

Research Article

Preparation and Characterization of Self-Assembled Manganese Dioxide Thin Films

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Thin films of manganese dioxide (MnO_2) were prepared by self-assembly of MnO_2 nanoparticles directly onto nickel-coated poly(ethylene terephthalate) flexible films using the newly developed horizontal submersion process. The thickness of deposited thin films was controllable by the deposition duration. This horizontal submersion deposition process for thin-film deposition is relatively easy, simple, and cost effective. Effects of deposition duration and calcination temperatures on the microstructure and electrochemical properties of self-assembled MnO_2 thin films were investigated. Optimized MnO_2 thin films exhibited high charge capacity, good cycling reversibility, and stability in a mild aqueous electrolyte and are thus promising electrode materials for the fabrication of thin-film electrochemical capacitors.

1. Introduction

Manganese dioxide- (MnO_2 -) based thin film electrochemical capacitors have received numerous attentions since Pang et al. reported a specific capacitance value of 720 F/g for ultra-thin MnO_2 films in a mild aqueous electrolyte [1, 2]. MnO_2 thin films appear to be a promising electrode material in batteries and electrochemical capacitors due to the low cost of raw materials, low toxicity and environmentally benign, and their excellent electrochemical properties [3, 4]. Many routes for the preparation of MnO_2 thin films have currently been developed, which include the sol-gel process, electrodeposition [5–7], and atomic layer deposition [8]. More recently, the self-assembly technique has emerged as one of the most promising methods for thin film fabrication [9]. Self-assembly is the spontaneous adsorption process by which molecules or nanoparticles are arranged into organized aggregates, networks, or patterns onto a supporting substrate. It is characterized as being relatively simple, inexpensive, and requires low energy consumption.

In this study, we have attempted to prepare self-assembled manganese dioxide (MnO_2) thin films directly on nickel-coated poly(ethylene terephthalate) (Ni/PET) flexible supporting substrate using the newly developed horizontal

submersion process under ambient conditions. This thin film deposition process is very cost effective, rapid, and conformal in the preparation of nanostructured thin films which are suitable for the fabrication of thin film electrochemical capacitors. Most notably, the thickness of deposited film is controllable simply by the duration of submersion or by repeating the deposition process a desired number of times. Physical and electrochemical characterization of manganese dioxide nanoparticles and self-assembled thin films was conducted using various established characterization techniques. The effect of deposition conditions on the microstructure and electrochemical properties of self-assembled manganese dioxide thin films were investigated.

2. Materials and Methods

2.1. Preparation of MnO_2 Colloidal Suspension (sol). Stable MnO_2 colloidal suspension (sol) was prepared based on a method reported in literature [10]. Typically, MnO_2 sol was prepared by mixing 4 mL of KMnO_4 (1.0×10^{-1} mol/L) and 8 mL of $\text{Na}_2\text{S}_2\text{O}_3$ (1.88×10^{-2} mol/L) in 38 mL ultrapure water (18.2 M Ω). The resulting dark-brown MnO_2 sol was

