Novel Na+ ion Diffusion Mechanism in Mixed Organic-Inorganic Ionic Liquid Electrolyte Leading to High Na+ Transference Number and Stable, High Rate Electrochemical Cycling of Sodium Cells.

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Abstract

Ambient temperature sodium batteries hold the promise of a new generation of high energy density, low-cost energy storage technologies. Particularly challenging in sodium electrochemistry is achieving high stability at high charge/discharge rates. We report here mixtures of inorganic/organic cation fluorosulfonamide (FSI) ionic liquids that exhibit unexpectedly high Na+ transference numbers due to a structural diffusion mechanism not previously observed in this type of electrolyte. The electrolyte can therefore support high current density cycling of sodium. We investigate the effect of NaFSI salt concentration in methylpropylpyrrolidinium (C3mpyr) FSI ionic liquid (IL) on the reversible plating and dissolution of sodium metal, both on a copper electrode and in a symmetric Na/Na metal cell. NaFSI is highly soluble in the IL allowing the preparation of mixtures that contain very high Na contents, greater than 3.2 mol/kg (50 mol%) at room temperature. Despite the fact that overall ion diffusivity decreases substantially with increasing alkali salt concentration, we have found that these high Na+ content electrolytes can support higher current densities (1mA/cm²) and greater stability upon continued cycling. EIS measurements indicate that the interfacial impedance is decreased in the high concentration systems, which provides for a particularly low-resistance solid-electrolyte interphase (SEI), resulting in faster charge transfer at the interface. Na+ transference numbers determined by the Bruce-Vincent method increased substantially with increasing NaFSI content, approaching > 0.3 at the saturation concentration limit which may explain the improved performance. NMR spectroscopy, PFG diffusion measurements and molecular dynamics simulations reveal a changeover to a facile structural diffusion mechanism for sodium ion transport at high concentrations in these electrolytes.