



# Abrupt change with surfactant concentration in the surface morphology of the electrodeposited manganese oxide films for electrochemical capacitors



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## ABSTRACT

Manganese oxide films are produced by electrodeposition on a graphite sheet from a solution of manganese oxide with tetradecyltrimethylammonium bromide (TTAB) added as a surfactant. Effects of TTAB concentration on electrochemical and morphological properties of the films are observed. Under the bath conditions used in this work, the specific capacitance of the electrodeposited manganese oxide films has a maximum value of 343 F/g for TTAB concentration of 0.01 M. Change in the specific capacitance of the films with TTAB concentration is found to be associated with corresponding changes in the surface morphology of the films at those concentrations. Addition of TTAB up to 0.01 M is observed to increase the surface area of electrodeposited manganese oxide films, as the surface of the films is well covered with flake-like or petal-shaped arrays of nanofibers forming a three-dimensional network. Higher concentrations of TTAB than 0.01 M reduce the surface area of the films due to agglomeration and collapse of the nanofibers. The addition of 0.01 M TTAB to an electrochemical bath also improves supercapacitor capability such as rate capability, cycling stability, and electrode series resistance.

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## 1. Introduction

Electrochemical capacitors, also called supercapacitors, have drawn much interest as energy storage devices because of their high power density, long cycle life (> 100,000 cycles), and rapid charging-discharging rates. Electrochemical capacitors are classified into two types according to their charge storage mechanisms [1,2]: electric double layer capacitor (EDLC) and redox supercapacitor (or pseudo-capacitor). EDLCs, which are based on carbonaceous materials, mainly utilize non-faradaic charge separation at the electrode/electrolyte interface. Redox supercapacitors make use of a reversible redox reaction that occurs at the electrode surface. The behavior of redox supercapacitors is typically called “pseudo-capacitance”. Transition metal oxides and conducting polymers belong to pseudo-capacitive materials.

Various noble and transition metal oxides (oxides of Ru, Mn, Co, Ni, Cr, Mo, V, Nb, etc.) have been employed as electroactive

materials for redox supercapacitors because these metals have several redox states or structures that contribute to the charge storage via fast redox reactions [3–16]. Among these materials, manganese oxides have received much attention for use in electrochemical capacitors applications because of their natural abundance and low cost [17–23]. However, the electrochemical performance of manganese oxides is sometimes unsatisfactory due to their dense morphology and poor electrical conductivity [24,25]; these aspects negate the advantages of the material. Many efforts have been made to improve the electrochemical performance of manganese oxides for electrochemical capacitors by incorporating various transition metals into the manganese oxides; these form binary and/or tertiary manganese oxide nanocomposites with controlled micro/nanostructures [26,27].

Surface modification can also be a key approach to improve the electrochemical performance of metal oxides for electrochemical capacitors by increasing their effective surface area. This is usually achieved by modifying the morphology of metal oxides without destroying their intrinsic properties. Control of process parameters is one method to manipulate the surface morphology. Chuang and Hu investigated the effect of the bath solution's pH on the surface

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morphology and electrochemical characteristics of manganese-cobalt oxides prepared by anodic deposition [28]. Xu et al. reported that calcination temperature greatly affected surface morphology and, correspondingly, specific surface area of manganese oxide films [29]. Addition of surfactant is another method to modify the surface morphology of metal oxides. Use of surfactants such as sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP), Pluronic P123, cetyltrimethyl ammonium bromide (CTAB), and sodium lauryl sulfate (SLS) in the fabrication of metal oxides has been reported in the literature [30–39]. The fabrication of manganese oxides in the presence of anionic surfactants (for example, SDS and SLS) has been obtained using various methods such as electrodeposition, co-precipitation, hydrothermal, organic aqueous interfacial synthesis, and so on [30,35–39]. However, only co-precipitation was reported for the preparation of manganese oxides in the presence of cationic surfactants (for example, CTAB) [33,34].

As an alternative to the previously reported surfactants, this work reports the use of tetradecyltrimethyl ammonium bromide (TTAB) as a cationic surfactant for electrodeposition of manganese oxide films on a graphite sheet. The change in the electrochemical performance of electrodeposited manganese oxide film as an electrochemical capacitor electrode with concentration of TTAB was observed and explained in terms of a change in surface morphology of the films.

## 2. Experimental

Manganese oxide films were electrodeposited on a commercially available graphite sheet. The graphite sheet was cut into a rectangular substrate ( $10 \times 50 \text{ mm}^2$  in size) and lacquered to expose an area of  $10 \times 20 \text{ mm}^2$  for electrodeposition. The exposed part of the substrate was polished with silicon carbide paper to increase surface roughness. The polished substrate was etched in a 20 wt% sulfuric acid solution at room temperature for 20 seconds, dipped into a 2 M methanol solution for 20 seconds to remove macro-level surface defects and contamination, and then cleaned with double-distilled water. Before electrodeposition, the substrate was dried in an oven at  $65^\circ\text{C}$  for 6 hours.

