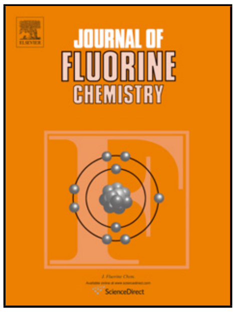

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Synthesis of new fluorinated imidazolium ionic liquids and their prospective function as the electrolytes for lithium-ion batteries

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Highlights

- Green pathway to prepare fluorinated ionic liquids.
- 1-(2,2,2-Trifluoroethyl)-3-methylimidazolium tosylate.
- 1-(2,2,2-Trifluoroethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.
- Both will be prospective electrolytes for lithium batteries.
- [CF_3CH_2MIm][Tf_2N] even showed a wider electrochemical window.

Abstract: Two fluorine-containing ionic liquids, 1-(2,2,2-trifluoroethyl)-3-methylimidazolium tosylate and 1-(2,2,2-trifluoroethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (TFSI anion), were obtained in good yields and high purity via a green pathway procedure free of solvent and hazardous catalyst. The incorporation of CF_3 moieties in imidazolium structure decreases the ILs TFSI melting point. The preliminary electrochemical results are very promising, a wide electrochemical stability up to 5.7 V vs Li^+/Li for the fluorinated imidazolium with TFSI anion.

Keywords: Fluorinated imidazolium; Ionic liquids; Lithium-ion battery; Electrolyte; Solvent-free pathway; Electrochemical stability.

1. Introduction

In recent years, there have been many studies focusing on developing new electrolytes for rechargeable lithium batteries to enhance its safety and longevity [1-3]. Some electrolytes based on solid and gel materials were developed but their poor ion conductivity has been the main obstacle which lessens the interest towards these materials [3-5]. Ionic liquids (ILs), alternatively, have been considered as the promising candidates because of their extraordinary characteristics such as non-volatility, non-flammability, high ion conductivity, and extremely thermal and electrochemical stability [6-8]. Especially, bis(trifluoromethanesulfonyl)imide based ionic liquids have attracted a greatest attentions due to their low viscosity as well as the broad electrochemical window [9-17]. In this study, we proposed a green pathway to prepare 1-(2,2,2-trifluoroethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([CF_3CH_2MIm][TFSI]) via the intermediate 1-(2,2,2-trifluoroethyl)-3-methylimidazolium tosylate ([CF_3CH_2MIm][OTs]) and studied their thermal and electrochemical properties for the first time to give initial evaluations on their potential of being used as new electrolytes for lithium batteries. Compared to previous reports, in which toxic solvent methylene chloride [18,19] or hazardous catalyst pyridine [20] was used, the procedure here in allowed to obtain [CF_3CH_2MIm][TFSI] under very mild conditions (solvent-free, cheap and non-hazardous catalyst, and less time-consuming). The thermal and electrochemical properties of synthesized ILs were initially characterized. The fluorinated imidazolium ILs exhibits very high electrochemical stability in oxidation.

2. Results and discussion

2.1. Synthesis of ionicliquids

In the three-step pathway illustrated in Scheme 1, the final product [CF_3CH_2MIm][TFSI] was planned to be derived from the precursor [CF_3CH_2MIm][OTs] which had been previously synthesized via the nucleophilic attack of 1-methylimidazole (**4**) to ester **3**. The first step, tosylation of 2,2,2-trifluoroethanol, was performed under ultrasound irradiation to afford the first isolatable compound **3**. The results from Table 1 showed that reaction temperature, reaction time, and molar ratio **1**:**2** affected the yield of **3** at different rates. In general, there was a slight increase in yield of compound **3** along with raising the reaction temperature or prolonging the reaction time. However, no complete conversion could be observed unless an excess amount of reactant **2** was used. Due to the high hydroscopic, at least 1.2 equiv. of compound **2** was used to ensure a quantitative conversion (entry 9, Table 1).

Scheme 1

Compared to other activation methods investigated in our works (entry 12-14, Table 1) and previous reports [21-25], sonication was the most appropriate method for such heterogeneous reactions to afford compound **3** in the best yield. In addition, the replacement of traditional toxic bases (e.g. pyridine, triethylamine, 4-DMAP, and DABCO) by K_2CO_3, an environmentally benign one, was also encouraged in the green chemistry.

Table 1

For the next step, it can be referred from Table 2 that the intermediate ionic liquid [CF_3CH_2MIm][OTs] could be obtained in the highest yield of 77% at 120 ^oC within 24 h (entry 9, Table 2). Increasing the temperature or extending the reaction time did not result in better yields (entry 5 and 10, Table 2). [CF_3CH_2MIm][OTs] was then ion-exchanged with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to provide the final product at 40 ^oC with a few minutes under the ultrasound irradiation (71%, entry 2, Table 3). The microwave irradiation and the conventional heating under the same conditions mentioned for the sonication did not further increase the yields of product (entry 8 and 9, Table 3).

