



# Carbon black/manganese dioxide composites synthesized by sonochemistry method for electrochemical supercapacitors



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## ABSTRACT

Carbon black (CB)/manganese dioxide ( $\text{MnO}_2$ ) composites are prepared by a sonochemical method from an aqueous solution of potassium bromate and manganese sulfate. The morphology, structure, physical properties and specific surface area of samples are examined by scanning electron microscopy (SEM), transition electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) method. Electrochemical properties of the synthesized composites with different carbon to manganese dioxide ratios are studied by cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS). Electrochemical data for the composites obtained in the 0.5 M  $\text{Na}_2\text{SO}_4$  solutions show the capacitive behavior in the voltage window of 0–1.0 V versus Ag/AgCl. When the mass ratio of  $\text{MnO}_2$  composite material is 65 wt% the specific capacitance of CB– $\text{MnO}_2$  composite calculated from the CV curves is  $313 \text{ F g}^{-1}$  at the scan rate of  $5 \text{ mV s}^{-1}$  whereas specific capacitance for pure  $\gamma\text{-MnO}_2$  prepared in the same conditions is  $257 \text{ F g}^{-1}$  at the scan rate of  $5 \text{ mV s}^{-1}$ . The CB– $\text{MnO}_2$  composites show higher energy density than pure  $\gamma\text{-MnO}_2$ . Also, they show a long cycle life in the potential range of 0–1.0 V and retain 78.3% of initial capacitance over 1000 cycles.

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## 1. Introduction

Electrochemical supercapacitors are new energy storage devices. These materials demonstrate suitable capacity, excellent reversibility, high power density, and long cycle life. Based on the charge storage mechanisms, the electroactive materials are classified to: (a) electric double-layer capacitors (EDLCs) that employ typical form of carbon or similar materials, and (b) pseudocapacitors, in which materials such as transition metal oxide compounds (e.g.  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{NiO}$ ,  $\text{Fe}_2\text{O}_3$ , etc.) or conducting polymers are used as electrodes [1–3]. Among the second category,  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  shows higher performance as an electroactive material for the supercapacitors. However, the shortage of abundance and cost of the precious metal (Ru) are main disadvantages for commercial production of  $\text{RuO}_2$  [4,5].

Electrochemical supercapacitors based on  $\text{MnO}_2$  are currently attracting great attention owing to the low cost of  $\text{MnO}_2$ , high theoretical specific capacitance ( $\sim 1380 \text{ F g}^{-1}$ ) and the fact that they use environmental friendly aqueous electrolytes [6–8]. The high relative resistance of  $\text{MnO}_2$  reduces charge storage thus its commercial use is limited [9–12]. In order to improve the conductivity of  $\text{MnO}_2$ , conductive fillers such as exfoliated graphite

[13,14], graphite nanoplatelet [15], graphene oxide [16], graphene [17,18], mesoporous carbon [19,20], carbon black [21], and carbon nanotubes [22,23] are blended with  $\text{MnO}_2$ . These composites may be prepared using various synthetic methods including microwave irradiation, sol–gel route, hydrothermal, electrochemical deposition, microemulsion process, in situ coating, chemical precipitation, and co-precipitation [13–23].

Sonochemistry methods have been successfully used for preparation of various nanostructured metal oxides [24–26], at room temperature, ambient pressure, and short reaction time. Ultrasonic waves create nanostructured materials based on acoustic cavitation; the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation causes bubble collapse, producing intense local heating, high pressures, and very short lifetimes. The temperature of these hot spots is about  $5000 \text{ }^\circ\text{C}$  at pressure of up to 500 atm. The rate of heating and cooling is greater than  $10^9 \text{ K s}^{-1}$ . Strong reductive and oxidative radicals are produced as result of cavitation and these radicals can cause secondary oxidation or reduction reactions [27–29].

In our previous work [29], a novel ultrasonic aided procedure was introduced to prepare excellent capacitance manganese dioxide with different crystalline structures:  $\gamma\text{-MnO}_2$  and a rather layered structure.

