Preparation and Electrochemical Performance of CNT Electrode with Deposited Titanium Dioxide for Electrochemical Capacitor

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To reduce polarization of electrochemical capacitor based on carbon nanotube, titanium oxide nanoparticles were deposited by ultrasound. The pore distribution of TiO2/CNT nanoparticle exhibited surface area of 341 m2 g−1 when TiO2 content was 4 wt %, which was better than that of pristine CNT with surface area of 188 m2 g−1. The analyses indicated that titanium oxide (particle diameter < 20 nm) was deposited on the CNT surface. The electrochemical performance was evaluated by using cyclic voltammetry (CV), impedance measurement, and constant-current charge/discharge cycling techniques. The TiO2/CNT composite electrode showed relatively better electrochemical behaviors than CNT electrode by increasing the specific capacitance from 22 F g−1 to 37 F g−1 in 1 M H2SO4 solution. A symmetric cell assembled with the composite electrodes showed the specific capacitance value of 11 F g−1 at a current loading of 0.5 mA cm−2 during initial cycling.

Key Words: Electrochemical capacitor, Titanium dioxide, CNT, Polarization

Introduction

Electrochemical capacitor is an electrochemical energy storage device utilizing the electric charges accumulated at the interface between the electrode and the electrolyte to form the electric double layer.1–5 It has been increasingly getting attention not only for the established applications as backup power to electronic equipments and mobile devices,6,7 but also for high power applications in pulsed lasers and electric vehicles.8,9

Advancement in energy-storage technologies can benefit from the shift from conventional to nanostructured electrodes. For electrochemical capacitors, focus has been on nanostructured carbons, nanotubes, and nanotemplates.10,11 Among these materials, carbon nanotubes (CNTs) have been considered ideal for electrochemical capacitors, owing to the advantages such as accessible surface area, excellent electronic conductivity, and good stability.12–17

On the other hand, CNT grows the polarization when CNT electrode reacts with electrolyte through the electrode/electrolyte interface. Generally, polarization is the change of potential of an electrode from its equilibrium potential upon the application of a current. The phenomenon of transportation of electrical charge from one part of the electrochemical cell to another, occurring mainly as electromigration of ions, but it can also occur by diffusion of ions.5,17 The specific capacitance of the electrochemical capacitor based on CNTs has been reported to present lower capacitance of about 20 ~ 30 F g−1. The lower capacitance is partially attributed to poor wettability of electrode material, which leads to a lower usable specific surface area for charge storage.18 As another reason, polarization may reduce charge accumulation of the ions on the double-layer. For these reasons, reducing the polarization of activated carbon by introducing TiO2 nanoparticles has been considered to be an effective approach to improve the capacitance of the double-layer capacitors.5 In this study, we considered that wettability and polarization of the nanocomposite electrode depend on the content of TiO2 deposited on CNT.

Experimental

The TiO2/CNT nanocomposite material was prepared by sol–gel process with ultrasound in 2-propanol. The starting material, titanium isopropoxide (Aldrich Co., Ltd.) was commercially available with purity of 99%. The average outer diameter of CNT (MWNT type, Iljinnanotech. Co., Ltd.) was 15 ~ 20 nm and the length was 10 ~ 20 µm. The CNT was chemically oxidized in 1M H2SO4 for 48 h at 80 °C and dried at 120 °C overnight. Titanium isopropoxide (0.2, 0.4, 0.6 and 0.8 M) and 1 g CNTs were mixed in 2-propanol (200 mL) with ultrasound, respectively. Then they were mixed with stirring under ultrasound for 30 min. The mixture was separated from the solvent by drying at 90 °C into vacuum oven overnight. The resultant was calcinated at 450 °C for 2 h in air at a heating rate of 5 °C/min to form TiO2/CNT nanocomposite. The samples were characterized by X-ray diffraction (XRD, SCINTAG DMS2000) and transmission electron microscope (TEM, model Joel-1020 Carl Zeiss TEM109) was used to monitor the particle size at each synthesis step. X-ray Photoelectron Spectroscopy (XPS, ESCALAB 210) was used to obtain the structure of nanocomposite.

