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$_2$R 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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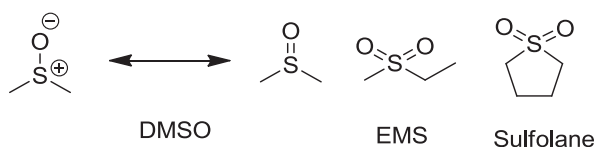
Fig. 1. Resonance structures of DMSO (left) and representative solvents containing S=O groups (right).

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$_2$SO$_2$), 3.00 (s, 3H, SO$_2$CH$_3$). ^{13}C NMR (125 MHz, CD$_3$Cl): δ 56.9 (s, BrCH$_2$), 41.9 (s, CH$_2$SO$_2$), 21.1 (s, SO$_2$CH$_3$).

2.2.2. Synthesis of 1-methyl-3-(2-(methylsulfonyl)ethyl)-1H-imidazol-3-ium bromide, [ImC$_2$HSO$_2$CH$_3$]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$_3$CN 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$_2$SO$_2$), 3.01 (s, 3H, SO$_2$CH$_3$). ^{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$_7$H$_{13}$BrN$_2$O$_2$S	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

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

2.2.3. Synthesis of [ImC$_2$HSO$_2$CH$_3$][TFSI] (2a)

To a solution of [ImC$_2$HSO$_2$CH$_3$]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$_3$CN): 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$_2$SO$_2$), 2.95 (s, 3H, SO$_2$CH$_3$). ^{13}C NMR (125 MHz, CD$_3$CN): 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).
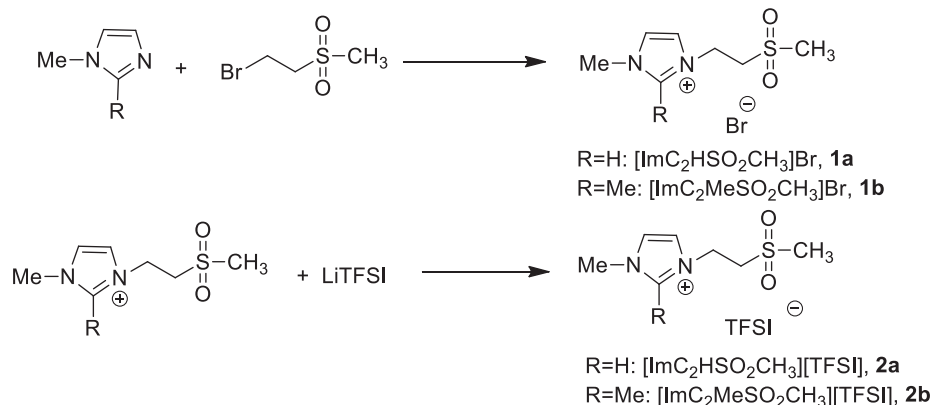
2.2.4. Attempted synthesis of [ImC$_2$MeSO$_2$CH$_3$]Br (1b)

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$_2$SO$_2$). 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

R=H: [ImC$_2$HSO$_2$CH$_3$]Br, **1a**
R=Me: [ImC$_2$MeSO$_2$CH$_3$]Br, **1b**

R=H: [ImC$_2$HSO$_2$CH$_3$][TFSI], **2a**
R=Me: [ImC$_2$MeSO$_2$CH$_3$][TFSI], **2b**

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

Table 2
Selected bond lengths (Å) and bond angles (°) for **1a**.

S1—O1	1.4506(12)	N1—C4	1.3294(18)
S1—O2	1.4464(11)	N2—C3	1.3821(19)
S1—C6	1.7820(15)	N2—C4	1.3339(19)
S1—C7	1.7504(15)	N2—C5	1.4690(18)
N1—C1	1.462(2)	C2—C3	1.358(2)
N1—C2	1.383(2)	C5—C6	1.527(2)
O1—S1—O2	116.22(7)	C3—N2—C4	108.94(12)
O1—S1—C6	108.48(7)	C3—N2—C5	125.48(13)
O1—S1—C7	109.56(7)	C4—N2—C5	125.52(12)
O2—S1—C6	109.09(7)	N1—C2—C3	106.94(13)
O2—S1—C7	109.64(8)	N2—C3—C2	106.79(13)
C6—S1—C7	103.03(7)	N1—C4—N2	108.40(13)
C1—N1—C2	125.35(12)	N2—C5—C6	113.49(12)
C1—N1—C4	125.52(13)	S1—C6—C5	112.16(10)
C2—N1—C4	108.92(12)		
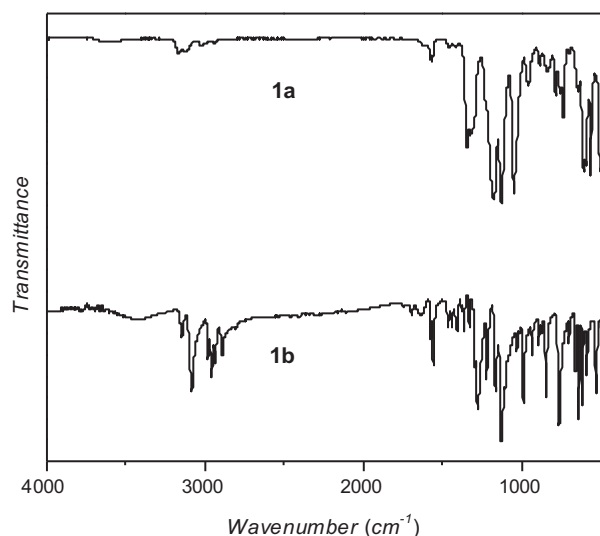
Fig. 3. FT-IR spectra of **1a** and **1b**.

