Electroactive imidazolium salts based on 1,4-dimethoxybenzene redox groups : synthesis, electrochemical characterization and overcharge protection in Li-ion batteries

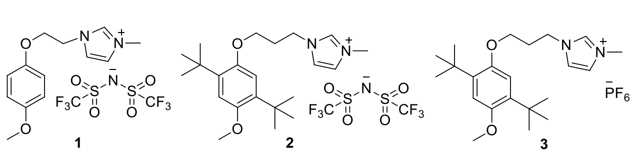
John C. Forgie*, Dominic Rochefort, Soumia El Khakani and Dean D. MacNeil

Département de Chimie, Université de Montréal
Montreal, Québec

The use of Lithium ion batteries in electronic devices continues to grow, the popularity stems from the excellent cycle life and the ability to store more energy per volume than any other portable rechargeable battery currently available.[1] However, one major problem of the Li-ion battery is preventing it from going into an abuse situation. An abuse situation is when a cell is overcharged; causing degradation of the battery and in some cases exothermic reactions at elevated temperatures.[2] There are however several safety mechanisms that can be employed to prevent the overcharge situation.

Redox shuttles,[3] dissolved electroactive species in the electrolyte, are the simplest of the current safety measures available. An ideal redox shuttle should have an oxidation 0.3 V above the potential of the cell. In normal working conditions the shuttle has no function but if the cell is about to get over-oxidized, the redox shuttle becomes oxidized instead receiving the excess charge. This new oxidized species then migrates to the opposite electrode to regenerate to the original redox shuttle. Despite the simplicity, one disadvantage of redox shuttles has always been the amount of the species that can dissolve into typical Li-ion electrolytes. Recent redox shuttles discussed in the literature, can only dissolved in low concentrations because of their poor, thus limiting the amount of current that can be passed via the redox shuttle in an overcharge situation.

In this presentation, we report three new redox-active imidazolium salts that have been synthesized based on 1,4-dimethoxybenzene (**1**) and 2,5-di-tert-butyl-1,4-dimethoxybenzene (**2** and **3**). These imidazolium salts are the first organic redox-active groups to be incorporated into an ionic liquid structure and have been designed to be employed as redox shuttles for Li-ion battery overcharge protection.



The advantage of ionic liquids with regards to Li-ion battery electrolytes is their miscibility with carbonate solvents over a wide range of molar fraction. Therefore, the incorporation of the redox group into an ionic liquid group allows a greater amount of redox shuttle to be added in solution, up to 1M. In comparison, the solubility of 2,5-di-tert-butyl-1,4-dimethoxybenzene in conventional carbonates (1.2 M $LiPF_6$ in ethylene carbonate : ethyl methyl carbonate (3:7 w/w)) is limited to 0.08 M, however it can be increased to 0.2 M in 0.5 M lithium bis-oxolatoborate dissolved in propylene carbonate : diethyl carbonate (1:2 v/v).[4]

Thus these redox-active imidazolium salts provide an electrolyte for lithium batteries that combines the low volatility and high thermal stability of ionic liquids with the overcharging protection of a redox shuttle present in higher concentrations.

We will present the synthesis, physiochemical, electrochemical and transport properties of these imidazolium salts as well as coin cell overcharge tests. Conductivity and viscosity measurements were performed in ethylene carbonate : diethyl carbonate (1:2 v/v) with a supporting electrolyte of either lithium bis(trifluoromethanesulfonyl)amide or lithium hexafluorophosphate, we show that a high concentration of these redox shuttles can be added to the solution without the viscosity becoming too great while still maintaining a conductivity that is above 50% of that of the electrolyte containing no redox shuttle. Cyclic voltammetry measurements were performed inside a glove box and show the onset of oxidation (ca. 3.81 – 3.94 V vs. Li/Li^+) at a high potential suitable for the overcharge protection of lithium iron phosphate cathodes in Li-ion batteries. Diffusion coefficients and heterogeneous rate transfer calculations show there are no negative effects on the transport properties by incorporating 2,5-di-tert-butyl-1,4-dimethoxybenzene into an electroactive imidazolium salt. Coin cell tests using imidazolium salts **2** and **3** showed protection over 23 and 56 cycles, respectively.

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