Electrochemical properties of arc-black and carbon nano-balloon as electrochemical capacitor electrodes

T Sato¹, Y Suda¹, H Uruno¹, H Takikawa¹, H Tanoue¹, H Ue², N Aoyagi³, T Okawa⁴ and K Shimizu⁴

¹ Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi Japan
² Tokai Carbon Co., Ltd. 394-1 Subashiri, Oyama, Sunto, Shizuoka, Japan
³ Daiken Chemical Co., Ltd. 2-7-19 Hanaten-Nishi, Joto, Osaka, Japan
⁴ Shonan Plastic Mfg. Co., Ltd. (31-27 Daikan, Hiratsuka, Kanagawa Japan

E-mail: suda@ee.tut.ac.jp

Abstract. In this study, we used two types of carbon nanomaterials, arc-black (AcB) which has an amorphous structure and carbon nano-balloon (CNB) which has a graphitic structure as electrochemical capacitor electrodes. We made a coin electrode from these carbon materials and fabricated an electric double-layer capacitor (EDLC) that sandwiches a separator between the coin electrodes. On the other hand, RuO₂ was loaded on these carbon materials, and we fabricated a pseudo-capacitor that has an ion insertion mechanism into RuO₂. For comparison with these carbon materials, activated carbon (AC) was also used for a capacitor electrode. The electrochemical properties of all the capacitors were evaluated in 1M H₂SO₄ aqueous solution. As a result of EDLC performance, AcB electrode had a higher specific capacitance than AC electrode at a high scan rate (≥ 100 mV/s). In the evaluation of pseudo-capacitor performance, RuO₂-loaded CNB electrode showed a high specific capacitance of 734 F/g per RuO₂ weight.

1. Introduction
Electrochemical capacitor (EC) has a high power density and a long lifetime. Then, EC is expected to be applicable to an electric vehicle. [1] ECs are distinguished by the difference of charging mechanism. There are two types of ECs: electric double-layer capacitors (EDLCs) and pseudo-capacitors (PCs). EDLC does not use a chemical reaction for charge/discharge and enables us to operate for a long cycle life. Commercial EDLCs employ inexpensive activated carbon (AC). On the other hand, PC, as represented by RuO₂ [2-6], has a different charge/discharge mechanism from EDLC, which is accompanied with a redox reaction and has a higher energy density than EDLC. However, Ru is expensive and Ru resources are limited.

Recently, novel carbon nanomaterials which have a high electric conductivity including carbon nanotube (CNT) [7-12], carbon nanofiber (CNF) [13-15], and graphene [16,17] are studied for EC. Fabrication of carbon nano-sheet is also studied for effective use of a high surface area of carbon materials. [12,16,17] Novel carbon nanomaterials have a lot of potential for EC application.

In this study, we used two types of carbon nanomaterials, arc-black (AcB) and carbon nano-balloon (CNB) which were developed in our laboratory, as EC electrodes and compared their electrochemical properties with activated carbon (AC). The applicability of AcB and CNB for EC
2.1. Electrochemical cell

The electrochemical cell used in this study is shown in Figure 1. The cell is made of two stainless steels and contains capacitor electrodes. When capacitor electrodes and liquid electrolyte are installed in the cell, the cell is evacuated by connecting with a rotary pump for degassing. The dimension of coin-shaped electrode for this cell was 20 mm diameter and 1 mm thickness. Two coin-shaped electrodes were separated by double sheets of polypropylene (PP) (Nippon Kodoshi Corporation, MPF0830). This separator has a role to separate between anion and cation in an electrolyte. 1M H$_2$SO$_4$ was used as an electrolyte.

2.2. Fabrication of EDLC

2.2.1. Preparation of carbon nanomaterials for EDLC

AcB was prepared by employing an arc discharge of graphite rod electrodes [18]. Carbon atoms and molecules vaporized by an arc discharge were cooled down in the chamber due to the collision with N$_2$ gas molecules and deposited on the chamber wall as AcB. CNB was prepared by calcination of AcB in Ar gas ambient at 2500°C.

