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Short communication

Ionic liquid electrolytes for lithium batteries: Synthesis, electrochemical, and cytotoxicity studies

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HIGHLIGHTS

- Ionic liquids are evaluated as potential electrolytes for Li/CF_x primary batteries.
- High discharge capacities and wide electrochemical windows are demonstrated.
- The studied ionic liquid electrolytes are relatively nontoxic to human health.

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ABSTRACT

We have synthesized and determined the electrochemical and thermal stabilities of a series of 1-methyl-3-alkoxyalkyl and 1-methyl-3-fluoroalkyl imidazolium and the corresponding pyrrolidinium-based ionic liquids and estimated the cytotoxicities of representative ionic liquids. The pyrrolidinium-TFSI based ionic liquids have wide electrochemical stability (>5.7–6.2 V vs. Li/Li^+) but show limited thermal stabilities and lithium cell discharge characteristics, as compared to those that are imidazolium-based (4.8–5.1 V vs. Li/Li^+). The fluoroalkyl-derived ionic liquids typically have superior thermal stability ($T_d > 350\ ^\circ C$) as compared to the alkoxyalkyl-substituted analogues. In all these cases, $TFSI^-$ anion-based ionic liquids are thermally and electrochemically more stable than the BF_4^- anion-based analogues. We have also shown that the imidazolium-based ionic liquids are relatively nontoxic and their EC50 values are comparable to their corresponding lithium salts.

1. Introduction

Li/CF_x primary lithium batteries using sub-fluorinated graphite (CF_x; $x < 1$) as cathode materials are of renewed interest due to their inherently high theoretical specific capacity and high energy density as compared to the other primary lithium batteries such as Li/MnO_2, Li/SO_2 or Li/$SOCl_2$ [1–3]. The main limitation of the primary Li/CF_x batteries is their poor discharge performance, especially at subambient temperatures and the flammability of the electrolyte solvents due to the high exothermicity during the discharge, which leads to thermal runaway explosion reactions. The state of the art carbonate-based electrolytes used in these batteries are, however, volatile, flammable and their electrochemical stability windows are relatively low.

Room temperature ionic liquids (RTILs) have attracted much attention as electrolytes in lithium/lithium ion batteries [4–7], proton exchange membranes in fuel cells [8], and high energy density supercapacitors [9–11], as they are relatively nonvolatile, less flammable or nonflammable, and have superior thermal and electrochemical stabilities. Due to the favorable physicochemical and electrochemical properties of the imidazolium, piperidinium, and pyrrolidinium-based ionic liquids, they are attractive targets as nonvolatile, nonflammable, and high voltage electrolyte materials for the primary lithium ion batteries [7,12–15]. However, due to their relatively high viscosities, their low-temperature performance often is not satisfactory for the design of commercial batteries. The ionic liquids based on the alkoxyalkyl-side chain groups or fluoroalkyl substituents typically have relatively lower

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viscosities as compared to dialkyl substituted ionic liquids [16–19], while the molecular mass of the corresponding ionic liquids is minimally altered due to these substituents. Further, the electron withdrawing alkoxyalkyl and fluoroalkyl substituents, due to their HOMO-energy lowering effect [20,21], would be expected to show moderate increase in the oxidation potentials of the ionic liquid electrolytes, which would complement the high voltage CF_x cathodes used in our studies. We have therefore chosen to explore the β-fluoroethyl- and ethoxymethyl-substituted imidazolium and pyrrolidinium-based ionic liquid electrolytes for lithium battery applications. We have ruled out the ionic liquid electrolytes with polyfluoroalkyl groups for lithium battery applications, as they may show deleterious effects due to their higher molecular mass and relatively higher viscosities [22].

Further, it is also important that the battery electrolytes are relatively nontoxic to human health. There are several studies on the relative toxicities of various imidazolium-based ionic liquids [23–25], using a variety of cell lines, including the HeLa cell lines [26,27], rat leukemia cell lines [28], bacterial cell cultures [29], or algae [30]. However, the alkoxylalkyl and fluoroalkyl-substituted imidazolium or pyhrrolidinium ionic liquids are relatively less explored for their human toxicity. The effect of the alkoxymethyl side chains on the toxicity of the imidazolium and pyrrolidinium salts needs to be thoroughly investigated in view of their relatively more favorable physicochemical and electrochemical properties. In general, the toxicity of the ionic liquids increases with the increasing alkyl chain length, and the nature of the anions also plays important role in the cytotoxicity [31]. Introduction of fluorine in organic molecules increases their lipophilicity and they are better able to penetrate the cellular membranes and thus the toxicities of these compounds are expected to be modulated by fluorine.

In order to meet the above goals in the design of ideal ionic liquid based electrolytes for primary Li/CF_x batteries, we have synthesized variously substituted alkoxyalkyl and fluoroalkyl derivatives of imidazolium and pyrrolidinium-based ionic liquids (compounds **1**–**6**; Fig. 1) and studied their thermal and electrochemical stabilities, and estimated their toxicities using human bronchoalveolar A 549 cell line. From these studies, we have identified fluoroalkyl-substituted imidazolium and pyrrolidinium-based ionic liquids that have exceedingly high thermal stabilities ($T_d > 350$ °C for ionic liquids **3** and **4**, and $T_d > \sim 250$ °C for all other ionic liquids except ionic liquid **6**). Most of these ionic liquids are ideally suited for the primary Li/CF_x batteries due to their relatively low vapor pressures and low- or non-flammability and high thermal stabilities. Our results show that the $TFSI^-$ anion-based ionic liquids are thermally and electrochemically more stable than the BF_4^- based ionic liquids. Importantly, some of our ionic liquid electrolytes show high discharge capacities (>700 mAh g^{-1}) in coin cells made with CF_x cathode, lithium anode and ionic liquid based electrolytes at room temperature, at low rates of discharge (*C*/100), comparable to that of the state of the art carbonate-based electrolytes [3]. Further our toxicity studies show that they are relatively nontoxic to human health (vide infra).

