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Physicochemical and electrochemical investigations of the ionic liquid *N*-butyl -*N*-methyl-pyrrolidinium 4,5-dicyano-2-(trifluoromethyl) imidazole

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ABSTRACT

A new ionic liquid formed by coupling 4,5-dicyano-2-(trifluoromethyl)imidazole (TDI^-) anion with *N*-butyl -*N*-methyl-pyrrolidinium (Pyr_{14}^+) cation is successfully synthesized and characterized by Raman spectroscopy, thermal and rheological analyses, as well as electrochemical techniques. The $Pyr_{14}TDI$-LiTDI mixture, melting at 49 °C, shows remarkable stability within the 50–250 °C range, as well as suitable ionic conductivity, lithium ion transport, and electrochemical stability window. Thus, it is proposed for application at 60 °C in a lithium cell with stable $LiFePO_4$ cathode. At this temperature, the electrolyte has viscosity of 65.8 mPa s, ionic conductivity of the order of 5 mS cm^{-1}, and limiting current density of 10^{-2} mA cm^{-2}. Lithium metal/$LiFePO_4$ cells with such an electrolyte offer promising results in terms of stable $LiFePO_4$/electrolyte interface, investigated by impedance spectroscopy, as well as delivered capacity above 160 mAh g^{-1} with 81% of retention after 80 galvanostatic cycles.

1. Introduction

The intrinsic risk of thermal runaway in lithium batteries is a recurring theme. Indeed, fire accidents and explosions are severe issues, especially for large-scale battery packs [1]. Therefore, the current lithium battery research is focusing on the investigation of new materials with higher safety characteristics than the conventional ones [2]. The present electrolytes for lithium batteries are based on alkyl carbonates, which are volatile and flammable, thus leading to potential danger under abuse conditions [3]. Furthermore $LiPF_6$, which is mostly employed as the electrolyte salt, has poor thermal stability and may react with H_2O traces unavoidably present in the cell to form HF, which attacks the positive electrode [4]. As for the common electrode materials, de-lithiated layered cathodes based on cobalt may release oxygen at high temperatures [3,5,6], which further increases the chemical reactivity of the battery. In this respect, the use of phospho-olivines like $LiFePO_4$, characterized by high thermal stability due to the strong covalent P—O bond, may partially decrease the thermal runaway hazards [7]. However, the application of conventional lithium batteries is presently limited to temperatures up to 50 °C [8].

Electrolytes based on ionic liquids (ILs), i.e., molten salts at room temperature, have attracted great attention as replacements of common carbonate-based electrolytes in lithium cells [9–15]. Indeed, IL-based electrolytes have shown enhanced safety characteristics with respect to the conventional ones due to higher thermal stability, negligible vapor pressure, and flame-retardant capability. In addition, they exhibit relatively high ionic conductivity and wide electrochemical stability window, suitable for lithium battery application [16–23]. Following this trend, one of the most investigated class of ionic liquids is that based on pyrrolidinium cations [24,25], yielding to IL-based electrolytes with relatively low viscosity and remarkable electrochemical stability. The above-mentioned cations have been combined with imide-based anions, such as bis(trifluoromethanesulfonyl)imide

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($TFSI^-$) and bis(fluorosulfonyl)imide (FSI^-), as well as with LiTFSI and LiFSI salts, respectively. The resulting electrolytes have revealed outstanding electrochemical performance in lithium-ion cells [26,27]. However, imidazole anions, such as 4,5-dicyano-2-(trifluoromethyl)imidazole (TDI^-), have shown suitable properties for application in safe lithium-ion batteries. Thus, the LiTDI salt has a remarkable thermal stability (>250 °C), negligible hydrolysis, high oxidation stability, and aluminum protection against corrosion [28–34]. Furthermore, Niedzicki et al. have recently reported new TDI-based ILs for lithium-ion battery application, which have shown promising electrochemical properties [35].

Herein we originally synthesize and investigate the *N*-butyl -*N*-methyl-pyrrolidinium 4,5-dicyano-2-(trifluoromethyl)imidazole ($Pyr_{14}TDI$) ionic liquid. This new IL is used for preparing a $Pyr_{14}TDI$-LiTDI electrolyte solution, which is fully characterized in terms of physicochemical and electrochemical properties by vibrational spectroscopy, thermal and rheological analyses, and electrochemical techniques, respectively. Hence, the IL-electrolyte used in Li/$Pyr_{14}TDI$-LiTDI/$LiFePO_4$ cells exhibits suitable electrode/electrolyte interface and promising behavior above room temperature.

