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ORIGINAL PAPER

Morpholinium-based ionic liquid mixtures as electrolytes in electrochemical double layer capacitors

Maciej Galinski · Izabela Stepniak

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Abstract Butyl-Methyl-Morpholinium bis(trifluoromethanesulphonyl)imide [ButMetMor][TFSI] and Ethyl-Methyl-Morpholinum bis(trifluoromethanesulphonyl)imide [EtMetMor][TFSI] and their mixtures with propylene carbonate (PC) were investigated as potential electrolytes in an electrochemical double layer capacitor (EDLC). Temperature dependencies of conductivity and electrochemical stability windows of ionic liquids (ILs) as well as their mixtures were determined. PC mixtures give higher conductivity with maximum ca. 1:4 (IL:PC) molar rate. Temperature dependencies of conductivity follow the Arrhenius type, showing higher energy activation for neat ILs rather than for mixtures. The EDLC was constructed based on activated carbon cloth (ACC, Kynol®) ca. 2000 $m^2 g^{-1}$ and IL:PC mixture giving specific capacitance of ca. 100–120 F g^{-1}.

Keywords Room temperature ionic liquid · Morpholinium ionic liquid · Electrolyte conductivity · Electrochemical double layer capacitor (EDLC)

Abbreviations

[EtMeMor][TFSI]	Etyl-Methyl-Morpholinium bis (trifluoromethanesulphonyl)imide
[ButMetMor][TFSI]	Butyl-Methyl-Morpholinium bis (trifluoromethanesulphonyl)imide
EDLC	Electrochemical double layer capacitor
PC	Propylene carbonate
AN	Acetonitrile
DMSO	Dimethylsulphoxide
DSC	Differential scanning calorimetry

1 Introduction

Room temperature ionic liquids (RTILs), or simply termed ionic liquids (ILs), have been developed and studied extensively during the last decade [1–5]. They are characterised by low-melting points, negligible vapour pressure and staying in a liquid phase in a wide range of temperatures. Their potential application has been studied in various aspects: they may serve as solvents for chemical reactions [6, 7] as well as electrolytes in electrochemical devices [8, 9].

The first extensively studied RTIL was 1-ethyl-3-methylimidazolium tetrachloroaluminate [EtMeIm][$AlCl_4$]. However, ionic liquids containing the [$AlCl_4$]$^-$ anion are easily hydrolysed by water. Non-chloroaluminate RTILs, resistant to moisture, based on imidazolium, alkylammonium, alkylphosponium, pyrydinium, piperidynium and pyrrolidynium cations [10–15] are known, cations therein have a acyclic or aromatic character. The variety of anions, such as tetrafluoroborate [BF_4]$^-$, triflate [OTf]$^-$, bis(trifluoromethanesulphonyl) imide [TFSI]$^-$ or bis(fluorosulfonyl)imide [FSI]$^-$ [16] are the most popular. The last two are the most promising for electrochemical applications; they create ionic liquids characterised by low melting points, low viscosities, high conductivities and wide electrochemical stability windows.

Morpholinium salts have already been obtained, tested [17, 18] and applied as gel polymer electrolytes [19, 20].

M. Galinski (✉) · I. Stepniak
Faculty of Chemical Technology, Poznan University of Technology, Pl. M.Sklodowskiej-Curie 5, 60 965 Poznan, Poland
e-mail: maciej.galinski@put.poznan.pl

The oxygen group present in the chain is expected to interact with a lithium ion, yielding an improved conductivity of the potential electrolyte [12] for lithium-based cells.

At the same time, electrochemical double layer capacitors (EDLCs), based on carbon materials having a very high-surface area, have been developed as energy storage devices with very promising results. Various liquid electrolytes, both aqueous and non-aqueous, as well as polymer electrolytes have been applied [21–23]. There are also available reports describing attempts to apply ionic liquids in EDLCs [10, 24–29] and also as mixtures with propylene carbonate (PC) [30, 31].

This article presents data on the application of [EtMetMor][TFSI] and [ButMetMo][TFSI] mixtures with PC as electrolytes in the EDLC application. EDLC devices based on activation carbon cloth (ACC, Kynol®) were constructed and tested.