The working electrode was prepared from a mixture paste of TiO2/CNT nanocomposite powder, ketijen black(KB) as an electronic conductor additive, and polyvinylidene fluoride (PVdF) binder mixed with the weight ratio of 85:10:5 in N-Methyl-2-Pyrrolidone (NMP). The electrode was dried under vacuum
at 120 °C for 24 h before electrochemical evaluation. Electro-
chemical measurements were conducted using conventional
three-electrode configuration and symmetrical full cell. The
TiO2/CNT composite on carbon paper electrode was used as
the working electrode. A Pt wire and KCl-saturated Ag/AgCl
were used as the counter and reference electrodes, respecti-
vely. The 1M H2SO4 aqueous solution was used as the electrolyte.
Cyclic voltammetry (CV) was measured on range of 0 ~ 800
mV. Scan rate was 50mVs⁻¹ and it was shown after 3 th cycle.
And cycling performance of the two electrodes in cell was mea-
sured at 0.5 mAcm⁻² between 0 and 1000 mV. All the measure-
ments were taken at room temperature and under nitrogen
atmosphere.

**Results and Discussion**

In order to show actual size and formation of deposited TiO2
particle, Fig. 1 (b) ~ (e) present TEM images of TiO2/CNT com-
posite materials with different TiO2 weight ratio. Some of the
shapes of these samples were classified as a part of a straight
form with a thick outer diameter and another rest as a curved
style with a narrow outer diameter. The TiO2/CNT composite
materials were different from the result in Fig. 1. From above
results, our attempt to prepare the TiO2/CNT composite materi-
als was successful. And the more the TiO2 was inserted, the more
the deposited TiO2 grains clumped together. The particles are
spherical with the size of about 10 ~ 20 nm in diameter.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the
CNT and the CNT on which TiO2 was deposited with contents of
4, 6, 17, and 32 wt %. After the stoichiometric precursor of TiO2/
CNT composite has been calcinated at 450 °C for 2 h in air, the
anatase phase of TiO2 has been appeared. The peaks located at
25.66° and 42.50° could be identified to the reflection from the
(002) and (100) planes of CNT and the additional peaks observ-
ed at 25.07°, 37.66°, 47.74°, 53.58°, 54.29° and 62.44° are cor-
responding to (101), (004), (200), (105), (211) and (204) planes
of anatase TiO2 (JCPDS no. 21-1272).19 All of broaden and
weaken peaks in Fig. 2 imply that TiO2/CNT composite materi-
als consisted of TiO2 and CNT nanoparticles belong to low-di-
mensional states. The CNT (002) reflection overlaps the anatase
TiO2 (101) reflection. As is seen in Fig. 2, the TiO2/CNT compo-
site shows CNT peak, and also anatase peaks of the composites
grow as the TiO2 content increases. And no peak of other phases
was observed, which indicates that the composite materials are
well crystallized.

The X-ray photoelectron spectroscopy (XPS) which was per-
formed to investigate the chemical bonding state of Ti in the
TiO2/CNT composite material prepared at 450 °C for 2 h is
shown in Fig. 3. The Ti 2p signal of the TiO2/CNT composites
shows a Ti 2p1/2 peak centered at 464.8 eV and a Ti 2p3/2 peak at
459 eV. The observed binding energies (B.E.) of Ti 2p1/2 and Ti
2p3/2 peaks for TiO2/CNT composites are near to those observed
for TiO2 (458.5 and 464.2 eV, respectively). The atomic % of
TiO2 nanoparticle (C₅) was calculated peak area from the equa-
tion (1):

$$C_{atomic} = \frac{[I_i / F_i]}{\Sigma(I / F)} \times 100$$  \hspace{1cm} (1)

where $I$ is the number of photoelectron per second in a specific
spectra peak, $F$ is the atomic sensitivity factor, $i$ is the TiO2
element. According to the XPS results, TiO2/CNT composites
contained TiO2 particle of correctly 4 wt %, 6 wt %, 17 wt % and
32 wt % on CNT, respectively.

