

Self-assembled Manganese Dioxide Thin Films as Novel Electrode Material for the Fabrication of Thin-Film Supercapacitors

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ABSTRACT

Self-assembled manganese dioxide thin films were deposited directly onto metalized plastic supporting substrates by a novel horizontal submersion process which entailed spontaneous self-assembly of preformed manganese dioxide nanoparticles under optimized deposition conditions. Desired film thicknesses were obtained simply by repeating the deposition process the desired number of times. Scanning electron micrographs had revealed that such self-assembled manganese dioxide thin films were nanoparticulate and highly porous in nature. Thin films with tailored microstructure were prepared through optimizing deposition conditions such as duration of submersion, temperature, pH, concentration and ionic strength of colloidal suspension, as well as the post-deposition calcination temperature. As shown by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) techniques, these films exhibit excellent capacitive behavior, and high cycling stability and reversibility within the potential range of 0.0 to 1.0 V (versus SCE) both in mild aqueous and gel electrolytes. The high pseudocapacitance was attributed to redox reactions involving homogenous intercalation and deintercalation of protons into and out of the oxide matrices during charge and discharge. Performance evaluation of 'proof-of-concept' prototypes had indicated high potential utility of such nanostructured manganese dioxide thin films as novel electrode material for the fabrication of high energy and power density thin-film supercapacitors. *Key words:* Manganese dioxide, nanoparticles, self-assembly, nanostructures, thin films, supercapacitor.

1 INTRODUCTION

Manganese dioxide (MnO_2) has long been established as the preferred electrode materials for the fabrication of primary and secondary batteries. Besides its favorable electrochemical characteristics, manganese dioxide is considered to be toxicologically benign and cheap¹⁻⁴. In recent decades, intense research interest have been focused on the utilization of MnO_2 as electrode material for the fabrication of energy-storage and conversion devices, most

notably, supercapacitors or electrochemical capacitors. Pang *et al.*⁵ and Chin *et al.*⁶ had demonstrated a specific capacitance of about 700 F/g at 50 mV/s for ultra-thin nanoparticulate manganese dioxide thin films prepared by the sol-gel process, thereby provided further impetus for intensified research on such nanoparticulate manganese dioxide thin films. Recent studies have concurred that nanoparticulate manganese dioxide thin films possess very favorable electrochemical properties and are therefore very promising electrode materials for the fabrication of high power and energy density electrochemical capacitors⁷⁻⁹.

Various chemical routes have been developed recently for the preparation of nanostructured manganese dioxide suitable for the fabrication of electrochemical capacitors. Among these methods include electrostatic spray deposition from KMnO_4 ¹⁰, sonochemical method⁷, and cathodic electrodeposition⁸. Nanostructured manganese dioxide prepared by these methods exhibited specific capacitance which ranged between 163 F/g and 425 F/g in Na_2SO_4 aqueous electrolyte. However, manganese dioxide thin films prepared by all these methods were found to suffers from several shortcomings, most notably, charge capacity fading upon prolong cycling, unfavorable frequency responses, as well as partial dissolution of electroactive materials into the electrolyte solution during cycling.

Research findings from numerous recent studies have shown that self-assembly is emerging as a versatile and effective strategy in chemical synthesis, and potentially capable of generating structures with dimensions of 1 to 100 nm range¹¹⁻¹³. Self-assembly approaches to materials synthesis which entails the spontaneous adsorption of molecules or nanoparticles onto a substrate, offers the possibility of controlling size, shape, crystal structure, orientation, and organization, and eventually leads to self-assembled films. As such, self-assembly approaches afford high versatility in the deposition of nanostructured and nanocomposite films comprising different nanoparticles which are suitable for the fabrication of functional devices.

The present study focuses on the physical and electrochemical characterization of self-assembled MnO_2 thin films as novel electrode materials for the fabrication of thin-film supercapacitors. Such films were deposited directly onto the metalized and flexible polyethylene terephthalate (PET) film using the novel horizontal submersion self-assembly process. The microstructure and

electrochemical properties of MnO₂ thin films were optimized by precisely controlling the deposition parameters. The electrochemical characteristics and performances of 'proof of concept' prototypes with various dual-planar configurations were investigated in order to evaluate the potential utility of such self-assembled MnO₂ thin films as novel electrode materials for the fabrication of thin-film supercapacitors.

