



Asymmetrical imidazolium-trialkylammonium room temperature dicationic ionic liquid electrolytes for Li-ion batteries

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ABSTRACT

This paper reports on the synthesis and characterization of novel dicationic ionic liquid electrolytes based on asymmetrical imidazolium-trialkylammonium ionic liquids. The results obtained indicate that the length of the alkyl chain attached to the nitrogen atom has a significant influence on the thermal and electrochemical properties of the electrolytes, as well as on parameters such as lithium ion coordination number and lithium ion transport number. All synthesized dicationic ionic liquids and the corresponding electrolytes are liquid at room temperature being thermally stable up to 300 °C; well above battery operation temperature. Room temperature ionic conductivities of the electrolytes are in the range of 0.8–7.2 × 10⁻⁵ S cm⁻¹, with an electrochemical stability window of 1.5 V–5.0 V vs. Li/Li⁺. Synthesized electrolytes have been tested in Li half-cells using LiMn₂O₄ (LMO) spinel as cathode material. Cyclic voltammetry, rate capability and galvanostatic cycling studies at 60 °C have been performed. Again, the alkyl chain length attached to the nitrogen atom plays a significantly role in the electrochemical performance of the LMO cells. Among the cells studied, the one assembled with the electrolyte 1M LITFSI doped IMI_{1,6}-TEA exhibits the best rate capability and the high cycling performance.

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1. Introduction

Li-ion batteries (LIBs) are currently the electrochemical energy storage technology most predominate in the market, for applications in portable electronic devices. However, their use in the automotive industry and in large-scale energy storage, require improvements in factors such as energy density, power density, durability and safety [1,2]. Carbonate solvents, typically used in Li-ion batteries, are responsible for the majority safety problems, as they have low thermal stability, toxicity, high volatility and inherent non flammability, restricting their battery operative use to temperatures below 60 °C [3,4]. Recent studies on alternatives to conventional organic electrolytes for Li-ion batteries have demonstrated that ionic liquids (ILs) consisting of large unsymmetrical organic cation such as imidazolium [5,6], pyrrolidinium [7,8],

piperidinium [9,10], phosphonium [11,12], quaternary ammonium cations [13,14] containing various substituents and weakly coordinated organic anions (PF₆⁻, BF₄⁻, CF₃SO₃⁻ (CF₃SO)₂N⁻), etc.), show significant promise to replace the highly volatile and flammable carbonate electrolytes. Room temperature ionic liquids (ILs) characteristics involve a negligible vapor pressure, wide liquid range, high thermal stability, non-flammability, good solubility of organic and inorganic compounds, high ionic conductivity and wide electrochemical stability window [15–17]. Another important factor is that all these parameters can also be tuned easily by appropriate design of the molecular structure of the component ions. However, problems associated to their high viscosity [18,19], especially when lithium salts have been added, low stability of the solid electrolyte interphase (SEI) [17,20], and high cost need to be solved before they are commercially viable. Currently, most room temperature ionic liquids tested as electrolyte solvents in rechargeable batteries are monocationic [21–24]. Dicationic ionic liquids, both symmetrical and asymmetrical, having two cationic moieties linked through a hydrocarbon linkage chain, have also being synthesized and characterized both thermally and electrochemically [25–28]. Compared

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to monocationic ILs, dicationic ILs exhibit much higher thermal degradation temperatures, wider liquid ranges, and electrochemical windows in the range of 4.3 V–4.7 V [29,30]. Several studies have been reported in the literature on the synthesis and characterization of dicationic ionic electrolytes [31–33], studying their potential application in devices such as electrochemical capacitors and solid state dye-sensitized solar cells but, up to now, only one paper checking the role of the ionic liquid as additive in a Li/1 M LiPF₆/EC-DMC/LiMn₂O₄ cell [34] and other using a solid polymeric ionic liquid electrolyte in a Li/LiFePO₄ device [35] have been published.

Imidazolium based ionic liquid electrolytes have received much attention because of their low viscosity and relatively high conductivity (usually greater than 10⁻³ S cm⁻¹ at 25 °C) [5,36]. However, their electrochemical stability window is generally limited to 4 V with a reduction potential at about 1 V vs. Li/Li⁺ [37]. Quaternary ammonium based ionic electrolytes have better electrochemical stability (low cathodic limiting potential) compared with imidazolium ones and their electrochemical stability window is usually greater than 5 V vs. Li/Li⁺, but the larger size of cations leads to high viscosity and low ionic conductivity [38]. In a previous study, Zhang et al. [34] reported on the synthesis of asymmetrical dicationic ionic liquids based on both imidazolium and aliphatic ammonium cations where the imidazolium and ammonium cations were linked by alkyl chains of different lengths and the role of the ionic liquid as an additive in LiMn₂O₄ half-cells. In this study, we report on the synthesis and characterization of a series of novel room temperature asymmetrical dicationic ionic liquid electrolytes, based on imidazolium-trialkylammonium cation moieties linked by a C6 aliphatic backbone, carrying different alkyl substituents in the ammonium cation. Characterization of the thermal, electrical and electrochemical properties of the electrolytes prepared will be presented. Electrochemical performance of Li-half cells assembled using the LiMn₂O₄ spinel (LMO) as cathode material and electrolyte based on the synthesized dicationic ionic liquid have been tested using cyclic voltammetry and galvanostatic charge/discharge tests. The influence of the alkyl chain length attached to the nitrogen on the cell performance have been evaluated.