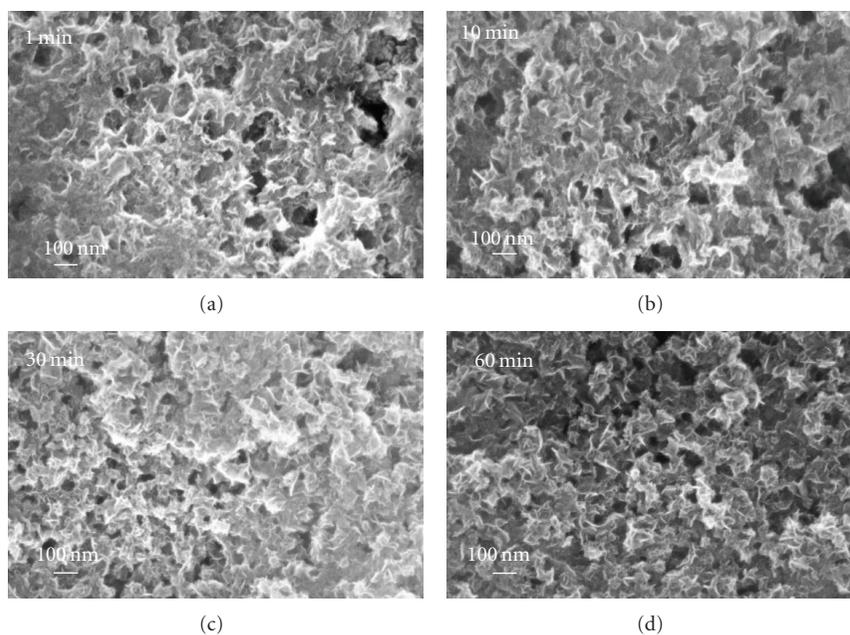


FIGURE 1: FESEM micrographs of self-assembled MnO_2 thin films deposited on Ni/PET substrates at various submersion durations (a) 1 min, (b) 10 min, (c) 30 min, and (d) 60 min.

being dispersed by sonication in order to enhance dispersion to form a stable colloidal suspension.

2.2. Preparation of Self-Assembled MnO_2 Thin Films. Self-assembled MnO_2 thin films were prepared on nickel-coated poly(ethylene terephthalate) supporting substrate (Ni/PET) using the newly developed horizontal submersion process. Precleaned Ni/PET substrate with a surface area of $\sim 3 \text{ cm}^2$ was positioned horizontally onto glass slides using adhesive tape and placed into petri dishes. The MnO_2 sol was sonicated for 5 minutes to ensure well-dispersed nanoparticles before being poured into the petri dishes. A measured volume of MnO_2 sol was then poured into each petri dish to completely submerge the substrate. Self-assembled MnO_2 thin films were formed spontaneously on the substrates upon submersion within the sol for the desired duration. The relative film thickness was controlled by the duration of submersion in the sol. All deposited films were air dried at ambient temperature and subsequently calcined in a tube furnace at various temperatures in air for an hour.

2.3. Characterizations of MnO_2 Nanoparticles and Thin Films. The surface morphology of MnO_2 nanoparticles and self-assembled thin films were characterized using a scanning electron microscope (SEM) (JEOL Model JSM 6390LA) and a field emission scanning electron microscope (FESEM) (LEO Model 1535), respectively, at various magnifications. All samples were coated with platinum using a sputtering device JFC-1100 E to reduce the inherent charging effect. A transmission electron microscope (TEM) (Model JEM-1230) was used to study the surface morphology of MnO_2 nanoparticles. The elemental composition of the MnO_2 nanoparticles was analyzed by FESEM-associated energy

dispersive X-ray microanalysis (EDX) operated with a beam energy of 10 kV.

The electrochemical characterization of self-assembled MnO_2 thin films was conducted using an advanced electrochemical analyzer (PARSTAT 2263). Sample evaluation by cyclic voltammetry (CV) was conducted using a standard three-electrode cell configuration. The reference electrode used was a saturated calomel electrode (SCE) fitted with a Vycor bridge, and the counter electrode was a platinum foil ($\sim 2 \text{ cm}^2$). A geometric electrode area of 0.1257 cm^2 of thin-film sample was being exposed to the electrolyte during all cyclic voltammetric experiments. Cyclic voltammograms were obtained by scanning over the potential range of 0.0 V–0.9 V (versus SCE), with a scan rate of 50 mV/s in 1.0 M Na_2SO_4 aqueous solution as electrolyte.

The mass loading of various self-assembled MnO_2 films was determined quantitatively by atomic absorption spectroscopy (AAS) after dissolving a known area of films in the $\text{H}_2\text{O}_2/\text{HNO}_3$ solution mixture. Based on the measured Mn concentration, the mass loading of MnO_2 per unit of electrode area was calculated using the formula weight of stoichiometric MnO_2 of 86.94 g/mol.

