



# Electrochemical characterization of MnO<sub>2</sub>-based composite in the presence of salt-in-water and water-in-salt electrolytes as electrode for electrochemical capacitors



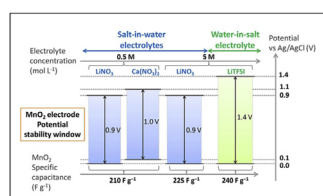
Axel Gambou-Bosca, Daniel Bélanger\*

Département de Chimie, Université du Québec à Montréal, Case Postale 8888, succursale Centre-Ville, Montréal, Québec, H3C 3P8, Canada

## HIGHLIGHTS

- Ca<sup>2+</sup> and Li<sup>+</sup> ions have similar effect on the electrochemical utilization of MnO<sub>2</sub>.
- 5 M LiTFSI as “water in salt” electrolyte for MnO<sub>2</sub> electrode.
- MnO<sub>2</sub> is characterized by a potential stability window of 1.4 V in 5 M LiTFSI.
- MnO<sub>2</sub> exhibits a specific capacitance of 239 F g<sup>-1</sup> in 5 M LiTFSI at 2 mV s<sup>-1</sup>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The effect of the electrolyte on the electrochemical utilization of manganese dioxide as active material for electrochemical capacitor was studied by cyclic voltammetry and electrochemical impedance spectroscopy. MnO<sub>2</sub>-based composite electrodes were characterized in salt-in-water (0.65 M K<sub>2</sub>SO<sub>4</sub>, 5 M LiNO<sub>3</sub>, 0.5 M LiNO<sub>3</sub> and 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub>) and water-in-salt (5 M LiTFSI (lithium bis-trifluoromethanesulfonimide)) electrolytes. Firstly, no effect of the cation valence on the specific capacitance was observed as similar values were measured in 0.5 M LiNO<sub>3</sub> and 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub> aqueous solutions at both low and high scan rate, when a MnO<sub>2</sub>-based composite electrode was cycled in the pseudocapacitive potential region. Secondly, it was found that in 5 M LiTFSI, a MnO<sub>2</sub> electrode is characterized by an extended potential stability window of about 1.4 V and exhibits a high specific capacitance of 239 F g<sup>-1</sup> per active material mass at a scan rate of 2 mV s<sup>-1</sup>. However due to the low ionic conductivity of this solution, the rate capability is limited at high scan rate.

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## 1. Introduction

Manganese dioxide-based electrode is characterized by its benign nature, good stability in aqueous electrolyte and a theoretical specific capacitance as high as 1233 F g<sup>-1</sup> for one electron redox reaction between Mn<sup>4+</sup> and Mn<sup>3+</sup> [1–10]. Due to these attractive features, MnO<sub>2</sub> has been studied as electrode material in

symmetric and in asymmetric electrochemical capacitor [1,4,5,11–26]. Moreover, MnO<sub>2</sub> has been synthesized under many amorphous [9,27–31] and crystalline [1,6,7,23,32,33] forms. Their specific capacitance values indicated a 20% electrochemical utilization of the metal oxide in aqueous electrolytes [3,6,9,34–37], for thick MnO<sub>2</sub>-based composite electrodes prepared with a polymeric binder and a conductive additive [8,37]. This limited specific capacitance is mainly due to the poor ionic and electronic conductivity of manganese dioxide [8,24]. To improve MnO<sub>2</sub> electrochemical utilization, aqueous electrolytes containing bivalent

\* Corresponding author.