Li$_{1.1}$[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]$_{0.9}$O$_2$(NCM) as the cathode, lithium metal as the anode, and a Celgard 3501 separator. The effective electrode area was 1.6 cm^2. The positive electrode was made of 84 wt% NCM, 8 wt% TB5500 carbon black, and 8 wt% polyvinylidene fluoride (PVDF, Kureha 7208). Performance data were acquired and analyzed by the software associated with the instrument. FTIR spectra were recorded on a Perkin-Elmer spectrum 100 instrument with an attenuated total reflection (ATR) sampling accessory.

2.3.2. Crystal structure determination of 1a by single-crystal X-ray diffraction

A colorless crystal of **1a** was mounted onto the tip of a with glass fiber with epoxy and placed on a Bruker APEX II 3-circle diffractometer equipped with an APEX II detector. The crystal temperature was maintained at 150(2) K through use of an Oxford Cryostream 700 Plus LT device. The analysis was carried out using
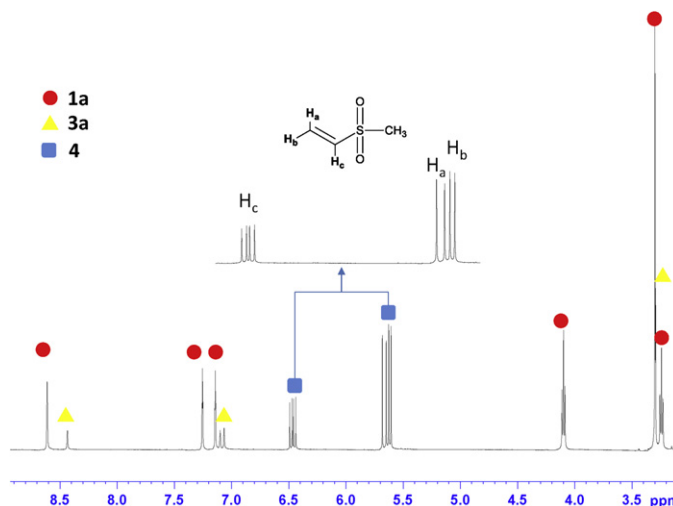

Fig. 4. ^{1}H NMR spectrum of a typical reaction mixture of **1a**, **3a** and **4** in the region of δ 9.0–3.0.

Moκα radiation (λ = 0.71073 Å) with a frame exposure time of 30 s and a detector distance of 5.00 cm. Five hemispheres were collected with 0.30° ω scans. The raw intensity data were corrected for absorption (SADABS) [10]. The structure was solved and refined by using SHELXTL [11]. A direct-method calculation provided most of atomic positions from the electron density map. Full-matrix least squares/difference Fourier cycles were performed to locate the remaining atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as "riding atoms" with relative isotropic displacement parameters. Structural and refinement parameters are provided in Tables 1 and 2.