Table 2

Table 3

2.2. Physical chemical and electrochemical properties of synthesized ionic liquids

2.2.1. Physical chemical properties

Two synthesized ionic liquids, through thermo-gravimetric analysis (TGA), were evaluated for the thermal stability. The ILs exhibit a high decomposition temperature, above 340 ^oC (Table 4). The DSC analysis showed that [CF_3CH_2MIm][TFSI] presents a lower melting temperature, about -16 ^oC instead of -15 °C for [CH_3CH_2MIm][TFSI]. The replacement of a CH_3 group by a CF_3 one induces a decrease in the IL melting point. The result is quite different with the work of M.L.P. Le et al [2,12]. However, it could be a good alternative to use CF_3 group incorporated in the imidazolium structure in order to decrease the melting point and the viscosity of ionic liquid.

Table 4

The density, viscosity and conductivity of [CF_3CH_2MIm][TFSI] was determined and compared to the electrolyte of [CF_3CH_2MIm][TFSI] + 0.25 M LiTFSI. The addition of LiTFSI induces a decrease of ionic conductivity. The addition of lithium salt decreases the ionic conductivity. This behavior may be due to the increase in the viscosity or association resulting from specific interaction involving the formation of ionic cluster [2].

Table 5

2.2.2. Electrochemicalproperties

One of the most important requirements for the use of ILs as liquid electrolyte is that they must have a wide electrochemical window to ensure that it is neither oxidized nor reduced in the operating voltage range of lithium batteries. This parameter can be easily evaluated by cyclic voltammetry.

Acetonitrile (ACN) and the mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 v/v) were used as solvents to evaluate firstly the electrochemical windows of synthesized ionic liquids, particularly [CF_3CH_2MIm][OTs] whose melting point is fairly high above the room temperature. Compared with a different supporting electrolyte 0.005 M TBAP/ACN, equimolar solutions of [CF_3CH_2MIm][TFSI] and [CF_3CH_2MIm][OTs] generated similar cyclic voltammograms in which reduction and oxidation peaks were approximately 2.7 and 4.3 V, respectively. However, for the ionic liquid dissolved in EC-DMC, the oxidation peaks were shifted to more positive potential (over 4.5 V) compared withthe solution containing TBAP/ACN at the same molar concentration. The electrochemical windows were expanded as the result. In addition, the presence of flat potential plateau also confirmed the high purity of the synthesized ionic liquids (Figure 1).

Figure 1

Thus, EC-DMC was chosen as an appropriate solvent for further investigations of [CF_3CH_2MIm][OTs] solutions at various molar concentrations. In Figure 2, the oxidation peaks were gradually shifted to more positive value while the reduction peaks remained almost unchanged when increasing the concentration of [CF_3CH_2MIm][OTs] solutions. This result proved that obtained oxidation-reduction signals were generated from ionic liquid [CF_3CH_2MIm][OTs], not from the solvent solution.

Figure 2

In order to compare with the conventional electrolyte 1 M $LiPF_6$/EC-DMC (1:1) used in lithium batteries, the cyclic voltammogram of pure [CF_3CH_2MIm][TFSI] was recorded. The voltammograms in Figure 3 showed that the pure [CF_3CH_2MIm][TFSI] started being oxidized at 5.7 V vs Li^+/Li while the 1 M $LiPF_6$/EC-DMC (2:1) solution was only stable within the potential range below 5.5 V vs Li^+/Li. When scanning to more positive potential over this limit, the oxidation current of $LiPF_6$ solution increased so rapidly that an oxidation wall was created. Besides, the oxidation stability of pure [CF_3CH_2MIm][TFSI] is higher than [CH_3CH_2MIm][TFSI] (about 5.8 V vs Li^+/Li). The electrochemical stability of imidazolium-based ILs seems insufficient in lithium batteries. Thus, it can be concluded that the incorporation of CF_3 moieties group in imidazolium structure improve well the ILs oxidation stability. The result is coherent with the work of M.L.P. Le et al [2,12].

The addition of lithium salt induces a remarkable decrease of oxidation current while the onset oxidation potential remains about 5.8 V vs Li^+/Li (inset in Figure 3). The role of Li^+ ions in the formation of surface films on different electrodes (glassy carbon, platinum,…) in IL was already discussed in the literature previously. It suggests that protective Li^+ containing are formed on a Pt metal surface due to the reduction of TFSI in the presence of Li^+ ion [27,28]. However, the formation of SEI film layer on the electrode materials during cycling test is still irrelevant for ILs containing Li salt.

Figure 3

3. Experimental

3.1. Chemicals and equipments

All chemical precursors and solvents were purchased from Sigma-Aldrich and employed without further purification. The synthesized ionic liquids were vacuum dried at 120 °C during 24 hours. The water contains of ILs, determined by Karl-Fisher was below 20 ppm. The ILs were stored in a glovebox ($[H_2O] < 3$ ppm). The structure of intermediate and final products were confirmed by ^1H NMR and ^{13}C NMR spectra measured on a Bruker 500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) in DMSO-*d6* or acetone-*d6*, and mass spectra recorded via GC-MS and LC-HR-MS techniques. GC-MS analyses were performed on an Agilent GC System 7890A, equipped with a mass selective detector Agilent 5973 and a capillary column HP-5MS (30 m x 0.25 mm x 0.25 μm). LC-HRMS analyses were performed on a Bruker micrOTOF-Q II.