The specific surface areas of carbon nanomaterials were measured by the Brunauer-Emmett-Teller (BET) method. The resistivities of carbon nanomaterials were measured by the compressive electrical resistivity method [19]. A 300 mg carbon nanomaterial was compressed under a load of 3.75 MPa when measured.

2.2.2. Fabrication of EDLC coin electrodes

Each of the carbon nanomaterial used (AcB, CNB, or AC) was mixed with a conductive carbon black (Ketjenblack : EC-600JD, Shanghai Fuhua Co., Ltd.) and a binder (PTFE). The mass ratio of carbon nanomaterial, Ketjenblack, and PTFE was 8:1:1, respectively. A 200 mg quantity of mixed material was placed in a jig and pressed at 14 MPa for 30 min to form a coin-shaped electrode. Two coin-shaped electrodes were separated with double sheets of polypropylene separators.

2.3. Fabrication of PC

2.3.1. Surface functionalization of carbon nanomaterials

Prior to RuO$_2$ supporting, the carbon nanomaterials were oxidized in 15% H$_2$O$_2$ aqueous solution at 120°C for 2 h to add surface functional groups such as the hydroxyl group (–OH) and carboxyl group.
The specific capacitance $C$ was calculated from the CV curve by the following formula [5]:

$$C = \frac{\int I \cdot dt}{2\Delta E}$$  \hspace{1cm} (1)

where $I$ is current, $dt$ is time step, and $\Delta E$ is operating voltage. The specific capacitance per electrode weight $C_m$ is given by the following formula:

$$C_m = \frac{C}{m}$$  \hspace{1cm} (2)

The specific capacitance per one electrode $C_s$ is given by the following formula:

$$C_s = 4C_m$$  \hspace{1cm} (3)

The internal resistance of the EDLC electrode $R$ was calculated by the following formula:

$$R = \frac{\Delta V}{I_{cd}}$$  \hspace{1cm} (4)

where $\Delta V$ and $I_{cd}$ are IR drop and discharge constant current, respectively. The charge/discharge current was 100 mA.

2.4. Characterization of carbon nanomaterials and analyses of EC performances

Thermogravimetric analysis was carried out to measure the supported amount of metal oxides in still air at a heating rate of 10°C/min with a thermal analysis instrument (TG/DTA: Shimadzu, DTG-60). The morphologies and structures of RuO$_2$ were analyzed by transmission electron microscopy (TEM: JEOL, JEM-2100F) and scanning electron microscopy (SEM: HITACHI, S-4500). The cyclic voltammetric (CV) behavior of the electrodes was determined using electrochemical analyzer systems (Hokuto Denko, HZ-5000).

The specific capacitance was calculated from the CV curve by the following formula [5]:

$$C = \frac{\int I \cdot dt}{2\Delta E}$$  \hspace{1cm} (1)

where $I$ is current, $dt$ is time step, and $\Delta E$ is operating voltage. The specific capacitance per electrode weight $C_m$ is given by the following formula:

$$C_m = \frac{C}{m}$$  \hspace{1cm} (2)

The specific capacitance per one electrode $C_s$ is given by the following formula:

$$C_s = 4C_m$$  \hspace{1cm} (3)

The internal resistance of the EDLC electrode $R$ was calculated by the following formula:

$$R = \frac{\Delta V}{I_{cd}}$$  \hspace{1cm} (4)

where $\Delta V$ and $I_{cd}$ are IR drop and discharge constant current, respectively. The charge/discharge current was 100 mA.

3. Results and discussion

3.1. Carbon nanomaterials used in this study

We used two types of carbon nanomaterial, arc-black (AcB) which has an amorphous structure and carbon nano-balloon (CNB) which has a graphitic structure as EC electrodes. Activated carbon (AC: YP-80F, Kuraray Chemical Co., Ltd.) was also used for comparison. Figure 2 shows SEM and TEM images of carbon nanomaterials. These properties are listed in Table 1. The AcB was diameter as large as CNB. The CNB resistance was lowest among all of carbon nanomaterials. The AC was largest specific surface area among three carbon nanomaterials.
3.2. EDLC performance