2 Experimental

2.1 Synthesis of ionic liquids

Methyl-Morpholinium, butyl-bromide, ethyl-bromide, acetonitrile (AN), dichloromethane, dimethylsulphoxide and PC were freshly distilled prior to their use. Lithium bis(trifluoromethylsulphonyl)imide was used as received. Redistilled water was used. Ethyl-Methyl-Morpholinium bis(trifluoromethylsulphonyl)imide [EtMetMor][TFSI] and Butyl-Methyl-Morpholinium bis(trifluoromethanesulphonyl)imide [ButMetMor][TFSI] were synthesized according to the mechanism [8] presented on Fig. 1. In both cases, the first step was carried out in AN as a solvent. The amount of 61 mL (0.81 mol) ethyl bromide was added to the solution of 47 mL (0.42 mol) 4-methyl morpholinium in 100 mL AN and the mixture was kept at 50 °C. When white precipitate appeared, it was decanted and washed four times with small portions of AN. The white solid was dried under vacuum at 60 °C. The same procedure was applied to obtain [ButMetMor][Br]; in both cases, double excess of alkylbromide was used. The second step was carried out in redistilled water. Water solutions of lithium bis(trifluormethanesulfonyl) imide were mixed with solutions of Ethyl-Methyl morpholinium bromide, [EtMet][TFSI] was extracted with the use of dichloromethane. The solution was washed with small portions of water to remove lithium bromide, while the $AgNO_3$ solution was used to indicate AgBr precipitate. A colourless, transparent liquid was obtained. Efficiencies of 86% and 85% of the 2nd steps of [EtMetMor][TFSI] and [ButMetMor][TFSI] were obtained, respectively. Water content, analyzed with a Karl Fischer titrant (HYDRANAL® Composite 1), was below the detection limit.

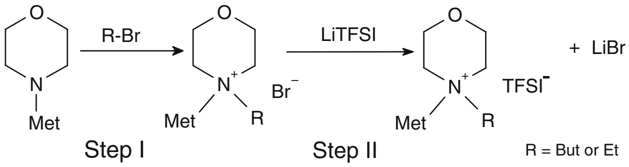

Fig. 1 Synthesis scheme of [EtMetMor][TFSI] and [ButMetMor][TFSI], R = Ethyl or Buthyl

2.2 Measurements

Differential scanning calorimetry (DSC) was performed using Haas DSC XP-10i 10 K min^{-1}. Electrolyte conductivity and temperature dependencies of conductivity were determined with the use of the impedance method (FRA, µAutolab, EcoChemie, The Netherlands). Measurements were taken in a cell with constant 4.8 cm^{-1} in a temperature range of 25–80 °C. The Arrhenius plot was used to describe temperature dependence on conductivity of ILs and their mixtures.

Electrochemical stability windows were tested using three electrode compartment cells (µAutolab, EcoChemie the Netherlands) with a 10 mV s^{-1} potential sweep rate. A platinum disc electrode (ca. 1.5 mm in diameter) was used as a working electrode and platinum foil (ca. 2 cm^2) as a counter electrode. A silver/silver(I) couple in dimethylsulfoxide (Ag/Ag^+ 0.01 mol dm^{-1} in DMSO) was used as a reference electrode—silver wire placed in a compartment filled with 0.01 M $AgClO_4$ solutions in DMSO separated from IL/through glass frit ($Ag|Ag^+$ DMSO).

Electrochemical double layer capacitor devices were prepared in a Swagelock® system that consists of a sandwich-like system. Electrodes were activated carbon cloth (ACC-5092-20—specific surface 2000 m^2 g^{-1}). Two electrodes of 12 mm in diameter (ca. 12 mg) were cut. Separated by a glass microfibre (Fisher) separator and placed in the Swagelock system, platinum discs were used as current collectors, filled with appropriate electrolytes.

Electrochemical double layer capacitors were tested using the galvanostatic charging–discharging method (Atlas-Sollich, POLAND). The 5 mA charging and discharging current was used and several hundred cycles were performed. Cyclic voltammetry was performed by the electrochemical system (µAutolab, EcoChemie, The Netherlands). Density was measured with a DMA 35N densitometer (Anton Paar, Austria). Densities were measured at 40 °C for neat ionic liquids with the densitometer placed in a thermostatic chamber and at 25 °C for mixtures with PC.