2 MATERIALS AND METHOD

Preparation of MnO₂ Colloidal Suspension

Stable MnO₂ colloidal suspension was prepared according to the method reported by Perez-Benito *et al.*¹⁴. Typically, predetermined volumes of KMnO₄ and Na₂S₂O₃ solutions were mixed in a known volume of ultrapure water (~18.2 MΩ). The resulting dark brownish MnO₂ formed was being dispersed by sonication to form stable colloidal suspension.

Deposition of MnO₂ Thin Films

MnO₂ thin films were deposited directly onto nickel coated polyethylene terephthalate (PET) supporting substrate by a horizontal submersion self-assembly process¹⁵. Briefly, nanostructured MnO₂ thin film was formed spontaneously on the PET substrate upon submersion into the MnO₂ colloidal suspension under controlled submersion conditions. Thin films of varying thicknesses were prepared through the layer-by-layer self-assembly process by simply repeating the horizontal submersion coating process the desired number of times. The deposited MnO₂ film was then left to air dry overnight prior to heat treatment at 200°C in air for an hour.

Characterization of MnO₂ Films

The loading and uniformity of self-assembled MnO₂ thin film was evaluated by dissolving a known area of film in a given volume of H₂O₂/HNO₃ solution mixture. The concentration of Mn in the solution was determined quantitatively using atomic absorption spectroscopy (AAS). The surface morphology of self-assembled MnO₂ thin films was studied using a field emission scanning electron microscope (FESEM, LEO 1525), whereas their electrochemical characteristics were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques with a computer interfaced frequency response analyzer (PARSTAT 2263). CV studies were performed in 1.0M Na₂SO₄ aqueous electrolyte using a standard 3-electrode configuration with platinum foil as the counter electrode and saturated Calomel electrode (SCE) as the reference electrode. The surface area of the working electrodes was fixed at 0.126 cm² and a scan rate of 50 mV/s within potential window of 0 – 1.0V (vs SCE) was used. The specific capacitance of the MnO₂ thin films was calculated by dividing the integrated anodic current (Q_a) with the mass of electroactive electrode material. Electrochemical impedance spectroscopy (EIS)

measurements for MnO₂ thin-film electrodes were performed within the frequency range of 1 MHz to 10 mHz. Specific capacitance was calculated from the impedance values at 100 mHz or 10 mHz and divided by the mass of electroactive electrode material.

Fabrication and Evaluation of Thin-film Supercapacitor Prototypes

Prototypes of thin-film supercapacitors with different dual-planar configurations were fabricated by patterning of self-assembled MnO₂ thin films deposited on flexible PET films. A novel rapid prototyping process have been developed for this purpose. Apart from using aqueous Na₂SO₄ electrolytes, and prototypes were also fabricated by depositing a thin layer of agar-based gel electrolytes directly onto the electrodes. The electrochemical characteristics of these prototypes were evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) techniques.

3 RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of self-assembled MnO₂ thin films deposited on the nickel-coated PET substrates under controlled conditions. Such self-assembled MnO₂ thin films were nanoparticulate and highly porous in nature. These films showed good adhesion to the nickel-coated PET substrates even without the use of any binders. However, cracks were observed on most film surfaces after heat treatment which could be attributed to film densification. Film densification through the heat treatment process could afford enhanced electronic connectivity and conductivity between nanoclusters thereby contributed to substantial reduction of the overall resistance of films.

The cyclic voltammograms (CV) of self-assembled MnO₂ thin-film electrodes showed almost rectangular shape indicating their good capacitive behaviors. The charge capacities were observed to increase with increasing number of coatings or increasing film thickness obtained by repeating the horizontal submersion process. The anodic/cathodic charge ratios were very close to unity which indicated excellent cycling reversibility of the self-assembled MnO₂ thin-film electrodes.

'Proof of concept' prototypes of thin-film supercapacitor with different dual-planar configurations were fabricated and evaluated in either 0.2M Na₂SO₄ aqueous electrolyte or polysaccharide-based gel electrolyte containing dissolved 0.2M Na₂SO₄ salt. All prototypes of thin-film supercapacitor were observed to exhibit excellent capacitive behaviors at the scan rate of 50 mV/s within the potential window of -0.9V to 0.9V as evidenced by the almost perfectly rectangular shape of the CV curves (Figure 2). No redox peaks were discernible in these CV curves even after prolong cycling of exceeding 1,000 cycles, indicating high phase stability and reversibility of the self-assembled MnO₂ thin films used in the fabrication of these

prototypes. These CV curves were almost the same that of prototype with liquid electrolytes. Polysaccharide-based gel electrolyte thin film appeared to possess high ionic conductivity and could potentially be used as electrolyte in the fabrication of thin-film supercapacitors or related electrochemical devices. All prototypes exhibited excellent cycling stability without any observable loss in their capacitance, albeit an overall increase in capacitance of about 2 to 4% upon cycling for 1,000 cycles was observed.