3. Results and Discussion

3.1. Effect of Submersion Duration. Figure 1 shows SEM micrographs of self-assembled MnO_2 thin films deposited on Ni/PET substrate by the horizontal submersion process at various submersion durations under ambient conditions. These films showed good adhesion to the substrate even without the addition of any binder. Self-assembled films deposited at shorter submersion duration were observed to be rather porous with loosely packed nanoclusters,

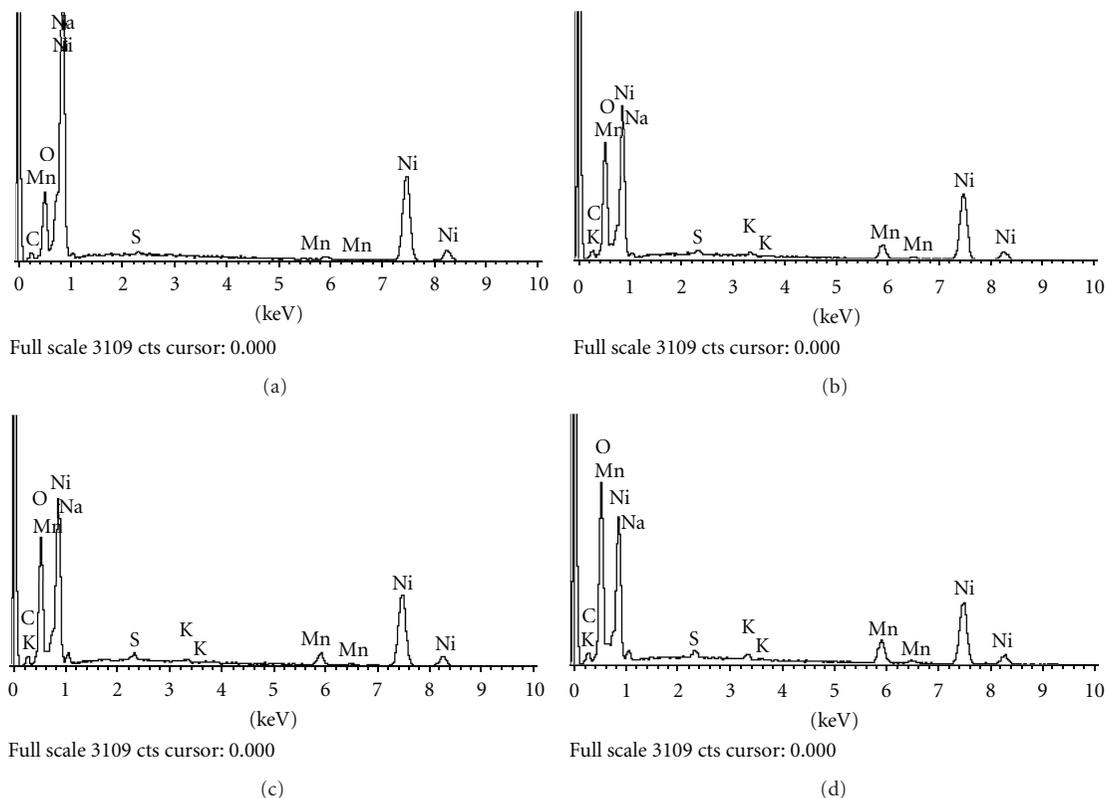


FIGURE 2: EDX spectra of self-assembled MnO_2 thin films on Ni-coated PET films at submersion duration of (a) 1 min, (b) 10 min, (c) 30 min, and (d) 60 min.

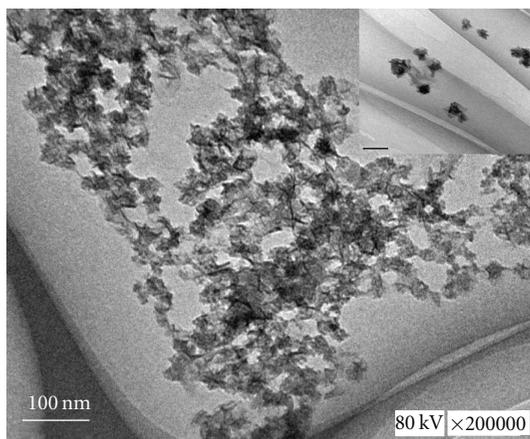


FIGURE 3: TEM micrographs of MnO_2 self-assembled thin films as deposited on Ni/PET supporting substrate. Inset showed well-dispersed nanoclusters and individual nanoparticles.

