling in an ionic liquid, contrary to conventional electrolytes, allows flexibility in ionic liquid electrolyte design to the benefit of battery manufacturers.

## 1. Introduction

A global focus towards alternative energy storage technologies has recently seen the 'beyond lithium' research area drastically expand. This is due to several drawbacks expected for future lithium ion technologies mainly pertaining to high cost, and low natural abundance/access of starting materials [1]. As sodium and lithium share similarities in their alkali metal electrochemistry, there is rationale for renewed interest in the area of sodium batteries. It is now envisioned that

sodium secondary cells, amongst others, will be implemented in parallel to lithium based devices in the near future [2,3]. However, in order to be competitive with future Li-ion technologies, it is essential to enable the highest possible energy densities for sodium based devices (1677 Wh kg<sup>-1</sup> Na-O<sub>2</sub>) [4]. In doing so, we may harness the sodium metal as an anode rather than hard carbon materials which are currently used (ca. 100–300 mAh g<sup>-1</sup>) [5]. The path towards enabling sodium metal anodes has proven difficult, mainly due to the reactivity of sodium with water and/or the flammable conventional electrolytes

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carried forward from Li-ion technologies [6]. In order to remove this safety concern from future sodium metal devices, a new class of electrolyte have shown promise, namely highly concentrated ionic liquid electrolytes [7–9].

Recent results have shown highly concentrated ionic liquid electrolytes allow a large amount of charge migration in both lithium and sodium plating and stripping [8]. In addition, the passing of large charges has been reported to prepare a surface with a stable electrode-electrolyte interface [7]. These ionic liquids are typically non-flammable and exhibit negligible vapor pressure thus promoting their use as safe electrolytes. Nonetheless, ionic liquid electrolytes still falter in their high viscosity and lower conductivity, the latter being compounded with the addition of such high salt concentrations [10]. Various additives are included to alleviate viscosity ( $H_2O$ ) [11–13], flammability (e.g. ionic liquids) [6], or promote beneficial interface formation via sacrificial breakdown (fluoroethylene carbonate, vinylene carbonate) [14]. Importantly, for ionic liquid electrolytes, a beneficial solid-electrolyte interphase has been shown to form without the use of such additives [15].

The effect of water has been studied in non-fluorinated ionic liquid electrolytes for both Li and Na cells [16,17]. Both of these reports concluded that an increase above ca. 100–200 ppm  $H_2O$  within the ionic liquid electrolyte was detrimental to cell cycling and that the water content should be kept to a controlled minimum. Herein we report for the first time the stable plating and stripping of sodium metal from *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide comprising of 50 mol% sodium bis(fluorosulfonyl)imide (1:1 NaFSI: $C_3$ mpyrFSI) with an additional 500 ppm  $H_2O$ . These results are compared with ionic liquids bearing the FSI<sup>-</sup> anion paired with an alkyl phosphonium or an alkoxy ammonium cation. With this higher concentration of  $H_2O$ , the viscosity and conductivity concern may be alleviated, enabling cells exhibiting lower overpotentials required for the  $Na^{0/+}$  redox process than previously reported for implementation in Na metal cells. Additionally, at a high concentration of 50 mol%  $Na^+$  salt the lower cost of NaFSI salt, compared to the IL, effectively reduces the cost of these electrolytes.

## 2. Results & discussion

The physicochemical properties of the neat  $C_3$ mpyrFSI ionic liquid and electrolyte systems are shown in Fig. 1 and describe the trend of improved conductivity and viscosity with the inclusion of water as an additive. The conductivity curves measured at 10 °C intervals in Fig. 1a show that neat  $C_3$ mpyrFSI maintains the highest conductivity values at all temperatures. As is common to this class of electrolyte, the conductivity for the system can be seen to steadily increase through three orders of magnitude in the temperature range  $-20$  °C to 120 °C. It is upon the addition of a high 50 mol% concentration of NaFSI that these

conductivity values decrease an order of magnitude when compared to the neat  $C_3$ mpyrFSI. This is clearly attributed to the rise in viscosity shown in Fig. 1b. This electrolyte still maintains a liquid phase as shown previously to be possible within highly concentrated ionic liquid systems [8].