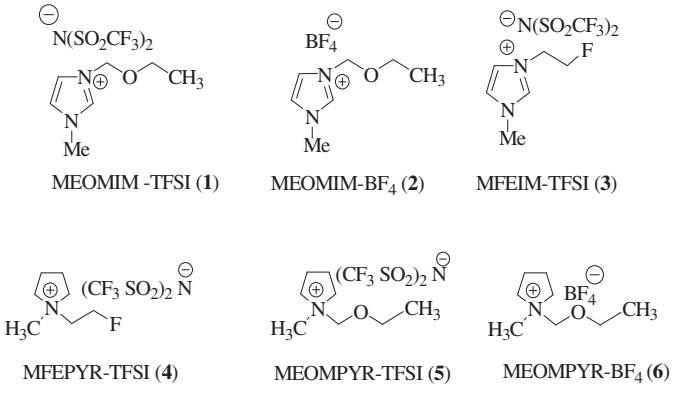


Fig. 1. Alkoxyalkyl and fluoroalkyl-derived imidazolium and pyrrolidinium ionic liquids investigated in this study.

2. Experimental

2.1. Materials and methods

Chloromethoxyethane, (>96%) and LiTFSI (>98%) were purchased from TCI America. 1-Methylpyrrolidine (>99%), $NaBF_4$, (>97%) 1-methylimidazole, (>99%), diethyl ether (anhydrous, ACS certified), acetone (ACS certified, >99.5 %), magnesium sulfate (anhydrous, 99.5%), silica gel (99%, 63–200 Å mesh size), and acetone-d_6 were purchased from Sigma–Aldrich and were used as received. 1-Bromo-2-fluoroethane (>98%) was purchased from AK Scientific.

Ham's F-12, (1×) modified medium, fetal bovine serum (FBS), penicillin–streptomycin mixture, trichloroacetic acid (TCA), acetic acid, dimethyl sulfoxide, and *tris*-hydrochloride, were purchased from Sigma–Aldrich. Trypsin–EDTA was purchased from Invitrogen Co. (Carlsbad, CA, USA). Sulforhodamine B was purchased from ICN Biomedicals (Irvine, CA, USA). The human bronchoalveolar carcinoma derived cell line (A549) was purchased from ATCC (Manassas, VA, USA).

2.2. General methods

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on an INOVA-Varian 400 MHz spectrometer at 400 MHz, 100 MHz and 376 MHz, respectively, in acetone-d_6 solvent. The δ^1H and δ^{13}C were referenced with respect to residual solvent signals or internal tetramethylsilane and the δ^{19}F were referenced to internal trichlorofluoromethane ($\delta CFCl_3 = 0$). The ^{13}C chemical shifts assignments were confirmed through their proton coupled ^{13}C spectra.

Thermogravimetric analysis (TGA), using TA Q500 instrument was conducted at a heating rate of 3 °C/min. Differential scanning calorimetry (DSC) analysis was performed using a TA Q200 instrument at a heating/cooling rate of 3 °C/min. Linear scan voltammetry analysis to determine the potential stability window of ionic liquids was performed using a VersaSTAT 3 instrument in a three electrode system, having glassy carbon as the working electrode, platinum as the counter electrode, and lithium metal as the reference electrode. Ionic conductivity values of ionic liquid electrolytes were measured using an YSI 3100 conductivity meter with platinum electrodes.

Preliminary investigation on the electrochemical performance of ionic liquid electrolytes in Li/CF_x system was done using 2016 coin cells. The cathode active material CF_x with $x \sim 1$ and an average particle size ~300 nm is synthesized using a carbon black precursor. The CF_x was synthesized at Contour Energy Systems using a proprietary technique involving a precise control of the fluorination kinetics and thermodynamics parameters including temperature, fluorine gas flow rate, pressure, and reaction time. The active material was mixed with 15 wt% Super-P carbon and 5 wt% PTFE binder to make cathodes with thickness ~100 μm, density ~0.8 g/cc, and area ~1 cm^2. A 200-μm thick lithium metal foil was used as the anode with a sheet of glass fiber (180 μm thick) as separator.

2.3. Synthesis of ionic liquids (general procedure) [32,33]

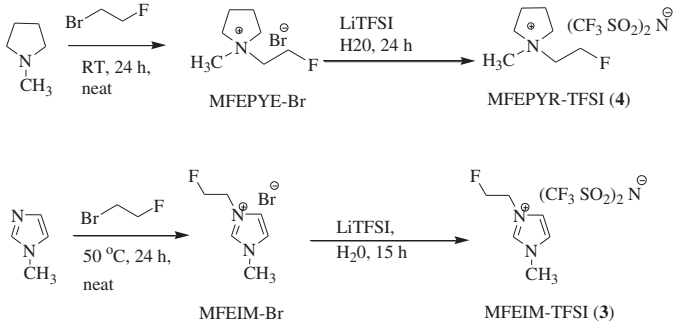
2.3.1. 1-Ethoxymethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (MEOMIM-TFSI, **1**)

To a stirred solution of chloromethoxyethane (11.2 g, 118 mmol) at 0 °C in a 50 mL round-bottom flask , 1-methylimidazole (7.5 g, 91 mmol), was added dropwise in an inert atmosphere, and stirred at 0 °C for 30 min, and at 50 °C for 1 h. The mixture was cooled to room temperature and washed with diethyl ether (28 mL). The product, 1-ethoxymethyl-3-methylimidazolium chloride (MEOMIM-Cl), was obtained as a light yellowish solid after filtration and drying in high vacuum (yield: 92%). The compound was used for the next step without further purification.

