Ionic liquids based on N-alkyl-N-methylmorpholinium salts as potential electrolytes†

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Ionic liquids (ILs) have received growing attention in recent years for applications as electrolytes and in fuel cells. Their wide electrochemical window, high conductivity, and wide operating temperature range make ILs attractive for electrolyte applications. However, various thermodynamic properties and electrochemical characteristics according to the species and combination of cation and anion have yet to be revealed.1,2

MacFarlane, Forsyth et al. developed plastic crystalline electrolytes based on ILs and opened a new field of lithium-doped plastic crystal ILs exhibiting fast Li+ ion conduction and plastic crystalline properties.3 However, the preparation of these lactam-based ILs appeared difficult, because the synthesis conditions are strict. Herein, we have synthesized N-alkyl-N-methylmorpholinum cation combined with bis(trifluoromethanesulfonyl)imide anion for the first time. The objective of this study is to evaluate the preliminary results on the physical and electrochemical characteristics for the newly synthesized morpholinium ILs.6

Morpholinium cation-based ILs could be potential electrolytes for the following reasons: (1) The oxygen group in the cation might dissociate Li salt and have interactions with Li+ ions leading to improved ionic conductivity. (2) Synthesis and purification processes are easy and product reproducibility is good. (3) The costs of 4-methylmorpholine as a source of cation are more economical compared to those of 1-vinyl-2-pyrrolidinone, 1-methylpyrrolidine, and 1-methylimidazole. Therefore, the use of morpholinum ILs will reduce the production costs.

N-Butyl-N-methylmorpholinum bis(trifluoromethanesulfonyl)imide (Mor1,2TFSI) and N-ethyl-N-methylmorpholinum bis(trifluoromethanesulfonyl)imide (Mor1,4TFSI) were prepared. The synthesis procedure was divided into two steps. The desired morpholinum cation was formed, and converted into the corresponding TFSI by anion exchange (Scheme 1). The overall reaction time was less than that of imidazolium salt. Preparative details for each IL are provided.† The 1H NMR and FAB mass spectra were recorded on a Bruker DME 600 MHz NMR spectrometer and FAB mass JMS-HX110A, respectively.‡ The possible presence of residual Br− was examined by a precipitation test of AgNO3 and ionic chromatography. (System: Bio-LC DX-300 ( Dionex, Sunnyvale, CA, USA), Detector: Suppressed Conductivity (PED2), Column: ICSep AN300 with ICSep ANSC guard). No discernable Br peaks were found in the TFSI salts.‡

The thermal stabilities of Mor1,2TFSI and Mor1,4TFSI were determined under nitrogen at a heating rate of 10 °C min−1 by a PA instrument TGA 2050. In each case, the samples showed high thermal stabilities and similar TGA tendencies, as shown in Fig. 1. Mor1,2TFSI and Mor1,4TFSI were stable until approximately 400 °C and decomposed rapidly between 410 and 470 °C. The temperature-dependent phase behaviors were examined in the range of −50 to 150 °C using a Dupont TA 2000 differential scanning calorimeter (DSC). Table 1 and Fig. 2 show the thermal properties of two ILs. All the salts were found to have a solid–liquid phase transition near room temperature. While Mor1,4TFSI has one melting point, Mor1,2TFSI exhibits multiphase transition characteristics like some pyrrolidinium salts investigated by MacFarlane and Forsyth.3,4,7,8 This compound appeared to form four different solid phases, where the highest temperature crystalline phase was assigned as phase I at 29.2 °C and for subsequent decrease to −4.0, −17.8 and −31.2 °C as phases II, III, and IV, respectively. The

† Electronic supplementary information (ESI) available: the method of measurement of ionic conductivities. See http://www.rsc.org/suppdata/cc/b4/b400198b/

‡ Br peaks were found in the TFSI salts.