Figure 3 shows the CV curves of EDLC electrodes of AcB, CNB and AC at 5 and 7000 cycle operations. Figure 4 shows cycle performance of these three electrodes. Almost no decrease in specific capacitances of all the electrodes was observed up to 7000 cycles. Figure 5 shows the CV curve of the EDLC electrodes at different voltage scan rates, 1 and 100 mV/s. Figure 6 shows the result of specific capacitances of the AcB, CNB, and AC electrodes at different voltage scan rates. In a lower scan rate region (≤ 50 mV/s), the AC electrode had the highest specific capacitance. This is explained by that a high surface area of AC resulted in a lot of sites for electric double-layer in the AC electrode. In contrast, specific capacitance of the AC electrode becomes the lowest in a high voltage scan rate region (≥100 mV/s). This result is still under consideration. However, Liu, et al has shown a similar experimental result where the specific capacitance of AC electrode significantly decreased at a high voltage scan rate [21]. They considered that the many channel is required for ion transportation as the voltage scan rate is increased. It is reasonable to say that the ion channel was not formed well in our AC electrode. Though the particle sizes of AcB and CNB are almost the same, the surface area of AcB is more than 4 times higher than that of CNB as shown in Table 1. This is the reason maybe that specific capacitance of the AcB electrode became the highest at higher voltage scan rate.

Figure 7 shows charge/discharge curves of the EDLCs composed of the carbon nanomaterials. The internal resistance of the EDLC electrode \( R \) in Figure 7 was calculated by formula (4). \( R \) of the AcB, CNB, and AC electrodes were 1.5, 1.2, and 1.5Ω, respectively. The CNB electrode had the lowest \( R \).
and this is correlated with the lowest resistivity of CNB among three carbon nanomaterials used in this study.

**Figure 3.** Cyclic voltammograms of AcB, CNB and AC EDLC electrodes at different cycle operations.

**Figure 4.** Cycle performances of AcB, CNB and AC EDLC electrodes.

**Figure 5.** Cyclic voltammograms of AcB, CNB and AC EDLC electrodes at different voltage scan rates: (a) 1 mV/s and (b) 100 mV/s.

**Figure 6.** Specific capacitances of AcB, CNB and AC EDLC electrodes at different voltage scan rates.

**Figure 7.** Charge/discharge curves of AcB, CNB and AC EDLC electrodes.
3.3. Characteristics of carbon nanomaterials as a support material of RuO$_2$ for PC

TEM images of the RuO$_2$-supported carbon nanomaterials are shown in Figure 8. The characteristics of RuO$_2$-supported carbon nanomaterials are listed in Table 2.

![TEM images of RuO$_2$ supported carbon nanomaterials: (a)AcB, (b)CNB, and (c)AC.](image)

Figure 8. TEM images of RuO$_2$ supported carbon nanomaterials: (a)AcB, (b)CNB, and (c)AC.

Figure 9 shows the cyclic voltammograms of RuO$_2$-supported carbon nanomaterial electrodes. Specific capacitances of the RuO$_2$/AcB, RuO$_2$/CNB, and RuO$_2$/AC electrodes are respectively calculated. then this became 178, 170, 225 F/g from the results in Figure 9 (a).

Subtracting the specific capacitance of carbon nanomaterials in RuO$_2$-supported carbon electrodes from that of the total capacitance, the specific capacitance of RuO$_2$ was calculated and listed in Table 3. Specific capacitances of the RuO$_2$/AcB and RuO$_2$/CNB were almost the same. The pseudo capacitance of the RuO$_2$-supported carbon electrodes was much higher than their electric double-layer capacitance. The RuO$_2$/CNB electrode showed the highest pseudo capacitance per the RuO$_2$ mass as shown in Table 3. This indicates that CNB is suitable for support material of RuO$_2$ in PC.

Figure 10 shows charge/discharge curves of the RuO$_2$/C in PC. The internal resistances $R$ of RuO$_2$-supported AcB (RuO$_2$/AcB), CNB (RuO$_2$/CNB), and AC (RuO$_2$/AC) were 0.8, 0.6, and 0.6 $\Omega$, respectively. Each $R$ of the RuO$_2$/C shows respectively lower than that of carbon nanomaterial without RuO$_2$. These have an advantage in low output loss.

