Performances of Electrochemical Hybrid Supercapacitor of RuO$_2$/Activated Carbon Nanofibers from Electrospinning

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Abstract: In this study, performances of hybrid supercapacitor with electrodes of RuO$_2$/carbon were investigated. Two preparation methods adopted were the RuO$_2$ deposition after activation of the carbon nanofibers and activation of RuO$_2$/carbon composite nano-fibers from electrospinning. Alternatively, multi-walled carbon nanotube (MWCNT) was dispersed in the solution of polyacrylonitrile (PAN) for the dope of the electrospinning. The performances of the electrodes were investigated in 6 M of aqueous KOH solution. The electrical conductivity of the PAN based activated carbon nanofibers (ACNFs) increased from 0.42 S/cm to 0.98 S/cm by dispersions of 3wt.% of MWCNT. The capacitances of the PAN only, MWCNT/PAN, RuO$_2$/PAN, RuO$_2$/MWCNT/PAN based ACNFs were 140, 180, 390, 530 F/g, respectively. The value was increased by 4 times by compositing of 3 wt.% of MWCNT and deposition of 20 wt. % of RuO$_2$. The electrodes of only RuO$_2$ composite without MWCNT showed a capacitance of 460 F/g exhibiting the cyclic voltamogram of combination double layer and REDOX type behaviors. The capacitance was more efficiently improved through the compositing than the depositing at lower than 15 wt.% RuO$_2$.

Key-Words: electrospinning, supercapacitor, carbon nanofiber, carbon nanotube

1. Introduction

Carbon fibers show wide varieties of electrical conductivities depending on the ordered structure ranged $10^{-2}$-$10^5$ S/cm. The order of the structure results from the molecular structure of the precursor materials and heat treatment temperature.

The main advantage of electrospinning is the ability to produce ultra-fine fibers ranging from nanometer to sub-micron diameters. Also, the electrospinning process is fast, simple and relatively inexpensive. Because of the extremely small diameters and excellent uniformity of the electrospun fibers, the non-woven fabrics produced by this technique have high porosities and large specific surface area.[1,2] These characteristics introduce many applications, such as filters and electrical double layer capacitors.

When the non-woven web was used as an electrode, it does not need a second processing step, adding a binder and electron conductor such as carbon black. Therefore the webs from electrospinning have important advantages such as an ease of handling, an increase in the energy density.
due to large specific surface area, an improvement of conductivity caused by enhanced density of the contact points and low cost of preparations of the electrodes.

In considerations of the electrical double layer capacitor (EDLC) electrode applications, ultra-fine diameter introduces short traveling distances of the ions associated with solvent molecules resulting reductions in charge transfer resistance during charging and discharging procedures.[1]

To expand the application area to hydrogen fuel cell vehicle, an improvement of capacitance is a crucial factor to be solved. One of the solutions could be from capacitance increases by combinations of double layer and faradaic process.

In this work, multi-walled carbon nanotube (MWCNT) or RuO$_2$ was dispersed in the polyacrylonitrile(PAN) solution, electrospun to be composite fibers and followed by activations. Alternatively, RuO$_2$ was deposited after activation of the PAN or MWCNT/PAN composite fibers (ACNFs). The electrodes prepared were evaluated in the 6M KOH aqueous solutions.

2. Experimental

PAN solution and that dispersed with MWCNT or RuO$_2$ were electrospun into nano fiber webs through the capillary positively charged using an electrospinning apparatus with DC 20kV power supply. The electrospun webs were stabilized by heating at 1 °C/min up to 280°C and holding for one hour under air flow. The stabilized webs heated at the rate of 5 °C/min and followed by activations for 60 minutes by supplying 30 vol.% of steam with a carrier gas of N$_2$.

The electrodes of the ACNFs deposited with RuO$_2$ (Fig. 1(a)) and also RuO$_2$/carbon composite electrode was prepared (Fig.1(b)).

Specific surface area and pore size distribution of the samples were evaluated by using the BET equation, after preheating the ACNFs at 150 °C for 2 h to eliminate water adsorbed.

A unit cell was prepared with a pair of the ACNF web separated by a filter paper. The EDLC performances were tested 6M KOH aqueous solutions. The cyclic voltamogram(CV) of the unit cell was performed in the potential range of 0 – 0.9 V at a scanning rate of 20mV/s. The discharge capacitance of the electrodes in EDLC were calculated on the basis of $C=4i\times\Delta t/(W\times\Delta V)$, where $i$ is the current, $\Delta t$ is the discharge time, $\Delta V$ is the voltage variation in the time range measured, and $W$ is the weight of the two electrodes used.

