Improvement in the cycle performance of lithium ion batteries by using bis(fluorosulfonyl)imide-based ionic liquids

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Electrolyte is a critical component which is involved in balancing energy and safety specifications of batteries. Electrolyte solutions normally contain organic solvents that are required to be replaced with thermally stable materials to control their flammability. Ionic liquids (ILs) have been recognized as potential alternatives for this purpose. ILs are entirely composed of ions, and Coulombic interactions between ions add to a negligible vapor pressure to ILs. In the present study, the ILs containing bis(fluorosulfonyl)imide ([FSI]) anions, which were selected due to their innate tendency to highly dissociate and in turn their high ionic conductivity, were designed as the electrolytes for lithium ion batteries.

1) Design of electrolytes   Ionic conductivity is known to be suppressed below the melting point of electrolytes. Therefore, FSI anions were combined with a series of the cation which contains an ether oxygen to suppress crystallization. The IL, *N*-ethoxyethyl-*N*-methylpiperidinium bis(fluorosulfonyl)imide ($[P_{1,2O2}][FSI]$), was newly synthesized and mixed with LiFSI in ratio of 9:1: (IL:LiFSI mol/mol). The electrolyte mixture was confirmed to possess the low glass transition temperature of -88.8 °C without a crystallization feature.

2) Performance in a Li | LiFePO₄ cell   Figure (a) shows the cycling performance of the cell at C/10, which contains the $[P_{1,2O2}][FSI]$-LiFSI as an electrolyte and $LiFePO_4$ as a cathode. The cell retained the high capacity, which reaches the nominal capacity of $LiFePO_4$ (150 mAh g^{-1}), with Coulombic efficiencies higher than 99 % from 3rd to 50th cycles. Also, a flat voltage profile essentially arose from $LiFePO_4$ was preserved during the course of cycling.

3) Diffusion coefficient   To understand the excellent performance of the cell, the Li | $[P_{1,2O2}][FSI]$-LiFSI | $LiFePO_4$ cell was analyzed by means of the cyclic voltammetry at different scan rates (Figure (b)). A diffusion coefficient was calculated by analyzing the plot based on Randles–Sevcik equation. A cell containing LP30 (1M LiPF$_6$ in ethylene carbonate / dimethyl carbonate 1/1 v/v) was also analyzed as a control. The diffusion coefficient was calculated to be 1.4×10^{-7} and 9.6×10^{-8} cm^2 s^{-1} for $[P_{1,2O2}][FSI]$-LiFSI and LP30, respectively. Surprisingly, the higher diffusion coefficient was found for the IL-based electrolyte mixture. As a consequent of this, sufficient lithium stripping-plating was realized, and thus $LiFePO_4$ exerted its intrinsic high performance by using $[P_{1,2O2}][FSI]$-LiFSI mixture as the electrolyte.
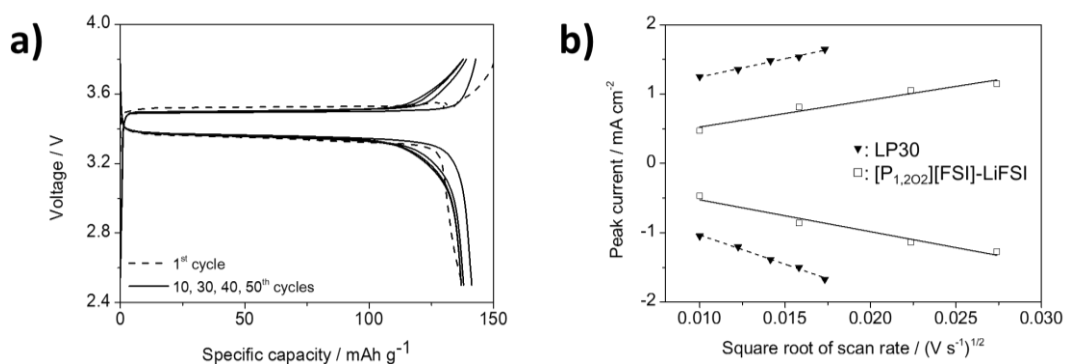

Figure (a) Cycling performance of the Li | $[P_{1,2O2}][FSI]$-LiFSI | $LiFePO_4$ cell at C/10 (1C equivalents to 0.847 mAh), and (b) peak current *versus* square root of scan rate that was obtained by means of cyclic voltammetry.