Electrophoretic Fabrication and Characterizations of Manganese Oxide/Carbon Nanotube Nanocomposite Pseudocapacitors

Chung Jung Hung, a Jeng Han Hung, b Pang Lin, a and Tseung Yuen Tseng b, z

aDepartment of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan
bDepartment of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu 300, Taiwan

This study reports the electrochemical performance and stability of MnO2-multiwall carbon nanotubes (MWCNTs) nanocomposite/Ni pseudocapacitor electrodes fabricated by a modified electrophoretic deposition (EPD) method. The nanocomposite electrode consisting of highly dispersed manganese oxide on MWCNTs was synthesized by a redox titration method at room temperature. The electrochemical properties of the electrode were demonstrated by cyclic voltammetry. The mean specific capacitances at a constant scan rate of 100 mV/s of MnO2-MWCNTs nanocomposites without and with heat treatment at temperatures 150, 200, and 250°C for 2 h are 378, 402, 445, and 469 F/g, respectively, which indicate an increase with increasing annealing temperature. During stability tests, the as-grown MnO2-MWCNTs nanocomposite electrode can preserve 80% of its original capacitance after 6000 cycles of operation which can be increased to 86% after annealing at 200°C for 2 h. The EPD MnO2/MWCNTs coaxial nanocomposite pseudocapacitors with manganese oxide ionized by H+ ion process exhibit high specific capacitance, fast reaction rate, high stability, and have high potential for practical applications.

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In recent years, manganese oxide (MnO2) has been widely investigated as a promising pseudocapacitive material because of its low cost, abundance, more friendly environmental nature and higher electrochemical activity than other transition metal oxides. But one major issue of MnO2 as a pseudocapacitive material is its intrinsically low electrical conductivity, which causes its poor specific capacitance. Therefore, the MnO2/MWCNT/Ni nanocomposite electrode was employed for pseudocapacitor applications in our previous study1 to enhance the specific capacitances. The specific capacitances were employed for pseudocapacitor applications in our previous study1 to enhance the specific capacitances. The specific capacitances were employed for pseudocapacitor applications in our previous study1 to enhance the specific capacitances. The specific capacitances were employed for pseudocapacitor applications in our previous study1 to enhance the specific capacitances. Therefore, the MnO2/MWCNTs nanocomposite electrode was synthesized by a redox titration method at room temperature. The purified MWCNTs were put in the 0.005 M KMnO4 solution and dispersed by ultrasonic agitation for 30 min. Then 0.016 M MnSO4 was added into the MWCNTs/KMnO4 solution drop by drop at room temperature. Such a solution was stirred for 6 h until the disappearance of its purple color. Finally, the nanocomposites were obtained via filtering the solution and cleaned by methanol (200 ml). The powders were dispersed well in the solution with 10% nitric acid solution for 30 min to obtain rough surface and cleaned with deionized (DI) water in an ultrasonic bath, and dried in an oven at 100°C for 12 h. The commercial MWCNTs (specific surface area: 40–300 m2/g, length: 5–20 μm) were purified by putting them in boiling 70% nitric acid solution for 24 h, cleaned with DI water and dried in an oven at 110°C for 12 h before synthesizing MnO2/MWCNTs nanocomposites.

The pseudocapacitor electrode material, MnO2/MWCNTs nanocomposite powders were synthesized by redox titration method at room temperature. The purified MWCNTs were put in the 0.005 M KMnO4 solution and dispersed by ultrasonic agitation for 30 min. Then 0.016 M MnSO4 was added into the MWCNTs/KMnO4 solution drop by drop at room temperature. Such a solution was stirred for 6 h until the disappearance of its purple color. Finally, the nanocomposites were obtained via filtering the solution and cleaned by DI water and dried in an oven at 110°C for 12 h. Then the MnO2/MWCNTs nanocomposite film was deposited on the Ni substrate via electrophoretic deposition (EPD). The electrolyte used in EPD was a mixture of 0.24 g MnO2/MWCNTs nanocomposite powders and 37% hydrochloric acid (0.4 ml) in isopropyl alcohol (200 ml). The powders were dispersed well in the solution by ultrasonic agitation for 30 min. Nickel and platinum foils were put in this solution as cathode and anode at a distance of 1 cm, respectively. The MnO2/MWCNTs nanocomposite powders were deposited onto 10 × 30 × 1 mm flat Ni substrates by electrophoretic deposition technique in this study. The Ni substrates were etched with 10% nitric acid solution for 30 min to obtain rough surface and cleaned with deionized (DI) water in an ultrasonic bath, and dried in an oven at 100°C for 12 h. The commercial MWCNTs (specific surface area: 40–300 m2/g, length: 5–20 μm) were purified by putting them in boiling 70% nitric acid solution for 24 h, cleaned with DI water and dried in an oven at 110°C for 12 h before synthesizing MnO2/MWCNTs nanocomposites.

