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COMMUNICATION

Anion Amphiprotic Ionic Liquids as Protic Electrolyte Matrices Allowing Sodium Metal Plating

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The sodium-ion battery (SIB) is proposed as a complementary technology to today's commercially dominant lithium-ion battery (LIB). While much know-how can be transferred from LIBs to SIBs, adjustments are still necessary, not the least for the electrolytes employed. Here the use of anion amphiprotic ionic liquid (AAIL) based electrolytes is proposed for SIB application. Two different AAILs, based on organic trifluoromethylsulfonylamide (TFSAm) and inorganic HSO₄⁻ anions, respectively, doped with NaTFSI salt have been studied, focusing on electrochemical stability and transport properties, complemented by studies of the ion-ion interactions, and final sodium-ion battery performance via stripping/plating vs. sodium metal electrodes.

The last three decades the lithium-ion battery (LIB) technology has risen in popularity to the point that today it totally dominates the market for modern rechargeable batteries, being used for portable electronics, electric cars and grid storage.^{1–5} However, continuing with lithium based technologies might not be the best solution for the future. The relatively limited resources of lithium and uneven global distribution cause high cost, large price fluctuations of the raw material and a dependency on a few countries willingness to share their natural resources.^{6–8} Therefore, development of complementary battery technologies to the LIB is crucial. Among the possibilities, sodium can be considered as a natural candidate to replace lithium, since these two elements are chemically very similar, paving the way for sodium-ion batteries (SIBs).^{9–12}

The non-aqueous electrolytes, necessary for SIB batteries, can be based on matrices of organic solvents^{13–15}, polymers^{16,17} or ionic liquids (ILs)^{18,19}. All have different advantages and

disadvantages. ILs and organic/IL hybrids in particular offer synergies between intrinsic safety and ion transport properties.^{20–23} Most attention has so far focused on aprotic ILs, due to their wider electrochemical stability windows,^{24,25} although recently also protic ILs have been reported with similar transport properties, but different interactions. Importantly they also offer reduced charge transfer resistance for insertion-extraction of charge carriers at the electrode/electrolyte interfaces for both LIBs and SIBs.^{26–28} The positive effect of the presence of a proton and its interactions have also been reported for modified anions; Armand *et al.* reported a less than fully fluorinated TFSI anion, *i.e.* [N(SO₂CF₂H)₂]⁻, to be beneficial for the cation transport, especially in PEO based polymer electrolytes, by virtue of special hydrogen bonds created.^{29,30} All this taken together turned our attention back to the concept of anion amphiprotic ILs (AAILs), which were originally designed as proton conducting materials for fuel cell application and distinguished by decoupled transport,³¹ and we now try to use them as electrolyte matrices for SIBs.

As 1-ethyl-3-methylimidazolium trifluoromethylsulfonylamide ([EMIm][TFSAm]) previously provided the highest conductivity,³¹ we have here used this AAIL and compare it with another more standard type of protic IL that analogously has a proton in its anion structure: 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIm][HSO₄], Fig. 1). Both AAILs were carefully dried to reach a water level <45 ppm and doped with sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) to create SIB electrolytes.

We started our analysis with the pure ILs and found that the AAILs have superior transport properties, as illustrated by the Walden plot (Figure 2), allowing us to consider them as superionic ILs.³² The origin of this has been analysed before by us and was postulated to be related to a proton exchange equilibrium.³¹ Our present DFT calculations confirm the existence of this critical process, with the equilibrium shifted much more towards the singly-charged anion structure for

Figure 1. Chemical structures of the AAILs.

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Figure 2. Walden plot of the studied ILs, with data for EMImTFSI from ref. ³⁹

[TFSAm]⁻ than for [HSO₄]⁻ (Figure 3). This has a huge impact on the electrochemical stability; the singly protonated structures are predicted to have stabilities against reduction of -1.17 and -0.76 V vs. Na⁺/Na⁰, respectively, while the doubly protonated structures are predicted to have poorer stabilities of 1.41 and 0.90 V vs. Na⁺/Na⁰, respectively, and the latter is for both structures related to the hydrogen evolution reaction (HER). Indeed, [EMIm][HSO₄] exhibits the lower electrochemical stability and is reduced at ca. 1.0 V vs. Na⁺/Na⁰ (Figure 4), having a two orders of magnitude higher concentration of the doubly protonated form – as derived from the calculated equilibrium constants. To further test the stability, adding a small piece of sodium metal into this IL leads to formation of bubbles at the metal surface. The analogous test with the [EMIm][TFSAm] IL gives no bubble formation and the CV demonstrates stability at the potential of sodium metal, with a small process at ca. 1 V vs. Na⁺/Na⁰, possibly related to the formation of a passivation layer, similarly to that of highly concentrated electrolytes based on TFSI. ^{33,34}

Looking at the pure ILs, the lowest ion conductivity is observed for [EMIm][HSO₄] – around half order of magnitude lower – likely primarily due to the much higher viscosity (Figure 5a). In contrast, [EMIm][TFSAm] exhibits a similar ion conductivity as that reported for the “standard” [EMIm][TFSI] IL.¹⁸ However, in Figure 5a there are different behaviours observed, likely related to different activation energies of the ion transport, and thus possibly different ion transport mechanisms. Doping of [EMIm][TFSAm] with NaTFSI causes a decrease in conductivity, connected with aggregation of the system, as observed for most ILs,³⁵ while for [EMIm][HSO₄] the introduction of NaTFSI increases the conductivity. For both the NaTFSI doped AAILs a local maximum in ion conductivity is observed for x=0.15 at 2.7 and 1.5 mS cm⁻¹, respectively, corresponding to concentrations of ca. 0.7-0.9 mol kg⁻¹ – quite typical of standard LIB (and SIB)

Figure 3. Proton exchange reactions in the AAILs; Equilibrium constants and reduction potentials obtained from DFT calculations.

