Electrodeposition of MnO₂ on Carbon Nanotube Thin Films as Flexible Electrodes for Supercapacitors

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Carbon nanotubes (CNTs) are a promising new material for electrodes of supercapacitors, owing to their unique internal structure, high surface area, remarkable chemical stability, and electrical conductivity. In this study, CNTs films with nanoporous structure were made by a filtration method. A nanostructured manganese dioxide layer was electrodeposited on a thin CNT film to form a flexible CNT/MnO₂ film electrode for supercapacitors. The morphology of the CNT/MnO₂ electrode was examined by SEM and TEM. Compared with a pure CNT film, the CNT/MnO₂ electrode shows a higher specific capacitance. The CNT network in the CNT/MnO₂ electrode acted as a substrate of good conductivity and high surface area. The nanostructured MnO₂ not only increased the surface area, but also has enhanced reactions with the cations in the electrolyte to increase specific capacitance.

Key words: Supercapacitor, MnO₂, Carbon nanotube, Electrodeposition

1. INTRODUCTION
Climate change and limited availability of fossil fuels have greatly affected the world economy and ecology. As a result, we are observing an increase in the production of renewable energy from the sun and wind, as well as in development of electric vehicles or hybrid vehicles with low CO₂ emissions. Because the sun does not shine in the night and the wind does not blow as we wished, energy storage systems, such as batteries and supercapacitors, are starting to play a larger part in our life. Supercapacitor, which is also called ultracapacitor or electrochemical double layer capacitor, is a kind of energy saving unit that can provide a huge amount of energy in a short period of time, making it indispensable for power delivery [1]. Supercapacitors are more suitable for energy storage because of their excellent cyclability and power performance. However, supercapacitors often suffer from low energy performance which is usually evaluated by specific capacitance and energy density. Therefore we need to improve their energy performance to meet the higher requirements of future systems, ranging from portable electronics to hybrid vehicles and large industrial equipment. In development of this kind of energy devices, nanostructured electrode materials have attracted great attention. Nanostructured electrode materials are key components in the advancement of future energy technologies, as they show not only higher capacities but also better response rates than traditional materials [2-3].

Carbon nanotubes (CNTs) are promising materials for the electrodes of supercapacitors, owing to their unique internal structure, high surface area, low mass density, remarkable chemical stability, and electrical conductivity. CNTs can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), both of which have been widely explored as a choice for high power electrode materials because of their good electrical conductivity and readily accessible surface areas. Moreover, their high mechanical resilience and open tubular network make them an ideal support for active materials. But the energy density is, however, a concern due to their relatively small surface area [4].

Nowadays, much research on supercapacitor is aimed at increasing power and energy densities as well as lowering fabrication cost and using environmentally friendly materials. For example, it has been found that RuO₂ exhibited prominent capacitive properties as a supercapacitor electrode material. However, its high cost prohibits it from wide applications. Instead, low cost materials such as MnO₂ and NiO₂ have been developed as the electrode materials, but their power performance need be enhanced [5-6]. MnO₂ can form many polymorphs such as α-, β-, γ- and δ-type, offering distinctive properties and wide applications as catalysts, ion-sieves, and especially as electrode in Li/MnO₂ and Zn/MnO₂ batteries [7-9]. On the other hand, MnO₂ is a promising material for pseudocapacitors due to its superior electrochemical performance, environmentally friendliness, and lower cost in production [10-14]. Over the past years, several nanostructured MnO₂, including nanocrystals of different shapes, nanowires, nanotubes, nanobelts, and nanoflowers, have been synthesized [15-16].
We combine both CNTs and MnO₂ to form a electrode of high power density and enhanced energy density. The MnO₂ needs be made into nanostructures because only the surface or near-surface areas (a few nanometers) can participate the redox reactions with the cations in the electrolyte. The bulk form of MnO₂ may lead to poor power performance due to the relatively poor conductivity of MnO₂. Our research strategy is shown schematically in Fig. 1. We first make an entangled CNT network which can act as the substrate for MnO₂. This conductive substrate can provide a high path for electrical conduction. What’s more, the CNT film can provide a porous structure for ion absorption and hosting MnO₂. Most important of all, the entangled film can provide a porous structure for ion absorption in the electrolyte. The bulk form of MnO₂ may strongly affect the amount of microtwinning. The (110) peak with a high magnification SEM image after MnO₂ coating; and (d) Low magnification image after MnO₂ coating.

Fig. 1 Procedure for preparation of nanostructured electrode using carbon nanotubes.

2. EXPERIMENTAL
2.1 Synthesis of CNT Film and Manganese Dioxide

The SWCNT samples were purchased commercially (Cheap Tube Inc. (purity >90%, amorphous carbon content < 3wt%). The specific area of the SWCNTs is 407 m²/g, the electrical conductivity is 100 S/cm, and their length is about 5-30 μm. The carbon nanotubes were used without any further treatment. For a conventional filtration, the SWCNTs would disperse in solutions. We used sodium dodecyl sulfate as the surfactant to help SWCNTs disperse in distilled water. Then the SWCNTs were filtrated to form a glassy filter paper (bucky paper).

