



Short communication

# Redox-active electrolyte supercapacitors using electroactive ionic liquids



Han Jin Xie, Bruno Gélinas, Dominic Rochefort\*

Département de Chimie, Université de Montréal, CP6128 Succ. Centre-Ville, Montréal, Québec H3C 3J7, Canada

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## ABSTRACT

Here we present redox ionic liquid supercapacitors (RILSCs) which use electrolytes made from ionic liquids modified with an electroactive function to increase the energy density of activated carbon electrodes via faradaic reactions. More specifically, two different ionic liquids were made by modifying either the imidazolium cation or the bis(trifluoromethanesulfonyl)imide anion with ferrocene in order to determine the importance of the electroactive ion's polarity. The functionalization of an ionic liquid with ferrocene led to high concentrations of redox moieties in the electrolyte (2.4 M) and a large maximum operating voltage (2.5 V). An energy density of up to 13.2 Wh per kg (both electrodes) was obtained which represents an 83% increase vs. the unmodified ionic liquid. When the ionic liquid's anion is modified with ferrocene, the self-discharge at the positive electrode is fully suppressed due to the deposition of a film on the electrode. The results presented herein demonstrate that electroactive ionic liquids constitute a promising alternative to conventional solute in solvent electrolytes found in energy storage devices, and are particularly well-suited for redox-active electrolyte supercapacitors.

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## 1. Introduction

Redox-active electrolyte supercapacitors (RESCs) are obtained by dissolving electroactive species in the electrolyte as a mean to increase the energy density of carbon-based capacitors [1–4]. Some of the most common redox centers previously used to modify carbon electrodes were also investigated as redox additives in RESCs. The oxidation of hydroquinone (at 0.38 M concentration in  $\text{H}_2\text{SO}_4$  electrolyte) into benzoquinone attained  $901 \text{ F g}^{-1}$  at low current density ( $2.65 \text{ mA cm}^{-2}$ ) during the charging step of a KOH-activated carbon capacitor, while the same electrode provided  $320 \text{ F g}^{-1}$  in the absence of hydroquinone [2]. Similar enhancements in capacitance were obtained by adding KI at 0.08 M in  $\text{H}_2\text{SO}_4$  electrolyte (increase from 472 to  $912 \text{ F g}^{-1}$  at  $2 \text{ mA cm}^{-2}$ ) [5]. Other redox additives with activated carbon electrodes reported in recent years include  $\text{VOSO}_4$ , *p*-phenylenediamine, acetylferrocene, and methylene blue [4,6,7]. RESCs are often based on aqueous electrolytes due to a higher solubility of redox molecules in water than in organic solvents. For the same reason, ionic liquids have not been extensively studied as electrolyte in RESCs despite the fact that they could present the advantage of an increased maximum operating voltage. For example, Sun et al. reported on the reduction of  $\text{Cu}^{2+}$  dissolved in 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMImBF}_4$ ) ionic liquid at porous carbon electrodes, providing a cell voltage of 2.0 V [8]. So far, a compromise must be done between fast transport and high solubility of the redox molecule (obtained in

aqueous electrolytes) and a high cell voltage (obtained with organic solvents and ionic liquids).

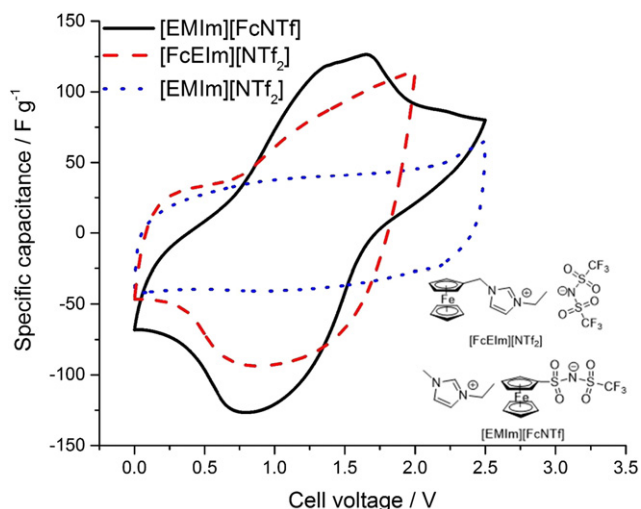
Clearly, RESCs may benefit from the development of electroactive electrolytes specifically formulated for this purpose, and which should *i*) allow high concentrations in redox species, *ii*) present a high maximum voltage, and *iii*) include a self-discharge suppression mechanism. This work demonstrates that electroactive ionic liquids, in which a redox moiety is covalently linked to one of the ions [9–11], may be used to meet these challenges. No study on redox ionic liquid supercapacitors (RILSCs) has ever been reported in the past, and the importance of the ionic liquid structure on charge storage and self-discharge requires investigation. Therefore, two redox ionic liquids (RILs) obtained by modifying either the cation or the anion with ferrocene, are studied here as redox-active electrolytes for carbon-based RILSCs. The RIL with the Fc attached on the cation was used to demonstrate self-discharge in RILSCs. Electrolytes based on these ionic liquids were applied in carbon-based supercapacitor cells to establish how the polarity of the electroactive ion impacts energy storage and self-discharge processes in RILSCs.