3. Results and discussion

Sulfone-functionalized imidazolium ionic liquids are synthesized by quarternization of the imidazole ring with appropriate halides followed by anion metathesis. Detailed analysis of the ^{1}H NMR spectrum of the reaction of 2-bromoethyl methyl sulfone [9] with 1-methylimidazole as illustrated in Fig. 2 indeed revealed the formation of the desired product **1a**. Workup of the reaction mixture and subsequent wash of the precipitate with diethyl ether afford the pure **1a** in a ∼80% yield. The CH$_2$—CH$_2$ linker between the imidazole ring and sulfone group gave rise to a pair of triplet peak at δ 4.66 ppm (N—CH$_2$) and 3.82 ppm (S—CH$_2$) respectively in the ^{1}H NMR spectrum of **1a**, indicating a significantly downfield shifting from 2-bromoethyl methyl sulfone (δ 3.70 ppm and δ 3.54 ppm). The chemical structure of **1a** and **1b** are characterized and confirmed by IR spectroscopy. FTIR spectra of **1a** and **1b** are shown in Fig. 3. The IR peaks at 1316 and 1124 cm^{-1} in the IR spectrum of **1a** belong to the ν_{asym}SO$_2$ and ν_{sym}SO$_2$ stretching bond respectively.
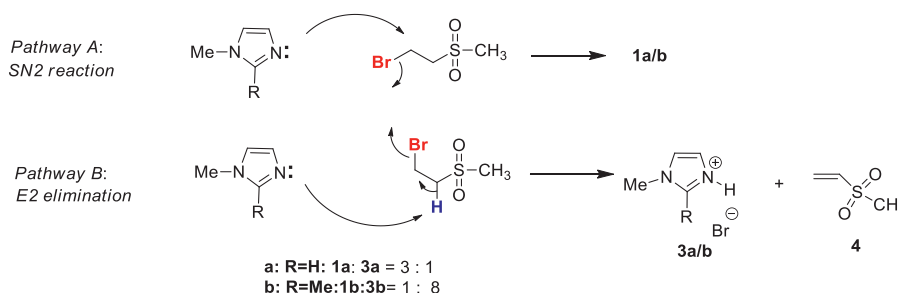
Fig. 5. Competing S$_N$2 reaction and E2 elimination in the synthetic process of precursor **1a** and **1b**.
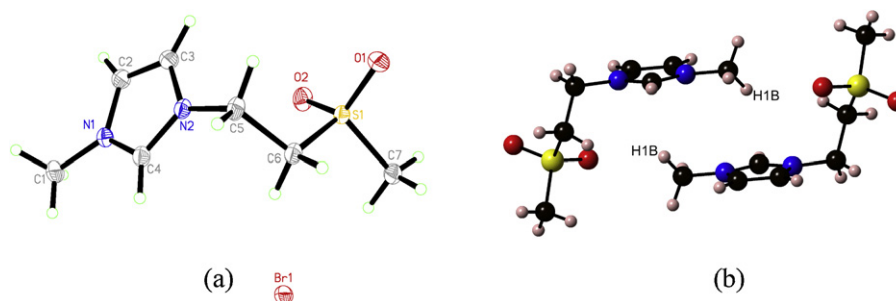
Fig. 6. (a) Thermal ellipsoid plot and atomic numbering scheme for the crystal structure of **1a**. Ellipsoids are drawn at 50% probability, with hydrogen atoms depicted as spheres of arbitrary radius; (b) the $ImC_2HSO_2CH_3^+$ cations pack as centrosymmetric dimmers with CH–π interactions in the solid state. Carbon (black), nitrogen (blue), sulfur (yellow), oxygen (red), and hydrogen (salmon) atoms are depicted as spheres of arbitrary radius. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
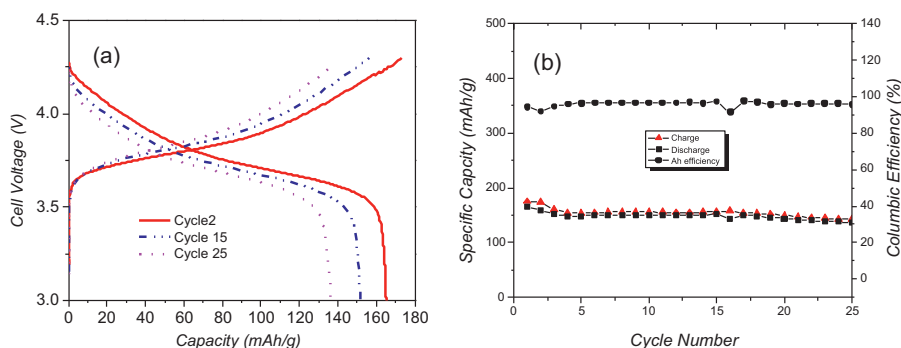
Fig. 7. (a) Charge/discharge voltage profiles of Li/NMC cell with 0.5 M LiTFSI/**1b** electrolyte; (b) capacity retention and the coloumbic efficiency of Li/NMC cells 0.5 M LiTFSI/**1b** (C/20, testing temperature: 55 °C).