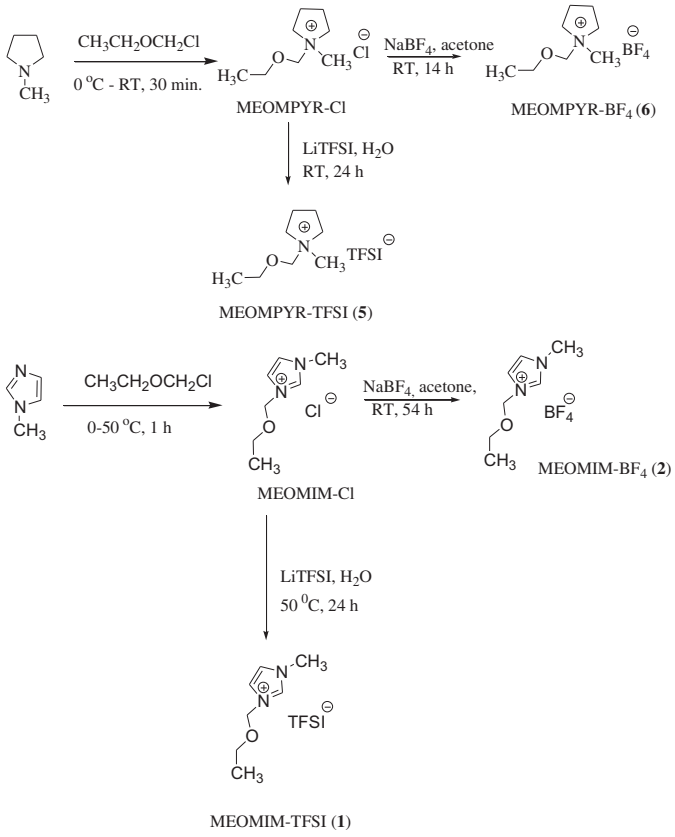
The above-prepared 1-ethoxymethyl-3-methylimidazolium chloride ((MEOMIM-Cl); 15.0 g, 85 mmol) was dissolved in water and stirred with lithium bis (trifluoromethanesulfonyl) imide (23.3 g, 81 mmol) for 24 h. The product was extracted from the reaction mixture using dichloromethane and the organic layer was dried over $MgSO_4$. The compound was eluted through a small column of silica gel for further purification. Removal of the solvent in high vacuum gave compound **1** as an off-white viscous liquid (85% yield); mp approximately −35 °C; T_d ~405 °C; ^{1}H NMR (400 MHz, acetone-d_6): δ 9.13 (s, 1 H imidazole-C_2H), 7.81 (bs, 1 H) and 7.73 (bs, 1H) imidazole-C4,5-H, 5.69 (s, 2H, N-CH_2), 4.07(s, 3H, −N-methyl), 3.64(q, J = 7 Hz, 2H, O-CH_2), 1.16 (t, J = 7 Hz, 3H, methyl); ^{13}C (100 MHz, acetone-d_6; ^{1}H, ^{19}F-coupled): δ 137.6 (d, J = 201 Hz imidazole-C2), 123.8 (d, J = 205 Hz) and 121.9 (d, J = 203 Hz), (imidazole-C4,5), 119.2 (q, J_{CF} = 320 Hz), 79.6 (t, J = 163 Hz), 66.2 (t, J = 144 Hz), 36.7 (q, J = 143 Hz), 14.2 (q, J = 126 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ −78.91(s).

2.4. Cell viability assay

Cytotoxicity was performed with the sulforhodamine B assay (SRB) that determines cell viability. The SRB assay [34,35] has been used to determine cell viability of various cancer cell lines [36,37]. The A549 cells were maintained in Ham's F-12 medium supplemented with 10% fetal bovine serum, and 100 μg/mL penicillin–streptomycin, and grown at 37 °C in the presence of a 5% CO_2 humidified environment. The A549 cells were plated into 24-well plates at a density of 1×10^4 cells per well in 1.0 mL culture medium and allowed to attach for 48 h. Then, ionic liquids of a series of concentrations (200–2500 μM ionic liquids in 0.02% DMSO) were applied to the cell-media for 48 h. After 48 h exposure, the experiment was terminated by removing medium and then fixing cells with 500 μL of cold 10% trichloroacetic acid (TCA) for 1 h. The TCA solution was then discarded. The cells were washed three times with distilled water followed by drying under nitrogen. Each well was treated with 500 μl of 0.2% SRB in 1% acetic acid to stain the cells for 30 min. The staining solution was discarded, and the cells were washed with 1% acetic acid to eliminate excess dye. After complete drying, the dye in each well was dissolved in 300 μL of cold 10 mM Tris buffer (pH 10.5). Then, 100 μL of dye solution was transferred into a 96-well plate. The absorbance was measured using a FLOUstar Optima (BMG Lab Technologies, Durham, NC, USA) microplate reader at 490 nm. The experiments were performed in triplicate and the data was expressed as mean ± SD (Fig. 6 and Table 3). The control groups include cells only and cells with DMSO.



Scheme 1. Synthesis of 1-methyl-1-fluoroethylpyrrolidinium and 1-methyl-3-fluoroethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids.



Scheme 2. Synthesis of 1-methyl-1-ethoxymethylpyrrolidinium and 1-methyl-3-ethoxymethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids.