whereas films deposited at longer submersion duration were denser with closely packed nanoclusters. Figure 2 shows the EDX spectra of self-assembled manganese oxide thin films on Ni/PET substrates. The presence of manganese and oxygen atoms in the elemental composition of deposited thin films confirmed the deposition of MnO_2 thin films. Besides, the weight percentages of Mn and O elements

within the deposited films were observed to increase with increased submersion durations, indicating the deposition of thicker films. The weight percentage of Mn was observed to have increased from 1.42% to 8.74%, whereas that of O was increased from 10.85% to 25.56% as the submersion duration was increased from 1 minute to 60 minutes.

Figure 3 shows TEM micrographs of self-assembled MnO_2 thin film as deposited on Ni/PET supporting substrate. Well-dispersed manganese dioxide nanoclusters and well-defined individual nanoparticles could be clearly discernable (insets of Figure 3). The mean average nanoparticle size was about 20–25 nm in diameter. Aggregated and dense nanofibrous structures were observed to radiate outward from the centre of each nanoparticle.

3.2. Effect of Calcination. The effect of calcination on the surface morphology of self-assembled MnO_2 thin films on Ni/PET supporting substrates was studied by FESEM and shown in Figure 4. The heat treatment was observed to have substantial effect on the surface morphology of MnO_2 thin films, with calcined films showing comparatively smoother surface morphology with densely packed nanoparticles. Apart from film densification, the calcination process could have effectively removed all physisorbed and chemisorbed water from MnO_2 thin films, as evidenced by the porous microstructure and occurrence of cracks due to the shrinkage of films. Such porous microstructures could serve to enhance ionic transport and redox reactions which underlie the

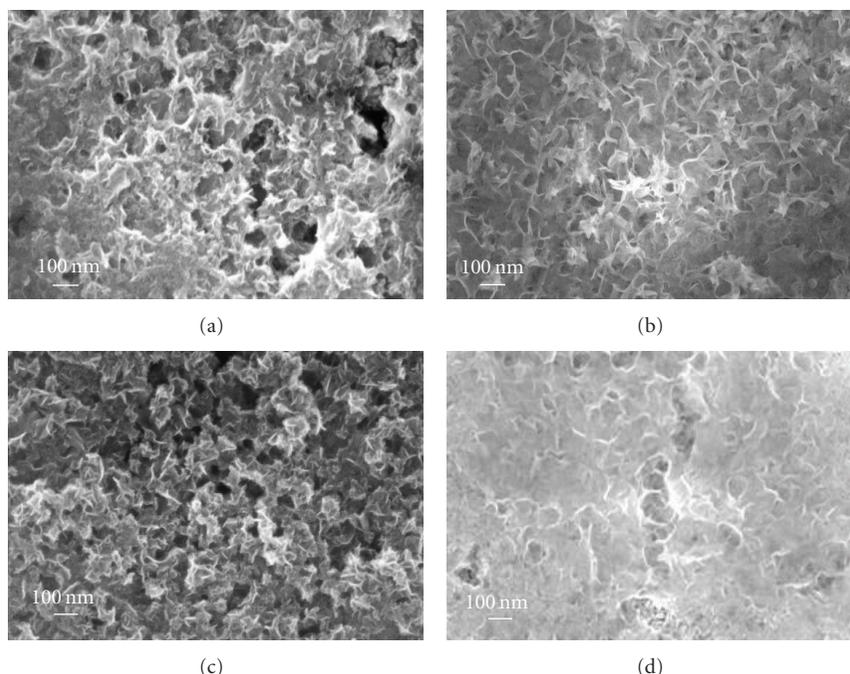


FIGURE 4: FESEM micrographs of MnO_2 thin films on Ni-coated PET films at deposition duration of (a) 1 min, before, (b) 1 min, after, and (c) 60 min, before, (d) 60 min, after calcination at 200°C in air for 1 hour.

charge storage mechanism [11]. The electrolyte ions could penetrate into the porous microstructure of manganese dioxide thin-film electrode during electrochemical reactions.