DSC measurements were performed using Mettler Toledo DSC1 Star. Samples of 10 mg were sealed in aluminiumpansin a glovebox. Each sample was heated from -80 °C to 100 °C at a heating rate of 10 °C.min^{-1}. Thermogravimetric measurements were carried outwitha TGA Q500 V20.10 Build. A few milligram of the sample was heated from the room temperature up to 600 °C at 10 °C.min^{-1} under oxygen flow.

The ionic conductivity and viscosity of ILs in glove box was measured by using Conductimeter OAKION CON 2700 and Ostwald viscometer CANNON.

Cyclic voltammetry of ILs at the scan rate of 1 mV.s^{-1} and 20 mV.s^{-1} was recorded on MGP2 Biologic instrument (France) by using a three-electrode cell. The counter electrode was a Pt wire and the working electrode was a Pt electrode with a diameter 1 mm and 25 μm for characterization of ILs solution and pure ILs. The reference electrode was a Ag wire in $AgNO_3$ 10 mM in acetonitrile + 0.1 M tetrabutylammonium perchlorate (TBAP). Preparation of electrolyte solutions was carried out in a glovebox to protect the ionic liquids from hygroscopicity. Potential can be converted to the Li^+/Li by adding 3.548 V [29].

The oxidation stability of lithium electrolyte containing pure ILs with LiTFSI was also studied for by cyclic voltammetry (CV). The lithium salt concentration is 0.25 M in order to compromise the ionic conductivity and viscosity of electrolyte.

3.2. Synthesis of ionic liquids

Ionic liquids were synthesized in a Branson 1510 ultrasonic bath, a Discover (CEM) microwave reactor, and an IKA magnetic stirrer.

*3.2.1. 2,2,2-Trifluoroethyl tosylate (**3**)*

3.2.1.1. Under ultrasonic irradiation

A glass capped test tube (10 mL volume) was charged with 2,2,2-trifluoroethanol (0.500 g, 5 mmol), tosyl chloride (1.144 g, 6 mmol), and potassium carbonate (1.382 g, 10 mmol). Then it was immersed into an ultrasonic bath and irradiated for 60 min at 55 ^oC. After finishing above steps, sodium hydroxide (0.200 g, 5 mmol) was added and the resulting mixture was continuously sonicated for further 5 min. The mixture was subsequently cooled to the room temperature and diluted with Et_2O. The ether solution was washed with water until neutralization, dried over Na_2SO_4, filtered, and concentrated under low pressure to afford product **3** as a white crystallized solid (92%). MS (EI) *m/z* (%): 254, 155, 91 (100), 65.

3.2.1.2. Under microwave irradiation

A 10 mL pressurized vessel was charged with the same materials as in the previous section. The mixture was then exposed to the microwave at 55 ^oC for 60 min in a Discover (CEM) microwave reactor. Upon the completion, the resulting mixture was worked up in the same manner described for the ultrasound-assisted reaction.

3.2.1.3. Under conventional heating

A flask (10 mL) was charged with the same materials as described above. Then it was assembled with a condenser whose upper end was fitted with a drying tube. This assembly was immersed in an oil bath, heated gently, and simultaneously stirred for 60 min at 55 ^oC. Upon completion, the resulting mixture was again worked up according to the procedure mentioned above.

3.2.1.4. Under grind condition

A mixture of the initial compounds as mentioned in previous sections was ground in a mortar for 60 min at room temperature. Upon completion, the work-up procedure was the same as above.

3.2.2. [CF_3CH_2MIm][OTs]

A mixture of compound **3** (1.271 g, 5 mmol) and 1-methylimidazole (0.411 g, 5 mmol) were charged into a flask (10 mL) assembled with a condenser. This montage was heated in an oil bath, and simultaneously stirred for 24 h at 120 °C. Upon completion, the resulting mixture was washed with Et_2O until all starting material were removed completely (checked by GC) and freeze-dried under vacuum to obtain [CF_3CH_2MIm][OTs] as a yellow solid at room temperature (77%). ^{1}H NMR (500 MHz, DMSO-*d6*): δ (ppm) 9.35 (s, 1H), 7.85 (s, 1H), 7.83 (s, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.40 (q, J = 9.0 Hz, 2H), 3.90 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, DMSO-*d6*): δ (ppm) 145.3, 138.4, 137.9, 128.1, 125.4, 124.4, 123.5, 122.7 (q, J = 276 Hz), 48.3 (q, J = 35 Hz), 36.1, 20.7; HRMS (ESI$^+$) *m/z* 165.0639 (165.0639 calcd. for $C_6H_8N_2F_3$); Anal. calcd. for $C_6H_8N_2F_3$: (%) C 43.62; H 4.89; N 16.97; F 34.53. Found: C 43.64; H 4.88; N 16.96; F 34.51. HRMS (ESI$^-$) *m/z* 171.0116 (171.0115 calcd. for $C_7H_7O_3S$); Anal. calcd. for $C_7H_7O_3S$: (%) C 49.12; H 4.12; O 28.06; S 18.70. Found: C 49.11; H 4.12; O 28.04; S 18.73.