Table 1 Physicochemical properties of morpholinium-based ionic liquids and mixtures

IL	Melting point (°C)	Density (g cm^{-3})	Conductivity (mS cm^{-1})[a]	Activation energy (kJ mol^{-1})
[EtMetMor][TFSI]	36.5	1.514[a]	2.4	35.5
[ButMetMor][TFSI]	35.0	1.439[a]	1.2	41.4
[EtMetMor][TFSI]:PC	–	1.312	11.8	17.5
[ButMetMor][TFSI]:PC	–	1.341	8.9	19.2

[a] Measured at 40 °C

3 Results and discussion

Temperatures of phase transitions were obtained from DSC measurements and they are in good agreement with those published earlier [12]; thus, they were considered redundant and are not shown in this article. [ButMetMor][TFSI] shows one melting point, whereas [EtMetMor][TFSI] shows several phase transitions described and explained earlier [12]. Temperatures of highest transitions are collected in Table 1. Melting temperatures exceeded room temperature for both ILs; thus, measurements of conductivity, density and electrochemical windows were performed at 40 °C. Density values of 1.51 and 1.44 g cm^{-3} are typical for room temperature densities of ionic liquids [5].

High-electrolyte conductivity, low viscosity and wide electrochemical stability windows are the parameters that have the marked influence on durability, efficiency and storage capacity of EDLC. Neat ionic liquids rarely meet such conditions and are rarely comparable to common non-aqueous electrolytes, such as tetrafluoroborate tetraethylammonium in PC (TEABF$_4$) [16]. Pure morpholinium salts exhibit too high-melting points to be applied as electrolytes in room temperature; thus, mixtures with PC were prepared at IL:PC—1:4 molar ratio. Such a concentration shows maximum conductivity for PC mixtures with several imidazolium-based ionic liquids [31]. Figure 2 shows electrochemical windows for [EtMetMor][TFSI] at 40 °C and the [EtMetMor][TFSI] mixture with PC (1:4 molar ratio) at room temperature (25 °C). Inspection of Fig. 2 shows a distinct decrease of electrochemical stability windows for mixtures of [EtMetMor][TFSI] with PC. Cathodic and anodic limits for neat ionic liquids and IL:PC mixtures are given in Table 2. The cathodic and anodic potential limits were set when the reduction or oxidation current reached 1 mA cm^{-2} at the scan rate of 10 mV s^{-1}. The same effect may be seen on Fig. 3 showing voltamograms for [ButMetMor][TFSI] and its mixture with PC. Potential of cathodic reduction of PC reduced electrochemical stability windows in both cases. The potential range of 5.3 and 5.6 V for [EtMetMor][TFSI] and [ButMetMor][TFSI] mixtures, respectively, is in both cases limited to 4.9 V by an addition of a molecular solvent.

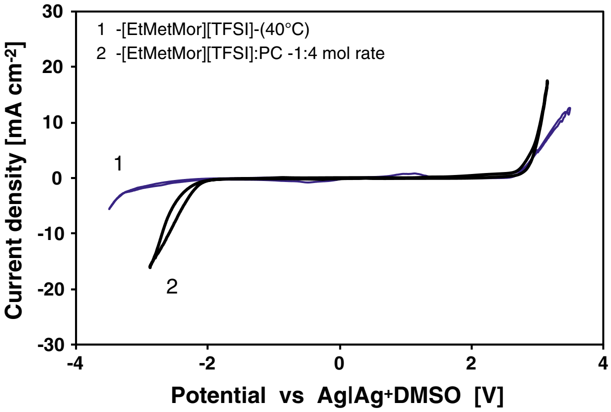

Fig. 2 Electrochemical stability windows of [EtMetMor][TFSI] and mixtures with PC (1:4 molar rate). Potential versus Ag|Ag^{+}DMSO reference electrode, sweep rate: 10 mV s^{-1}

Table 2 Electrochemical stability windows on the Pt electrode of morpholinium-based ionic liquids and mixtures

Electrolyte	Cathodic limit (V)	Anodic limit (V)	Voltage range (V)
[EtMetMor][TFSI][a]	−2.6	2.7	5.3
[ButMetMor][TFSI][a]	−2.9	2.7	5.6
[EtMetMor][TFSI]:PC	−2.2	2.7	4.9
[ButMetMor][TFSI]:PC	−2.2	2.7	4.9