3. Results and discussion

The SEM of the ACNFs are shown in fibers were Fig 2, PAN (a), MWCNT/PAN deposited with RuO2(b), and RuO2/PAN composite (c) based.

Fig. 1. Experimental procedures of activated nanofiber preparations (ACNFs).
aggregation of RuO$_2$ was observed from the deposition process, at high magnification. On the other hand, at high magnification (Fig.3), the deposition of is evenly distributed with the size of 2-3nm. The RuO$_2$/PAN composite based ACNFs shows the structure covered with RuO2 furs through the activation of the composite fibers(refer Fig.2-c).

The BET specific surface areas of the ACNFs were summarized in Table 1.

Table 1. BET specific surface areas of the ACNFs.

<table>
<thead>
<tr>
<th>RuO$_2$ (%)</th>
<th>*SSA (m$^2$/g)</th>
<th>RuO$_2$ (%)</th>
<th>*SSA (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1030</td>
<td>0</td>
<td>2180</td>
</tr>
<tr>
<td>15</td>
<td>434</td>
<td>15</td>
<td>912</td>
</tr>
<tr>
<td>20</td>
<td>314</td>
<td>20</td>
<td>675</td>
</tr>
</tbody>
</table>

* SSA: specific surface area

The specific surface area of the ACNFs decreased significantly with an increase in RuO$_2$ concentration. The electrical conductivity of the PAN based activated carbon nanofibers(ACNFs) increased from 0.42S/cm to 0.98S/cm by dispersions of 3wt% of MWCNT. And the electrical conductivity of the RuO$_2$/PAN composite ACNFs increased from 0.4 to 4.5 S/cm as the RuO$_2$ concentration increases up to 20%.

The capacitance of the electrode form various sources are summarized Table 2. The capacitances of the PAN only, MWCNT/PAN, RuO$_2$(20wt%)/PAN, RuO$_2$(20wt%)/MWCNT(3wt%)/PAN based ACNFs were 140, 180, 390, 530 F/g, respectively.

The value was increased by 4 times by addition of 3wt% of MWCNT and deposition of 20wt % of RuO$_2$. The electrodes of only 15wt.% RuO$_2$ composite without MWCNT showed a capacitance of 460F/g. The capacitance was more efficiently improved through the compositing than the depositing at lower than 15 wt% RuO$_2$.

Fig. 2. SEMs of ACNFs from various sources.
(a) PAN only, (b) MWCNT/PAN deposited with RuO2, (c) RuO2/PAN based composite ACNFs

![20 nm TEM image](image)

**Fig. 3.** TEM of the fiber deposited with RuO2 on the MWCNT/PAN based ACNFs

**Table 2.** Specific capacitance of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacitance (F/g)</th>
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<tbody>
<tr>
<td>PAN/10% RuO2</td>
<td>365</td>
</tr>
<tr>
<td>PAN/15% RuO2</td>
<td>460</td>
</tr>
<tr>
<td>PAN/20% RuO2</td>
<td>390</td>
</tr>
<tr>
<td>PAN/3% MWCNT/15% RuO2</td>
<td>400</td>
</tr>
<tr>
<td>PAN/3% MCNT/20% RuO2</td>
<td>530</td>
</tr>
</tbody>
</table>

The cyclic voltamogram shows the energy storage mechanisms (Fig.4). The CV of RuO2 deposited ACNF electrode shows that the capacitance was mostly contributed by double layered mechanism that represented by the absence of the faradaic reaction peak (Fig.4(a)). On the other hand, CV for the RuO2 composite ACNF shows REDOX reaction peaks representing the combined mechanisms, i.e., double layer and faradaic process (Fig. 4(b)).

![Cyclic voltamograms](image)

**Fig. 4.** Cyclic voltamograms of the samples.

(a) MWCNT/PAN deposited with RuO2,
(b) RuO2/PAN based composite

The Nyquist plots of the electrodes represent the various resistances (Fig.5). The internal resistance was reduced by the compositions with MWCNT as indicated by the smaller value on the X-axes for MWCNT/PAN in the absence of RuO2 than the PAN based ACNF. The mass transfer resistance represented by the slope of the Nyquist plots. The value increased by a deposition of the RuO2 (Fig. 5(a)), on the other hand, the RuO2 composite ACNF
electrodes showed a decrease with an increase in RuO2 concentration (Fig. 5(b)). The behaviors would be dependent not only on the internal resistance of the electrode but also surface characteristics of the electrode.

Acknowledgements
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References

Fig. 5. The Nyquist plots of the electrodes;
(a) MWCNT/PAN deposited with RuO2,
(b) RuO2/ PAN based composite