

# EFFECT OF CARBON SURFACE STRUCTURE FOR ENHANCEMENT OF PSEUDO-CAPACITANCE: RuO<sub>2</sub> ON CNFS

*Taegon Kim, Hyung-Kuk Kim, Seongyop Lim, Yukihiro Motoyama, Masaharu Tsuji, Isao Mochida,  
Seong-Ho Yoon, IMCE, Kyushu University, Kasuga, Fukuoka 816-8580, Japan  
Choong Kyun Rhee, Dept. of Chemistry, Chungnam National University, Yuseong-Gu, Daejeon 305-764,  
Korea*

## Abstract

The pseudo-capacitance of RuO<sub>2</sub>, NiO, and MnO<sub>2</sub> 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<sub>2</sub>·xH<sub>2</sub>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<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> 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

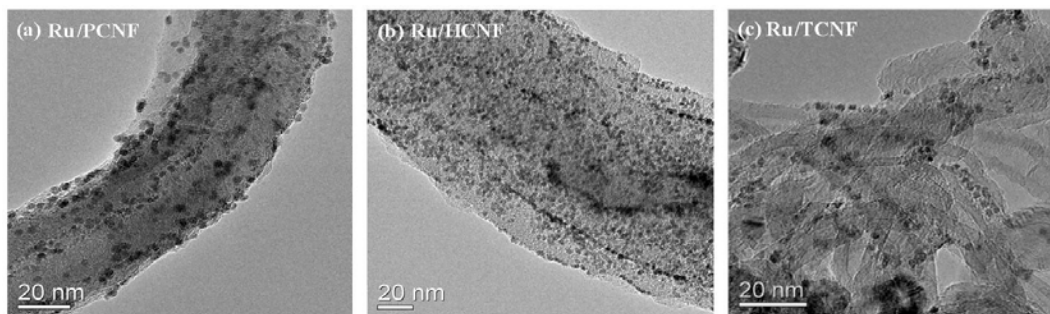
CNFs were facilely supported by thermal decomposition of organometallic precursor  $\text{Ru}_3(\text{CO})_{12}$  into CNFs by refluxing with toluene under argon atmosphere. The ICP-MS analysis revealed Ru contents of Ru/PCNF (1.6-1.7 wt%), Ru/HCNF (1.1-1.6 wt%) and Ru/TCNF (1.1-3.8 wt%), respectively [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  $\text{H}_2\text{SO}_4$  solution (Min. 95.0 %, Wako, Japan), Ag/AgCl electrode ( $[\text{Cl}^-] = 1 \text{ M}$ ) as a reference electrode and Pt gauze (52 mesh,  $25 \times 25 \text{ mm}^2$ , Johnson Matthey, USA) as a counter electrode, were employed to carry out.

### **Results and discussion**

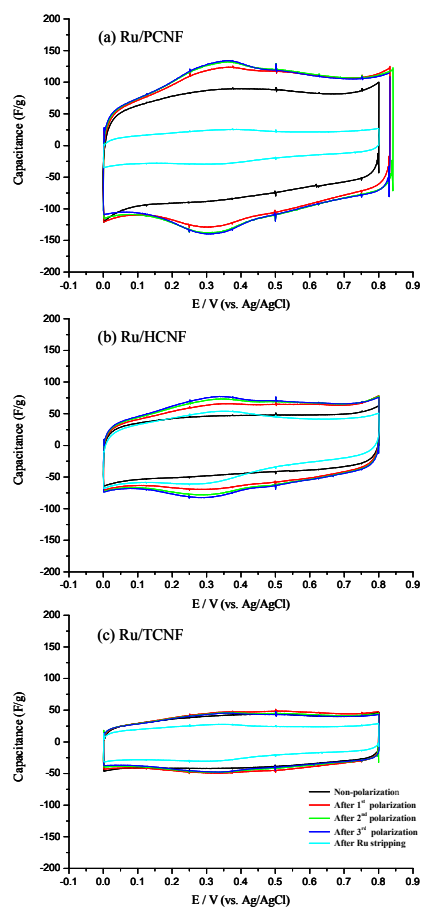
Figure 1 shows TEM images of Ru/CNFs. Ru particles were well dispersed on surface of PCNF, HCNF and TCNF types. PCNF and HCNF provided homogeneous dispersions of ruthenium nanoparticles on the surface edges, whereas TCNF showed them both inside of the tube and on the basal surface. The XPS showed two Ru  $3d_{5/2}$  signals of the zero-valence ruthenium and oxidized  $\text{RuO}_2$ .