## 2. Experimental section

The synthesis and characterization of both electroactive ionic liquids are detailed in previous studies [12,13]. The unmodified ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide,  $[\text{EMIm}][\text{NTf}_2]$  was purchased from Iolitec and used without further purification. The water content of all ILs was found between 144 and 170 ppm after vacuum drying, which are typical values [14]. The electrodes were prepared by mixing activated carbon (Black Pearl 2000, Cabot) [15],

\* Corresponding author. Tel.: +1 514 343 6733.

E-mail address: [dominic.rochefort@umontreal.ca](mailto:dominic.rochefort@umontreal.ca) (D. Rochefort).



**Fig. 1.** Cyclic voltammograms recorded with two-electrode cells with 80 wt.% of the ionic liquid in acetonitrile. Each carbon electrode weighed 3.5 mg and contained 80 wt.% of activated carbon. The curves were obtained at a scan rate of  $10 \text{ mV s}^{-1}$  at a temperature of  $25^\circ\text{C}$ .

acetylene black (Alfa Aesar), graphite (Alfa Aesar) and PTFE ( $1 \mu\text{m}$  particles, Sigma-Aldrich) in a mortar, at a ratio of 80:7.5:7.5:5 based on weight. The mixture was then pressed into a film, from which  $15 \text{ mm}$ -diameter disks were cut. These electrodes were assembled in Swagelok cells in a glovebox, with four stacked paper disks soaked with the electrolyte used as separators. For the three-electrode setup, a Pt wire (quasi-reference electrode) was inserted between the paper disks to prevent contact with the electrodes. Cyclic voltammograms and galvanostatic charge/discharge measurements were made with a VMP3 potentiostat from Biologic.

### 3. Results and discussion

Two imidazolium redox ionic liquids (RILs), each with one ion modified with ferrocene, were selected to provide faradaic reactions and increase the specific energy ( $W_g$ ,  $\text{Wh kg}^{-1}$ ) of carbon-based supercapacitors. The structures of their reduced form are presented in Fig. 1. The redox ionic liquid 1-(methylferrocenyl)-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide, [FcElm][NTf<sub>2</sub>], presents a ferrocene on the cation which forms a dication upon oxidation and remains in the liquid phase. The details of the synthesis and characterization of the electrochemical properties of [FcElm][NTf<sub>2</sub>] were previously published [12]. The second RIL was obtained by modifying ferrocene with an anionic function, the structure of

which is inspired by the NTf<sub>2</sub> anion (Fig. 1). In 1-ethyl-3-methylimidazolium ferrocenylsulfonyl-(trifluoromethylsulfonyl)imide, [EMIm][FcNTf], the anion is the electroactive species and has been shown to deposit on electrodes when oxidized to the zwitterion  $[\text{Fc}^+ \text{NTf}^-]^0$  [13].

