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Novel choline-based ionic liquids as safe electrolytes for high-voltage lithium-ion batteries

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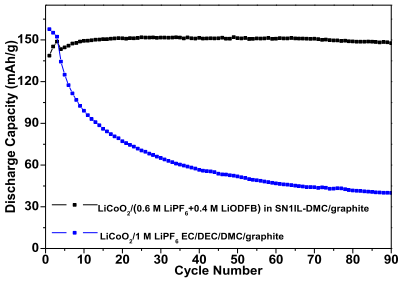
HIGHLIGHTS

- Novel choline-based ionic liquids synthesized as safe electrolytes for Li-ion batteries.
- Delivered a stable capacity of 152 mAh g^{-1} over 90 cycles at a cut-off voltage of 4.4 V.
- Displayed a lower propagation rate than the commercial carbonate electrolyte.

GRAPHICAL ABSTRACT



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ABSTRACT

Three choline-based ionic liquids functionalized with trimethylsilyl, allyl, and cynoethyl groups are synthesized in an inexpensive route as safe electrolytes for high-voltage lithium-ion batteries. The thermal stabilities, viscosities, conductivities, and electrochemical windows of these ILs are reported. Hybrid electrolytes were formulated by doping with 0.6 M LiPF6/0.4 M lithium oxalydifluoroborate (LiODFB) as salts and dimethyl carbonate (DMC) as co-solvent. By using 0.6 M LiPF6/0.4 M LiODFB trimethylsilylated choline-based IL (SN1IL-TFSI)/DMC as electrolyte, LiCoO2/graphite full cell showed excellent cycling performance with a capacity of 152 mAh g^{-1} and 99% capacity retention over 90 cycles at a cut-off voltage of 4.4 V. The propagation rate of SN1IL-TFSI)/DMC electrolyte is only one quarter of the commercial electrolyte (1 M LiPF6 EC/DEC/DMC, $v/v/v = 1/1/1$), suggesting a better safety feature.

1. Introduction

Ionic liquids (ILs) have a unique suite of properties such as low volatility, and high electrochemical and thermal stabilities, which makes them as important candidates for a number of energy storage and conversion related applications, such as super-capacitors, dye sensitised solar cells and batteries. Advantages that they offer for advanced lithium-ion batteries (LIBs) to replace the anodic limited and high flammable organic-carbonate electrolytes are their low volatility and non-flammability, making it possible to formulate electrolytes with enhanced safety without compromise of cyclic stability [1]. Based on the types of cations, ILs could be primarily categorised into sulfonium, imidozonium, phosphonium

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and ammonium [2]. Amongst them, quaternary ammonium ILs are widely investigated as electrolytes for LIBs because of their high cathodic stablility. For instance, cyclic pyrrolidinium and piperidinium bis(trifluoromethylsulfonyl)imide (TFSI) ILs are typically less viscous and cathodically stable than ILs with aliphatic cations, thus show highly efficient lithium cycling [3,4]. While the lack of the ability of forming a stable solid electrolyte interface (SEI) on graphitic anode before lithium intercalation can be effectively overcame by the incorporation of ethylene carbonate (EC) [5] or other well-known additives such as vinyl carbonate [6,7], fluoroethylene carbonate [8], lithium bis(oxalato) borate [9] and lithium oxalyldifluoroborate (LiODFB) [10], the design and synthesis of novel ILs with low viscosity, advanced electrochemical performance and especially low cost is still a challenge.

Choline chloride is an ammonium based ionic liquid produced in industry scale with competitive price, and is environmentally benign and biocompatible [11,12]. Thus choline chloride and its derivatives are vastly used in foodstuff [13,14], biodegradation [15], catalysis [16], electrochemical synthesis [17] and surfactants [18]. However, choline chloride ionic liquid cannot be directly used as electrolyte in lithium-ion batteries, due to its poor compatibility with highly reductive anodes and oxidative cathodes because of its hydroxyl group and chloride ion. Additional modification, therefore, is necessary to use it as electrolyte in LIBs. Fortunately, the electrochemical compatibility of ILs could be tuned by integrating various groups [19,20], *e.g.* organosilicon, double bond and cyano groups. Besides that, organosilicon offers good biocompatibility [21], double bond SEI film forming capability [22] and cyano group protective effect for aluminum collector [23]. Meanwhile, different anions [2] have been used to functionalize ILs, such as BF_4^- [24], $B(CN)_4^-$ [25], PF_6^- [26], $ODFB^-$ [27], bis(fluorosulfonyl)imide [28] and bis(trifluoromethylsulfonyl)imide ($TFSI^-$) [29]. It is demonstrated that TFSI anion exhibits superior stability against oxidation and reduction, which offers wide electrochemical window [30].

