



## In search of an appropriate ionic liquid as electrolyte for macroporous manganese oxide film electrochemistry

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### HIGHLIGHTS

- There is no difference among the surface areas films of differing pore sizes.
- Capacitances are due both surface charge compensation and intercalation processes.
- The best cycling performance was observed for  $\text{Li}^+/\text{[BMMI][Tf}_2\text{N]}$  electrolyte.
- Oxide dissolution occurs in  $\text{Li}^+/\text{[Et}_2\text{OMMI][Tf}_2\text{N]}$  and  $\text{Li}^+/\text{[BMMI][BF}_4\text{]}$ .

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### ABSTRACT

Macroporous manganese oxide films were produced via template-assisted electrodeposition methodology employing polystyrene spheres with different diameters as template, thereby producing films with different pore sizes. The obtained films were true casts of the template(s) employed, as evidenced by Field Emission Scanning Electron Microscopy. The influence of pore size on capacitive behavior was assessed by cyclic voltammetry experiments in conventional propylene carbonate/ $\text{LiClO}_4$ . Besides the influence of pore size, four different ionic liquids (ILs) were studied as electrolytes, showing that the physico-chemical nature of IL strongly affects the capacitive behavior of macroporous manganese oxide films, particularly in terms of stability throughout successive charge/discharge cycles. Optimal performance was obtained using 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ( $\text{[BMMI][Tf}_2\text{N]}$ ), in which a constant increase in capacitance was observed for the first 700 charge/discharge cycles. This capacitance remained constant, at least until the 1,000 cycle, and was higher than the capacitance achieved using conventional organic solvents. Moreover, the electrochemical window obtained using  $\text{[BMMI][Tf}_2\text{N]}$  was widened (from 0.9 V to 1.5 V), corresponding to a significant gain (up to 75%) in terms of energy density. Thus, the development of electrochemical capacitors may significantly benefit from macroporous manganese oxide film electrochemistry employing ionic liquids as electrolytes.

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### 1. Introduction

Because of their advantageous properties, such as low flammability, negligible vapor pressure and high ionic conductivity [1], ionic liquids (ILs) have been extensively studied for use as electrolytes in electrochemical devices such as lithium batteries [2–6]. In addition to these advantageous characteristics, ILs are stable throughout a wide electrochemical window, which is extremely important given that energy and power density are strongly affected by cell voltage.

Another advantage of ILs is their potential to combine several cations and anions, thus making it possible to modify the ILs' properties according to the desired particular applications [7]. However, in spite of attempts to understand the relationship between structure(s) and properties, it is still a considerable challenge to determine which IL is the best suited electrolyte for a given system.

Some studies have demonstrated the use of ILs as electrolytes in electrochemical capacitors [8–10]. In contrast to lithium batteries, in which charge compensation is primarily obtained via the  $\text{Li}^+$  ions provided by the salt added to the IL, in electrochemical capacitors the ions from the IL itself can take part in this process, which typically occurs at the surface of the electroactive material. Recently, Li and co-workers have demonstrated that adding small ions such as  $\text{Na}^+$ ,  $\text{H}^+$  and  $\text{Cl}^-$ , thereby providing electroactive sites

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**Table 1**  
Prepared ionic liquids and their physico-chemical properties at 25 °C.

Ionic liquid	Full name	$\sigma$ /mS cm <sup>-1</sup>	$\eta$ /mPa s	Ref.
[BMMI][Tf <sub>2</sub> N]	1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	1.6	93	[23]
[Et <sub>2</sub> OMMI][Tf <sub>2</sub> N]	1-Ethoxyethyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	2.3	67	[24]
[BMP][Tf <sub>2</sub> N]	N-n-Butyl-N-methylpiperidinium bis(trifluoromethanesulfonyl)imide	1.2	183	[23]
[BMMI][BF <sub>4</sub> ]	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	0.9	515	[25]

that are unavailable via the more voluminous ions in the IL, can improve the capacitance in systems containing manganese oxide as the electrode material and an IL as the electrolyte [11].