3.2.3. [CF_3CH_2MIm][TFSI]

3.2.3.1. Under ultrasonic irradiation

A mixture of [CF_3CH_2MIm][OTs] (0.336 g, 1 mmol) and deionized water (1 mL) was charged into a glass test tube (10 mL) and then immersed into an ultrasonic bath. A solution of LiTFSI (0.2871 g, 1 mmol) in deionized water (1 mL) was added dropwise to the above ionic liquid solution. The mixture was irradiated for 10 min at 40 °C. Upon completion, the resulting mixture consisted of two phases, the upper aqueous phase was removed and the lower phase was diluted with dichloromethane. This organic solution was then washed with deionized water until no remaining starting materials (LiTFSI and [CF_3CH_2MIm][OTs]) as well as by-product (LiOTs) was detected, concentrated under low pressure, and finally freeze-dried under vacuum to give [CF_3CH_2MIm][TFSI] as a yellow liquid at room temperature (71%). ^{1}H NMR (500 MHz, acetone-*d6*): δ (ppm) 9.23 (s, 1H), 7.85 (s, 1H), 7.82 (s, 1H), 5.36 (q, J = 9.0 Hz, 2H), 4.12 (s, 3H); ^{13}C NMR (125 MHz, acetone-*d6*): δ (ppm) 138.4, 124.4, 123.6 (q, J = 276 Hz), 123.4, 121.0 (q, J = 319 Hz), 50.1 (q, J = 36 Hz), 37.3. HRMS (ESI$^+$)

m/z 165.0639 (165.0639 calcd. for $C_6H_8N_2F_3$); Anal. calcd. for $C_6H_8N_2F_3$: (%) C 43.62; H 4.89; N 16.97; F 34.53. Found: C 43.64; H 4.88; N 16.96; F 34.51. HRMS (ESI$^-$) m/z 279.9153 (279.9172 calcd. for $C_2O_4NF_6S_2$); Anal. calcd. for $C_2O_4NF_6S_2$: (%) C 8.57; O 28.06; N 5.00; F 40.72; S 18.70. Found: C 8.59; O 28.05; N 5.01; F 40.71; S 18.69.

3.2.3.2. Under conventionalheating

The same materials as in the previous section were charged into a flask (5 mL) which was subsequently immersed in an oil bath, heated gently, and simultaneously stirred for 10 min at 40 ^{o}C. Upon completion, the resulting mixture was worked up according to the procedure mentioned above.

3.2.3.3. Under microwave irradiation

A 10 mL pressurized vessel was charged with the same mixture as described before. The mixture was then exposed to microwave at 40 ^{o}C for 10 min in a Discover (CEM) microwave reactor. Upon completion, the resulting mixture was worked up in the same manner described for previous methods.

4. Conclusion

We successfully synthesized [CF_3CH_2MIm][TFSI] and its precursor, [CF_3CH_2MIm][OTs] by the ultrasonic irradiation without using solvents, hazardous catalysts and in the short reaction time. Both of the synthesized ionic liquids showed the good thermal and electrochemical stability. These behaviors are crucially required for the electrolytes in lithium batteries. [CF_3CH_2MIm][TFSI] exhibits a wide electrochemical window in comparison with the conventional electrolyte (1 M $LiPF_6$/EC-DMC). The primarily result is very encouraging, that the incorporation of CF_3 group in imidazolium structure enhance the oxidation stability and decrease the melting point as well as viscosity of ILs. The electrolyte of [CF_3CH_2MIm][TFSI] + 0.25 M LiTFSI exhibits a remarkable decrease of oxidation current even through the onset oxidation potential remains (about 5.8 V vs Li^+/Li). Our further works will focus on the electrolyte – electrode interface during cycling performance.

