Ionic Liquid-based electrolyte mixtures for high-voltage lithium batteries with enhanced safety and cycle-life

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With a growth of the need for high energy density lithium-ion batteries, there are strong demands on improved reliability and safety. The electrolyte is a critical component, determining safety specifications. Important challenges are aimed to replace alkyl carbonate solvents with non-volatile ionic liquids (ILs) to control the flammability [1].

Here we propose N-butyl-N-methylpyrrolidinium hexafluorophosphate ($Py_{14}PF_6$) as an additive for 1M $LiPF_6$ in ethylene carbonate - dimethyl carbonate (commercially, LP30). This IL was considered to be one of the most suitable for adding to LP30 [2], because of the analogous anions structure and high electrochemical stability of the IL cation.

Different amounts of the IL in LP30 were considered, namely 30, 50 and 70 wt.%. The highest IL concentrations (i.e., 50 and 70 wt.%) allowed the suppression of any crystallization features and shifted the flash point of the mixtures well above room temperature, thus enlarging the temperature limits for a safe applicability. Good ionic conductivity, approaching 10^{-2} Scm^{-1}, was retained at around room temperature even for the most concentrated solutions.

The most favorable electrochemical properties, in terms of interfacial stability versus lithium and carbonaceous electrodes, were found for the 50 wt.% mixture. Due to the enhanced electrochemical stability window of the IL-added solution, the mixture with 50 wt.% of $Py_{14}PF_6$ in LP30 was tested as electrolyte in high voltage lithium-metal batteries, adopting the spinel $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) cathode. A good rate capability of the quoted cell was found, with a stable, reversible capacity as high as 130 mAh/g and 110 mAh/g under C/10 and 1C current density, respectively.

Improved cycling tests were obtained with a modified, in-house made LMNO material, having a finely tuned stoichiometry containing iron and chromium dopants [3]. This allowed a Li-cell with a fast charging behavior, up to 10C, very long cycle life and good capacity retention (≥120 mAh/g) when using the 30 wt.% $Py_{14}PF_6$-LP30 electrolyte mixture.

References:

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