E-mail address: [belanger.daniel@uqam.ca](mailto:belanger.daniel@uqam.ca) (D. Bélanger).

cations such as  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  have been proposed [38–42]. Although the concentration of  $\text{Na}^+$  ions was twice that of  $\text{Ca}^{2+}$  ions, the specific capacitance measured in 0.1 M  $\text{Ca}(\text{NO}_3)_2$  was 1.6 times higher than in 0.2 M  $\text{NaNO}_3$  [38,39]. The specific capacitance of a  $\text{MnO}_2$  electrode could be improved by replacing monovalent cations by bivalent cations, because the latter can contribute to store two electrons [40]. Later, an increase of the specific capacitance was observed with an increase of charge of the solution cations (for 0.1 M  $\text{NaNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{La}(\text{NO}_3)_3$ ) [41]. On the other hand, Brousse and coworkers [23,34] have reported superior  $\text{MnO}_2$  electrochemical utilization in presence of  $\text{Li}^+$  ions, among monovalent cations. They reported a specific capacitance of  $145 \text{ F g}^{-1}$  in 5 M  $\text{LiNO}_3$  [34] that corresponds to  $\sim 220 \text{ F g}^{-1}$  (per active material mass), which is close to the capacitance value recorded in  $\text{Mg}(\text{NO}_3)_2$  [41]. Furthermore, Anouti and coworkers [43], reported the electrochemical performance of different  $\text{MnO}_2$  materials in ten lithium salts electrolytes with a concentration yielding the maximum ionic conductivity. Although the best capacitance retention (when cycling up to  $50 \text{ mV s}^{-1}$ ) was obtained with aqueous 5 M  $\text{LiNO}_3$  and 1.8 M  $\text{LiClO}_4$ , good pseudocapacitive behavior was also observed in 2 M  $\text{Li}_2\text{SO}_4$  and 2.5 M  $\text{LiTFSI}$ .

Since aqueous electrolytes are only useful in hybrid or asymmetric devices, which can overcome the  $\sim 1.23 \text{ V}$  thermodynamic limit of water decomposition [12,13], non-aqueous electrolytes are often preferred in symmetric devices [2]. Nonetheless, innovative “water-in-salt” mixtures consisting in a very high concentration of salt (eg. molality  $> 20 \text{ m}$   $\text{LiTFSI}$  (lithium bis-trifluoromethanesulfonimide) in water have been recently proposed as electrolyte for aqueous lithium-ion battery [44,45]. In “water-in-salt” electrolyte, the number of water molecules in the solvation shell is much lower than that existing for lower salt concentration and the structure of the interphasial region is also very different [44,45]. With this definition, highly concentrated (eg. 5 M) lithium based electrolyte such as  $\text{LiNO}_3$  does not fit this class of electrolyte. Moreover, it was suggested that “water-in-salt” electrolyte can increase the voltage window of aqueous electrolyte-based lithium-ion battery, and be competitive with non-aqueous electrolytes due to their facile preparation, being safer and environmental friendly [44].

Here, we report the effect of the cation charge on the electrochemical performance of  $\text{MnO}_2$  electrode, investigated by cyclic voltammetry and electrochemical impedance spectroscopy, in salt-in-water electrolyte (0.65 M  $\text{K}_2\text{SO}_4$ , 0.5 M  $\text{LiNO}_3$  and 0.5 M  $\text{Ca}(\text{NO}_3)_2$ ) and for the first time in a highly concentrated  $\text{LiTFSI}$  water-in-salt electrolyte (5 M  $\text{LiTFSI}$ ). Finally, preliminary results of an asymmetric carbon/ $\text{MnO}_2$  electrochemical capacitor in the water-in-salt electrode are presented.

## 2. Experimental section

### 2.1. Preparation of the manganese oxide materials

Poorly crystalline manganese dioxide was synthesized by precipitation by mixing a 60 ml aqueous solution containing 1.58 g of  $\text{KMnO}_4$  with a 100 ml solution containing 3.68 g of  $\text{Mn}(\text{CH}_3\text{COO})_2$ , at  $25^\circ\text{C}$ . The resulting solution was stirred for 6 h during, and a dark-brown precipitate was formed. Once the stirring was stopped, the precipitate was rinsed several times with distilled water and filtered under vacuum. Then, the wet powder was dried at  $110^\circ\text{C}$  for 12 h and milled in an agate mortar [5,8].