Fig. 4 shows the nitrogen adsorption isotherms of the (a)
CNT and the CNT on which TiO2 was deposited with contents of
(b) 4, (c) 6, (d) 17, and (e) 32 wt %. An increase in the TiO2 con-
tents a great enhancement in the nitrogen adsorption capacity. Fig. 5 shows the BET surface area of the pristine CNT and TiO\textsubscript{2}/CNT nanocomposites with various deposited TiO\textsubscript{2} contents. After deposition of TiO\textsubscript{2}, surface area raises the porosity of the TiO\textsubscript{2}/CNT composite to improve BET specific surface area. When comparing those TiO\textsubscript{2}/CNT composites, 4 wt % TiO\textsubscript{2}/CNT composites and 6 wt % TiO\textsubscript{2}/CNT composites have higher specific surface area. The pore distribution of TiO\textsubscript{2}/CNT nanocomposites is exhibited in Table 1. As seen in this Table, the 4 wt % and 6 wt % TiO\textsubscript{2}/CNT composites showed most excellent values of specific surface area (341 m\textsuperscript{2}g\textsuperscript{−1}) and micro pore area (17 m\textsuperscript{2}g\textsuperscript{−1}) compared with the pristine CNT, respectively. But higher contents of deposited TiO\textsubscript{2} decreased both specific surface area and micro pore area.

The effect of TiO\textsubscript{2} on the capacitance property of the TiO\textsubscript{2}/CNT composite material was measured by cyclic voltammetry. Fig. 6 shows the cyclic voltammograms in 1 M H\textsubscript{2}SO\textsubscript{4} electrolyte in the range of 0 ~ 800 mV at 50 mVs\textsuperscript{−1}. In order to determine a good composition ratio of the TiO\textsubscript{2}/CNT electrode, the capacitances with different ratios of TiO\textsubscript{2} contents were measured in 1M H\textsubscript{2}SO\textsubscript{4}. The specific capacitance \( C \) can be calculated from the cyclic voltammetry according to the equation (2):

\[
C = \left[ \frac{(i_c + i_a)}{2 / \nu} \right] / w
\]

where \( i_c \) and \( i_a \) are currents at 0.0 V during the cathodic and anodic sweeps, respectively, \( \nu \) is the sweep rate, and \( w \) is the total weight of the active material in one electrode. The anomalous increase in the current was caused by an enhancement of the electronic and/or ionic transfer between TiO\textsubscript{2}/CNT nanocomposite electrode and electrolyte. When TiO\textsubscript{2} content was small, its double layer capacitance was only slightly higher than that of pristine CNT. But with increasing the TiO\textsubscript{2} content ratio, the capacitance was decreased on account of improvement in diffusion resistance from impedance analysis of Fig. 7. From the result, we suggest the optimized content of TiO\textsubscript{2} to be 4 wt % in H\textsubscript{2}SO\textsubscript{4} electrolyte. The specific capacitance of the pristine CNT and TiO\textsubscript{2}/CNT composite electrodes are listed in Table 1. The 4 wt % TiO\textsubscript{2}/CNT composite electrode delivered a specific capacitance of 37 Fg\textsuperscript{−1} which is higher than CNT electrode by 15 Fg\textsuperscript{−1}.
It has been reported\(^\text{20}\) that the capacitance of an electrochemical capacitor is proportional to ion concentration and inversely proportional to the thickness of the double-layer, and the ion concentration is affected by the voltage between CNT electrodes and electrolyte. Based on above results, the increase of the capacitance in Table 1 could be attributed to the reduced polarization of CNT electrodes, which is believed to relate to the concentration of electric charges on TiO\(_2\) surface with increasing wettability. And electric field adsorption of electrolyte on the CNT composite electrode was significantly enhanced by TiO\(_2\) introduction due to the increase in the charge density of ions under electric field.\(^\text{21}\)

A more detailed estimation of the electrochemical properties of the pristine CNT and TiO\(_2\)/CNT composite electrodes can be carried out by analysis of the impedance spectra. Fig. 7 shows Nyquist plots of the pristine CNT and TiO\(_2\)/CNT composite electrodes in 1M H\(_2\)SO\(_4\). The plot is composed of a semicircle at high frequency and a nearly vertical line at low frequency. The
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Figure 5. BET Surface area of the pristine CNT and TiO$_2$/CNT nanocomposites with various deposited TiO$_2$ contents.