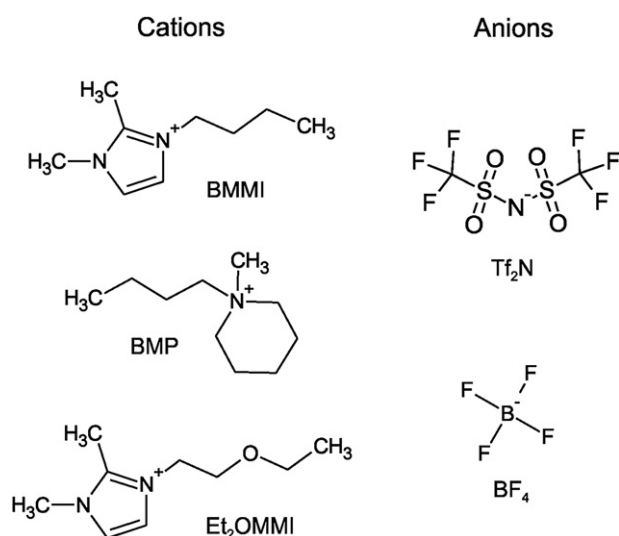
Due to its high theoretical capacitance and low cost, manganese oxide was widely studied for use in supercapacitor [12,13]. However, due to its relatively poor experimental capacitance (compared to theoretical values), most recent work involved synthesizing materials with increased surface areas to increase their electrochemical performance [14–17]. Among others strategies, electrodeposition of films around a colloidal crystal template was suggested as a good alternative for producing macroporous materials with high surface areas [18–20]. Initial studies regarding template-assisted electrodeposition of macroporous manganese oxide employed polystyrene spheres was done, and the resulting film was electrochemically characterized using aqueous electrolytes [21,22]. However, only one sphere size was used in these studies; therefore, there was no investigation or discussion regarding the effect(s) of pore size on electrochemical performance.

Based on these assumptions, the goals of the present contribution are both to study the influence of pore size on capacitive behavior of manganese oxide films as well as the influence of physico-chemical nature of different ionic liquids on the electrochemical performance of manganese oxide macroporous films.

## 2. Experimental

### 2.1. Syntheses of ILs

Ionic liquids were prepared and purified according to procedures described in previously published studies. The procedures used are shown in Table 1 and their cations and anions structures are showed in Fig. 1.



**Fig. 1.** Structures of cations and anions of ionic liquids.

In general, after the imidazole compound was reacted with the longer chain bromide to give the IL cation bromide, an ionic exchange reaction with the desired anion was performed. After synthesis, the water content of each IL was measured via Karl-Fischer titration with a Metrohm – 831 KF Coulometer; a value between 200 and 1000 ppm was obtained in all cases.

### 2.2. Preparation of manganese-oxide macroporous films

A scheme presenting the preparation of manganese oxide macroporous films is presented in Fig. 2.

#### 2.2.1. Assembly of polystyrene spheres over a gold substrate

Aqueous suspensions (10% (w/w)) of polystyrene nanospheres with differing diameters (300, 460, 600 and 800 nm) were diluted to 0.5% using Triton-X 100 aqueous solutions of differing concentrations (depending on the sphere sizes used). Three 10- $\mu$ L aliquots of the obtained suspensions were placed (via micropipette) on the substrate, which consisted of the gold surface of a 6 MHz, AT-cut, overtone polished, piezoelectric quartz crystal (Valpey-Fisher) with a diameter of 25 mm and a piezo-active electrode area of 0.31 cm<sup>2</sup> (integral sensitivity factor,  $K = 6.45 \times 10^7$  cm<sup>2</sup> Hz g<sup>-1</sup> [26]). The surfactant used was important to ensure homogeneous assemblage of the polystyrene spheres over the substrate. After each 10  $\mu$ L aliquot application and prior to the subsequent application, the gold surface was slowly dried at room temperature in a saturated-humidity atmosphere. After the last aliquot was applied and the surface was dry, the deposits obtained were submitted to thermal treatment at 100 °C for varying times, depending on the particular sphere size employed. The Triton-X 100 concentrations and thermal treatment times for each sphere size are given in Table 2.

#### 2.2.2. Electrodeposition of manganese oxide around the polystyrene spheres

Manganese-oxide films were obtained via oxidation (at a constant voltage) of 2 mmol L<sup>-1</sup> MnSO<sub>4</sub> + 50 mmol L<sup>-1</sup> LiClO<sub>4</sub> aqueous solution (as electrolyte) [27]. Immediately prior to electrodeposition, the substrate containing the polystyrene template was immersed in the electrodeposition solution for 1 h to completely swell the voids among spheres within the electrode. Electrodeposition was obtained by applying 1 V (vs. an Ag/AgCl/KCl<sub>sat</sub> reference electrode) and increasing the charge until it reached 180 mC cm<sup>-2</sup> (using an Autolab PGSTAT 30 potentiostat). After the electrochemical process was complete, the substrate containing the MnO<sub>2</sub> deposit was rinsed with deionized water and dried with N<sub>2</sub> gas.

To remove the polystyrene template, the electrode was immersed in tetrahydrofuran, which was then stirred for 45 min, after which the electrode was washed with ethanol and dried under N<sub>2</sub> flow. The mass of the electrodeposited material was obtained by measuring the resonance frequency of the quartz crystal before the deposition of polystyrene spheres and after their removal. Frequency shifts were measured using a Stanford Research Systems Model SR620 instrument connected to an oscillating circuit (serial mode) and a microcomputer for data acquisition. Complete removal of polystyrene spheres from the manganese oxide film was confirmed via FESEM using a Jeol microscope, model JSM-7401F.

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