

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

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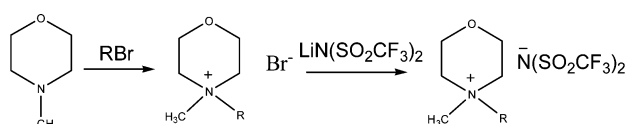
Ionic liquids based on *N*-alkyl-*N*-methylmorpholinium salts have been synthesized and the physical and electrochemical characteristics of this family of ionic liquids have been investigated for use as electrolytes.

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.^{3,4} In our previous work, we suggested several ILs based on *N*-vinyl- γ -butyrolactam exhibiting high ion conduction and plastic crystalline properties.⁵ However, the preparation of these lactam-based ILs appeared difficult, because the synthesis conditions are strict. Herein, we have synthesized *N*-alkyl-*N*-methylmorpholinium 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 morpholinium salts will reduce the production costs.

N-Butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide (Mor_{1,4}TFSI) and *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide (Mor_{1,2}TFSI) were prepared. The synthesis procedure was divided into two steps. The desired morpholinium 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 DMX 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),



Scheme 1

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

Column: ICsep AN300 with ICsep ANSC guard). No discernable Br peaks were found in the TFSI salts.†

The thermal stabilities of Mor_{1,2}TFSI and Mor_{1,4}TFSI 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. Mor_{1,2}TFSI and Mor_{1,4}TFSI 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 Mor_{1,4}TFSI has one melting point, Mor_{1,2}TFSI 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

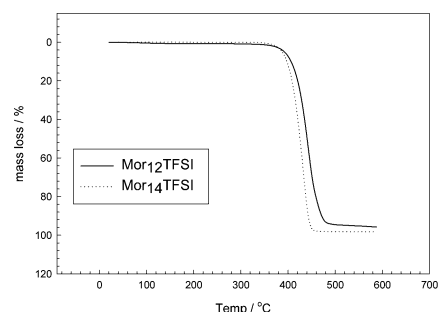


Fig. 1 Thermogravimetric analysis (TGA) under nitrogen of Mor_{1,2}TFSI and Mor_{1,4}TFSI.

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

Compound	$T_{IV-III}/^{\circ}\text{C}$	$T_{III-II}/^{\circ}\text{C}$	$T_{II-I}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$
Mor _{1,2} TFSI	-31.2	-17.8	-4.0	29.2
Mor _{1,4} TFSI				28.7

T_m = melting temperature, T_{IV-III} , T_{III-II} , T_{II-I} = summary of peak maximum temperatures for thermal transitions.

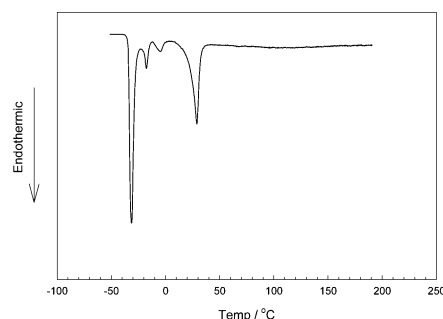


Fig. 2 DSC traces of Mor_{1,2}TFSI.

existence of multiphase transitions in Mor_{1,2}TFSI suggests the material possesses plastic crystalline characteristics. This plasticity implied that Mor_{1,2}TFSI can act as a matrix inducing fast conduction of the ion doped into the matrix *via* rotatory and vacancy motions.^{3,7}

The conductivity data of morpholinium salts measured by complex impedance analysis using a Solartron 1260A frequency response analyzer (FRA) are presented in Fig. 3. The conductivity values increase with increasing temperature. For both salts, the continuous curve shapes indicate that the discontinuity of conductivity between solid and liquid phases might occur at a lower temperature than the melting point.⁹

The electrochemical behaviour of these salts is illustrated by a cyclic voltammogram in Fig. 4. The stability was analyzed using a cyclic voltammetry Solartron 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_{1,2}TFSI and Mor_{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.^{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_{1,4} is in the liquid state at room temperature, P_{1,2} 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 some doubts about their electrochemical stability. The 1-alkyl, 2-alkyl, 3-alkyl Im salts overcome this problem, but represent low conductivity.^{3c}

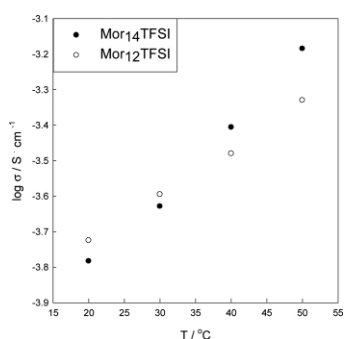


Fig. 3 Ionic conductivities as a function of temperature for Mor_{1,2}TFSI and Mor_{1,4}TFSI.

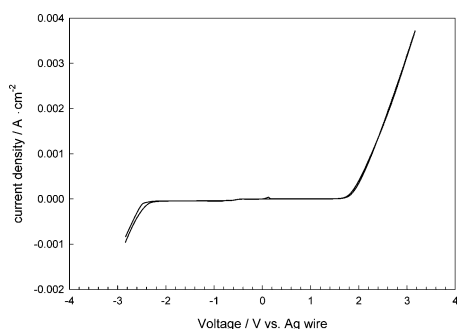


Fig. 4 Cyclic voltammogram of Mor_{1,2}TFSI.

In conclusion, the morpholinium salts were proven to be highly conductive and thermally and electrochemically stable. Moreover, Mor_{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(trifluoromethanesulfonyl)imide (Mor_{1,2}TFSI).

Under vigorous stirring, 147 g (1.35 mol) of 1-bromoethane was added dropwise to a solution of 101 g (1 mol) of 4-methylmorpholine in 200 mL of acetonitrile, and N₂ 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_{1,2}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. 32 g of the product was obtained (yield 80%): ¹H-NMR (D₂O, δ/ppm relative to TMS): 4.08 (s, 4H), 3.59–3.50 (m, 6H), 3.19 (s, 3H), 1.41 (t, 3H). FAB MS: *m/z* = 130 [Mor_{1,2}]⁺. Br⁻ content: no precipitation of AgBr and not detected by ion chromatography.

N-Butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide (Mor_{1,4}TFSI): ¹H-NMR (D₂O, δ/ppm relative to TMS): 4.08 (s, 4H), 3.56–3.47 (m, 6H), 3.21 (s, 3H), 1.82–1.80 (m, 2H), 1.46–1.42 (m, 2H), 1.01–0.98 (t, 3H). FAB MS: *m/z* = 158 [Mor_{1,4}]⁺. Br⁻ content: no precipitation of AgBr and not detected by ion chromatography.

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