Figure 4. Electrochemical stability of the two AAILs. WE: Pt, RE: Ag, CE: SS. Potential of Ag calibrated vs. ferrocene, E_{Ag} = -0.18 V vs. Fc⁺/Fc⁰.

electrolytes. A further increase in salt concentration, into the highly concentrated electrolyte (HCE) regime, results in another two maxima in ion conductivity: at 4.0 mS cm⁻¹ for (NaTFSI)_{0.5}[(EMIm)[TFSAm])_{0.5} and 6.1 mS cm⁻¹ for (NaTFSI)_{0.4}[(EMIm)[HSO₄])_{0.6}, respectively. At higher NaTFSI concentrations in [EMIm][HSO₄] a huge decrease in ion conductivity at lower temperatures is observed as the material partly crystallizes (melting point ca. -20 °C, Figure S4). This also affects the glass transition temperature (T_g) decreasing from ca. -65 to -90 °C. Much more of a glassy behaviour was recorded for the NaTFSI-[EMIm][TFSAm] system where no melting/crystallization is observed up to x=0.4 and with a glass transition temperature more or less fixed at ca. -72 °C (Figure S4). The appearance of crystalline phase (T_m = 160 °C) for x=0.5 decreases T_g down to -84 °C, that also can explain the higher ion conductivity, while a further increase in NaTFSI concentration increases the T_g to -62 °C, nicely correlated with a reduced ion conductivity.

Clearly the organic AAIL based system outperforms the inorganic for properties important for battery application. The [HSO₄]⁻ based system indeed has some crucial drawbacks: low electrochemical stability, low ion conductivity, and ample crystallization, why only the TFSAm based system is targeted for SIBs. A detailed analysis show significant changes in the structure in this system upon salt addition (Supporting Information). Aggregation around Na⁺ leads to the formation of a Na_xTFSAm_y phase, as seen also by DSC (Figure S4), together with a weaker intermolecular H-bonding, related to an increasing competition with Na⁺ coordination to the oxygen atoms of the anion (Figure S6). This is also confirmed by MD simulations, with a major contribution from TFSAm in the Na⁺ coordination and formation of densely packed Na_xTFSAm_y clusters.

Finally, some plating/stripping tests in Na|Na cells were performed for the electrolytes x_{NaTFSI} = 0.15 and 0.5 at 60 °C, a temperature used to compensate for the overall low ion conductivities (Figure 6). For the former electrolyte, the cycling was less stable, with significant potential increases during single cycles suggesting quite low sodium transference numbers, while the latter showed lower overpotentials that only slightly increased during subsequent cycles. This is a behaviour similar to other HCE IL based sodium conducting systems, where sodium conductivity has been inferred to occur through highly

Figure 5. Conductivity curves for neat ILs (a), AAILs doped with NaTFSI (b), and corresponding isotherms for (NaTFSI)_x([EMIm][TFSAm])_{1-x} (c) and (NaTFSI)_x([EMIm][HSO₄])_{1-x} (d). Data for EMImTFSI taken from ¹⁸.

aggregated clusters.^{36–38} We speculate that the introduction of a proton in the anion structure may further support/facilitate this ion transport inside the cluster by a proton – sodium exchange at the basic oxygen centres enabling de-coordination of sodium and further improve the Na⁺ mobility.

The results presented here show on possibilities for successful application of AAILs as matrices for Na-salts to create SIB electrolytes. The perhaps expected restricted diffusion of the relevant charge carrier and limited electrochemical stability window, due to H-bonding related increases in viscosity and proton reduction directly at the anionic structure, were both shown to be overcome due to a unique amphiprotic anion design. The pure [EMIm][TFSAm] AAIL shows ample electrochemical stability together with adequate transport properties and moreover, after addition of NaTFSI the electrolyte contains sodium cation based aggregates, Na_xTFSAm_y clusters, as shown spectroscopically and supported

both by DFT and MD simulations. This results in high ion conductivity, as for other HCEs, especially for the equimolar mixture of [EMIm][TFSAm] and NaTFSI, which also provides acceptable sodium plating/stripping performance. Altogether this proves that the strategy to apply AAIL based battery electrolytes is promising and calls for further development and improvement.

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Figure 6. Na|Na cycling of (NaTFSI)_{0.15}([EMIm][TFSAm])_{0.85} (a) and (NaTFSI)_{0.5}([EMIm][TFSAm])_{0.5} (b) at 60 °C.

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Conflicts of interest

There are no conflicts to declare.

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