# Ionic liquid-1,2-dimethoxyethane mixture as electrolyte for high power density supercapacitors

Q1  A. Jänes*, J. Eskusson, T. Thomberg, T. Romann, E. Lust

*Institute of Chemistry, University of Tartu, 50411 Tartu, Estonia*

ABSTRACT

In this work we have studied the effect of 1,2-dimethoxyethane (1,2-DME) addition (from 0 to 90 vol%) on the electrochemical behaviour of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide (EMImTFSI) as an electrolyte for supercapacitors, using cyclic voltammetry, electrochemical impedance spectroscopy and constant power methods. Also, the ionic conductivity and viscosity of EMImTFSI and 1,2-DME have been measured and discussed. The conductivity of the EMImTFSI could be increased from 5.67 mS/cm up to 24.21 mS/cm by mixing EMImTFSI with 1,2-DME. The stored power values for supercapacitors increased from 13 kW/kg to 20.5 kW/kg (correspond to 2 s application line), when the concentration of 1,2-DME increased up to 40 vol%. The supercapacitors based on the 40 vol% of 1,2-DME deliver the higher power density at the constant energy density, showing an excellent characteristics applicable in high rate supercapacitor devices. Nearly ideal capacitive behaviour has been established at potential scan rates $v \leq 10$ mV/s and cell potential $\Delta E \leq 2.7$ V.

© 2016 Science Press and Dalian Institute of Chemical Physics. All rights reserved.

## 1. Introduction

The most recent activated carbon based supercapacitors (SCs) on the market use electrolyte solutions based on aprotic solvents, typically acetonitrile (AN) or organic carbonate-based solvents (propylene carbonate (PC), ethylene carbonate, ethyl methyl carbonate etc.) with cell voltage up to 2.85 V. In the area of energy management room temperature ionic liquids (RTILs) have been studied for many years as alternative electrolytes in various devices, including Li-ion batteries [1,2], electrochemical actuators [3,4] and supercapacitors [5–8]. A major limitation of RTILs for widespread applications is their relatively high viscosity [9] as this property has a major impact on the ionic mass transport rate. Currently, commercially available RTILs do not have sufficient conductivity and so, several approaches have been undertaken in order to decrease their viscosity and improve their ionic conductivity [10–14]. Krause and Balducci studied high voltage electrochemical double layer capacitor containing mixtures of ionic liquids and propylene carbonate as electrolytes [15]. Using a mixture of PC/PYR$_{14}$TFSI as electrolyte, supercapacitors with an operative voltage of 3.5 V and electrochemical series resistance comparable with that of conventional electrolyte have been realized and the use of PC/PYR$_{14}$TFSI mixture also guarantees a remarkable cycling stability, as evidenced by a capacitance loss of only 5% after 100,000 cycles carried out at 3.5 V [15]. Also Pohlmann and co-workers proposed the use of the azepanium based ionic liquids and N-butyl-N-methylpyrrolidinium tetrafluoroborate (PYR$_{14}$BF$_4$) for propylene carbonate based electrochemical double layer capacitors [16,17]. Jarosik and co-workers [18] have explored the effect of binary blends. They reported that binary mixtures of 1-ethyl-3-methyl imidazolium trifluoromethane sulphonate triflate with 1-ethyl-3-methylimidazolium bis (trifluoromethane sulphonylimide) sometimes displayed small synergistic improvements. They observed higher conductivity than the conductivity of each RTIL by itself, and even higher than the conductivity expected from the weighted ratio of the two RTILs. Ruiz and co-workers studied the ionic liquid–solvent mixtures as supercapacitor electrolytes for extreme temperature operation [19]. Brandt et al. [20] studied mixtures of the trimethyl-sulphonium bis[(trifluoromethyl)sulphonyl]imide (Me$_3$STFSI) and PC as electrolytes for carbon-based electrochemical double layer capacitors (EDLC). They demonstrated that the EDLC cycle life strongly depends on the concentration of Me$_3$STFSI in the mixture. From Conway et al. [21], it appears that for the 1 M (C$_2$H$_5$)$_4$NBF$_4$ in propylene carbonate, possibly mixed with 1,2-dimethoxyethane decreases its viscosity and thus raises the ionic mobilities.