In this paper, we report the synthesis of three new choline-based ionic liquids prepared by substituting hydroxyl group with trimethylsilyl, allyl or cyanoethyl groups and exchanging chlorine with TFSI anions, aiming to combine the inexpensive features of choline ILs and the high-voltage feature of these functional moieties (Scheme 1). The thermal stabilities, viscosities, ionic conductivities and electrochemical windows are characterized. Using hybrid electrolytes formulated by doping the ionic liquids with $LiPF_6$/LiODFB as salts and taking dimethyl carbonate (DMC) as co-solvent, high-voltage $LiCoO_2$ (LCO)/graphite full cells are tested with an upper cut off voltage of 4.4 V. And the effect of this IL on electrochemical properties is analysed in detail by electrochemical impedance spectroscopy (EIS), Fourier transform infrared (FTIR) and scanning electron micrograph (SEM). The flammability of these electrolytes is characterized by measuring the flame propagation rate and compared with a commercial carbonate electrolyte.

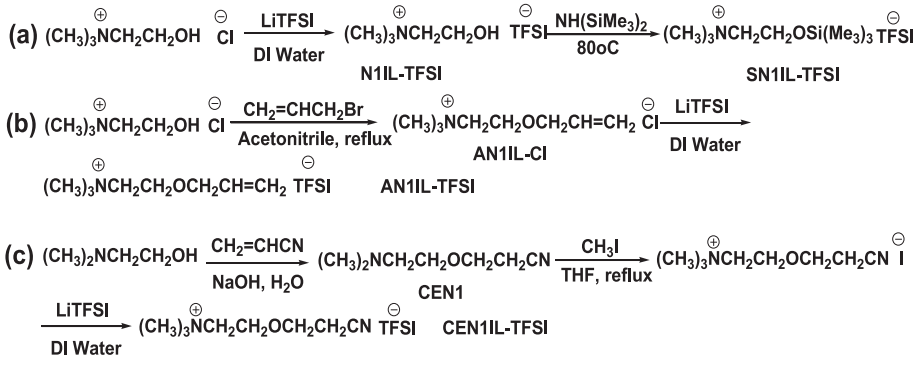
2. Experimental

2.1. Materials

Choline chloride, hydroxylethyldimethylamine, methyl iodide, acrylonitrile, acetonitrile, allyl bromide, sodium hydroxide, *N*-methyl-2-pyrrolidone (NMP) and hexamethylsilazane were purchased from Aladdin Reagent Co. (China). Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was bought from Acros Organics Co. (USA). DMC, $LiPF_6$, LiODFB and a conventional electrolyte of 1 M $LiPF_6$ EC/DEC/DMC ($v/v/v = 1/1/1$) were donated by Dongguan Shanshan Battery Materials Co. (China) and used as received. Artificial graphite powder and high-voltage LCO powder were offered by Amperex Technology Co. (China). Celgard 2400 (Celgard, USA) microporous polypropylene membrane was used as separators.

2.2. Apparatus

^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra were taken on a Bruker avance 400 spectrophotometer. The water content of the synthesized ionic liquids was less than 10 ppm, determined by Karl-Fisher coulometric moisture titrator (831 KF, Metrohm Co., Sweden). Viscosity (η) measurements were performed on SPb-2 Viscometer (Nirun Intelligent Technology Co., China). Thermal gravimetric analysis (TGA) measurements were conducted on a STA409C/PC-PFEIEFFER VACUUMTGA-7 analyzer (NERZSCH-Gertebau GmbH, Germany) in an Ar atmosphere with a flow rate of 30 mL min^{-1} from 40 °C to 450 °C at a heating rate of 10 °C/min. Variable temperature conductivity measurements of the prepared ionic liquids were conducted using a conductivity meter (model DDS-310, Dapu Instru. Co., China), utilizing an oil bath to control temperatures between 0 °C and 90 °C. Linear scanning voltammetry (LSV) experiments using an electrochemical workstation (BAS-ZAHNER IM6, Germany) were performed in a custom-made three-electrode cell with a platinum as working electrode, a lithium metal as reference and a lithium metal counter electrode at a scan rate of 5 mV s^{-1} between −0.5–6.7 V. Electrochemical impedance spectroscopy (EIS) measurements were conducted on a electrochemical workstation (BAS-ZAHNER IM6, Germany) by applying an alternative voltage of 5 mV over the frequency ranging from 0.01 to 10^5 Hz. Fourier transform infrared spectroscopy (FTIR) was recorded on a TENSOR 27 spectrometer (Bruker, Germany) from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. The morphology of the electrodes was observed by a scanning electron microscopy (Hitachi S-



Scheme 1. Synthesis routes of the functionalized choline ILs: (a) SN1IL-TFSI, (b) AN1IL-TFSI and (c) CEN1IL-TFSI.