Lithium electrolyte based on quaternary ammonium ionic liquids for high voltage lithium batteries

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Organic solvents are widely used in commercial lithium batteries as electrolyte with high electrical conductivity and good compatibility with electrode materials. Nevertheless, the reactivity and volatility of organic electrolyte are disadvantageous to its commercial applications [1]. In addition, they are all oxidized at potential up to 4.5 V vs Li/Li, which can't be used for high voltage electrode materials such as $LiNi_{0.5}Mn_{1.5}O_4$ (worked at 5 V vs Li^+/Li) [2]. The use of ILs in lithium batteries has been greatly investigated more than one decade [3]. Given their interesting properties, such as nonvolatility, non-flammability, high thermal stability, wide liquid range and wide electrochemical window. In addition, the choice of cation and anion can be made to tailor properties such as ionic conductivity, viscosity and electrochemical stability [4,5,6].

Among the various ILs, we focus on ILs based on ammonium cations (quaternary ammonium, pyrrolidinium and piperidinium) combined with anion TFSI (bis trifluoromethanesulfonyl imide). The structures of these ILs are presented in Figure 1. These ILs were reported to be more stable in oxidation than imidazolium based ILs, at least 5 V vs Li^+/Li. The fluorinated ammonium ILs increase the oxidation potential about 500 mV compared to the non-fluorinated ammonium [5,6]. However, the high viscosity of ILs based quaternary ammonium remains big challenge for application as lithium electrolyte. One solution to design safer electrolytes based on ionic liquids which exhibit simultaneously all the required properties (i.e. low viscosity, electrochemical stability, non-flammablity), is the addition of molecular additive (organic solvent such as: EC, acetonitrile,…). In our previous report, the incorporation of 20 wt% EC has no positive effect on the pure IL dissociation, but decreases the viscosity as well as improves the electrochemical window stability. Thus, the EC-ILs mixture constitutes an interesting alternative and safe solvents for application in lithium batteries [7].

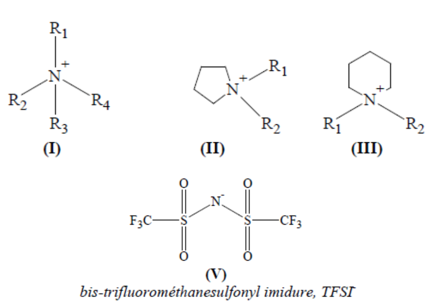

Figure 1. Structures of ILs with different cations: (I) quaternary ammonium, (II) pyrrolidinium; (III) piperidinium.

To further explore the potential application of ammonium quaternary (QA) based ILs, we focus on cycling behavior and evolution of impedance characteristics of lithium cell ($Li_4Ti_5O_{12}$//ILs + 0.75M LiTFSI or ILs-EC + 0.75M LiTFSI //$LiNi_{0.5}Mn_{1.5}O_4$) using Swagelok prototype. The Li^+ insertion/desinsertion into electrode materials has also studied by cyclic voltammetry in lithium electrolyte based ILs.

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