3.3. Electrochemical Characterization of Self-Assembled MnO_2 Thin Films

3.3.1. Effect of Calcination. The effect of heat treatment on the capacitive behavior of self-assembled MnO_2 thin films on Ni/PET films was investigated by heating them in air at various temperatures for 1 hour. The calcination temperature did not exceed 200°C since the melting point of pure PET was 241°C [12]. Calcination temperature was observed to have a positive effect on the charge capacity of MnO_2 thin films as shown by the increase in areas of cyclic voltammograms for films calcined at higher temperatures (Figure 5). The charge capacities of MnO_2 thin films were observed to increase moderately with increasing calcination temperatures up to 200°C . A maximum charge capacity of 34 mF/cm^2 was achieved for films calcined at 200°C . Previous studies reported that annealing temperature could affect the crystal structure of the electrochemically deposited manganese oxide [13]. Chemically bound water within the MnO_2 films was thought to have played a major role in the observed variation of charge capacity. As chemically bound water is essential for the transportation of active ionic species, the pseudocapacitance of oxide material is dependent upon its water content [14]. Water content in manganese oxides is known to affect the electrochemical reactivity and thermodynamic stability of various manganese dioxide phases as it causes variation of crystal lattice and

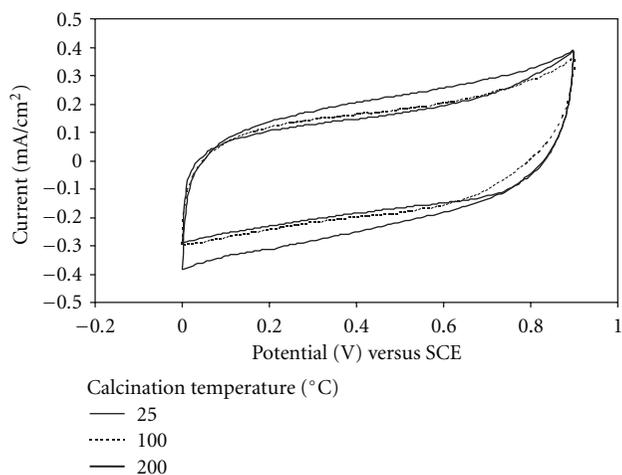


FIGURE 5: Cyclic voltammograms of self-assembled MnO_2 thin films calcined at various temperatures.

consequently of electrical conductivity and electrode potential [15]. Although the presence of structural water promotes proton diffusivity in manganese oxide, its resistivity increases with increasing water content. As such, heat treatment of MnO_2 films at 200°C in air for 1 hour could have resulted in lowering their structural water content within the oxide lattice and consequently led to increase in the electronic conductivity and hence the observed higher charge capacity.

3.3.2. Effect of Film Thickness. Figure 6 shows the cyclic voltammograms of MnO_2 films coated on Ni/PET substrates

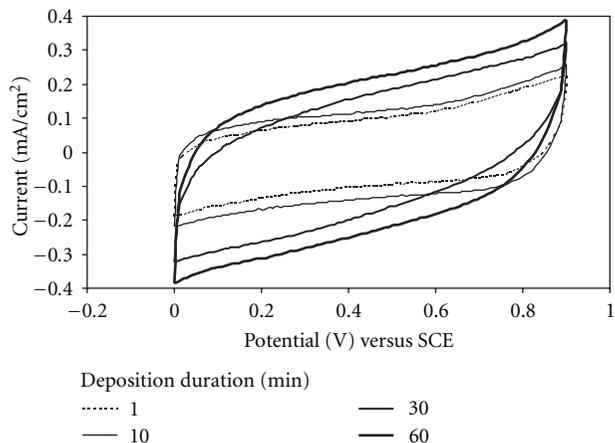


FIGURE 6: Cyclic voltammograms of self-assembled manganese dioxides thin films deposited at different submersion durations.