3. Results and discussion

3.1. Synthesis

We have synthesized a series of imidazolium- and pyrrolidinium-based ionic liquids containing monofluoroethyl and ethoxymethyl substituents (**1**–**6**; Fig. 1). 1-Methylimidazole and 1-methylpyrrolidine were reacted with the corresponding alkyl and alkoxy halides and the resulting halide salts were metathesized with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and sodium tetrafluroborate ($NaBF_4$) to give their TFSI salts and tetrafluoroborate salts,

Table 1
Room temperature ionic conductivity of ionic liquid electrolytes.

Ionic liquid	Conductivity (Neat IL) (mS cm^{-1})	Conductivity + 0.5 M LiTFSI or LiBF$_4$* (mS cm^{-1})
MEOMIM-BF_4 (**2**)	2.9	1.8*
MEOMPYR-BF_4 (**6**)	3.8	2.8*
MEOMIM-TFSI (**1**)	4.1	2.3
MEOMPYR-TFSI (**5**)	4.4	2.2
MFEIM-TFSI (**3**)	4.3	2.5
MFEPYR-TFSI (**4**)	3.0	1.3

The asterisk ones are for + 0.5 M LiBF4 and values without asterisk are for + 0.5 M LiTFSI.

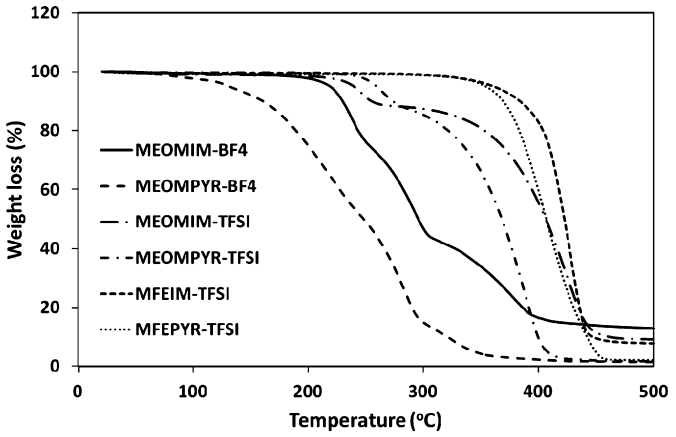


Fig. 2. TGA plots of neat ionic liquids.

respectively (Schemes 1 and 2), using a modified procedure [32,33]. These ionic liquids were obtained as liquids at room temperature after silica gel purification and drying in vacuum, and were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

We have observed that the melting points of these ionic liquids are substantially dependent on the nature of the counter-anions; bis(trifluoromethanesulfonyl)imide ($TFSI^-$) anions lower the melting points significantly as compared to their tetrafluoroborate (BF_4^-) analogues. Differential scanning calorimetry (DSC) analysis of these ionic liquids shows a wide liquid range for these materials.

3.2. Conductivity

Table 1 lists the ionic conductivity values of ionic liquid electrolytes investigated in this study. The conductivity values are found to be in the mS cm^{-1} range, similar to the organic solvent-based commercial battery electrolytes. The neat ionic liquids show moderately higher ionic conductivity values in the range of 3 to 5 mS cm^{-1}. In general, when mixed with 0.5 M Li-salt, the conductivity of ionic liquids decreases due to an increase in viscosity.

3.3. Thermal stability

Fig. 2 shows the thermogravimetric analysis (TGA) plots of all the ionic liquids investigated in this study. In general, the $TFSI^-$ based ionic liquids are found to be thermally more stable than the