Manganese dioxide was deposited onto the as-prepared SWCNT film by using a triple-electrode electrodeposition method. Before coating, the prepared SWCNT electrode was washed with ethanol and distilled water before dried at 60 °C for 12 hours. An Ag/AgCl electrode was used as the reference electrode and a Pt plate was used as the counter electrode. The electrolyte consists of 0.1 M N₂SO₄ and 0.1 M Mn(CH₃COO)₂ at PH = 5.5 for avoiding production of Mn(OH)₂ in the electrolyte. We also used a potentialstatic technique for 5 min for activation and then used cyclic voltammetry to synthesize MnO₂ by cycling for 200, 500, and 700 cycles under the scan rate of 250 mV/s on the CNT film.[11]

2.2 Characterization

Morphologies of the CNT film and manganese dioxide were examined by scanning electron microscopy (SEM, JSM-6500). The nanostructure of MnO₂ was examined using transmission electron microscopy (TEM, JEM-2100). Characterization of the crystal structure of manganese oxide was based on x-ray diffraction (XRD, RINT-2500). Electrochemical measurements in an aqueous electrolyte (1 M KCl) were conducted by a triple-electrode cell where Ag/AgCl is used as a reference electrode and a Pt plate is used as a counter electrode.

3. RESULTS AND DISCUSSION

3.1 Microstructure of CNT/MnO₂ Electrode

The proposed electrode is a three-dimensional structure, including a CNT network and a nanostructured manganese oxide coating. Fig. 2(a) shows the cross-sectional morphology of the prepared CNT network by filtration. The thickness of the CNT network is about 10 μm. Fig. 2(b) shows typical plan-view morphology of the CNT network. We can see that the carbon nanotubes entangled into bundles and form a rather smooth web with a three-dimensional nanoporous network structure which is desired for ion absorption. Fig. 2(c) shows a high magnification SEM image after MnO₂ coating, where the MnO₂ nanocactuses were deposited quite uniformly on the SWCNT bundles. Fig. 2(d) shows a low magnification image after MnO₂ coating.

An XRD pattern of the MnO₂ deposited on a gold coated glass slide is shown in Fig. 3(a) indicating the formation of γ-MnO₂. Despite the poor crystallinity of the sample, we could still observe the (110) and (002) Bragg reflections, confirming that the as-prepared products are γ-MnO₂.[18]. The x-ray diffraction pattern is strongly affected by three factors: 1) lattice parameters of γ-MnO₂; 2) concentration of De Wolff defects; and 3) the amount of microwinning. The (110) peak with a d-spacing of 4.072 Å in ramsdellite is shifted to higher 20 by De Wolff disorder. The γ-MnO₂ prepared by electrochemical methods has some different features in the x-ray diffraction pattern which are governed by two
kinds of defects that modify both the shape and the position of most diffraction peaks. For our case, we observed a broadened peak at 2θ = 25º since the microcrystal growth on the crystal faces, which includes the De Wolff defects, causes a small increase of 2θ. There is also a sharp peak of (110)-type that is located beside the broadened one indicating that there is some γ-MnO₂ with good crystallinity. The reflection intensities are very low due to the poor crystallinity the γ-MnO₂ structure synthesized by electrodeposition in solution. Fig. 3(b) shows a TEM image of the MnO₂ structure.

Figs. 4(a) and (b) show denser MnO₂ nanostructures on the CNT network prepared under different experimental conditions. There are two types of microstructures. One is nanowire (Fig. 4(a)) and the other is nanocactus (Fig. 4(b)). Both structures have very uniform morphologies that will benefit the electrochemical performance. We also found the element of both Mn and O from the Energy-dispersive x-ray spectrum (EDS).

3.2 Electrochemical Properties

Cyclic voltammetry (CV) tests were performed to investigate the electrochemical properties of both the CNT film and the CNT/MnO₂ electrode in an aqueous electrolyte, which is shown in Fig. 5. It can be seen from Fig. 5(a) that both the CNT film and CNT/MnO₂ show the typical rectangular CV curves at the scan rate of 10 mV/s indicating an ideal electrochemical behavior of the two electrodes. We also observed that the specific capacitance and energy density which are in proportion to the current is increased by about three times with the MnO₂ coating. The specific capacitance and energy density are calculated by Equation (1) and Equation (2) given below, respectively. Figs. 5(c) and (d) are the cyclic voltammetry results of the CNT film and CNT/MnO₂ electrode, respectively. They were measured at different scan rates ranging from 10 to 100 mV/s in a 1 M KCl aqueous electrolyte. The CNT/MnO₂ electrode shows a very good rectangular form which indicates very fast current responses even at high scan rates. It is attributed to a high electron conduction of the CNT substrate with a large surface area. We also calculated the specific capacitance under different scan rates as shown in Fig. 5(b). The specific capacitance improved significantly under every scan rate. The MnO₂ coating on CNTs is therefore a very effective modification to increase the energy performance of the supercapacitor.

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C = \frac{I}{dv/dt} \quad (1)
\]

\[
E_{\text{density}} = \frac{1}{2} CV^2 \quad (2)
\]

4. CONCLUSIONS

γ-MnO₂ nanostructures have been electrochemically deposited on a single-walled carbon nanotube film.
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(Received December 28, 2009; Accepted May 6, 2010)

substrate with a three-dimensional nanoporous structure. Through a comparative study of CNT film and CNT/MnO$_2$ electrodes in 1M KCl aqueous electrolyte, the CNT/MnO$_2$ electrode shows a much higher specific capacitance than the pure CNT electrode and it exhibits a very good current response at high scan rate. This is attributed to the construction of a three-dimensional nanoporous structure that consists of tiny MnO$_2$ nanostructures on CNT film substrate. This study indicates that nano-architected electrode is very useful in high performance supercapacitors. This kind of nanostructured hybrid electrodes has great potentials to lead to a new class of light, flexible, and wearable charge storage devices.

5. ACKNOWLEDGEMENT
We wish to thank financial support from the JSPS Grants-in-Aid for Scientific Research No. 19710101, 2008 Research for Promotion Technological Seeds of Japan Science and Technology Agency, and the “Nanotechnology Network Project” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

6. REFERENCES

(Received December 28, 2009; Accepted May 6, 2010)