In the present work, CB– $\text{MnO}_2$  composite electrode materials with different mass ratios were prepared by a sonochemistry method. These films were characterized by XRD, TGA, BET, SEM,

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and TEM. The electrochemical performances of CB–MnO<sub>2</sub> composite electrode for supercapacitors were investigated. The CB–MnO<sub>2</sub> composite electrodes are expected to provide improved energy and power density for various applications.

## 2. Experimental

### 2.1. Synthesis

100 ml of aqueous solutions of 0.25 M MnSO<sub>4</sub> (Merck, research grade), 0.5 M KBrO<sub>3</sub> (Merck, research grade), and various amounts of acetylene black (Alfa Aesar, >99.9%, S.A. 80 m<sup>2</sup> g<sup>-1</sup>) were irradiated ultrasonically. A 24-kHz ultrasound horn transducer system (UP 200 H, Dr. Hielscher GmbH) with a 2-mm microtip (titanium alloy) and a sonic power density of 480 W cm<sup>-2</sup> was employed. During the synthesis, the solution temperature was at 53 ± 1 °C.

### 2.2. Structural characterization

The crystallographic structures of the materials were determined by a X-ray diffractometer (Bruker, D8-advance) at 2θ = 4–70° with monochromatized Cu Kα radiation (λ = 1.541874 Å) operated at 40 kV/30 mA. TGA for samples were recorded in the temperature range from 20 °C to 900 °C in air at a heating rate of 10 °C per min using TG 209 F1 (Netzsch) tester. The morphologies of the MnO<sub>2</sub> and CB–MnO<sub>2</sub> composites were observed by SEM (Philips, XL30). The CB–MnO<sub>2</sub> composites electrode was examined using TEM (Zeiss, EM900, 80Kev). N<sub>2</sub> adsorption–desorption isotherms were measured using BELSORP-minill at liquid nitrogen temperature (77 K). The specific surface area were evaluated using the Brunauer–Emmett–Teller (BET) method, and pore size distributions were calculated using the Barret–Joyner–Halenda (BJH) method on the desorption branch.

### 2.3. Electrochemical measurement

Electrodes were prepared by mixing of the CB–MnO<sub>2</sub> powder as active material with 27 wt% of graphite (Alfa Aesar, conducting grade, ~200 mesh) and 6 wt% of polytetrafluoroethylene (PTFE) dried powder (Merck). A few drops of ethanol were added to this mixture in order to make a more homogeneous mixture. Graphite improves the conductivity of the electrodes, and reduces the resistance of the composite. The resulting slurry mixture was pasted on a steel grid (0.75 cm<sup>2</sup>) and then pressed at 15 MPa for 30 min.

All electrochemical measurements were performed using a potentiostat/galvanostat (PGSTAT 100, Autolab, EchoChemie) in a three-electrode glass cell with a CB–MnO<sub>2</sub> coated steel mesh working electrode, a platinum foil counter electrode and Ag/AgCl (Metrohm AG 9101 Herisau, 3 M KCl, 0.207 V versus SHE at 25 °C) reference electrode. The measurements were carried out in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte at pH 3.3. The solution temperature was maintained at 25 °C by means of a water thermostat (RE 104 Ecoline, LAUDA).

## 3. Results and discussion

### 3.1. Structure characterization

Typical XRD patterns for MnO<sub>2</sub> and CB–MnO<sub>2</sub> composites with different ratios are shown in Fig. 1. The diffraction peaks of MnO<sub>2</sub> in Fig. 1a correspond to the (120), (131), (230), (300), (002), (160), (242), (421) and (003) planes, from left to the right, respectively. All the peaks can be indexed to pure orthorhombic γ-MnO<sub>2</sub> (JCPDS card 14-644, a = 6.36 Å, b = 10.15 Å, c = 4.09 Å). No characteristic peaks were observed for other impurities such

as α- or β-MnO<sub>2</sub>, Mn(OH)<sub>2</sub>, and Mn<sub>2</sub>O<sub>3</sub> [29]. The broad and diffused peak in the XRD patterns of γ-series indicates that the oxide has a low level of crystallinity due to the absence of long-range order of the MnO<sub>6</sub> octahedral framework. The peak at 2θ = 25.34° can be indexed to carbon black phase where decreasing the CB content of the composites resulted in a decrease in the intensity of this peak.