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electrophoretically deposited on the Ni substrate after a direct current (DC) voltage of 30 V was applied for 40 min. After EPD, the nanocomposite film formed on Ni substrate was dried in an oven at 100 °C for 12 h, which names as-grown nanocomposite electrode. The weight of the deposited nanocomposite film was measured by a microbalance (PRECISA XR125SM-FR) with an accuracy of 0.1 μg. The loading of nanocomposites film on Ni substrate was about 47.5 ± 5.7 μg.

In order to know the effect of annealing temperature on capacitive behavior of MnOx/MWCNTs nanocomposite pseudocapacitors, the as-grown nanocomposite films were annealed at 150, 200, and 250 °C in air atmosphere for 2 h, respectively.

A field emission scanning electron microscope (FESEM, JEOL JSM-6500) and X-ray diffractometer (XRD, Bode D1) were used to analyze surface morphology and crystallization of the film, respectively. The oxidation states of manganese oxide film were examined by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI Quantera SXM). Field emission transmission electron microscope (FETEM, JEOL JEM-2100F) was used to observe the coaxial structure of MnOx/MWCNTs nanocomposite material. The specific surface area of the nanocomposite material was determined by BET (Brunauer, Emmett and Teller method) surface area analyzer. Thermal analysis was performed from 50 to 800 °C at 4 °C/min ramping rate under air atmosphere using thermogravimetric analyzer (TGA, TA Instruments Q500).

The electrochemical performance of the pseudocapacitors were measured by cyclic voltammetry (CV), galvanostatic charge/discharge cycling (CC) and electrochemical impedance spectroscopy (EIS) using CH Instruments 618B electrochemical analyzer. Electrochemical measurements were carried out in a three-electrode cell with a saturated calomel reference electrode (SCE), a counter electrode of platinum sheet, and aqueous 0.1 M Na2SO4 as the electrolyte. CVs were recorded between 0 and 0.8 V versus SCE at a scan rate varied from 5 to 100 mV/s. The CC testing was recorded between 0 and 0.8 V versus SCE at a constant current 1 mA. The values of the specific capacitance (F/g) were estimated from cyclic voltammetric curve by using the following equation

\[
C = \frac{Q}{\Delta E \times m}
\]

where \(m\) is the mass of the active material, \(Q\) the voltammetric charge within the working voltage, and \(\Delta E\) the width of the potential window.

Impedance spectroscopy investigation was performed in the frequency range of 1 mHz ~100 kHz at a voltage of 100 mV with an AC amplitude of 5 mV.

**Results and Discussion**

The FESEM surface morphology of as-grown nanocomposite film is shown in Fig. 1a, indicating that a highly porous MnOx-MWCNTs nanocomposite layer electrophoretically deposited on the Ni substrate. It shows that the MnOx is homogeneously uniformly coated on the MWCNTs surface by redox titration method.

The average specific surface area of MnOx-MWCNTs nanocomposites from BET measurement is 170.88 m²/g. This surface area is much larger than that (59–131 m²/g) reported in our previous study, in which the MnOx nanoparticles were deposited on MWCNTs by using EPD. Such a porous MnOx-MWCNTs nanocomposite film would provide a large redox reaction area. The density and the thickness of the nanocomposite film are about 0.41 g/cm³ and 1167 nm, respectively. The average thickness of MnOx layer in the nanocomposite film is about 4 nm according to the TEM image shown in Fig. 1b.