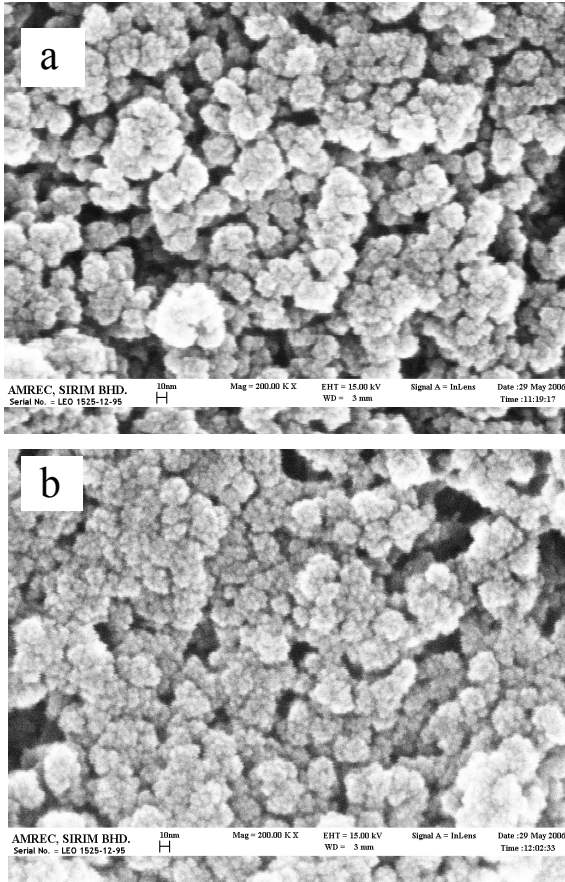


Figure 1: SEM micrographs of self-assembled MnO₂ thin films (a) before and (b) after heat treatment.

Self-assembled MnO₂ thin films were also observed to exhibit excellent cycling stability without any observable structural modification nor dissolution of electroactive material throughout the cyclic voltammetric cycling for exceeding 1,000 cycles. Such high cycling stability and reversibility of these films could be attributed to the combination of amorphous nature and microstructure of these films, as well as the optimal potential scan window of -0.9V to +0.9V used. The maximum specific capacitance achieved for all these prototypes ranged between 123 F/g and 141 F/g.

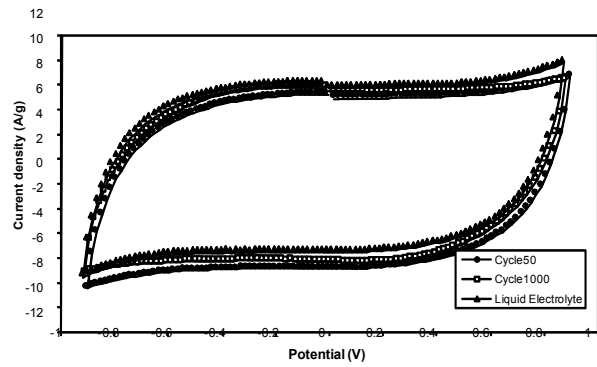


Figure 2: Cyclic voltammograms of thin-film supercapacitor prototypes with liquid or gel electrolytes.

Figure 3 shows the Nyquist plots for supercapacitor prototypes of dual-planar configuration and were evaluated in either liquid electrolyte or polysaccharide-based gel electrolyte. All supercapacitor prototypes exhibited the typical semicircular and steep vertical impedance responses in the high and low frequency regions, respectively. Prototypes with liquid electrolyte (0.2M Na₂SO₄) and polysaccharide-based gel electrolyte containing dissolved salt (0.2M Na₂SO₄) did not show any distinctive differences in the electrolyte resistance at high frequency regions (inset of Figure 3). As such, polysaccharide-based gel electrolyte with dissolved Na₂SO₄ salt exhibited comparable ionic conductivity with that of 0.2M Na₂SO₄ liquid electrolyte. However, the impedance plots for prototypes with polysaccharide-based gel electrolyte were observed to have shifted slightly to higher real impedance Z_{real} as compared to that with liquid electrolyte at the lower frequency region.