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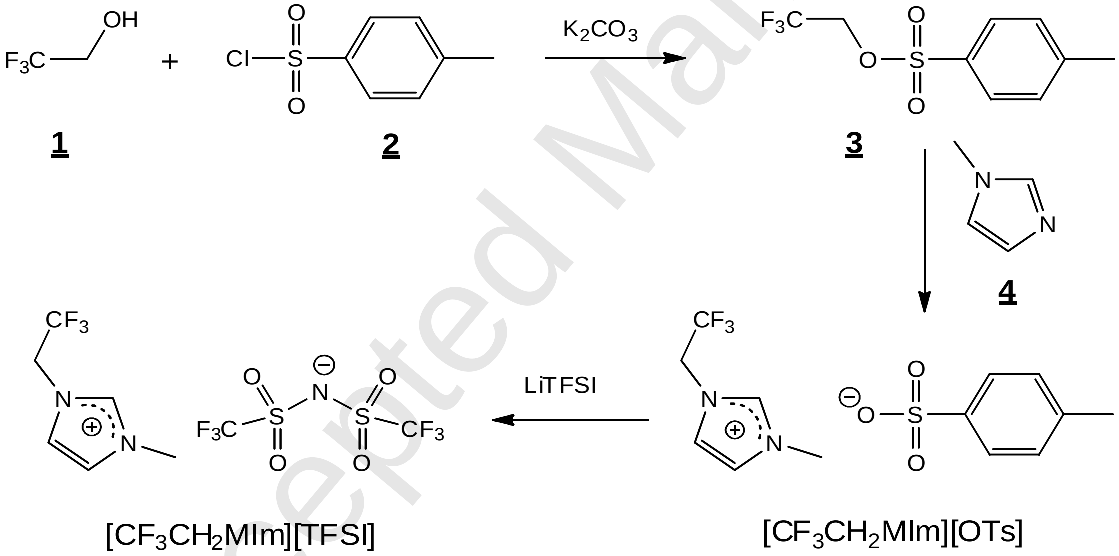
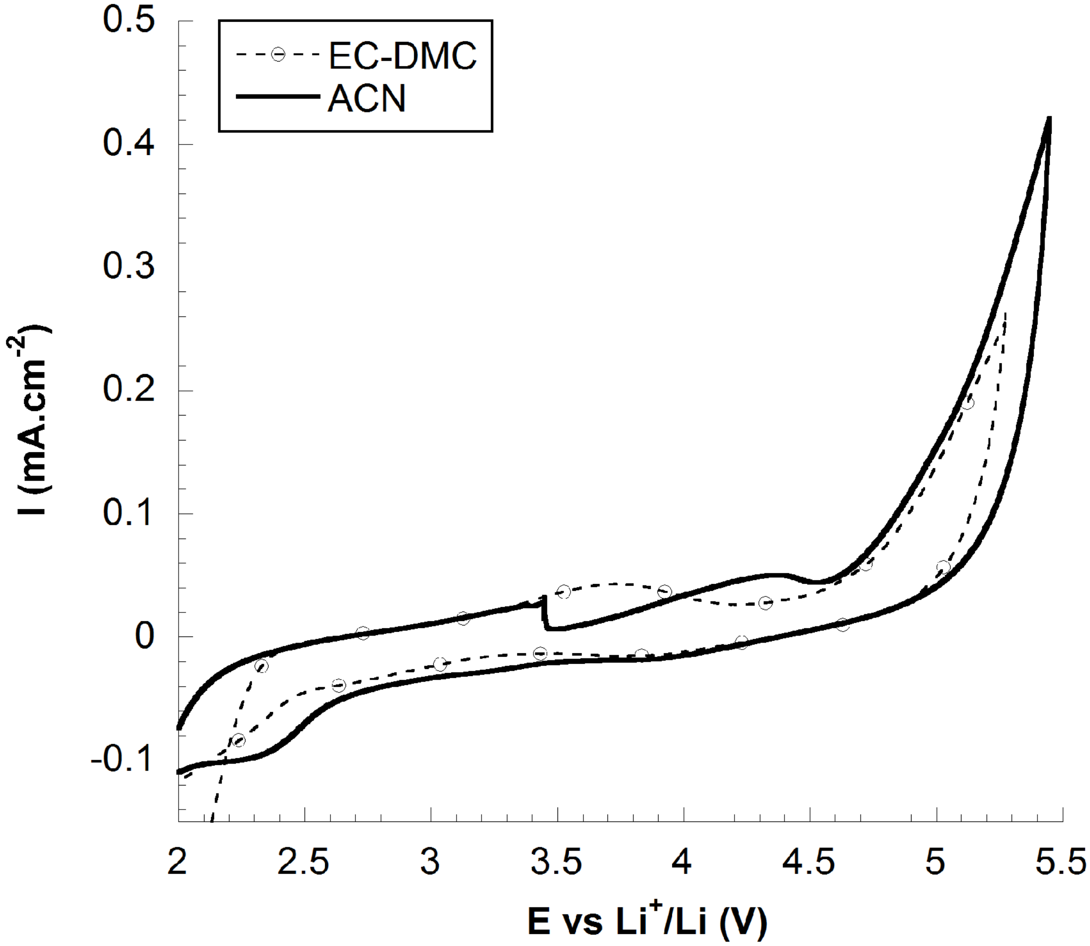
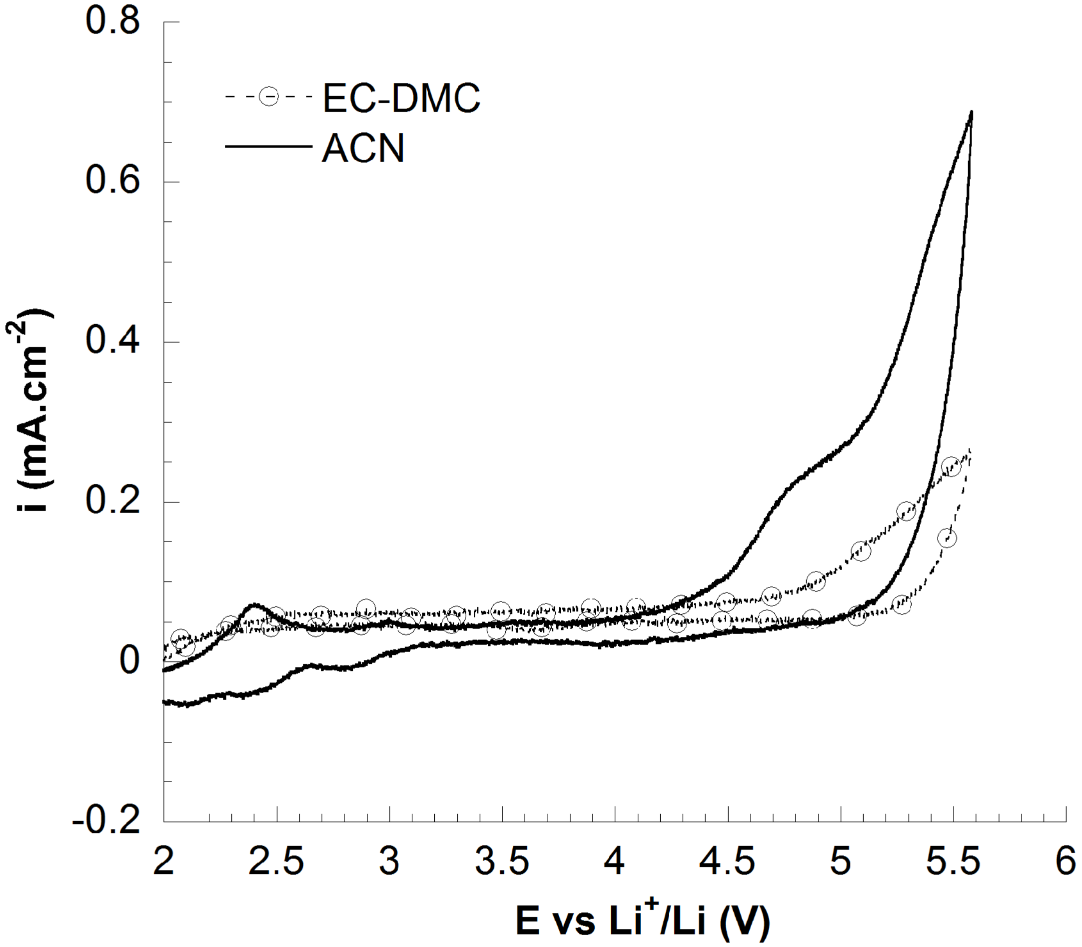