The frequency values agrees well with that observed for other aliphatic sulfones (i.e. propyl sulfone: 1314 and 1132 cm^{-1}). Imidazolium cations can be identified by the spectra features at 1174 cm^{-1} (imidazole C—C, C—N stretching), 1048 cm^{-1} (in-plane antisymmetric C—N stretching of N—CH$_3$). The FTIR spectrum of **1b** is more complicated due to the presence of sulfone group in TFSI anions. The resonance peaks at 1360–1300 cm^{-1} can be ascribed to $\nu_{asym}SO_2$ in the immidazolium cation while the resonance peak at 1283 cm^{-1} is associated with $\nu_{asym}SO_2$ from the TFSI anions.

The quarternization process of 2-bromoethyl methyl sulfone with 1-methylimidazole generated byproducts and their structures were identified by the NMR spectroscopy. As shown in Fig. 4, ^{1}H NMR resonance peaks in the vinyl proton region appear as a doublet of doublet at δ 6.95 ($J = 17$ Hz and 10 Hz) and two doublets at δ 6.3–6.1. This ABC pattern in the ^{1}H NMR spectra is characteristic of the monosubstituted terminal alkenes **4**. ^{1}H NMR resonance arising from the imidaole ring region was identified as three singlets with upfield shift from the corresponding protons of **1a**. Based on the detailed NMR analysis, we proposed the competitive pathways between classic S$_N$2 substitution and E2 elimination during the synthesis of **1a** and the reaction mechanism is shown in Fig. 5. Apparently, the parent imidazole can act both as a nucleophile and a base. Both S$_N$2 mechanism and E2 mechanism result in the release of Br$^-$, which is a good leaving group. The competition is kinetic in nature and can be affected by the substrate. For 1-methylimidazole, the ratio of **1a/3a** is 3/1. However 1,2-dimethylimidazole favors the elimination reaction. The ratio of the resulting **1b/3b** is about 1/8, which makes the isolation of pure **1b** not feasible. This may be attributed by the stronger basicity and increased steric bulkiness of 1,2-dimethylimidazole. The S$_N$2/E2 competition pathways generally have been ignored in the synthesis of ILs. There is a chance that the elimination product could be carried over to the subsequent steps existing as trace of impurities in the final product of ILs if no special cautions have been taken to remove it.

1a crystallizes in triclinic space group P-1 with the asymmetric unit containing one $ImC_2HSO_2CH_3^+$ cation and bromide anion. Crystal data and structure refinement of complex **1a** is summarized in Table 1. The molecular structure of **1a** is illustrated in Fig. 6(a), and selected bond distance and angles are provided in Table 2. While this is the first crystal structure reported of the $ImC_2HSO_2CH_3^+$ cation, the geometry of the 1,3-dimethylimidazolium moiety is similar to that previously reported [12–14]. As illustrated in Fig. 6(b), in the solid state, the $ImC_2HSO_2CH_3^+$ cations pack as centrosymmetric dimers stabilized by a weak C—H. . .π hydrogen bond (2.69 Å between the ring centroid and the hydrogen atom) between a methyl hydrogen atom and the imidazolium ring π-system along the (0 1 0) direction. The aromatic ring centroid separation is 4.6202(9) Å with the perpendicular separation between these rings being 3.3461(6) Å and a slippage of 3.186 Å.

The anion metathesis of isolated **1a** with LiTFSI afforded the final product of sulfone-substituted imidazolium ILs **2a**. After LiTFSI salt dissolved in **2a**, an IL electrolyte containing 0.5 M LiTFSI was examined as a potential electrolyte material for Li-ion battery. A typical slope-like voltage profiles were observed (Fig. 7(a)) in Li/Li$_{1.1}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{0.9}$O$_2$ (NCM) cells employing 0.5 M LiTFSI/**2a** as electrolyte. Fig. 7(b) is the representative capacity retention profile of Li/NCM cell using the same electrolyte. The initial specific charge and discharge capacities are about 175 and 165 mAh/g, respectively, which are close to the literature value. The initial coulombic efficiency is low (~94%) but maintains at >98% in the subsequent cycles with a specific discharge capacity of 145 mAh/g.

4. Conclusion

In conclusion, we investigated the first synthesis of sulfone-functionalized ionic liquid from the direct quaternization reaction (S$_N$2) of imidazole and alkyl bromide. The competition pathways

between S_N2 nucleophilic substitution and E2 elimination during the synthesis of ionic liquid showed a substrate-dependent selectivity. 1,2-Dimethylimidazole shows reversed preference of S_N2 reaction as observed for 1-methylimidazole. Such side reactions probably are less pronounced if simple alkyl halides are used as the substrates. Our study thus magnifies the "side effect" of the most common synthetic route for ILs and emphasizes the importance of extra purification process to remove possible impurities. The initial electrochemical examination in Li battery demonstrated that sulfone-functionalized ionic liquid has good compatibility with NCM cathode material.

Acknowledgments

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