TGA thermograms of γ-MnO<sub>2</sub> and CB–65% MnO<sub>2</sub> powder are shown in Fig. 2. TGA thermogram of γ-MnO<sub>2</sub> powder shows an initial 15% weight loss at ca. 150 °C, which corresponds to the dehydration of the sample. The weight loss in the range of 150–500 °C can be attributed to the loss of the crystallization water. The small weight loss in the range of 500–550 °C observed in the TGA data is attributed to the loss of oxygen from MnO<sub>2</sub> lattice resulting in phase transition from MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub> [30]. The small step in the range of 850–900 °C is attributed to the formation of the Mn<sub>3</sub>O<sub>4</sub> [31]. TGA thermogram of CB–65% MnO<sub>2</sub> powder is remarkably different and shows a slight decrease (7%) at temperatures up to 150 °C, which again can be related to the dehydration of the physically adsorbed water. A sharp weight loss in the range of 400–500 °C observed in the TGA data is related to the remove of carbon from the composite.

### 3.2. Morphology characterization

The CB, MnO<sub>2</sub> particles, and CB–MnO<sub>2</sub> composite prepared in this work were examined using SEM and TEM (Fig. 3). Fig. 3a shows the SEM image of as-prepared samples. It can be seen in the image that the particles, which are originally in the range of 40 and 80 nm, are agglomerated into larger aggregations. Fig. 3b shows the SEM of the CB powder. MnO<sub>2</sub> particles in the carbon composites are estimated in the range of 20–60 nm (Fig. 3c). The TEM micrograph of the CB–MnO<sub>2</sub> composite is presented in Fig. 3d. The CB particles have a granular appearance and the MnO<sub>2</sub> particles appear as dark deposits onto the CB surface.

### 3.3. Nitrogen adsorption

The specific surface area (*A<sub>s</sub>*) is determined by:

$$A_s = (V_m/22414)N_a\sigma \quad (1)$$

where *N<sub>a</sub>* is the Avogadro number and σ is the area covered by one nitrogen molecule (0.162 nm<sup>2</sup>) [32]. *V<sub>m</sub>*, the monolayer volume, can be estimated by a three-parameter BET equation:

$$V_m = V_{\text{ads}} \frac{(1 - (P/P_0))(1 + (C - 1)(P/P_0))}{C(P/P_0)} \quad (2)$$

with the parameters of *P/P<sub>0</sub>* (relative pressure), *V<sub>ads</sub>* (adsorbed volume), and *C* (constant). The BET and corresponded pore size distribution curves (BJH method) of the CB–MnO<sub>2</sub> composite with mass ratios of 35/65 are shown in Fig. 4. The isotherms of CB–65% MnO<sub>2</sub> composite belong to type IV of isotherms (based on the IUPAC classification) and show an obvious capillary condensation step (hysteresis loop) [33]. The specific surface area of CB–65% MnO<sub>2</sub> composite calculated by BET equation represents a high specific surface of 117 m<sup>2</sup> g<sup>-1</sup>. The large BET surface area enables the extended interface of the composite to adsorb/desorb protons or alkali cations between active materials and electrolytes. *r<sub>c</sub>*, the radius for cylindrical pores, can be obtained by the Kelvin equation [34]:

$$\gamma_c = \frac{-2\gamma w_m \cos \theta}{RT \log(P/P_0)} \quad (3)$$

where γ is the surface tension, *w<sub>m</sub>* is the molar volume, and θ is the contact angle.

The pore size distributions are shown in the inset of Fig. 4. The vertical axis in this diagram represents the volume of the pores at a

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