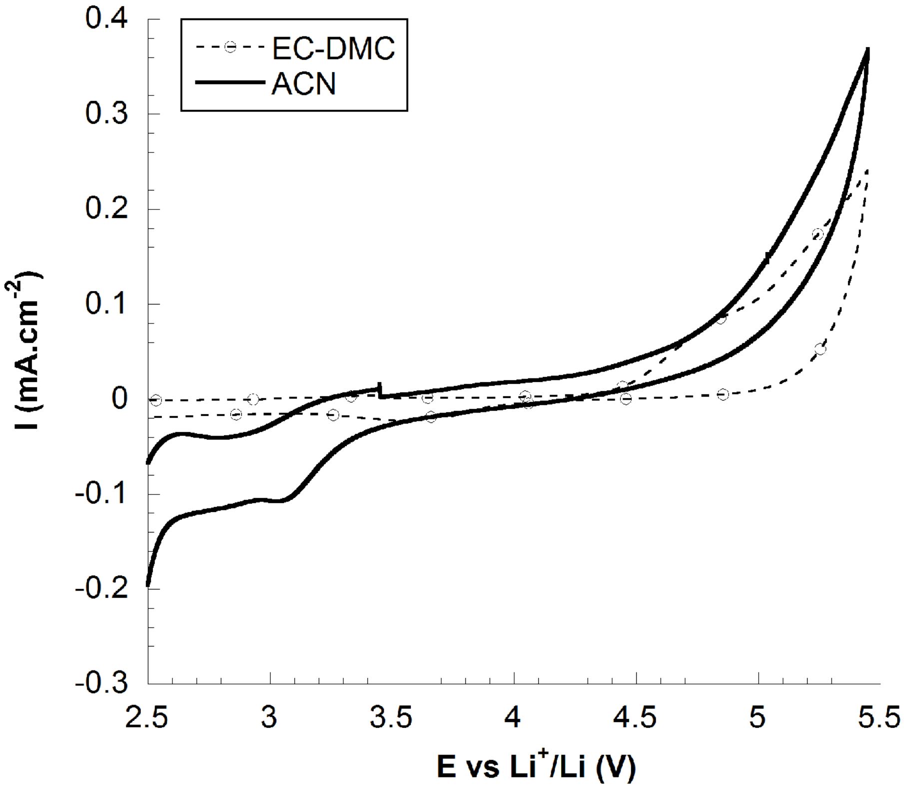
Scheme 1. The strategy for preparation of $[CF_3CH_2MIm][TFSI]$



(a)



(b)



(c)

Figure 1: Cyclic voltammograms of 0.005 M TBAP solution (a), 0.005 M [CF_3CH_2MIm][OTs] (b) and [CF_3CH_2MIm][TFSI] (c).Cyclic voltammetry of ILs at the scan rate of 20 mV.s^{-1} was recorded by a three-electrode cell (Pt wire as counter electrode, Pt with diameter 1 mm was used as working electrode and reference electrode was a Ag wire in $AgNO_3$ 10 mM in acetonitrile + 0.1 M tetrabutylammonium perchlorate). Acetonitrile (ACN) and the mixture of ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 v/v) were used as solvents.