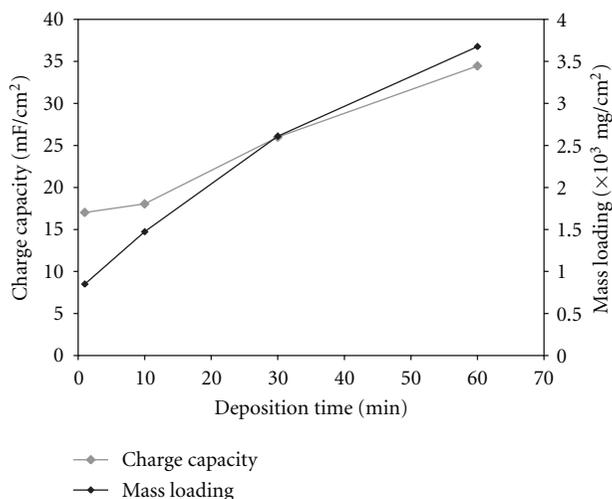


FIGURE 7: Charge capacity and mass loading of MnO₂ thin films deposited at various submersion durations.

at different submersion duration. The relative film thickness was controlled by the submersion duration which was being varied between 1 minute and 60 minutes. All cyclic voltammograms obtained were almost rectangular in shape with symmetrical anodic and cathodic halves. Such rectangular cyclic voltammograms indicated that self-assembled MnO₂ films exhibited almost ideal capacitive behaviors. It is clear from Figure 6 that there were no redox peaks observed within the potential range between 0 and 0.9 V (versus SCE) which could be attributed to the phase stability of electrode materials and the high reversibility of pseudocapacitive electrochemical reactions.

Figure 7 shows the average mass loading and charge capacities of self-assembled MnO₂ thin films deposited on Ni/PET substrates at various submersion durations. The mass loading of self-assembled MnO₂ films deposited on the supporting substrate was used as an indication of their relative film thickness. The mass loadings of MnO₂ films deposited on Ni/PET substrates were determined using AAS

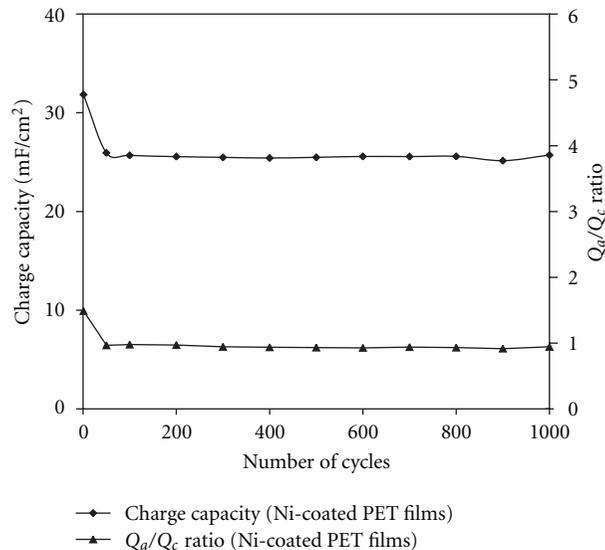
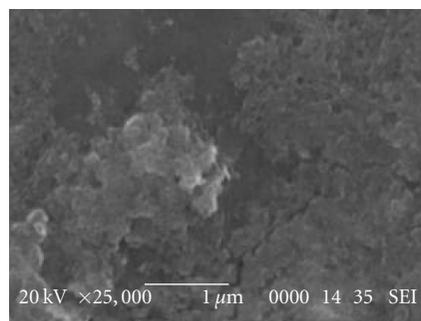
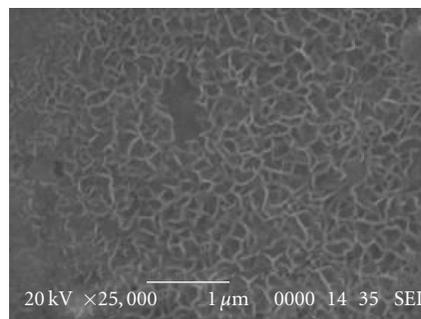


FIGURE 8: Charge capacity and cycling reversibility of self-assembled MnO₂ thin films as a function of cycle numbers.