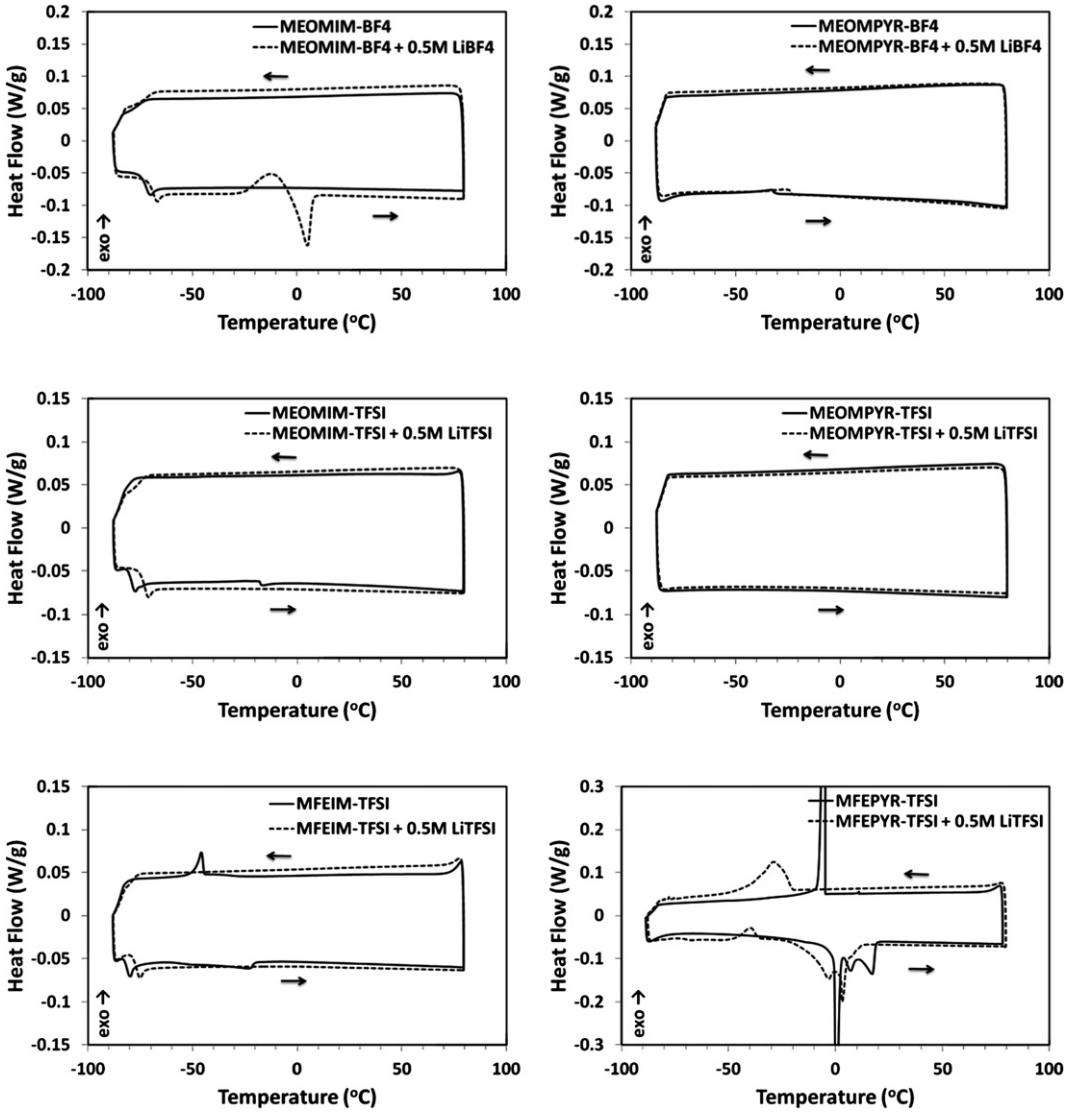


Fig. 3. DSC plots of neat ionic liquids and their 0.5 M Li-salt containing electrolytes.

BF_4^- analogues. Of the ionic liquids with BF_4^- anion, MEOMIM-BF_4 (**2**) is stable up to 200 °C, while MEOMPYR-BF_4 (**6**) starts to decompose above 50 °C. Of the ionic liquids with $TFSI^-$ anion, the alkoxyalkyl-derived ionic liquids (MEOMIM-TFSI (**1**) and MEOMPYR-TFSI (**4**)) are stable up to 200 °C, while the fluoroalkyl-derived ionic liquids (MFEIM-TFSI (**3**) and MFEPYR-TFSI (**4**)) show a superior thermal stability up to 350 °C. In general, the ether-functionalized imidazolium-based ionic liquids have relatively lower thermal stabilities and lower melting temperatures as compared to those of their alkyl-side chain derived ionic liquids [19]. Addition of lithium salt to ionic liquids to form electrolytes is not expected to drastically affect their thermal stabilities. The high thermal stability and nonvolatile nature of the ionic liquid based electrolytes is beneficial to the high temperature performance of batteries.

Fig. 3 shows the differential scanning calorimetry (DSC) curves of the neat ionic liquids and their 0.5 M Li-salt containing electrolytes. Of the BF_4^- based ionic liquids, neat MEOMIM-BF_4 (**2**) does not show any melting or freezing down to −60 °C, below which it undergoes glass transition. However, when the latter ionic liquid is mixed with 0.5 M $LiBF_4$ salt, the DSC of the mixture shows a freezing point around −10 °C and a melting point at 5 °C. On the other hand, both the neat MEOMPYR-BF_4 (**6**) and its Li-BF_4 salt solution (0.5 M) do not show any freezing/melting behavior down to −80 °C. We have also observed an unexpected minor irreversible exothermic peak near −30 °C in their DSC plots.

Of the alkoxyalkyl-derived ionic liquids with $TFSI^-$ anion, neat MEOMIM-TFSI (**3**) ionic liquid and its 0.5 M Li-TFSI salt containing electrolyte do not show any freezing/melting behavior down to −60 °C. Solidification of neat MEOMIM-TFSI (**3**) at −75 °C has been confirmed using a chloroform/dry ice mixture. An unexpected minor irreversible endothermic peak appears in the DSC of the neat MEOMIM-TFSI (**3**) at about −15 °C, as observed also for the ionic liquid **6**. From their DSC it is evident that neither the neat MEOMPYR-TFSI (**5**) nor its 0.5 M Li-TFSI salt solution shows any freezing/melting behavior up to −80 °C.

The DSC of the fluoroalkyl-derived neat MFEIM-TFSI (**3**) shows a freezing point at about −50 °C and a melting point at −20 °C. Its solution with 0.5 M LiTFSI salt does not show melting or freezing behavior up to −70 °C, below which it undergoes glass transition. However, the DSC of the pyrrolidinium analogue, neat MFEPYR-TFSI (**4**), shows a very distinct freezing point around −10 °C and a melting range between 0 °C and 20 °C. The DSC of the 0.5 M LiTFSI solution of the latter ionic liquid, on the other hand, shows relatively small decrease in its freezing point (about −20 °C) and melting point (about 10 °C). These DSC observations for the ionic liquid-LiTFSI salt solutions indicate the formation of eutectic phases, in accordance with the reported slightly lower melting temperatures for the 1,1-dialkylpyrrolidinium-TFSI/LiTFSI solutions [38]. However, in the case of MEOMIM-BF_4 (**2**), unexpectedly, higher freezing and melting points are observed, when mixed with $LiBF_4$, as described above.