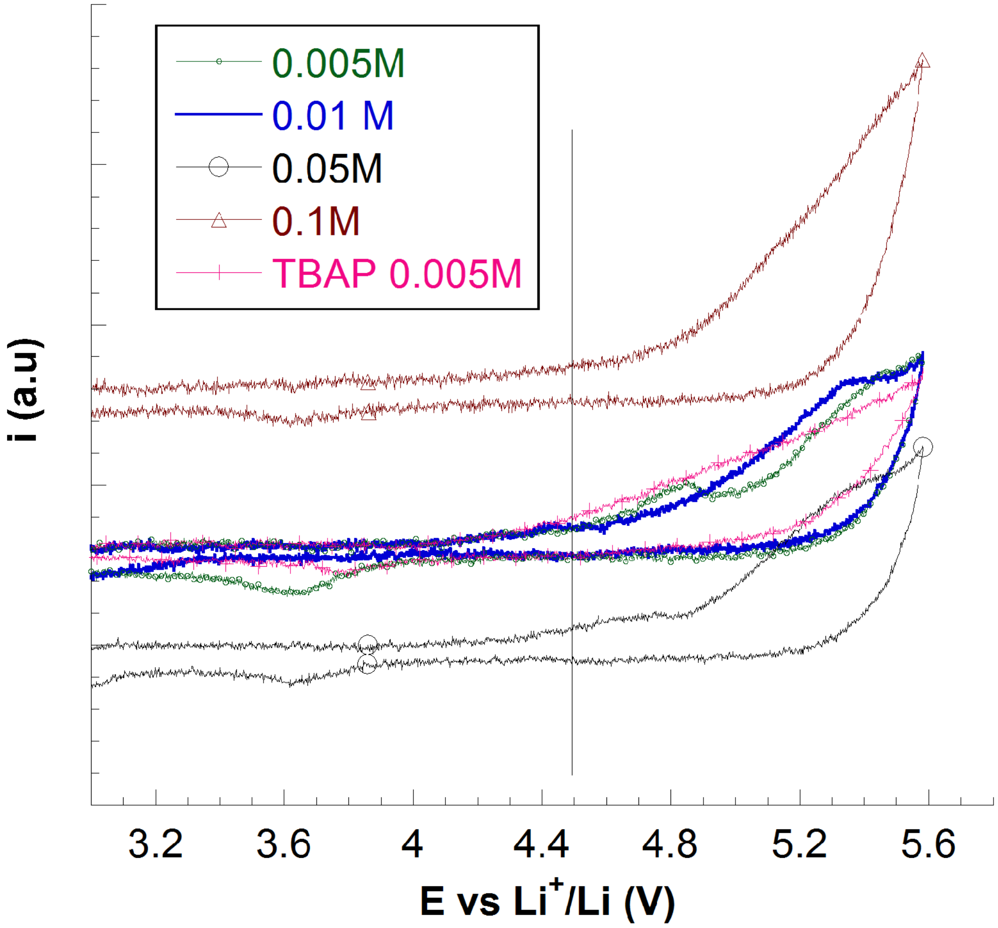


Figure 2. Cyclic voltammograms of [CF_3CH_2MIm][OTs] solution at different concentrations. Cyclic voltammetry of ILs at the scan rate of 20 mV.s^{-1} was recorded by a three-electrode cell (Pt wire as counter electrode, Pt with diameter 1 mm was used as working electrode and reference electrode was a Ag wire in $AgNO_3$ 10 mM in acetonitrile + 0.1 M tetrabutylammonium perchlorate).