(a)



(b)

FIGURE 9: Effect of voltammetric cycling on the microstructure of MnO₂ films (a) before cycling; (b) after cycling.

by dissolving these films in HNO₃/H₂O₂ mixture. Generally, the mass loading of MnO₂ was observed to increase in submersion durations. A maximum mass loading of 3.68 × 10⁻³ mg/cm² of MnO₂ was deposited on Ni/PET substrates at the submersion duration of 60 minutes. Both mass loading and charge capacity of self-assembled MnO₂ thin films were observed to increase in tandem with submersion durations. Such increase in charge capacity was associated

with the higher mass loading of manganese dioxide for thicker films, as also evidenced by the higher weight % of Mn as determined by both the EDX and AAS analyses for films deposited at longer submersion durations (Figure 2). The voltammetric charge of the electrochemically oxidized MnO₂ films was observed to increase with increasing film thickness, which corresponded to increase in their charge capacity. It was observed that self-assembled MnO₂ films possessed highly porous microstructure with high specific surface area and hence favored the proton/cation diffusion and adsorption/desorption during the redox transitions.

3.3.3. Effect of Long-Term Cycling. The effect of long-term cycling of self-assembled MnO₂ thin films deposited on Ni/PET substrates in 1.0 M Na₂SO₄ aqueous solution is shown in Figure 8. The charge capacity was observed to decline rather rapidly for the initial 100 cycles but only decreased gradually thereafter upon long-term cycling. The overall net loss in charge capacity of MnO₂ thin films was observed to be about 19% of their initial charge capacity upon cycling for 1,000 cycles. Such decline in charge capacity could be attributed to delamination and partial dissolution of manganese dioxide films into the electrolytes during cycling rather than any structural or chemical degradation. Dissolution of MnO₂ during discharge in neutral electrolyte occurred by both the disproportionation reaction and solid-phase diffusion [1]. However, it is speculated that other factors may also be involved, such as changes in the electronic conductivity of the film during cycling associated with changes in oxidation states or structural water content [2]. The decrease in capacity after cycling can also be attributed to increased electrode resistance with increasing cycle number [16]. The charge capacity was observed to decline rather rapidly for the initial 100 cycles but only decreased gradually thereafter upon long-term cycling. The overall net loss in charge capacity of self-assembled MnO₂ thin films was observed to be about 19% of their initial charge capacity upon cycling for 1,000 cycles.

Figure 9 shows the SEM micrographs of self-assembled MnO₂ thin films deposited on Ni/PET films before and after cycling for 1000 cycles. The surface morphology of MnO₂ film after cycling was more porous and fibrous in nature. Similar observations had been reported by Nagarajan et al. [17]. The higher porosity could be resulted from partial dissolution and redeposition of manganese oxide during cycling. Since the charge/discharge process in MnO₂ involves a redox reaction between the III and IV oxidation states of Mn, the reactivity (or utilization) of the oxide can be enhanced with increased accessibility of electrolyte ions within materials [16, 17]. In addition, some of the MnO₂ inevitably dissolved into the 1.0 M Na₂SO₄ electrolyte and then redeposited onto the substrate. The redeposited oxide layer was highly porous and showed a distinctive petal-like surface morphology. This could be attributed to the anodized film caused by back and forth sweeps of the applied cycling potential.

4. Conclusion

Self-assembled manganese dioxide thin films have been successfully deposited onto Ni/PET films using the newly developed horizontal submersion process under ambient conditions. These films were shown by cyclic voltammetry to exhibit excellent capacitance behavior, high cycling reversibility, and stability within the potential range of 0.0 to 0.9 V versus SCE in mild NaSO₄ aqueous electrolyte. Thin film with desired thickness, good uniformity and tailored microstructure, and enhanced electrochemical properties could be prepared through optimizing deposition conditions such as submersion duration and calcination temperature.

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