Table 1 Thermal properties of N-alkyl-N-methylmorpholinium salts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tmiv/°C</th>
<th>Tin/°C</th>
<th>Tf/°C</th>
<th>Tm/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mor1,2TFSI</td>
<td>−31.2</td>
<td>−17.8</td>
<td>−4.0</td>
<td>29.2</td>
</tr>
<tr>
<td>Mor1,4TFSI</td>
<td></td>
<td></td>
<td></td>
<td>28.7</td>
</tr>
</tbody>
</table>

Tm = melting temperature, Tiv–iii–IV, Tin–II–III, Tf = summary of peak maximum temperatures for thermal transitions.

Fig. 1 Thermogravimetric analysis (TGA) under nitrogen of Mor1,2TFSI and Mor1,4TFSI.

Fig. 2 DSC traces of Mor1,2TFSI.
existence of multiphase transitions in Mor\textsubscript{1,2} TFSI suggests the material possesses plastic crystalline characteristics. This plasticity implied that Mor\textsubscript{1,2} TFSI can act as a matrix inducing fast conductivity between solid and liquid phases might occur at a lower temperature than the melting point.\textsuperscript{3,7}

The electrochemical behaviour of these salts is illustrated by a cyclic voltammogram in Fig. 4. The stability was analyzed using a cyclic voltammetry Solatron 1287A potentiostat/galvanostat at room temperature. A glassy carbon working electrode 3 mm in diameter was used with a platinum wire as a counter electrode and a silver wire as a reference electrode. The cyclic voltammograms of Mor\textsubscript{1,2} TFSI and Mor\textsubscript{1,4} TFSI are almost overlapped and stable in the range of −2.5 to 2 V, indicating an electrochemical window of ~4.5 V.

It is also of interest to indicate the overall comparisons between Mor TFSI and imidazolium (Im) or pyrrolidinium (P) TFSI.\textsuperscript{3c,10} All these salts are thermally stable. The Mor salts melt near room temperature and the melting points of Im salts are recorded below 0 °C. In the case of P salts, while P\textsubscript{1,4} has high melting point (86 °C), Mor and P salts which show plastic crystalline characteristics represent lower conductivity values than those of Im salts. However, the possible reactions of C(2) carbon in 1-alkyl, 3-alkyl Im salts might cause conductivity values than those of Im salts. However, the possible reactions of C(2) carbon in 1-alkyl, 3-alkyl Im salts might cause some doubts about their electrochemical stability. The 1-alkyl, 2-alkyl, 3-alkyl Im salts overcome this problem, but represent low conductivity.\textsuperscript{3e}

In conclusion, the morpholinium salts were proven to be highly conductive and thermally and electrochemically stable. Moreover, Mor\textsubscript{1,2} TFSI possessed plastic crystalline characteristics. Because of these unique characteristics, the newly proposed morpholinium ILs might be promising candidates as electrolytes for batteries.

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Notes and references

† Representative synthesis: N-ethyl-N-methylmorpholinium bis(trifluoromethanesulfonylimide) (Mor\textsubscript{1,4} TFSI).

Under vigorous stirring, 147 g (1.35 mol) of 1-bromooctane was added dropwise to a solution of 1 g (1 mol) of 4-methylmorpholine in 200 mL of acetonitrile, and N\textsubscript{2} bubbling was used. The mixture was stirred at 60 °C for 5 h. The molten salt was placed in a freezer at −20 °C. The acetonitrile was decanted from the solids and recrystallized from acetone to yield white crystalline solids, which were dried in vacuum at 30 °C to give 190 g of product (yield 90%). 29 g (0.1 mol) of LiTFSI was added to 21 g (0.1 mol) of Mor Br in 150 mL of dichloromethane. The mixture was stirred for 1 day, and the LiBr filtered from the reaction mixture. The resulting ionic liquid was stirred with activated charcoal for 12 h. The IL was subsequently passed through a neutral aluminium oxide and silica gel columns to give colorless IL, which was dried under vacuum at 40 °C.

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\section{Notes and references}


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