The TGA and DSC curves were used to detect the thermal stability of the as-grown MnOx-MWCNTs nanocomposites. From the TGA curve of Fig. 2, the weight loss below 250 °C is attributed to evaporation of physically adsorbed water. The DSC curve depicts that the removal of volatile ingredient and water from the as-grown nanocomposites results in about 68% weight loss.

Figure 3 shows the XRD patterns of the as-grown and annealed MnOx-MWCNTs nanocomposite/Ni substrate electrodes. The annealing temperatures are 150, 200 and 250 °C. Excluding peaks at 44.5, 51.9, and 76.5° corresponding to the diffraction peaks of pristine Ni substrate, no other Bragg peaks appear. It demonstrates that the MnOx-MWCNTs nanocomposites without and with annealing process exhibit amorphous structure. It has been shown in the previous paper that the better electrochemical performance was obtained for the pseudocapacitor with oxide electrode containing higher amount of amorphous structure. Such amorphous structure could cause the electrolyte inserting into the matrix easily, leading to an increase in the reaction area between electrolyte and active electrode materials. The amorphous structure of manganese oxide, used in the pseudocapacitors as an electrode is expected to have a rapid oxidation-reduction reaction rate.

In this work cyclic voltammetry measurement (CV) was employed to understand the capacitive behavior of the pseudocapacitor materials. Figure 4 shows the CV curves of the MnOx-MWCNT nanocomposite/Ni substrate electrode in neutral aqueous electrolyte (0.1 M Na2SO4) at 25 °C in the potential range 0 < E < 0.8 V versus SCE with scan rates of 5, 25, 50, 75 and 100 mV/s. The typical CV curves of the nanocomposite electrode are almost a near-ideal rectangular and symmetric profile and no redox peaks appear in the cycling potential from 0 to 0.8 V. It has been well established that the nanocomposite electrode exhibits excellent capacitive behavior.

The variation of measured specific capacitances with scan rate is indicated in the inset of Fig. 4. It is shown that the mean specific capacitances of the electrode with scan rates of 5, 25, 50, 75, and 100 mV/s are 480, 432, 411, 393, and 378 F/g, respectively.
specific capacitance at the potential scan rate of 100 mV/s of the nanocomposite electrode is 78.8% of that measured with a scan rate of 5 mV/s.

Figure 5 depicts the CV curves of the MnOx-MWCNTs nanocomposite electrodes annealed at different temperatures with a constant scan rate of 100 mV/s. The typical CV curves are a nearly rectangular profile and some redox peaks in the curves appear as the annealing temperature increase. The CV loop area increases with an increase in the annealing temperature due to the enhancement of the capacitance. The mean specific capacitances of the as-grown and 150, 200, and 250°C annealed nanocomposite electrodes are 378, 402, 445, and 469 F/g, respectively, at a constant scan rate 100 mV/s. The specific capacitance increases around 25% as shown in the inset of Fig. 5 after the nanocomposite is annealed at 250°C.

For the purpose of observation on the connection between oxidation state of Mn in manganese oxide film and charge storage mechanism, the nanocomposite electrodes annealed at different temperatures were analyzed by XPS. Figure 6 indicates the Mn2p 3/2 spectra of the as-grown and 150, 200, and 250°C annealed nanocomposite electrodes. The curve fitting of the obtained XPS curve demonstrates that the manganese oxide film and charge storage mechanism is explained as follows. Two chemical reactions at 25°C are proposed to explain the MnO2 or Mn3O4 charge storage behavior

\[ \text{MnO}_2 + \text{H}_2\text{O} + e^- = \text{MnO} \cdot \text{OH} + \text{OH}^- \quad \Delta G = -5.305 \text{ kcal mol}^{-1} \]

\[ \text{MnO}_3 \cdot \text{OH} + \text{H}^+ + e^- = \text{Mn}^{2+} + \text{H}_2\text{O} \quad \Delta G = 13.370 \text{ kcal mol}^{-1} \]