Electrodeposition was carried out in an electrochemical bath containing manganese sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) and tetradecyltrimethylammonium bromide ( $\text{C}_{17}\text{H}_{38}\text{BrN}$ , TTAB), used as sources of manganese and surfactant, respectively. Concentrations of TTAB from zero to 0.05 M were used, while the concentration of manganese sulfate was fixed at 0.1 M throughout the study. The bath was produced by dissolving the above chemicals in deionized water and stirred for 12 hours at room temperature ( $24 \pm 1^\circ\text{C}$ ). The pH of the bath was 5.5. All chemicals were analytical reagent grade supplied by Sigma–Aldrich and were used as-received. Prior to electrodeposition, the solution was de-aerated by nitrogen gas for 5 min.

A standard three-electrode cell system was used for the electrodeposition of the manganese oxide films. A saturated Ag/AgCl electrode was used as a reference electrode and a platinum-coated titanium mesh ( $2.5 \text{ cm}^2$  in size) was used as a counter electrode. Electrodeposition was carried out at a constant potential of 1.1 V versus Ag/AgCl at room temperature, using a computer-controlled potentiostat (Princeton Applied Research, VSP). Deposition time was 60 seconds for all cases. After deposition, the samples were washed with a deionized water jet and dried with flowing nitrogen gas. To improve adhesion of the electrodeposited manganese oxide film to the substrate, samples were annealed in an oven at  $200 \pm 1^\circ\text{C}$  for 3 hours. The amount of electrodeposited manganese oxide was determined by weighing the samples before and after deposition, using a microbalance with an accuracy of  $10 \mu\text{g}$ . The mass of the electrodeposited manganese oxide was measured to be in the range of 0.9–1.4 mg.

Surface morphology of the films was examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). Nitrogen adsorption-desorption measurements were made using an adsorption analyzer (Micromeritics, ASAP 2010) to obtain the surface area and pore size of the electrodeposited manganese oxide films. Samples were outgassed for 6 hours at  $200^\circ\text{C}$  prior to measurements. Surface area and pore size of the films were calculated based on the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) desorption methods.

Electrochemical analysis of the manganese oxide films as an electrode for electrochemical capacitors was done using the same three-electrode cell system in which a platinum-coated titanium mesh ( $2.5 \text{ cm}^2$  in size) and a saturated Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. The electrodeposited manganese oxide films were used as a working electrode and 0.5 M  $\text{Na}_2\text{SO}_4$  as an electrolyte. The entire surface of the electrodeposited film was used for the electrochemical analysis. Before electrochemical analysis, the electrolyte was de-aerated by nitrogen gas for 5 min. Cyclic voltammograms (CVs) were recorded between  $-0.5$  and  $1.2 \text{ V}$  vs. Ag/AgCl at a scan rate of  $20 \text{ mV/s}$ . The charge/discharge behavior was investigated chronopotentiometrically at a current density of  $1 \text{ A/g}$ . The electrode was discharged to  $-0.2 \text{ V}$  (at the fully discharged state) in the first cycle and charged to  $1.1 \text{ V}$  (at the fully charged state) in the second cycle. The electrochemical impedance spectroscopy (EIS) was measured under open circuit potential vs. Ag/AgCl over the frequency range from  $100 \text{ kHz}$  to  $55 \text{ mHz}$ . During the electrochemical analysis, pH of the electrolyte was 6.

The specific capacitance ( $C_s$ ) of an electrode can be calculated from the equation;

$$C_s = \frac{I \times t}{m \times \Delta V} \quad (1)$$

where  $I$  is the constant discharge current,  $t$  is the discharge time,  $m$  is the mass of the electrode materials, and  $V$  is the discharging potential range.

## 3. Results and discussion

The performance of the electrodeposited manganese oxide films as an electrochemical capacitor electrode was investigated by cyclic voltammetry and a charge–discharge test. Fig. 1 shows cyclic

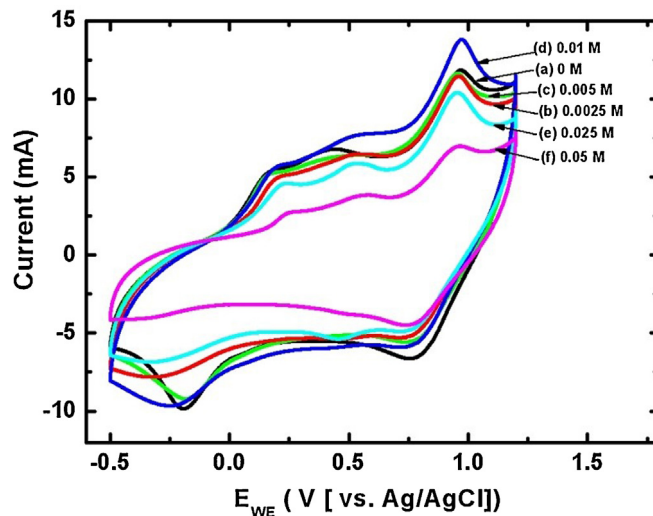


Fig. 1. Cyclic voltammograms of the manganese oxide films electrodeposited at TTAB concentrations of (a) 0 M, (b) 0.0025 M, (c) 0.005 M, (d) 0.01 M, (e) 0.025 M, and (f) 0.05 M. The cyclic voltammograms were measured in 0.5 M  $\text{Na}_2\text{SO}_4$  at a scan rate of  $20 \text{ mV/s}$ .

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