[a] Measured at 40 °C, all measurements versus Ag|Ag^{+}DMSO reference electrode

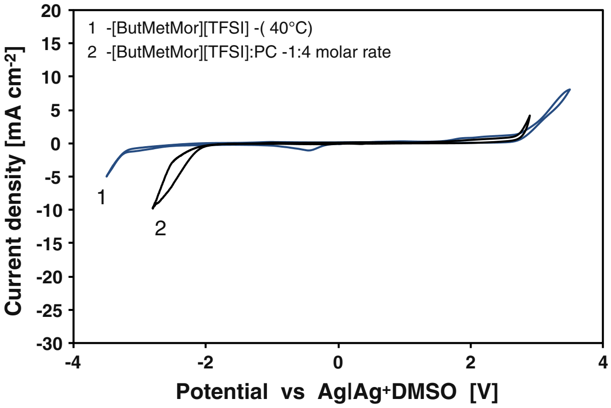

Fig. 3 Electrochemical stability windows of [BuMetMor][TFSI] and mixtures with PC (1:4 molar rate). Potential versus Ag|Ag^{+}DMSO reference electrode, sweep rate 10 mV s^{-1}

Electrochemical capacitors are based on high-surface carbon materials, containing undefined function groups, which result in real voltage being smaller than electrochemical stability windows measured at platinum electrodes [5].

Figure 4 shows temperature dependencies on conductivity of pure salts and mixtures with PC. An addition of PC increased conductivity from 2.4 to 11.8 mS cm^{-1} for [EtMetMor][TFSI] and from 1.2 to 8.9 mS cm^{-1} for [ButMetMor][TFSI] at 40 °C. The linear trend for all the four electrolytes is also presented in Fig. 4. Values of energies activation calculated from Arrhenius equations for the conducting process are included in Table 1. Neat ionic liquid activation energies are ca. 36 and 41 kJ mol^{-1}, whereas an addition of molecular solvent reduced these values to 18 and 19 kJ mol^{-1}. Such a behaviour and obtained values are in good agreement and typical of ionic liquid mixtures [31]

Electrochemical double layer capacitors based on Kynol fibres (ACC-5092-20) were constructed and tested. Figure 5 presents cyclic voltammetry of EDLCs devices based on PC mixture electrolytes. Box-like shapes in the 3.2 V range show a typical capacitor-like behaviour. EDLC based on pure [EtMetMor][TFSI] ionic liquid and the same carbon material has been constructed and tested in 85 °C. The comparison (see Fig. 5) shows similar capacitor-like shape. Figure 6 presents the 200–205th charging–discharging cycles, and Fig. 7 shows dependencies of specific capacitance on cycle number. Values of specific capacities calculated from voltammograms are ca. 136 F g^{-1} for both PC mixtures, being a little higher than those obtained from charging–discharging measurements, ca. 112 F g^{-1}.

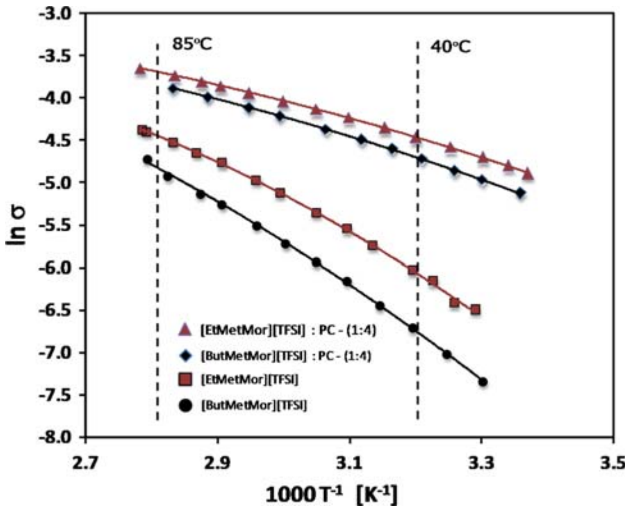

Fig. 4 Temperature dependencies of conductivity for neat ILs: *filled square*—[EtMetMor][TFSI], *filled circle*—[ButMetMor][TFSI] and their mixtures with propylene carbonate: *filled triangle*—[EtMetMor][TFSI]:PC—(1:4) and *filled diamond*—[ButMetMor][TFSI]:PC—(1:4)