Table 1. BET surface area, specific capacitance and discharge capacitance of the CNT and TiO$_2$/CNT nanocomposites

<table>
<thead>
<tr>
<th>Content (TiO$_2$ wt %)</th>
<th>BET (m$^2$g$^{-1}$)</th>
<th>Micro pore area (m$^2$g$^{-1}$)</th>
<th>Specific capacitance (Fg$^{-1}$)</th>
<th>Discharge capacitance (Fg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>181</td>
<td>10</td>
<td>22</td>
<td>8</td>
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<tr>
<td>4</td>
<td>341</td>
<td>13</td>
<td>37</td>
<td>11</td>
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<tr>
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<tr>
<td>32</td>
<td>188</td>
<td>2</td>
<td>23</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 6. Cyclic voltammograms of the pristine CNT and TiO$_2$/CNT composite electrodes at scan rate of 50 mVs$^{-1}$ in 1M H$_2$SO$_4$ electrolyte.

Figure 7. Nyquist plots of the pristine CNT and TiO$_2$/CNT nanocomposites with various deposited TiO$_2$ contents.

Figure 8. Cycle life performance of the pristine CNT and TiO$_2$/CNT electrodes at 0.5 mAcm$^{-2}$ in 1M H$_2$SO$_4$ electrolyte.

High frequency intercepts the real-axis bulk resistance of composite electrodes. The semicircle consists of electrode resistance of the pristine CNT and TiO$_2$/CNT composite electrodes. The bulk resistance of the capacitor built from CNT electrode was 1.7 ~ 1.8 Ω at 5.6 kHz. The resistances of the CNT electrodes with TiO$_2$ ratio of 4 wt %, 6 wt %, 17 wt %, and 32 wt % showed 3.8, 2.3, 2.4, and 2.4 Ω at 7.9, 12.5, 7.9, and 5 kHz, respectively. The resistances of the electrode/electrolyte interface on TiO$_2$/CNT composite electrodes were slightly higher than CNT electrode. The considerable effect of the Warburg impedance on the 4 wt % TiO$_2$/CNT composite electrode shows a good capacitor-like behavior of near vertical slope to 10 mHz. The Warburg impedance represents that the more the sloping line nears to the imaginary-axis, the more bulk resistance decreases. A Warburg diffusion element is incorporated in the circuit to emphasize the distributed resistance for ion diffusion in the micropores. The results indicate that the composite material reduced the polarization and improved the hydrophilicity of the CNT surface, resulting in the decrease of internal resistance between electrode and electrolyte and increase of the efficiency of charge and mass transfer on the electrode/electrolyte interface.

This result of Nyquist plot agreed well with that from the cycle life performance. Fig. 8 shows the variation in unit discharge capacity as a function of cycle number (voltage range...
for the TiO2/CNT composite electrodes and CNT electrode are
loss in the first 10 cycles, and then remained almost constant as
charge capacity with cycle : all capacitances showed a small
symmetric cells showed the similar variation trend in unit dis-
mass of the composite material, and
where
and TiO2 nanoparticles (< 20 nm) were partly deposited onto
CNT. Nanocomposites electrodes with 4 ~ 6 wt % of deposited
TiO2 shows higher capacitance and surface area than
pristine CNT. From the result, it is indicated that increasing
content of TiO2 nanoparticle. Table 1 summarizes the
surface area and reducing polarization increase specific capaci-
tance.

The dependence of specific capacitance on TiO2 contents is
shown in Fig. 9. The CNT composite electrode with 4 wt % and 6 wt % de-
position of TiO2 nanoparticles on the CNT. This conclusion
attributed to the decrease in electric polarization, caused by the
deposition of TiO2 nanoparticles on the CNT.

The specific capacitance of the composite electrode increased from 22 Fg\(^{-1}\) to 37 Fg\(^{-1}\) in comparison
with the pristine CNT from cyclic voltammogram. And cycle life performance of the symmetric cell showed increase in capacitance from 8 Fg\(^{-1}\) to 11 Fg\(^{-1}\) and maintained an excellent cycling stability. We suggest the optimized content of TiO2 to be 4 wt % and the increase in specific capacitance can be attributed to the decrease in electric polarization, caused by the deposition of TiO2 nanoparticles on the CNT. This conclusion is supported by the Warburg impedance behavior showed near vertical slope to 10 mHz.

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References

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