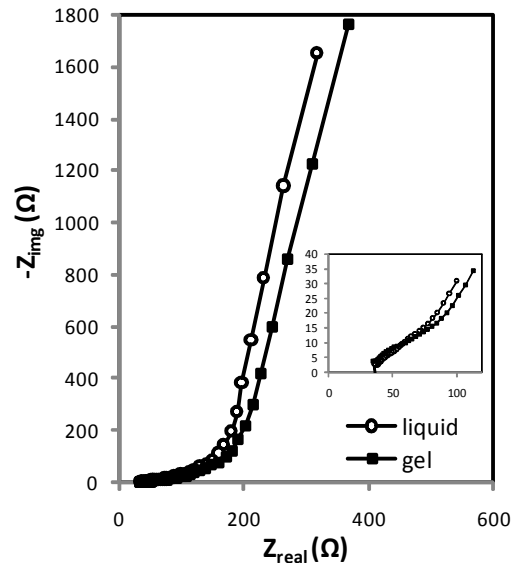


Figure 3: Nyquist plots of thin-film supercapacitor prototypes with liquid and gel electrolytes. Inset: Impedance plots at the high frequency region.

Based on these impedance data, the highest specific capacitance calculated for thin-film supercapacitor prototypes with different configurations 1, 2, and 3 were 133 F/g, 125 F/g, and 152 F/g, respectively (Table 1). Specific capacitance values for all these thin-film supercapacitor prototypes were generally observed to be about 15 to 30 F/g higher after cycling for 1,000 cycles. These results agreed closely with specific capacitance values obtained by the cyclic voltammetry technique.

Table 1: Comparison of electrochemical characteristics of supercapacitor prototypes with different configurations.

Prototype configuration	Specific Capacitance (F/g)		
	Cyclic voltammetry	Impedance	Spectroscopy
	Max.	100 mHz ⁺	10 mHz ⁺
Prototype 1	134 (+4.0)*	112	133
Prototype 2	126 (+1.8)*	108	125
Prototype 3	141 (+2.6)*	129	152

* % change in specific capacitance after 1,000 cycles.

+ Specific capacitance calculated at various frequency

Galvanostatic (Chronopotentiometry) Charge-Discharge

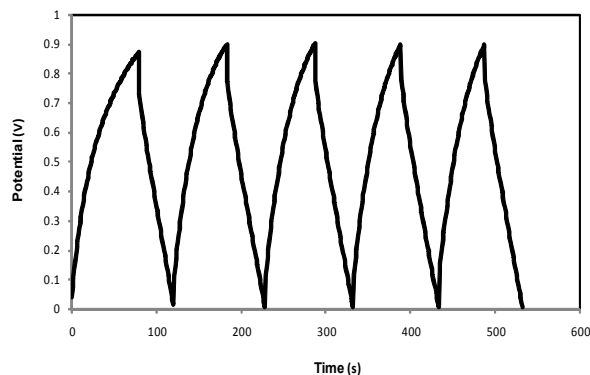


Figure 4: Typical chronopotentiometry charge-discharge curves of a supercapacitor prototype with polysaccharide-based gel electrolyte.

Figure 4 shows the chronopotentiograms of a thin-film supercapacitor prototype with polysaccharide-based gel electrolyte which was being charged/discharged at a constant current of 0.08 mA for five consecutive charge-discharge cycles. A sharp increase and drop in voltage were observed at the initial charging and discharging of the prototype devices. The linear discharging slopes substantiated the typical capacitive behaviour of supercapacitor prototypes. The coulombic efficiency achieved for various supercapacitor prototypes fabricated in the present study was within the range of 86-90 %.

4 CONCLUSION

Self-assembled manganese dioxide thin films prepared by the novel horizontal submersion self-assembly process were nanoparticulate and highly porous in nature. The

microstructure and electrochemical properties of self-assembled films could be tailored through optimization of the deposition parameters and conditions. Prototypes of thin-film supercapacitors fabricated with self-assembled manganese dioxide thin films exhibited excellent capacitive behavior with high cycling stability and reversibility for exceeding 1,000 charge-discharge cycles. As such, self-assembled manganese dioxide thin films are very promising electrode materials for the fabrication of high power and energy density thin-film supercapacitors and related electrochemical devices.

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