3.4. Electrochemical stability

Fig. 4 shows the linear scan voltammetry analysis of some of the neat ionic liquids investigated in this study. The electrochemical stability window of the BF_4^- anion containing ionic liquids is in general narrower than the $TFSI^-$ anion-based analogues (Table 2). The significantly lower anodic stability of MEOMPYR-BF_4 (**6**) electrolyte as compared to that of the TFSI salt reflects the relatively lower basicity of the TFSI anion, and the consequent lowering of its HOMO-energy levels [21]. In case of $TFSI^-$ anion containing ionic liquids, pyrrolidinium-based ionic liquids have typically wider electrochemical stability windows than their imidazolium-based analogues. Impressively, alkoxyalkyl-derived ionic liquid,

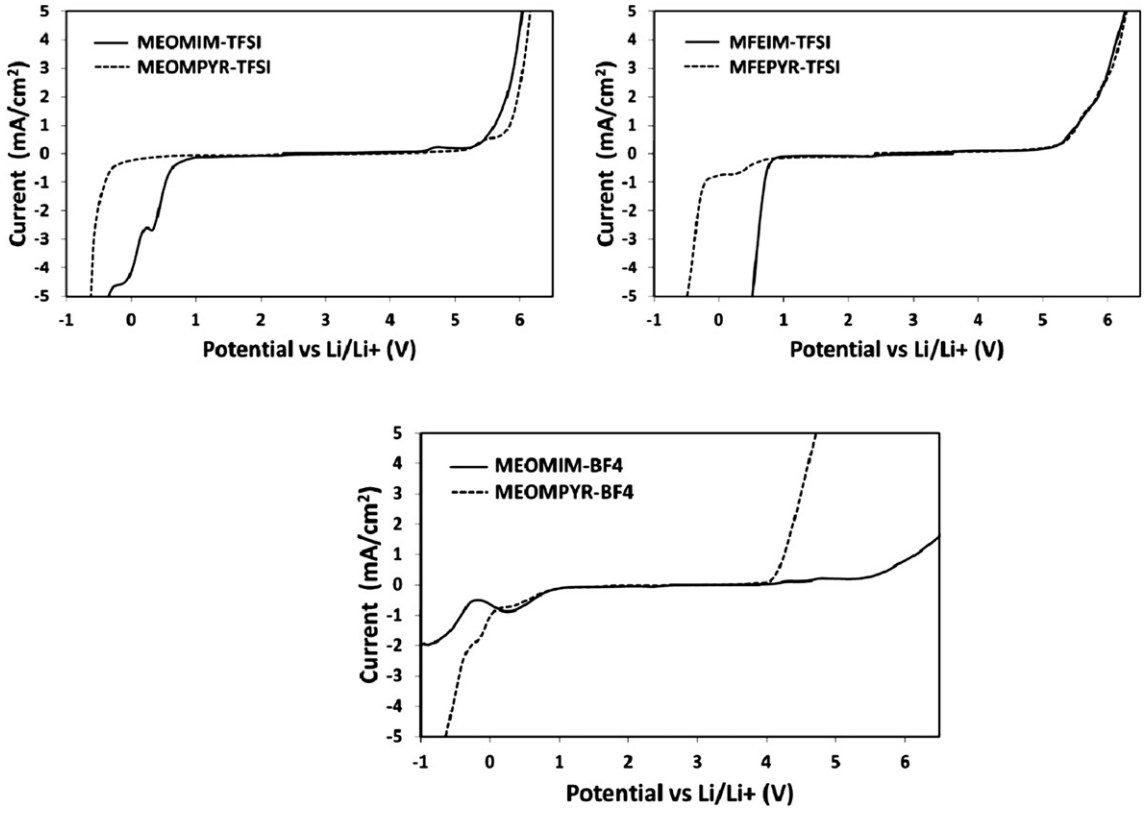


Fig. 4. Linear scan voltammetry analysis of $TFSI^-$ anion-based ionic liquids.

Table 2
Electrochemical stability window of novel ionic liquids.

Ionic liquid	Cathodic limit[a] (V)	Anodic limit[a] (V)	Electrochemical window (V)
MEOMIM-BF_4 (**2**)	0.8	5.4	4.6
MEOMPYR-BF_4 (**6**)	0	4.2	4.2
MEOMIM-TFSI (**1**)	0.5	5.6	5.1
MEOMPYR-TFSI (**5**)	−0.4	5.8	6.2
MFEIM-TFSI (**3**)	0.7	5.5	4.8
MFEPYR-TFSI (**4**)	−0.2	5.5	5.7

[a] Potential where the current density exceeds 1.0 mA cm^{-2}.

MEOMPYR-TFSI (**5**) has the widest stability window ranging from −0.4 V to 5.8 V vs. Li/Li^+ and the fluoroalkyl-derived ionic liquid, MFEPYR-TFSI (**4**), has similarly a wide electrochemical stability window, −0.2 V to 5.5 V vs. Li/Li^+. Similar, but relatively smaller electrochemical windows are recently reported in case of 1,1-dialkylpyrrolidinium TFSI salts [13,39].

For most of the ionic liquids investigated in this study, the discharge potential of the CF_x cathode lies within the stability window, thus preventing any electrolyte oxidation at the cathode. Although the potential of the lithium anode is outside the stability window of some of the ionic liquids, the electrolyte reduction at the anode could be suppressed by the formation of an SEI layer on the anode surface.

3.5. Lithium cell performance

Preliminary investigation on the electrochemical performance of ionic liquid electrolytes in Li/CF_x primary battery system was done using 2016 coin cells. Fig. 5 shows the constant-current discharge performance of coin cells using CF_x cathode, lithium anode, and ionic liquid based electrolytes. CF_x is a low-to-medium rate primary cathode material with a theoretical discharge capacity of 864 mAh g^{-1} for $x = 1$. Among the cells employing the BF_4^- anion containing ionic liquids, the imidazolium-based electrolyte, MEOMIM-BF_4 (**2**), demonstrated a high discharge capacity of ~800 mAh g^{-1} with a nominal voltage of ~2.4 V, at *C*/100 rate. Even at high discharge currents (*C*/20 rate), the cell retained a capacity of ~700 mAh g^{-1} and a nominal voltage of ~2.2 V.