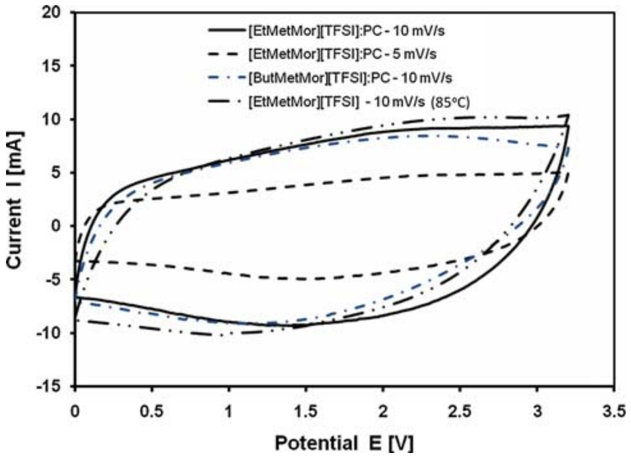

Fig. 5 Cyclic voltammetric curves of capacitors based on [EtMetMor][TFSI]:PC and [ButtMetMor]:PC mixtures (IL:PC—1:4 molar rates) as well as cyclic voltammetric of a capacitor based on neat [EtMetMor][TFSI] as electrolyte in 85 °C. Electrode material: ACC Kynol® (5092-20), 2000 m^2 g^{-1}

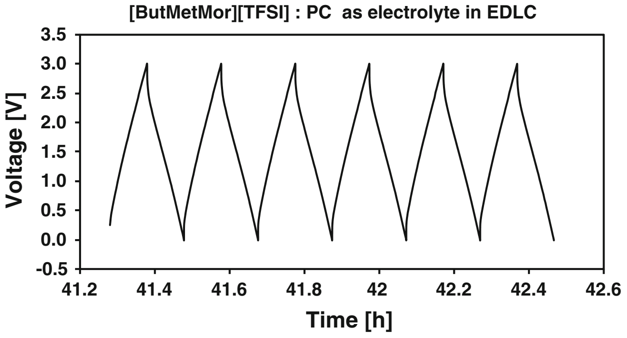

Fig. 6 Galvanostatic charging–discharging of EDLC devices: two ca. 12 mg Kynol ACC (5092-20; 2000 m^2 g^{-1}) electrodes and [ButMetMor][TFSI]:PC mixtures as electrolyte. 200–205th cycles, current: 5 mA

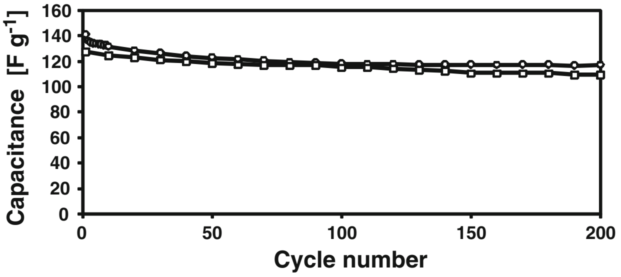

Fig. 7 Capacitance dependencies on cycle number calculated from galvanostatic charging curves of EDLC devices: two ca. 12 mg Kynol® cloth (5092-20; 2000 m^2 g^{-1}) electrodes and *open circle* [ButMetMor][TFSI]:PC and *open square* [ButMetMor][TFSI]:PC mixtures as electrolyte

Inspection of Fig. 7 shows that after several cycles specific capacitance becomes stable at the similar levels of 120 and 113 F g^{-1}, respectively.

4 Conclusions

Morpholinium-based ionic liquids with [TFSI] anions have melting points above room temperature; thus, they may not be applied as pure electrolytes in EDLCs. The addition of PC increases conductivity, to the level of ca. 10^{-2} S cm^{-1}, while it simultaneously decreases melting points, making them good electrolytes in electrochemical double layer capacitor applications.

Specific capacitance of both morpholinium-based ionic liquid mixtures and high-surface activated carbon fibres is ca. 120 F g^{-1}.

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