![Cyclic voltammograms of RuO$_2$/C electrodes at different voltage scan rates: (a)1 mV/s and (b)100 mV/s.](image)

Figure 9. Cyclic voltammograms of RuO$_2$/C electrodes at different voltage scan rates: (a)1 mV/s and (b)100 mV/s.
4. Conclusions
AcB and CNB electrodes of EDLC were shown to operate for a long cycle life. The AcB electrode for EDLC indicated the highest specific capacitance among all the carbon nanomaterials in a high voltage scan rate region (≥ 100 mV/s). The RuO$_2$/CNB electrode showed the highest pseudo capacitance per the RuO$_2$ amount among all the RuO$_2$/C electrode. These results indicate that AcB and CNB are respectively suitable for EDLC electrode and support material of RuO$_2$ in PC.

5. References
[1] Kandalker S G, Gunjakar J L, and Lokhande C D 2008 Applied Surface Science 254 5540-5544
[2] Hong J H, Han S, Hyeon T and Oh S M 2003 J. Power Sources 123 79-85
[3] Yue F S, Feng W, Li Y B and Zhao H Y 2007 New Carbon Materials 22(1) 53-58
[4] Kuratani K, Kiyobayashi T and Kuriyama N 2009 J. Power Sources 189 1284-1291
[5] Hu C C and Huang Y H 2001 Electrochimica Acta 46 3431-3444
[6] Ramania M, Harana B S, Whitea R E, Popova B N and Arsovb L 2001 J. Power Sources 93 209-214
[7] Chen J H, Li W Z, Wang D Z, Yang S X, Wen J G and Ren Z F 2002 Carbon 40 1193-1197

Table 2. Characteristics of RuO$_2$/Carbon electrodes

| RuO$_2$ load (wt.%) | Particle size of RuO$_2$ (nm) |
|---------------------|-------------------------------|
| RuO$_2$/AcB         | 20.4                          |
| RuO$_2$/CNB         | 21.2                          |
| RuO$_2$/AC          | 20.8                          |

Table 3. Specific capacitances of RuO$_2$/C electrodes

| Total specific capacitance (F/g) | component of carbon nanomaterials (F/g) | component of RuO$_2$ (F/g) |
|----------------------------------|-----------------------------------------|----------------------------|
| RuO$_2$/AcB                     | 178                                     | 37                         |
| RuO$_2$/CNB                     | 170                                     | 20                         |
| RuO$_2$/AC                      | 225                                     | 101                        |

Figure 10. Charge/discharge curves of RuO$_2$/C electrodes.
[8] Ma R Z, Liang J, Wei B Q, Zhang B, Xu C L and Wu D H 1999 J. Power Sources 84 126-129
[9] Liu C G, Fang H T, Li F, Liu M and Cheng H M 2006 Journal of Power Sources 160 758-761
[10] Lu W, Qu L, Henry K and Dai L 2009 J. Power Sources 189 1270-1277
[11] Ye J S, Liu X, Cui H F, Zhang W D, Sheu F S and Lim T M 2005 Electrochemistry Communications 7 249-255
[12] Y Honda et al 2008 J. Power Sources 185 1580-1584
[13] Kim C, Park S H, Lee W J and Yang K S 2004 Electrochimica Acta 50 877-881
[14] Seo M K and Park S J 2009 Materials Science and Engineering B 164 106-111
[15] Kim B H, Yang K S, Kim Y A, Kim Y J, An B and Oshida K 2011 J. Power Sources 196 10496-10501
[16] Li Y, Zijll M V, Chiang S and Pan N 2011 J. Power Sources 196 6003-6006
[17] Chen Y, Zhang X, Yu P and Ma Y 2010 J.Power Sources 195 3031-3035
[18] Oke S et al 2009 Chem. Engineering 146 434-438
[19] Ikeda T et al 2011 Jpn. J. Appl. Phys. 50 01AF13
[20] Uruno H et al 2010 IEEJ Trans. Fund. and Materials 130-A(3) 293-294
[21] Liu G, Kang F, Li B, Hang Z and Chuan X 2006 J.Phys. and Chem. of Solids 67 1186-1189