Unexpectedly, the pyrrolidinium-based electrolyte, MEOMPYR-BF_4 (**6**), does not show any significant discharge capacity. Although the cause of the poor cell performance of MEOMPYR-BF_4 (**6**) electrolyte is not evident, it could be related to the morphology of LiF formed during discharge that may increase the impedance of the cell. Further, the low-temperature performance of the imidazolium-based electrolyte, MEOMIM-BF_4 (**2**), could be limited by the relatively high melting temperature of ~5 °C for its $LiBF_4$ salt solution (*vide supra*).

Among the cells employing the $TFSI^-$ anion containing ionic liquids, the alkoxyalkyl-derived (MEOMIM-TFSI (**1**) and MEOMPYR-TFSI (**5**)) electrolytes typically exhibit a high discharge capacity of ~800 mAh g^{-1} and a nominal voltage of ~2.3 V, at C/100 rate. However, at a high C/20 discharge rate, they show a moderate capacity of ~450 mAh g^{-1} and a nominal voltage of ~2 V.

In spite of their high thermal and electrochemical stability, the fluoroalkyl-derived ionic liquid electrolytes, (MFEIM-TFSI (**3**) and MFEPYR-TFSI (**4**)), exhibit a limited discharge capacity of <120 mAh g^{-1} even at low rates of discharge. Although the ionic conductivity of these fluoroalkyl-derived ionic liquids are comparable with other ionic liquids, the limited discharge performance of these cells could be due to a highly resistive interface between the electrode and the fluoroalkyl-derived ionic liquids. Intercalation of these salts or their degradation products on the cathode surfaces and the morphology of LiF formed during discharge might be a contributing factor for the decreased discharge capacity and further studies on the electrode surface characterization are needed to clarify this hypothesis. Improvement on their rate capability performance could be achieved in the presence of a small amount of carbonate-based electrolytes, and further studies on the fluoroalkyl-derived ionic liquids are in progress in our laboratories.

3.6. Toxicity studies

Imidazolium-based ionic liquids are expected to be relatively nontoxic and environmentally benign. However, recent studies

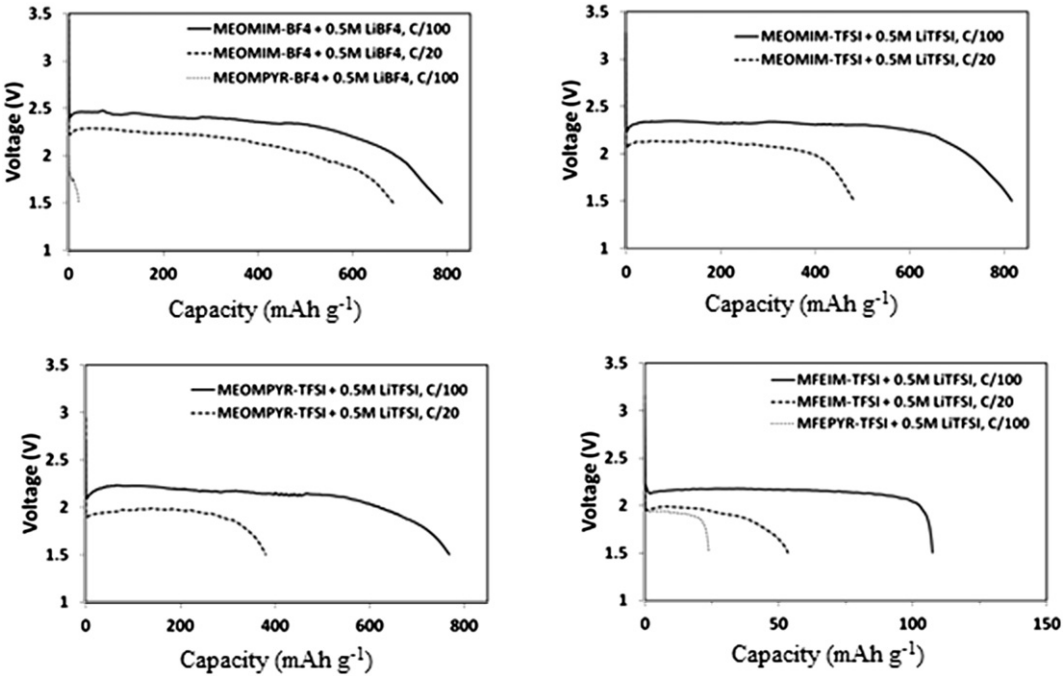


Fig. 5. Constant-current discharge performance of coin cells made with CF_x cathode, lithium anode, and ionic liquid based electrolytes, at room temperature.