In this work we have studied the effect of 1,2-dimethoxyethane (1,2-DME) addition (from 0 to 90 vol%) on the electrochemical behaviour of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide (EMImTFSI) as an electrolyte for supercapacitors, using cyclic voltammetry, electrochemical

* Corresponding author. Tel.: +372 737 5178; fax: +372 737 5264.
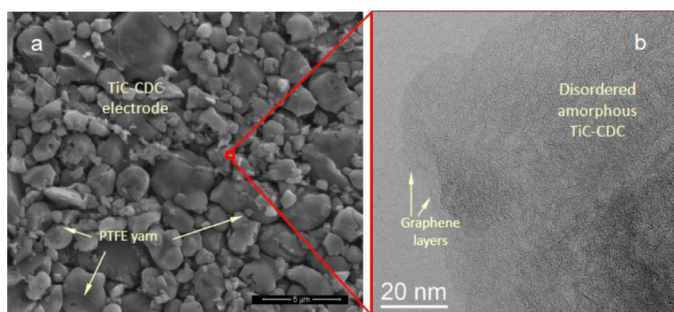  *E-mail address:* alar.janes@ut.ee (A. Jänes).

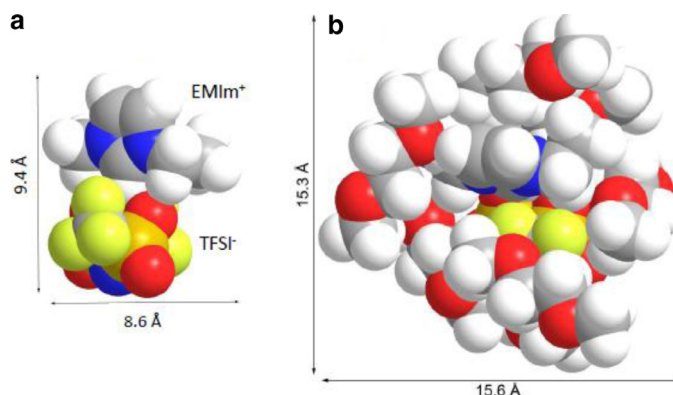**Fig. 1.** SEM (a) and HRTEM (b) images of TiC-CDC electrode material used.



**Fig. 2.** "Space Filled" representation of bare EMImTFSI (a) and 1,2-DME with 7 ligand (solvent) molecules (b), height and width have been calculated using Gaussian DFT B3LYP 3-21 G. Atoms are denoted as follows: hydrogen–white, nitrogen–blue, carbon–grey, fluorine–yellow, sulphur–brown and oxygen–red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

impedance spectroscopy and constant power methods. Also, the ionic conductivity and viscosity for (EMImTFSI) and 1,2-DME have been measured and discussed.

## 2. Experimental

### 2.1. Chemicals and supercapacitor test cells

All the experiments discussed were made inside the glove box MBraun Labmaster sp at very clean and dry conditions ($O_2$ and $H_2O$ concentration lower than 0.1 ppm). The two-electrode system was set in a hermetic aluminium test cell (Hohsen Corporation, Japan) to ensure the gas tightness of the cell. Between working electrodes the 25 $\mu$m thick Nippon Kodoshi TF4425 separator sheet was used.

The pure argon (6.0, AGA) has been used for saturation of the anhydrous 1,2-dimethoxyethane (1,2-DME, 99.5% (Sigma-Aldrich), melting point –58 °C, boiling point 85 °C, moisture content by Karl Fischer titration method less than 30 ppm) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide (EMImTFSI, assay 99.9 % (Solvionic), melting point –16 °C) mixtures under study.