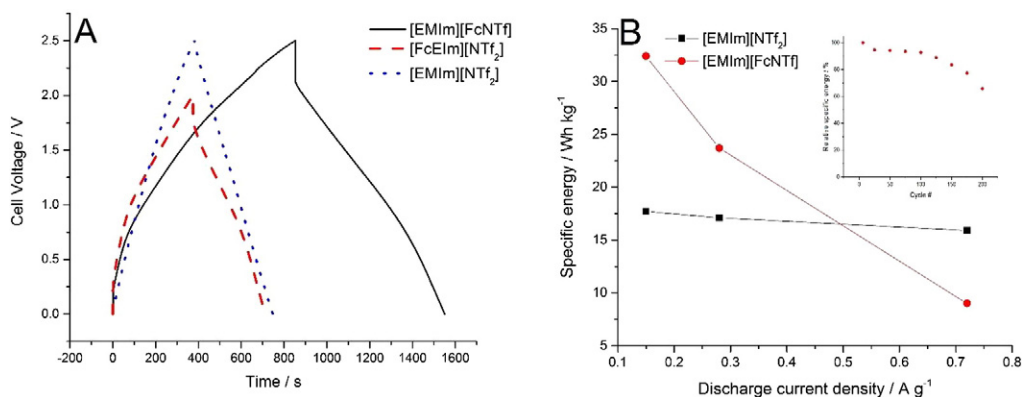
Fig. 1 shows the cyclic voltammograms obtained with three different solutions composed of 80 wt.% of ionic liquid in acetonitrile. The oxidation and reduction of the ferrocenyl moiety in [FcElm][NTf<sub>2</sub>] and [EMIm][FcNTf] appear clearly on the CV, while the unmodified [EMIm][NTf<sub>2</sub>] yielded a featureless, rectangular curve typical of double-layer charging. The use of RILs-CH<sub>3</sub>CN mixtures results in higher cell reproducibility, due to the former's high melting points ( $>55^\circ\text{C}$ ) and high viscosity ( $>1000 \text{ cP}$  at  $60^\circ\text{C}$ ). Mixtures with RIL concentration between 10 and 80 wt.% in CH<sub>3</sub>CN were evaluated and while the 40 wt.% provided the highest specific energy (compromise between concentration and viscosity) the 80 wt.% will be studied in details hereon due to its ability to prevent self-discharge (discussed later) which was not observed in more diluted mixtures. These 80 wt.% mixtures in acetonitrile have a concentration of  $2.4 \text{ M}$  in ferrocene centers, a figure three times higher than the ferrocene concentration in acetonitrile at saturation [16].

Galvanostatic charge–discharge (GCD) experiments were carried out to evaluate the energy density of the devices employing the two different electroactive ionic liquids (Fig. 2). The redox processes observed in Fig. 1 with both [FcElm][NTf<sub>2</sub>] and [EMIm][FcNTf] RILs are also evidenced in the curvature of the GCD profiles in Fig. 2A. The gravimetric specific energy ( $W_g$ ) for discharge was calculated from the integration of area under the curve (see Table 1), according to Eq. 1, rather than by evaluating the capacitance which tends to overestimate charge storage involving faradaic processes [17]:

$$W_g = \frac{I}{w} \int_{t=0}^{t=t} U(t) dt \quad (1)$$

where  $I$  is the current (A),  $w$  is the total weight of both electrodes (kg), and  $U(t)$  is the non-linear function of the voltage over time (V s).

The gravimetric specific energy values, based on total weight of both electrodes for the RILSCs presented here, are presented in Table 1. The values obtained with the [EMIm][FcNTf] redox ionic liquid represent a significant increase from equivalent double-layer devices using either the unmodified ionic liquid [EMIm][NTf<sub>2</sub>] or the conventional electrolyte  $1 \text{ M}$  TBAP in CH<sub>3</sub>CN. No significant gain in energy was obtained with the RIL [FcElm][NTf<sub>2</sub>] because of a less efficient oxidation of the Fc-based cation and of self-discharge (see below). To better understand the reactions involved at each electrode during GCD, the charge–discharge profiles obtained with [EMIm][FcNTf] RIL in a three-electrode Swagelok setup with a Pt wire quasi-reference inserted in the separator



**Fig. 2.** A: GCD profiles of supercapacitors with different ionic liquids ( $i = 1 \text{ mA}$ ). B: Effect of discharge rate on the  $W_g$  for the RILSC ([EMIm][FcNTf]) and EDLC ([EMIm][NTf<sub>2</sub>]). Inset of B shows the  $W_g$  losses over the first 200 cycles.

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