According to the areas of XPS peaks, the ratio of MnO2/Mn3O4 for as-grown nanocomposite can be estimated to be 1.88. With increasing annealing temperature up to 200°C, the MnO2/Mn3O4 ratio rapidly increases to 4.29. The correlation among the specific capacitance, MnO2/Mn3O4 ratio and charge storage mechanism is explained as follows. Two chemical reactions at 25°C are proposed to explain the MnO2 or Mn3O4 charge storage behavior

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The charge/discharge mechanism of manganese oxide has been also proposed in literature.

\[ \text{MnO}_4(\text{OH})_y + 5\text{H}^+ + 6e^- \rightarrow \text{Mn}^{2+} + (\text{OH})_y + 6 \]

where MnO4(OH)y and MnO4_d(OH)3_y indicate the higher and lower oxidation state of Mn, separately. Based on above equations, the manganese oxide is transformed into the hydrated manganese oxide, MnO-OH before charge/discharge process. From thermodynamic point of view, it is a spontaneous process from MnO2 to MnO-OH according to reaction 1, due to a negative Gibbs free energy change while the Mn3O4 to MnO-OH process is a non-spontaneous reaction according to reaction 2, where Gibbs free energy change is a positive value. Therefore, the specific capacitance of the MnO4-MWCNT nanocomposite/Ni substrate electrode is increased with an increase in annealing temperature which is due to the higher MnO2 content in the nanocomposite electrode heat treated at higher temperature.

The effect of annealing temperature on the electrochemical characteristics can be demonstrated from electrochemical impedance spectrum and the corresponding equivalent circuit model. The Nyquist plots of the AC impedance responses for the nanocomposite electrodes annealed at various temperatures in 0.1 M Na2SO4 electrolyte are shown in Fig. 7, indicating that all spectra contain a semi-circle (inset of Fig. 7) in the high frequency region (>25.7 Hz), a straight line inclined at a constant phase in the mid-frequency region (3.7 ~ 25.7 Hz), and an almost vertical capacitive line in the low frequency region (<3.7 Hz). Such a pattern of the impedance spectra can be fitted by an equivalent circuit shown in the inset of Fig. 7. Here, Rs represents the bulk resistance of the electrochemical system, which is used to account for electrical conductivity of the electrolyte and electrodes; Rct and Cdl are the charge-transfer resistance on the surface of the electrode in contact with the electrolyte and its...
relative double layer capacitance, respectively, corresponding to the semicircle at high frequencies; \( W \) is the Warburg impedance related to a combination of the ionic diffusion at the interface between the active electrode material and electrolyte\(^{20–22} \) which is employed to fit the straight line at intermediate frequencies (Fig. 7). Followed by a near-vertical line at low frequency region (close to 0.001 Hz), it is a typical capacitive behavior.

A vertical straight line in the imaginary positive part (\(-\text{Im}(Z) > 0\)) of the Nyquist plot basically corresponds to an ideal capacitance element. In fact, the MnO\(_x\)-MWCNTs nanocomposite electrode regards as a pseudocapacitor with capacitance originating from faradic reaction rather than an electrical double layer capacitor (EDLC). Therefore, the semicircle appearing at high frequencies should be related to above electrochemical reaction 3 used for to explaining the charge/discharge mechanism of MnO\(_2\). Additionally, based on the inset of Fig. 7, it can be seen that the radius of the semicircle is declined when annealing temperature increased. It means that the reduction of charge transfer resistance \( R_{ct} \) that is considered as a barrier of Na\(^+\) insertion/extraction lead to more MnO\(_x\) available to charge and discharge during cycling. From impedance analysis the increase in specific capacitance after thermal treatment can be referred to enlargement of suitable redox sites for Na\(^+\) ions.

We have developed a novel method of ionizing the surface of MnO\(_x\) with hydrogen ion as surfactant to substitute polymer by electrophoretic deposition method. Furthermore, the preparation of nanocomposite pseudocapacitor electrode with the binder-free or the surfactants-free was regarded as the method to decrease the charge transfer resistance and to increase efficient charge/electron transport from the current collector to the active materials.

In our experiment, the long-term stability test of the MnO\(_x\)-MWCNTs nanocomposite electrode for pseudocapacitors was a

![Figure 6.](image-url) (Color online) Mn2p\(^{3/2}\) spectra of the as-grown and annealed MnO\(_x\)/MWCNTs nanocomposite electrodes with annealing temperatures indicated.