The increased viscosity and concomitant drop in conductivity of the system can be reversed through the addition of water to the electrolyte. Here, a concentration of 500 ppm water within the 50 mol% electrolyte exhibits conductivity values close to that of the neat  $C_3$ mpyrFSI -albeit with greater viscosity. Practical applications of batteries cause internal heat generation which in turn raises the device temperature above ambient conditions. These intermediate temperatures can allow improved electrode kinetics in the full device, and it is only the fact that the traditional organic electrolytes lead to instabilities at elevated temperatures which has limited battery operation to room temperature [18]. Fig. 1a reveals that at a temperature of 50 °C the 500 ppm water containing electrolyte is within the same order of magnitude to the neat electrolyte. This 50 °C intermediate temperature then used as a controlled temperature for all cell cycling herein, consistent with our previous reports for the purpose of drawing comparison [8,19].

The symmetrical cell cycling for these three 50 mol% NaFSI in  $C_3$ mpyrFSI electrolytes shown in Fig. 2a compares the polarization of the cell containing < 20 ppm  $H_2O$  against those considered ‘wet’, comprising of 100 ppm and 500 ppm of water. The electrolyte containing less than 20 ppm is considered dry in this instance. The initial polarization for each cell begins at high values, larger than 250 mV, with the highest belonging to the cell with dry electrolyte at ca. 360 mV. As is consistently observed with ionic liquid electrolytes this overpotential relaxes upon continued cycling to values ca. 100 mV after 20 cycles. It is at this point after cycling that the effect of water as an additive can be observed clearly.

The overpotentials upon completing the final polarization step are ca. 80 mV, 100 mV, 150 mV for the electrolyte systems comprising of ca. 500 ppm < dry < 100 ppm respectively, and are shown in Fig. 2b. It is this most ‘wet’ electrolyte which exhibits the highest stability in the voltage profile during the 20 plating and stripping cycles, suggesting that the (i) electrode-electrolyte interface formed has lowest resistance, and/or that (ii) the addition of water to the electrolyte promotes diverse speciation and an increased diffusion for the  $Na^+$  ion. Investigations to determine the strength of these proposed mechanisms for beneficial cycling are currently underway in our labs. Unlike the dry and 100 ppm electrolyte, this cell's voltage-time curve shows very little sign of tailing at the completion of each polarization step. This is indicative of a beneficial solid-electrolyte interphase (SEI) which permits the ingress/egress of sodium without Coulombic inefficiency. If this were not the case, the tailing (which is seen predominantly in the dry cell) would be more apparent at the completion of cell cycling, and suggestive of pristine sodium being stripped from the counter electrode [20]. This

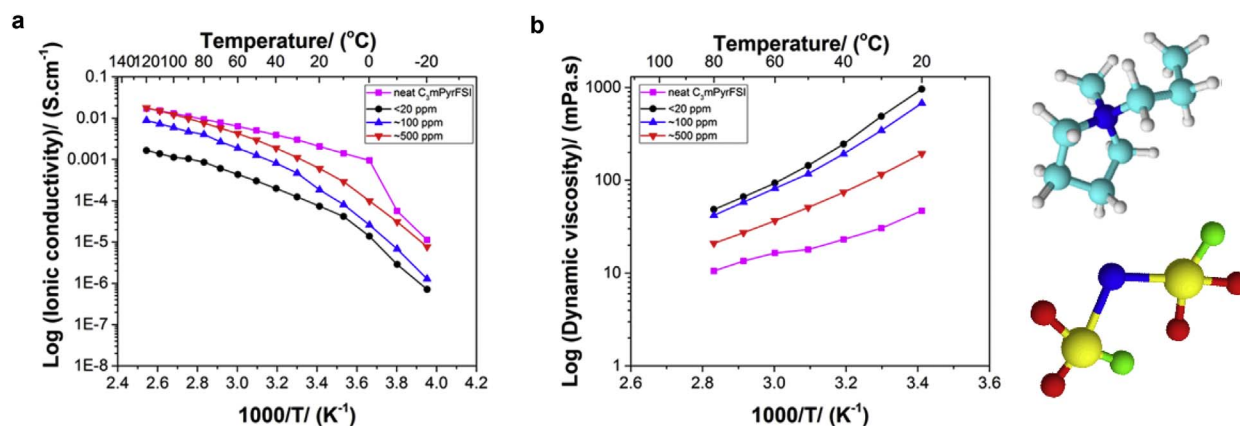


Fig. 1. (a) Conductivity and (b) viscosity values for the  $C_3$ mpyrFSI ionic liquid (shown at right) and the 50 mol% NaFSI containing electrolytes including increased amounts of water.

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