**Figure 1.** TEM images of ruthenium oxide on well-defined CNFs : (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  $\text{H}_2\text{SO}_4$  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.



**Figure 2.** Cyclic voltammograms of ruthenium oxide on well-defined CNFs in 0.5 M H<sub>2</sub>SO<sub>4</sub> :

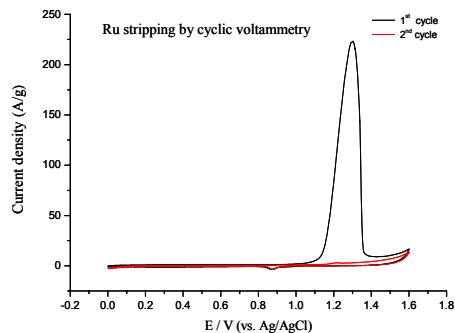
(a) Ru/PCNF, (b) Ru/HCNF and (c) Ru/TCNF (Scan rate: 10 mV/sec).

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

	Electrochemical capacitances of Ru/CNFs (F/g)			
	Non-polarized	Polarized	After Ru stripping	Pristine CNF
Ru/PCNF	79.0 ± 5.3	109.0 ± 3.1	22.5 ± 1.5	12.5 ± 1.2
Ru/HCNF	54.7 ± 3.2	67.4 ± 2.2	44.0 ± 1.0	23.4 ± 2.9
Ru/TCNF	38.4 ± 2.3	47.1 ± 2.7	28.6 ± 2.4	4.5 ± 0.6

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 2<sup>nd</sup> polarization.



**Figure 3.** Cyclic voltammograms of Ru stripping test in 0.5 M H<sub>2</sub>SO<sub>4</sub> (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.

## Acknowledgment

The work performed in Japan was carried out partially within the framework of CREST program. The authors in Japan acknowledge the financial support of Japan Science and Technology Corporation of Japan. On the other hand, the work performed in Korea was supported by the Next Generation Growth Engine Program funded by the Korean Government (MOCIE) (100283558).

## References

- Hansung, Kim and Branko, N. P. 2003. *J. Electrochem. Soc.*, 150, A1153-A1160.
- A.G. Pandolfo and A.F. Hollenkamp. 2006. *J. Power Source*, 157, 11-27.
- T.G. Kim, S.Y. Lim, K.H. Kwon, S-H. Hong, W. Qiao, C.K. Rhee, S-H. Yoon and I. Mochida. 2006. *Langmuir*, 22, 9086-9088.
- J.P. Zheng, P.J. Cygan and T.R. Jow. 1995. *J. Electrochem. Soc.*, 142, 8, 2699-2703.

- T.G. Kim, S.Y. Lim, K.H. Kwon, S-H. Hong, C.K. Rhee, S-H. Yoon and I. Mochida. 2006. *ACS National Meeting*, Division of Fuel Chemistry, 203, San Francisco, USA, September 10-14.
- A. Tanaka, S-H. Yoon and I. Mochida. 2004. *Carbon*, 42, 591.
- A. Tanaka, S-H. Yoon and I. Mochida. 2004. *Carbon*, 42, 1291.
- S-H. Yoon, S.Y. Lim, Y. Song, Y. Ota, W. Qiao, A. Tanaka and I. Mochida. 2004. *Carbon*, 42 (8-9), 1723-1729.
- Y. Motoyama, M. Takasaki, K. Higashi, S-H. Yoon, I. Mochida and H. Nagashima. 2006. *Chemistry Letters*, 35, 8, 876-877.