



Short Communication

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

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ARTICLE INFO

Article history:

Received 29 January 2014

Received in revised form 17 May 2014

Accepted 21 May 2014

Available online 28 May 2014

Keywords:

Fluorinated imidazolium

Ionic liquids

Lithium-ion battery

Electrolyte

Solvent-free pathway

Electrochemical stability

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 CF₃ 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.

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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 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 ([CF₃CH₂MIm][TFSI]) via the intermediate 1-(2,2,2-trifluoroethyl)-3-methylimidazolium tosylate ([CF₃CH₂MIm][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 [CF₃CH₂MIm][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.

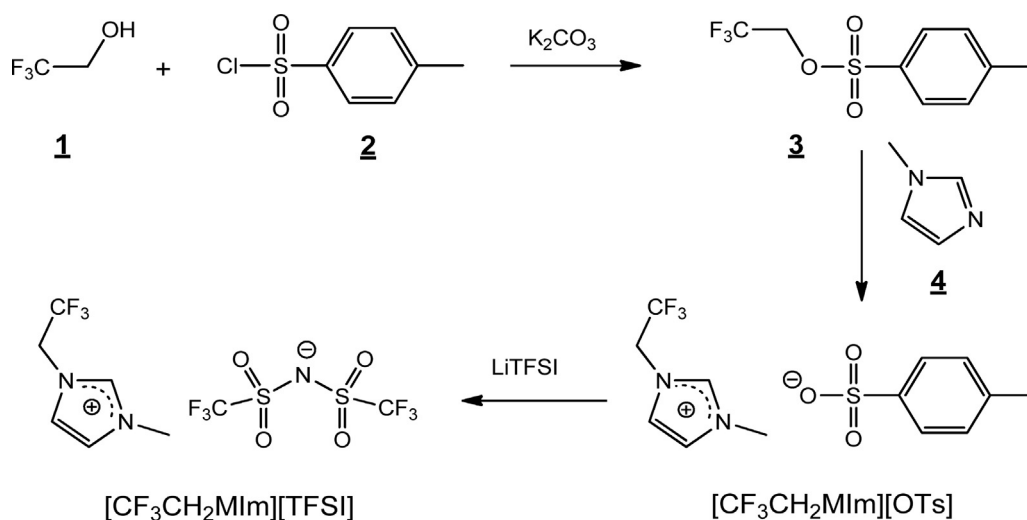
2. Results and discussion

2.1. Synthesis of ionic liquids

In the three-step pathway illustrated in Scheme 1, the final product [CF₃CH₂MIm][TFSI] was planned to be derived from the precursor [CF₃CH₂MIm][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

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Scheme 1. The strategy for preparation of $[\text{CF}_3\text{CH}_2\text{MIm}][\text{TFSI}]$.

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).

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.

For the next step, it can be referred from Table 2 that the intermediate ionic liquid $[\text{CF}_3\text{CH}_2\text{MIm}][\text{OTs}]$ could be obtained in the highest yield of 77% at 120 °C 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). $[\text{CF}_3\text{CH}_2\text{MIm}][\text{OTs}]$ was then ion-exchanged with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to provide the final product at 40 °C with a few minutes under the ultrasound irradiation (71%, entry 2, Table 3). The microwave irradiation and the conventional heating under the same conditions yields mentioned for the sonication did not further increase the yields of product (entry 8 and 9, Table 3).

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.

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 °C (Table 4). The DSC analysis showed that $[\text{CF}_3\text{CH}_2\text{MIm}][\text{TFSI}]$ presents a lower melting temperature, about -16 °C instead of -15 °C for $[\text{CH}_3\text{CH}_2\text{MIm}][\text{TFSI}]$. 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 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.

The density, viscosity and conductivity of $[\text{CF}_3\text{CH}_2\text{MIm}][\text{TFSI}]$ were determined and compared to the electrolyte of $[\text{CF}_3\text{CH}_2\text{MIm}][\text{TFSI}] + 0.25 \text{ M LiTFSI}$. 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. Electrochemical properties

One of the most important requirements for the use of ILs as liquid electrolyte is that they must have a wide electrochemical

Table 2
Preparation of ionic liquid $[\text{CF}_3\text{CH}_2\text{MIm}][\text{OTs}]$.^a

Entry	Temp. (°C)	Time (h)	Yield of $[\text{CF}_3\text{CH}_2\text{MIm}][\text{OTs}]$ (%) ^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.

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