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Synthesis and electrochemical property of sulfone-functionalized imidazolium ionic liquid electrolytes

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ABSTRACT

Sulfone-functionalized imidazolium ionic liquids were synthesized from direct nucleophilic substitution for the first time. Detailed NMR analysis of the products revealed the competition pathways of classic S_N2 substitution and E2 elimination in the synthesis reaction. Impurities from E2 elimination can easily be overlooked during the conventional method of ionic liquid preparation via S_N2 substitution. Initial electrochemical examination of the synthesized ionic liquids shows good compatibility with $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ cathode material.

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1. Introduction

Sulfur containing solvents such as dimethyl sulfoxide (DMSO) and sulfolane have been widely used in various applications due to their good solvation ability for a wide range of inorganic and organic substrates [1]. The resonance structures of the S=O double bond afford dipolar character with negative charge centered on the oxygen atom (Fig. 1). The high polarity and high dielectric constant (DMSO: 46.7; sulfolane: 44) of the solvents make them promising candidates for the dissociation of electrolyte salts. For example, ethyl methyl sulfone (EMS) based electrolytes display a better anodic stability (>5.5 V vs. Li^+/Li) than the conventional carbonate solvents [2]. Good cycling performance can be achieved for 5 V $LiNi_{0.5}Mn_{1.5}O_4$ cathode materials using a sulfone/linear carbonate binary electrolyte [3]. More recently, DMSO has been studied as an electrolyte solvent for Li-O_2 batteries due to its superior stability against superoxides [4,5].

Ionic liquids (ILs) represent an important family of solvents as safe replacements for the carbonate solvents [6]. ILs have negligible vapor pressure and good thermal stability. They are non-flammable and can be easily recycled. Numerous studies have been conducted on room temperature ILs based on quaternary ammonium or phosphonium cations and weakly-coordinating anions such as PF_6^-, BF_4^-, and $TFSI^-$ [$TFSI^-$ = bis(trifluoromethanesulfonyl)imide]. It has also been shown that the interface between electrode and IL electrolyte is the key factor that determines the electrochemical performance of the batteries. One obvious way to improve the interfacial properties is by adding solid-electrolyte-interphase (SEI) forming additives (i.e. vinylidene carbonate). Besides that, the introduction of various functional groups such as —CN, —OR, —CO_2R has also been proved to be an effective method to improve the electrochemical properties of lithium-ion batteries (LIBs). In our previous studies [7], a disiloxane-functionalized phosphonium based ionic liquid displayed exceptional stability with lithium transition metal oxide cathode and graphite anode.

In continuation of our previous work, this communication seeks to study sulfone functionalized ILs as potential electrolyte for LIBs. Ionic liquids with tethered sulfone groups are known. However, only one study investigated the synthesis of sulfone tethered ionic liquid via rather complicated sequences of reaction comprising the oxidation of the corresponding thioether tethered cation using strong oxidizing agent – *m*-chloroperoxybenzoic acid (*m*CPBA) [8]. Interestingly, the rather "remote" sulfone group was shown to have important effects on IL solvent properties (i.e. polarity, H-bonding, etc.). However, sulfone tethered ILs has not been evaluated as lithium-ion electrolytes even though it possesses enhanced safety characteristics. Herein, we reported the synthesis of new sulfone-functionalized ionic liquids via a simplified synthetic route which employs conventional nucleophilic displacement reaction [3]. The competing pathways in the formation of sulfone tethered ILs has been investigated and identified. Electrochemical property of the synthesized ILs was examined as new lithium-ion battery electrolytes.

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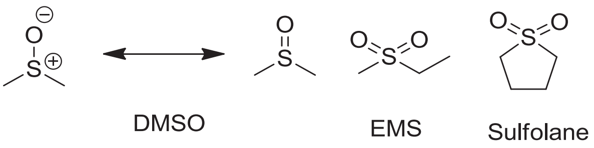

Fig. 1. Resonance structures of DMSO (left) and representative solvents containing S=O groups (right).

2. Experimental

2.1. Chemical and materials

All manipulations were carried out under a nitrogen atmosphere, using standard Schlenk techniques and dried solvents. All reagents were purchased from Aldrich and used as received. ^{1}H and ^{13}C NMR experiments were performed on a Bruker model DMX 500 NMR spectrometer (11.7 T).

2.2. Ionic liquid synthesis

2.2.1. Synthesis of 2-Bromoethyl methyl sulfone [9]

PBr_3(20 g, 0.074 mol) was added slowly to 2-methylsulfonyl ethanol (25 g, 0.2 mol) with vigorous stirring under Ar atmosphere. The reaction mixture was stirred at room temperature for 4 days to afford a dark-blue solution. Millipore water (30 mL) was carefully added to quench the reaction. The aqueous solution was stored frozen for 1 h and crystalline compounds were formed from slow thawing at ambient temperature. Yield: 16 g (43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (t, J = 7 Hz, 2H, $BrCH_2$), 3.54 (t, J = 7 Hz, 2H, CH_2SO_2), 3.00 (s, 3H, SO_2CH_3). ^{13}C NMR (125 MHz, CD_3Cl): δ 56.9 (s, $BrCH_2$), 41.9 (s, CH_2SO_2), 21.1 (s, SO_2CH_3).