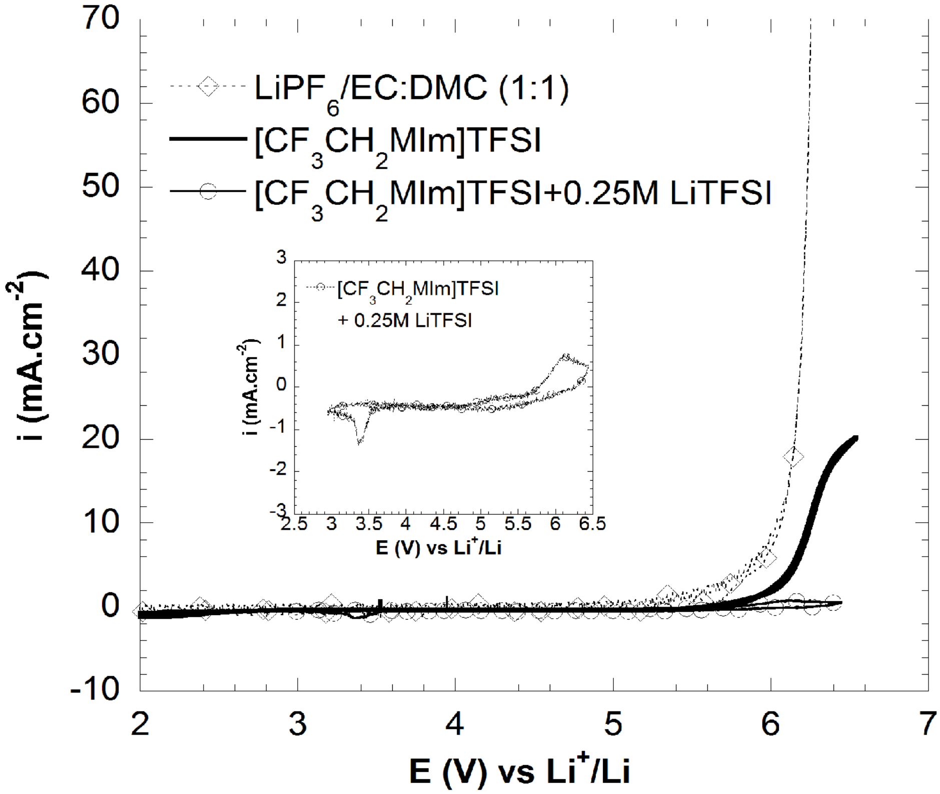


Figure 3. Cyclic votammograms of pure [CF_3CH_2MIm][TFSI], [CF_3CH_2MIm][TFSI] + 0.25 M LiTFSI vs 1 M $LiPF_6$/EC – DMC (2:1) solution. Cyclic voltammetry of ILs at the scan rate of 1 mV.s^{-1} was recorded by a three-electrode cell (Pt wire as counter electrode, Pt with diameter 25 μm was used as working electrode and reference electrode was a Ag wire in $AgNO_3$ 10 mM in acetonitrile + 0.1 M tetrabutylammonium perchlorate).

Table 1. Preparation of 2,2,2-trifluoroethyl tosylate (**3**)

Entry	Method[a]	**1**:**2**[b]	Temp. (°C)	Time (min)	Yield of **3** (%)
1	UI	1:1	40	30	33
2	UI	1:1	45	30	44
3	UI	1:1	50	30	58
4	UI	1:1	55	30	62
5	UI	1:1	60	30	61
6	UI	1:1	55	45	65
7	UI	1:1	55	60	74
8	UI	1:1	55	75	75
9	UI	1:1.2	55	60	92
10	UI	1:1.4	55	60	93
11	UI	1:1.6	55	60	95
12	MI	1:1.2	55	60	66
13	CH	1:1.2	55	60	26
14	G	1:1.2	r.t.	60	61

[a] UI: ultrasound irradiation, MI: microwave irradiation, CH: conventional heating, G: grinding; [b] Molar ratio.

Table 2. Preparation of ionic liquid [CF_3CH_2MIm][OTs] [a]

Entry	Temp. (°C)	Time (h)	Yield of [CF_3CH_2MIm][OTs] (%) [b]
1	60	3	no reaction
2	80	3	11
3	100	3	28
4	120	3	46
5	140	3	40
6	120	6	50
7	120	9	56
8	120	12	64
9	120	24	77
10	120	36	77

[a] Reaction conditions: conventional heating, 2,2,2-trifluoroethyl tosylate:1-methylimidazole was 1:1; [b] Isolated yield.

Table 3. Preparation of ionic liquid [CF_3CH_2MIm][TFSI] [a]

Entry	Method[b]	Temp. (°C)	Time (min)	Yield of [CF_3CH_2MIm][TFSI] (%) [c]
1	UI	35	10	54
2	UI	40	10	71
3	UI	45	10	63
4	UI	50	10	58
5	UI	40	5	51
6	UI	40	15	68
7	UI	40	20	67
8	MI	40	10	61
9	CH	40	10	22

[a] [CF_3CH_2MIm][OTs]:LiTFSI was 1:1; [b] UI: ultrasound irradiation, MI: microwave irradiation, CH: conventional heating; [c] Isolated yield.

Table 4. Properties of imidazolium ionic liquids [a]

ILs	T_m/°C	T_d/°C
[CF_3CH_2MIm][OTs]	35/45	340
[CF_3CH_2MIm][TFSI]	-22/-12	417
[CH_3CH_2MIm][TFSI]	-9	-

[a] T_m: melting point; T_d: degradation temperature.

Table 5. Properties of imidazolium ionic liquids

	Viscosity (mPa.s) 35 °C	Conductivity (mS.cm^{-1}) 35 °C	Density (g.ml^{-1}) 35 °C
[CF_3CH_2MIm][TFSI]	55.1	1.92	1.54
[CF_3CH_2MIm][TFSI] + 0.25 M LiTFSI	-	1.56	1.67

Graphical Abstract

Two fluorine-containing ionic liquids, 1-(2,2,2-trifluoroethyl)-3-methylimidazolium tosylate and 1-(2,2,2-trifluoroethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (TFSI anion), were obtained in good yields and high purity via a green pathway procedure free of solvent and hazardous catalyst. The incorporation of CF_3 moieties in imidazolium structure decreases the ILs TFSI melting point. The preliminary electrochemical results are very promising, a wide electrochemical stability up to 5.7 V vs Li^+/Li for the fluorinated imidazolium with TFSI anion.