2. Experimental

2.1. Synthesis of the ionic liquid and electrolyte preparation

$Pyr_{14}TDI$ ionic liquid (IL) was synthesized by a two-step synthesis route via ion exchange in aqueous solution [36–38] (Fig. 1). *N*-butyl-*N*-methyl pyrrolidinium bromide ($Pyr_{14}Br$) was prepared by *N*-alkylation of *N*-methylpyrrolidine (Sigma-Aldrich). For such reaction, butyl bromide (Sigma-Aldrich, freshly distilled prior to use) was added to N-methylpyrrolidine. The second step of the synthesis route was the cation exchange reaction to transform LiTDI (Solvionic) into AgTDI. This was performed dropping an aqueous solution of LiTDI into a vigorously stirred aqueous solution of excess $AgNO_3$ (Sigma-Aldrich, >99.0%). The obtained photosensitive, milky-white AgTDI was filtered off and washed with deionized water. The final step of the IL synthesis consisted in dropping an aqueous solution of $Pyr_{14}Br$ into a vigorously stirred suspension of AgTDI ($Pyr_{14}Br$:AgTDI molar ratio 0.95:1). Excess AgTDI and AgBr were filtered off. The IL was subsequently purified by alumina and charcoal [39] to obtain a colorless liquid. Water was removed with a rotary evaporator at 50 °C, followed by drying at 60 °C via oil pump (10^{-3} Pa) for 24 h and turbomolecular pump (10^{-6} Pa) for additional 24 h. Karl–Fischer titration, performed with the automatic coulometer titrator (Mettler Toledo), indicated water content below 10 ppm in the dried IL sample. Inductively coupled plasma-optical emission spectrometry (ICP-OES) indicated the silver content to be below the detection limit (0.03 ppm).

The electrolyte solution ($Pyr_{14}TDI$:LiTDI) was prepared by dissolving LiTDI in $Pyr_{14}TDI$ in the molar ratio of 1:9. Proper weight amounts of LiTDI and $Pyr_{14}TDI$ were determined through a XS105 Analytical Balance. The estimated error of the molar composition is <0.05%. The electrolyte density at room temperature is 1.37 g/cc, as determined by an Ultrapyc 1200e (standard deviation on 10 runs of 0.05 g/cc).

2.2. Characterization methods

Sample preparation and electrochemical testing were carried out in a dry room (dew point < −60 °C). Raman measurements were performed through a RAM II FT-Raman module of a Bruker Vertex 70 FT-IR spectrometer with a laser wavelength of 1064 nm. Each recorded spectrum is the average of 500 scans at an optical resolution of 2 cm^{-1}. The analyzed samples were sealed in glass tubes under vacuum.

Differential scanning calorimetry (DSC) was carried out by using a TA Instruments Q2000 with liquid N_2 cooling. The samples were hermetically sealed in Al pans inside the dry room [20]. The samples were extensively cycled between −150 °C and +150 °C before performing the heating ramp at a rate of 10 °C min^{-1}.

Thermogravimetric analysis (TGA) was carried out by using a TA Instruments Q5000. The samples were heated at a rate of 5 °C min^{-1} from room temperature to 500 °C under a nitrogen purge. The samples were hermetically sealed inside the dry room in aluminum pans, which were punched immediately prior to measurement. Additional TGA–mass spectrometry (MS) experiments were performed through a TG209 F1 Libra, Netzsch, coupled with QMS 403D Aeolos, Netzsch (see the Supplementary Information for further details). Before the measurements, vacuum was applied three times to remove the ambient atmosphere trapped in the probe. Samples were heated from 40 °C to 500 °C at a heating rate of 5 °C min^{-1} under He flow (20 mL min^{-1}). The MS detection was performed in the m/z range from 10 to 74.

Rheological analysis was performed in the dry room (dew point < −60 °C) through an Anton-Paar Physica MCR102 rheometer, by applying constant shear rates and using a Peltier system for cooling/heating. The sample was heated above the melting point and kept 1 h at 60 °C before starting the test. Viscosity measurements were performed every 5 °C upon sample heating after 15 min of equilibration at constant temperature.

The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) in the 50 kHz–100 Hz frequency range through an automated conductometer equipped with a

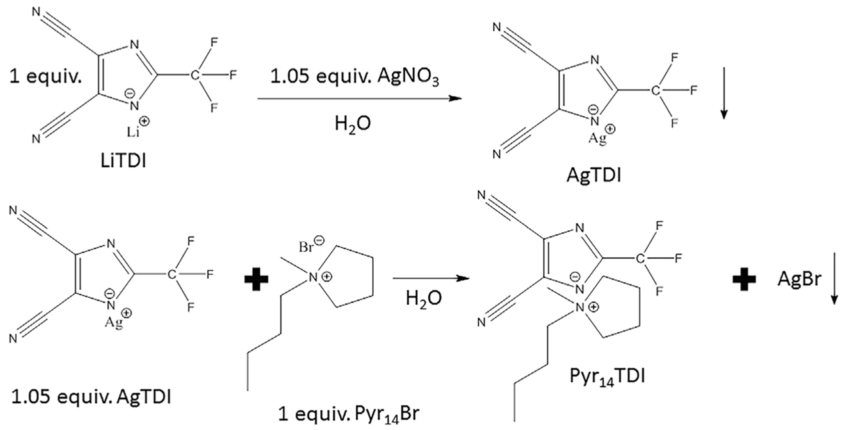

Fig. 1. Synthesis pathway of the ionic liquid $Pyr_{14}TDI$ via the silver salt route.