2.2.2. Synthesis of 1-methyl-3-(2-(methylsulfonyl)ethyl)-1H-imidazol-3-ium bromide, [$ImC_2HSO_2CH_3$]Br (***1a***)

A mixture of 1-methylimidazole (2 g, 0.024 mol) and 2-bromoethyl methyl sulfone (4.62 g, 0.024 mol) was charged into a round-bottom flask equipped with a condenser. The mixture was stirred at 60 °C for 24 h. The resulting yellow and viscous oil was washed with CH_3CN and then dried under vacuum. Yield: 4.54 g (83%). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.22 (s, 1H), 7.84 (t, J = 2 Hz, 1H), 7.72 (t, J = 2 Hz, 1H), 4.66 (t, J = 7 Hz, 2H, N—CH_2), 3.85 (s, 3H, N—CH_3), 3.82 (t, J = 7 Hz, 2H, CH_2SO_2), 3.01 (s, 3H, SO_2CH_3). ^{13}C NMR (125 MHz, d_6-DMSO): δ 137.3 (s), 123.6 (s), 122.7 (s), 52.5 (s), 42.6 (s), 41.0 (s), 35.9 (s).

Table 1
Crystal data and structure refinement of complex **1a**.

Formula	$C_7H_{13}BrN_2O_2S$	a (Å)	6.7476(2)
M_W	269.16	b (Å)	7.5071(2)
Cryst. syst.	Triclinic	c (Å)	11.0657(3)
T (K)	150(2)	α (°)	101.982(1)
Wavelength	0.71073 Å	β (°)	92.5430(1)
Space group	$P-1$	Z	2
μ (mm^{-1})	4.133	ρ ($g\,cm^{-3}$)	1.722
F(0 0 0)	272	$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0262, 0.0751
GoF	1.193	$R1$, $wR2$ (all data)	0.0267, 0.0774

$R1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$; $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(N_{obs} - N_{var})]^{1/2}$.

2.2.3. Synthesis of [$ImC_2HSO_2CH_3$][TFSI] (***2a***)

To a solution of [$ImC_2HSO_2CH_3$]Br (12.36 g, 0.046 mol) in distilled water (30 mL) was added lithium bis(trifluoromethanesulfonyl)imide (13.2 g, 0.046 mol). The reaction mixture was stirred for 24 h at ambient temperature. Distilled water (100 mL) was added to the mixture and the bottom layer was extracted with dichloromethane. The organic layer separated was washed with fresh distilled water, dried over $MgSO_4$. The crude solution was stirred with decolorizing charcoal and filtered through a plug of celite and then a plug of activated alumina. The solution was concentrated by removing the solvent under reduced pressure and dried at 100 °C under vacuum. Yield: 12 g (62%). ^{1}H NMR (500 MHz, CD_3CN): δ 8.49 (s, 1H), 7.45 (br, s, 1H), 7.34 (br, s, 1H), 4.59 (t, J = 7 Hz, 2H, N—CH_2), 3.82 (s, 3H, N—CH_3), 3.57 (t, J = 7 Hz, 2H, CH_2SO_2), 2.95 (s, 3H, SO_2CH_3). ^{13}C NMR (125 MHz, CD_3CN): δ 136.7 (s), 123.8 (s), 122.7 (s), 119.7 (q, $^1J_{C-F}$ = 319 Hz, TFSI), 52.6 (s), 42.8 (s), 41.1 (s), 36.0 (s).

2.2.4. Attempted synthesis of [$ImC_2MeSO_2CH_3$]Br (***1b***)

A mixture of 1,2-dimethylimidazole (7.2 g, 0.075 mol) and 2-bromoethyl methyl sulfone (14 g, 0.075 mol) was charged into a round-bottom flask equipped with a condenser. The mixture was stirred at 60 °C for 24 h. The resulting yellow and viscous oil was analyzed by ^{1}H NMR, which showed that 2a constitute ca. <20% of the resulting mixture. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 2 Hz, 1H), 7.46 (d, J = 2 Hz, 1H), 4.77 (t, J = 6 Hz, 2H, N—CH_2), 3.92 (t, J = 6 Hz, 2H, CH_2SO_2). Identification and assignment of the full set of the ^{1}H NMR resonance of **1b** was not possible because of the presence of other compounds.

2.3. Instrumentation and Procedures

2.3.1. Electrochemical testing

The charge–discharge cycling performance was tested on a Maccor Electrochemical Analyzer using 2032 coin cells with

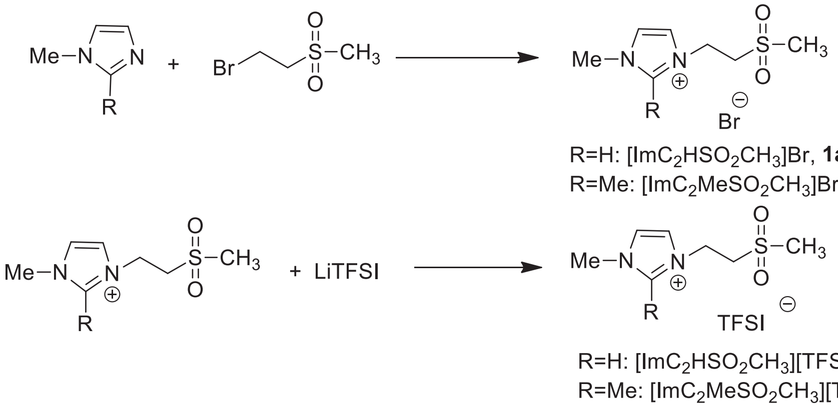

Fig. 2. Reaction scheme for the synthesis of sulfone-functionalized ionic liquid.