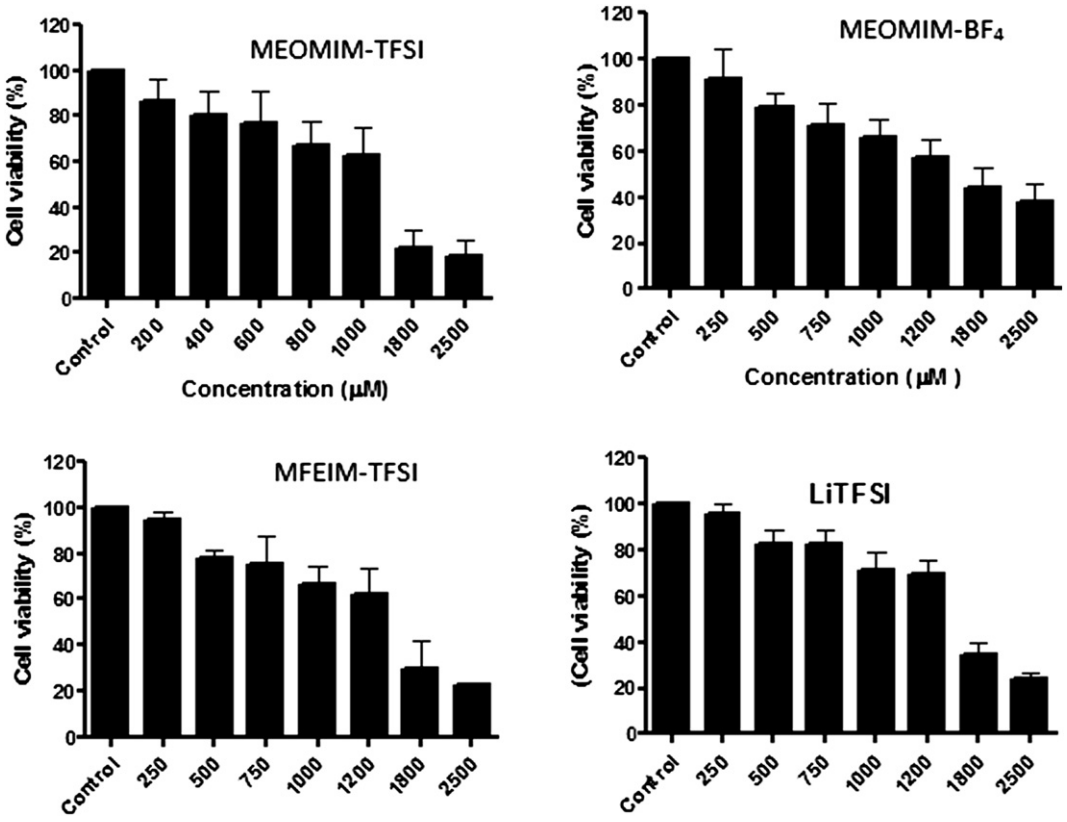


Fig. 6. Cell viability of A549 cells, treated with various concentrations (0.2–2.5 mM) of ionic liquids in Ham's F-12 medium supplemented with 10% fetal bovine serum (FBS), and 1% penicillin–streptomycin, and grown at 37 °C in the presence of 5% CO_2 humidified environment in for 24 h. The measured cell viability values are shown as mean ± SD from four independent experiments, each experiment is done in triplicate.

show that some of the RTILs may not be as environmentally benign as originally considered [40]. Thus development of novel type of RTILs without adverse environmental impact or human toxicity is crucial for the successful application of these solvents for industrial scale processes, especially in lithium/lithium ion battery technology. In this study, we have measured the toxicity of the representative alkoxymethyl- and fluroalkyl-substituted imidazolium-based ionic liquids MEOMIM-TFSI (**1**), MEOMIM-BF_4 (**2**) and MFEIM-TFSI (**3**) in human bronchoalveolar A549 cells, using the reported sulforhodamine B assay [41]. Cells not exposed to ionic liquids served as controls in each of these experiments. The results are shown in Fig. 6 and the estimated EC50 vas are shown in Table 3.

As can be seen from Table 3, the imidazolium-based ionic liquids have EC50 values comparable with that of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), ranging from 1.2 mM to 1.9 mM. Counter-anions BF_4^- or $TFSI^-$ have minimal effect on the EC50 values of these ionic liquids. As these toxicity assays were based on the human bronchoalveolar cancer A549 cell lines they are more directly related to their effect on human health as compared to other previously reported toxicity data of related ionic liquids.

Table 3
Toxicity data for the ionic liquids **1**–**3** and LiTFSI in human bronchoalveolar A549 cells.

Compound	Solvent (100 μL)	EC50 ± SD/(mM)
MEOMIM-TFSI (**1**)	DMSO	1.194 ± 0.001
MEOMIM-BF4 (**2**)	DMSO	1.320 ± 0.002
MFEIM-TFSI (**3**)	DMSO	1.927 ± 0.002
LiTFSI	Water	1.482 ± 0.001

4. Conclusions

In summary, a series of ionic liquids with bis(trifluoromethanesulfonyl)imide ($TFSI^-$) and tetrafluoroborate (BF_4^-) as the counter-anions have been synthesized and evaluated as potential electrolytes for primary Li/CF_x batteries. Most of these novel ionic liquids and their Li-salt containing electrolyte mixtures show no freezing/melting behavior up to −60 °C (by DSC analysis), and are thermally stable up to at least 200 °C (by TGA analysis). In general, the fluoroalkyl-derived ionic liquids typically have superior thermal stability ($T_d > 350$ °C) than their alkoxyalkyl-derived analogues, and the $TFSI^-$ anion-based ionic liquids are thermally and electrochemically more stable than the BF_4^- anion-based electrolytes. Some of these ionic liquid electrolytes exhibit high discharge capacities (>700 mAh g^{-1}) at low rates of discharge ($\sim C/100$), comparable to those of the state of the art carbonate-based electrolytes [3]. However, at high current rates and for fluoroalkyl-derived ionic liquids, the discharge capacity is limited.

The sulforhodamine B assay of the representative fluoroalkyl- and alkoxyalkyl-derived imidazolium ionic liquids and LiTFSI show that these ionic liquids are relatively nontoxic to human health and their toxicities are comparable to that of the corresponding lithium salt, LiTFSI.

Appendix A. Supplementary data

Supplementary data related to this article can be found at doi:10.1016/j.jpowsour.2013.02.002.

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