2. Experimental

2.1. Materials

N-Methyl-N-hexylimidazolium bromide was synthesized according to the literature [39]. LiTFSI (3 M, Fluorad HQ115) was dried at 80 °C under vacuum, then stored in an argon-filled dry-box. All other reagents were purchased at the highest commercial quality and used without further purification. LMO spinel powder (MTI Corporation), carbon black (Super P, TIMREX) and polyvinylidene fluoride binder (PVDF, Aldrich, Mw ~534000) were used as received.

Fig. 1 display the molecular structures and nomenclature of the synthesized dicationic ionic liquids. Synthesis procedure involves the addition of the correspondent amine to a solution of N-Methyl-N-hexylimidazolium bromide in acetonitrile under reflux followed by anion exchange with LiTFSI in aqueous solution. The resulting product was purified using column chromatography to afford the desired ionic liquid as light yellow viscous oil. NMR spectra were recorded on Mercury-400 and Bruker-300 instruments. The water content in the ionic liquids was measured according to Karl-Fischer method being in all cases below 12 ppm. 1M LiTFSI doped ionic liquid electrolytes were obtained directly by dissolving the appropriate amount of lithium salt to the respective ionic liquids.

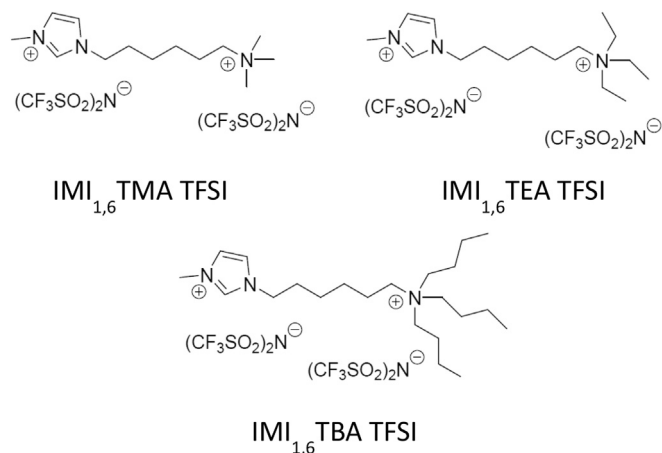


Fig. 1. Molecular structures and nomenclature of the synthesized asymmetrical imidazolium-trialkylammonium dicationic ionic liquids.

2.2. Physicochemical measurements

DSC measurements were made using a Mettler TA4000 calorimeter. The samples, housed in sealed aluminum pans, were cooled down from room temperature to -150 °C at 10 °C min⁻¹ and then heated (10 °C min⁻¹) up to 100 °C, under a nitrogen flow. Thermogravimetric analyses (TGA) were carried out using a TA Q500 equipment. Samples of approximately 10–15 mg were heated at a rate of 10 °C · min⁻¹ to 800 °C under a nitrogen atmosphere. The Raman spectra of the samples were collected with a confocal Raman microscope (Renishaw InVia Reflex Raman system), using a solid state diode laser (785 nm wavelength) as the excitation source. The spectra were evaluated using the Wire program and a Gaussian-Lorentzian band fit.

2.3. Electrochemical measurements

The temperature dependence of the ionic conductivity was measured within the -40 to 100 °C temperature range by using a Novocontrol Alpha dielectric analyzer in combination with a Novocontrol Quatro temperature controller. Experiments were performed over the frequency range 10⁷–10⁻¹ Hz using a hermetically sealed homemade stainless steel cell. An ac perturbation of 10 mV was applied to the cell. Data were collected during steps of 5 °C after a stabilization time of 10 min at each temperature. The real and imaginary parts of the complex impedance were plotted and the ionic conductivity was calculated by using the ZPlot fitting software. The electrochemical stability window of the electrolytes was determined by cyclic voltammetry using an Solartron 1470 potentiostat/galvanostat equipment on sealed homemade cells, using lithium metal as counter and reference electrodes and stainless steel as current collectors. The measurements were performed at room temperature in the potential range from -1 to 6 V vs. Li/Li⁺ at 2 mV s⁻¹ scan rate.

The room temperature lithium ion transference number of the ionic liquid based-electrolytes was measured using symmetric Li/ionic liquid electrolyte/Li Swagelok[®] type cells, where the electrolyte is soaked in a Whatman BSF-80 glass fiber paper. Values of *t*_{Li⁺} were evaluated by dc potentiostatic measurements in conjunction with ac impedance spectroscopy by using a Solartron 1470 potentiostat/galvanostat equipment provided with a 1255B frequency response analyzer. A 50 mV dc voltage was applied until a steady current was obtained (2 h in this study). The impedance spectra of the cell were obtained before and after polarization over the

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