### 2.2. Physical characterization of electrode material and preparation of supercapacitor electrodes

Specific surface area, pore size distribution, micropore volume, micropore area and other parameters were measured using the Micromeritics ASAP 2020 (Micromeritics, Inc.) system and calculated according to the methods discussed in Ref. [22]. Some more important characteristics obtained demonstrate that the TiC-CDC is mainly microporous amorphous material with micropore area, $S_{micro} = 1661$ m$^2$/g and micropore volume, $V_{micro} = 0.83$ cm$^3$/g, however including a noticeable amount of mesopores ($S_{meso} = 414$ m$^2$/g and $V_{meso} = 0.07$ cm$^3$/g). The surface structure and morphology of TiC-CDC were examined by scanning electron microscopy (SEM) using the FIB-SEM Helios$^{TM}$ Nanolab 600 system, by the high resolution transmission electron microscopy methods (HRTEM), exploiting a Tecnai 12 instrument operated at a 120 kV accelerating voltage (Fig. 1).

The supercapacitor electrodes were constituted of the microporous titanium carbide derived carbon (TiC-CDC), covered by the very pure Al layer from one side by the electromagnetron sputtering method. The limits of ideal polarizability of Al layer have been established by cyclic voltammetry as well as by impedance spectroscopy methods, and are wider than that for TiC-CDC electrode used. Before assembling of the symmetrical supercapacitor cells, the Ti-CDC was heated at $T = 300$ °C during 48 h under reduced pressure ($p < 10^{-3}$ atm). The electrode area used was 2 cm$^2$ and the medium thickness was $\sim 100$ $\mu$m.

## 3. Results and discussion

### 3.1. Quantum chemical study of EMImTFSI and 1,2-DME mixtures

By quantum chemical study applying to Gaussian DFT B3LYP 3-21 G, it was found that it is energetically favourable to form solvent-ion and ion-pair-solvent clusters, compared to the bulk ionic liquid or single ions. While the solvation layer, fully covering the ionic liquid or ions, would consist of ~10–12 1,2-dimethoxyethane ligands, energetically most stable is the complex with 5–7 ligands (~50–60 vol% solvent) (Fig. 2). Also, the energy differences for clusters with 1–7 1,2-DME ligands are quite small, i.e. first solvent molecule addition gives lowest energy (–66 kJ/mol versus single components), but fifth added solvent molecule gives only –13 kJ/mol and 7th gives +4 kJ/mol. Thus, it might be concluded that a medium 1,2-DME content (~60 vol%) stabilizes best the ionization of the RTIL ions. In pure EMImTFSI, ions move as ion|few ion-pair complexes [23] and only a small amount of ionic liquid is actually ionized. When adding molecular solvent, the solvated ions may become smaller and the amount of ionized particles increases.

### 3.2. Dynamic viscosity and specific conductivity of electrolytes

The dynamic viscosities, $\eta$, of pure EMImTFSI and mixtures with 1,2-DME were measured at fixed temperatures from –20 to 60 °C using U-shaped viscometer with flow pipe diameter 0.82 mm (Fig. 3a). The viscometer was calibrated with Milli-Q$^+$ water at $20.0 \pm 1$ °C. The dynamic viscosity significantly decreases with the rise of 1,2-DME vol% in mixed system. Fig. 3(b) demonstrates the dependence of specific conductivity on 1,2-DME vol% in mixed system. As it can be seen in Fig. 3(b), $\kappa$ nearly exponentially increases up to 60 vol% 1,2-DME in mixed system and then decreases. Lower viscosity for the ionic liquid + solvent mixture the first approximation can be explained by the smaller solvation shell in 1,2-DME containing solutions. Thus to the increase of ionic conductivity can be explained by the decrease of viscosity and, based on the quantum chemical study, also as a decrease of the sizes of solvated ions. In other words there are more dissociated ions in ionic liquid + solvent mixture and these solvated ions can move faster. A small or medium amount of solvent stabilizes ions better than the ionic liquid itself forming very big complexes. When the amount of ionized particles increases, it improves conductivity and differential capacitance as well. Thus ions and ion-pairs move in narrow carbon pores favourably as partially desolvated/solvated ions