![Figure 7.](image-url) (Color online) Impedance analysis of the as-grown and annealed MnO\(_x\)/MWCNTs nanocomposite electrodes with annealing temperatures indicated. The insets show the enlargement portion of selected part indicated and equivalent circuit of the pseudocapacitor, respectively.

![Figure 8.](image-url) (Color online) Typical Bode plots for the MnO\(_x\)-MWCNTs nanocomposite electrode (a) \( \log|Z| \) vs. \( \log f \), (b) phase angle (degree) vs. \( \log f \).
charge/discharge test with 1 mA constant current. The dependence of the maintenance efficiency on specific capacitances for the as-grown and annealed nanocomposite electrodes is shown in Fig. 9. It is indicated that the specific capacitance of the as-grown and annealed nanocomposite electrodes all slightly decrease to 93% of the initial values after about 1000 cycles. Finally, it displays that they all can maintain above 80% after long cycling and the maintenance efficiency of the capacitance increases with increasing annealing temperature up to 200 °C and the highest efficiency can reach about 86% after 6000 cycles for both 200 and 250 °C annealed electrodes. The above results are attributed to the enhancement of the amount of MnO2 species after annealing and good adhesion between manganese oxide and MWCNTs of the nanocomposite electrode, leading to reduced dissolution of MnO2 film during the charge/discharge process.

Figure 9. (Color online) Stability test of the as-grown and annealed MnOx-MWCNTs nanocomposite electrodes with annealing temperatures indicated via a constant current 1 mA charge/discharge process.

TEM observation is carried out to understand the influence of long cycling on the morphology of the as-grown nanocomposite electrode. The TEM image of the nanocomposite after galvanostatic charge/discharge 6000 cycles is shown in Fig. 10. The thickness of manganese oxide decreases from 4 nm before cycling (Fig. 1b) to around 2 nm after cycling. When measuring from 0.8 to 0 V during cycling, the MnOx film is reduced and some is dissolved into the electrolyte as Mn2+ cations. During scanning from 0 to 0.8 V, some of the dissolved Mn2+ cations transform into MnO2 and deposit on the electrode’s surface again. Comparing to our previous study in which the capacitance of the nanocomposite kept only at 79% after 1000 cycles due to some MnOx nanoparticles detached from the nanocomposite, this study shows much better stability result. This low degradation of specific capacitance is attributed to better adhesion between MnOx and MWCNTs, which can reduce the dissolution of MnOx film and remain the surface morphology after 6000 cycling test.

Conclusions

In summary, we have developed a novel method of ionizing the surface of manganese oxide with hydrogen ion instead of polymer material surfactant to fabricate pseudocapacitor electrode by EPD. The nanocomposites composed of high dispersion of MnOx on the surface of MWCNTs were synthesized by redox titration method at room temperature. With the help of such nanocomposite electrode, the degradable capacitance caused by dissolution and detachment of MnOx during the charge/discharge process can be significantly improved. The as-grown MnOx-MWCNTs nanocomposite electrode can keep about 80% of its original capacitance after 6000 charge/discharge cycles.

The amorphous structured nanocomposite electrode annealed at 250 °C allows Na+ ion to fast insert and extract. The XPS analysis result indicates that the MnOx film is composed of MnO2 and MnO4. The amount of MnO2 species in the nanocomposites increased with an increase of annealing temperature. The mean specific capacitance at 100 mV/s of as-grown nanocomposite, 378 F/g can increase to 469 F/g for the nanocomposite after annealing at 250 °C for 2 h. This enhancement is attributed to the MnO3/MnO2 ratio changed from 1.88 (as-grown) to 4.29 (250 °C annealed). The charge transfer resistance (a barrier for Na+ insertion and extraction) decreases with such an increase of MnO2 on the basis of impedance analysis. The 200 °C annealed MnO3-MWCNTs nanocomposite electrode can maintain about 86% of its original capacitance after 6000 charge/discharge cycles. Our EPD MnOx/MWCNTs coaxial nanocomposite pseudocapacitors exhibiting the high specific capacitance, fast reaction rate, and high stability, have high potential for practical applications.

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References