Electrochimica Acta

Available online 12 February 2018

In Press, Accepted Manuscript — Note to users

The effect of cation chemistry on physicochemical behaviour of superconcentrated NaFSI based ionic liquid electrolytes and the implications for Na battery performance

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Received 29 August 2017, Revised 5 February 2018, Accepted 10 February 2018, Available online 12 February 2018

https://doi.org/10.1016/j.electacta.2018.02.052

Highlights

- Physicochemical properties of novel ionic liquid electrolytes for sodium batteries have been evaluated.
- The electrolytes were paired with sodium cathodes to make prototype devices.
- The electrolyte properties were linked to the device performance.

Abstract

There is growing interest in ionic liquid based electrolytes for Na metal and Na-ion batteries. Here we compare three quite distinct bis(fluorosulfonyl)imide (FSI) anion based ionic liquids with small alkyl phosphonium (trimethyl *iso*butyl phosphonium, methyl tri-*iso*butyl: P_{111i4}, $P_{1i4i4i4}$) or alkoxy ammonium counter cations (*N*-ethyl-2-(2-methoxyethoxy)-*N*,*N*-bis(2-(2-methoxyethoxy)ethyl)ethan-1-ammonium bis(fluorosulfonyl)imide: $N_{2(2O2O1)3}$) mixed at near 1:1 mol ratio with NaFSI. The conductivities of these electrolytes range from 4.4 $mScm^{-1}$ for the smallest P_{111i4}FSI:NaFSI system to 0.3 $mScm^{-1}$ for the $N_{2(2O2O1)3}$FSI:NaFSI mixture at 50 °C. This difference in conductivity is interestingly not reflected in the cyclic voltammetry for Na/Na^+ where the maximum peak current density of 10 $mAcm^{-2}$ is surprisingly high for the poorly conductive $N_{2(20201)3}$FSI:NaFSI solution (e.g. 17 $mAcm^{-2}$ for P_{111i4}FSI:NaFSI). The overpotentials observed for Na symmetric cell cycling show very little differences after initial stabilising/conditioning for the three electrolytes being 50 mV for P_{111i4}FSI:NaFSI and 100 mV for the others (at 0.1 mA cm^{-2}). Also the Na^+ transport number is similar for the three electrolytes ranging from 0.33 to 0.37. Full cells were prepared with layered transition metal oxide cathodes: O3-$Na_{2/3}(Fe_{2/3}Mn_{1/3})O_2$), P2-$Na_{2/3}(Fe_{2/3}Mn_{1/3})O_2$ and P2-$Na_{2/3}(Mn_{0.8}Fe_{0.1}Ti_{0.1})O_2$. While for the O3/P2-$Na_{2/3}(Fe_{2/3}Mn_{1/3})O_2$ structures the device performance is consistent with the electrolyte properties, with the P2-$Na_{2/3}(Mn_{0.8}Fe_{0.1}Ti_{0.1})O_2$ cathode the $N_{2(2O2O1)3}$FSI:NaFSI electrolyte cycling extremely well. The P_{111i4}FSI and $N_{2(2O2O1)3}$FSI yield almost equivalent specific capacities of approximately 180 and 160 $mAhg^{-1}$ respectively at C/10 rate.