### 2.2. Physical characterization

The crystallographic structure of  $\text{MnO}_2$  was characterized by XRD with an X-ray diffractometer (X'Pert system, Philipps) at

$2\theta = 15\text{--}85^\circ$  using monochromatic  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.541874 \text{ \AA}$ ) operated at 50 kV/40 mA controlled by X'Pert Data Collector software. SEM micrographs were obtained with a scanning electron microscope (JEOL JSM-7600F) for  $\text{MnO}_2$  materials as well as for composite electrodes. The nitrogen adsorption–desorption isotherms were measured at 77 K using Autosorb–1 (Quantachrome instruments, USA) controlled by AS1 software. The BET surface area  $S_{\text{BET}}$  was evaluated using the Brunauer–Emmett–Teller (BET) method. The electrolyte conductivity was measured at  $20^\circ\text{C}$  using a conductivity meter (conductivity meter CDM80). The pH was measured using a pH meter (sympHony, VWR). The ionic conductivity was measured for both water-in-salt and salt-in-water electrolytes with a pH of about 6, except for the  $\text{Ca}(\text{NO}_3)_2$  solution which is one pH unit lower (5.0) than the other solutions. Finally, the electrolyte viscosity was measured at room-temperature for aqueous 5 M  $\text{LiNO}_3$  and 5 M  $\text{LiTFSI}$  solution using a VC-10 viscosimeter (A&D, Japan) with an accuracy of  $\pm 1\%$  of reading.

### 2.3. Electrode preparation

$\text{MnO}_2$  film electrode was prepared by mixing the as-prepared manganese dioxide powder (60 wt%) with 10 wt% PTFE binder (poly(tetrafluoroethylene), Aldrich) and 30 wt% acetylene black carbon (Alfa Aesar) in 1 mL ethanol (Aldrich). A series of composite electrode of  $0.25 \text{ cm}^2$  cold rolled thick film were prepared by pressing at  $9 \times 10^5 \text{ Pa}$  for 60 s in a stainless steel grid (80 mesh, 0.127 mm, Alfa Aesar) used as current collector. Secondly, a similar procedure was used to prepare the negative carbon electrode, but with a 90:10 ratio of Black Pearls 2000 carbon (BP,  $1500 \text{ m}^2 \text{ g}^{-1}$ , Cabot) and PTFE. Then, in the asymmetric device, typical loadings of  $\text{MnO}_2$  and BP active materials were 2.9 and  $9.7 \text{ mg cm}^{-2}$ , respectively. These loadings were calculated by considering the specific voltammetric charge and the appropriate potential windows of each separate electrode active material. Finally, the  $\text{MnO}_2$  and BP films ( $0.25 \text{ cm}^2$  each) were pressed at 900 MPa on a stainless steel grid.

### 2.4. Electrochemical characterization

#### 2.4.1. Characterization of composite electrode

Cyclic voltammetry and electrochemical impedance spectroscopy were performed using a standard three electrode cell containing either a 0.65 M  $\text{K}_2\text{SO}_4$ , 5 M  $\text{LiNO}_3$ , 0.5 M  $\text{LiNO}_3$ , 0.5 M  $\text{Ca}(\text{NO}_3)_2$  or 5 M  $\text{LiTFSI}$  aqueous solution, degassed with purified nitrogen gas at room temperature prior and during the experiment. A composite electrode was used as the working electrode, with platinum gauze and the  $\text{Ag}/\text{AgCl}$  (3 M  $\text{NaCl}$ ) as the counter electrode and the reference electrode, respectively. Each cyclic voltammogram shown below is the 10th cycle that corresponds to a stable electrochemical response. The capacitive behavior of the electrodes was studied by cyclic voltammetry within different potential range at various scan rates between 2 and  $200 \text{ mV s}^{-1}$ . To calculate the specific capacitance ( $C$ ), the cathodic voltammetric charge ( $Q$ ) was evaluated by integration of a cyclic voltammogram, and divided by the mass of electrode ( $m$ ) and the width of the potential window ( $\Delta V$ ):

$$C = Q/m\Delta V \quad (1)$$

The capacitance per mass of  $\text{MnO}_2$  was evaluated by subtracting the capacitance contribution of the carbon from the total electrode specific capacitance:

$$C_{\text{MnO}_2} = (C - yC_{\text{AB}})/x \quad (2)$$

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