EFFECT OF CARBON SURFACE STRUCTURE FOR ENHANCEMENT OF PSEUDO-CAPACITANCE: RuO$_2$ ON CNFS

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Abstract

The pseudo-capacitance of RuO$_2$, NiO, and MnO$_2$ nano-particles supported on the various carbon nanofibers were examined. Among various CNFs, CNF with relatively higher crystallinity and better arranged edges on surface showed higher pseudo-capacitance than those with basal surface. Surface morphology and the particle size of metal oxide were characterized by HR-TEM and XPS. The electrochemical capacitance was evaluated using self-designed electrochemical experimental apparatus with cyclic voltammetry.

Introduction

Super-capacitor is classified into electrical double layer capacitor and pseudo-capacitor. Electrical double layer capacitance is formed by the charge separation between an electrode and an electrolyte. The pseudo-capacitance, in contrast, is originated by the chemisorption of active ion or the faradaic redox reaction of ions on the transition metal oxides and conductive polymers [Kim, H., 2003, Pandolfo, A.G., 2006].

Recently, the present authors reported the capacitive behaviors of EDLC on well-defined carbon nanofibers (CNFs) distinguished as edge and basal surfaces [Kim, T.G., 2006]. The CNF with edge surface was found to be more effective in electrochemical capacitive performance compared to the CNF with basal plane surface by a factor of 3-5. In this presentation, we tried to examine the effect of surface of CNF on the performance of pseudo-capacitance of RuO$_2$·xH$_2$O [Zheng, J.P., 1995].

Experimental

Preparation of highly dispersed and size-controlled ruthenium nanoparticles on CNFs

The carbon nanofibers of platelet-type CNF (PCNF), herringbone-type (HCNF) and tubular-type (TCNF) were synthesized through the pyrolysis of CO/H$_2$ or C$_2$H$_4$/H$_2$ on the catalysts of Fe, Ni-Cu (8:2) or Fe-Ni (2:8) [Tanaka, A., 2004, Yoon, S-H., 2004]. The ruthenium nanoparticles on the three types of
CNFs were facilely supported by thermal decomposition of organometallic precursor Ru₃(CO)₁₂ into CNFs by refluxing with toluene under argon atmosphere. The ICP-MS analysis revealed Ru contents of Ru/PCNF (1.6-1.7 wt%), Ru/HCNF (1.1-1.6 wt%) and Ru/TCNF (1.1-3.8 wt%), respectively [Motoyama, Y., 2006].

**Electrochemical measurement by cyclic voltammetry**

The capacitances of ruthenium oxide supported on PCNF, HCNF and TCNF were estimated by cyclic voltammetry on HZ-3000 automatic polarization system (Hokudo Denko, Japan). Adequate amounts of Ru/CNFs, distilled water and 5 wt% nafion solution (Wako, Japan) were mixed and sonicated to produce Ru/CNFs slurries. A certain aliquot of the slurry was spread uniformly on an Au disk, and dried under a halogen lamp for 20 min. Conventional three electrode system with 0.5 M H₂SO₄ solution (Min. 95.0 %, Wako, Japan), Ag/AgCl electrode ([Cl⁻] = 1 M) as a reference electrode and Pt gauze (52 mesh, 25 × 25 mm², Johnson Matthey, USA) as a counter electrode, were employed to carry out.

**Results and discussion**

Figure 1 shows TEM images of Ru/CNFs. Ru particles were well dispersed on surface of PCNF, HCNF and TCNF types. PCNF and HCNF provided homogeneous dispersions of ruthenium nanoparticles on the surface edges, whereas TCNF showed them both inside of the tube and on the basal surface. The XPS showed two Ru 3d₅/₂ signals of the zero-valence ruthenium and oxidized RuO₂.

![Figure 1](image_url)  
*(a) Ru/PCNF, (b) Ru/HCNF and (c) Ru/TCNF.*

Figure 2 shows the electrochemical capacitances of Ru/CNFs. Table 1 summarized measured capacitance values of Ru/CNFs. Ru/PCNF showed largest pseudo-capacitance of 79.0 F/g. The cyclic voltammograms of Ru/CNFs actually show symmetrical mirror-like shapes in 0.5 M H₂SO₄ electrolytes. The pseudo-capacitance increment by increased surface area of ruthenium oxide also brings increase of electrical double layer capacitance together [Zheng, J.P., 1995]. The electrical double layer capacitances
which induced from pristine CNFs were estimated to 12.5 (PCNF), 23.4 (HCNF) and 4.5 F/g (TCNF), respectively [Kim, T.G, 2006]. The pseudo-capacitances of ruthenium oxide on CNFs showed great increase by a factor of 3-8 with only 2 wt% loading.

![Cyclic voltammograms of ruthenium oxide on well-defined CNFs in 0.5 M H$_2$SO$_4$](image)

**Figure 2.** Cyclic voltammograms of ruthenium oxide on well-defined CNFs in 0.5 M H$_2$SO$_4$:

(a) Ru/PCNF, (b) Ru/HCNF and (c) Ru/TCNF (Scan rate: 10 mV/sec).

**Table 1.** Electrochemical capacitances of the ruthenium oxide on well-defined CNFs

<table>
<thead>
<tr>
<th></th>
<th>Electrochemical capacitances of Ru/CNFs (F/g)</th>
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<tbody>
<tr>
<td></td>
<td>Non-polarized</td>
</tr>
<tr>
<td>Ru/PCNF</td>
<td>79.0 ± 5.3</td>
</tr>
<tr>
<td>Ru/HCNF</td>
<td>54.7 ± 3.2</td>
</tr>
<tr>
<td>Ru/TCNF</td>
<td>38.4 ± 2.3</td>
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</tbody>
</table>

For further enhancement of the pseudo-capacitance, Ru/CNFs were polarized for 10 seconds at 1.1 V. The voltage of polarization was selected by the Ru stripping test, as shown in Figure 3. The capacitances
of Ru/CNFs with electrochemical polarization were further increased by a factor about 1.5 compared to non-polarized Ru/CNFs. In after-polarization, the capacitance was more increased to result in maximum capacitance after 2nd polarization.

![Cyclic voltammograms of Ru stripping test in 0.5 M H₂SO₄](image)

**Figure 3.** Cyclic voltammograms of Ru stripping test in 0.5 M H₂SO₄ (Scan rate was 10 mV/sec).

### Conclusions

The capacitances of ruthenium oxide on PCNF, HCNF and TCNF were evaluated as 79.0, 54.7 and 38.4 F/g, respectively. Suggesting edge surface of PCNF was more effective for the revelation of pseudo-capacitance. After electrochemical polarization, the capacitance of ruthenium oxide was further enhanced to 109.0. Well arranged edge of PCNF should be a important on the revelation of high pseudo-capacitance.

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### References


