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Improving the characteristic of electric double layer capacitors using oxidized carbon nanoballoon

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ABSTRACT

Carbon nanomaterials are used as an electrode of electric double layer capacitors (EDLCs). In this research, we used arc black (AcB) and carbon nanoballoon (CNB) as the electrode material. AcB was produced by an arc discharge of graphite in N_2 atmosphere, and CNB was formed by a heat treatment of AcB. CNB is graphitic, and the particle shape is hollow. CNB has a higher specific capacitance than AcB at a high scan rate. In order to increase the specific capacitance of EDLC, CNB was oxidized at 625 °C in the air. By oxidization, the outer shell of CNB forms wrinkle. We call this material oxidized CNB (Ox-CNB). AcB, CNB, and Ox-CNB were used for the EDLC electrodes and were compared with commercially available activated carbon (AC). Cyclic voltammetry and electrochemical impedance spectroscopy of the EDLC electrodes were measured by an electrochemical measurement system. The specific capacitance of Ox-CNB (29 F/g) was larger than that of AC (16 F/g) at a scan rate of 500 mV/s. Furthermore, Ox-CNB had a high conductivity as a result of impedance measurement. Ox-CNB is an excellent electrode material of EDLC when using at a high charge/discharge rate.

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1. Introduction

The reduction of CO_2 emissions from cars has recently become an important issue, and the development of rechargeable batteries and fuel cells for powering hybrid electric vehicles (HEVs) or electric vehicles (EVs) is now in progress [1]. The Li-ion battery has a high energy density and therefore is widely used [2,3]. However, it is beset with problems, such as deterioration of a battery when using in large-current as a regeneration brake system or fast charge as acceleration of a vehicle [4]. The hybridization of electrochemical capacitors and rechargeable batteries has been proposed and discussed by several authors in order to reduce the deterioration of rechargeable batteries [5,6]. In this research, we study electric double layer capacitors (EDLCs) which have an advantage in quick charge/discharge like the rapid acceleration/deceleration of a vehicle. EDLCs perform charge and discharge by the electric double layer which arises in the interface of an electrode and electrolyte. Furthermore, any metal materials are not used for the electrode. EDLCs do not use redox reactions. Therefore, EDLCs have advantages that provide higher specific power and perform longer cycle life compared with rechargeable batteries [7–9]. Because the discharge amount of EDLCs depends on the electron transport between electrodes, the conductivity of an electrode is strongly related to the charge and discharge capability of EDLCs. Additionally, the amount of electric charge stored is proportional to the number of adsorbed ions. Simply, the specific surface area of electrode materials is large, so the specific capacitance of the EDLC is large [10]. Activated carbon (AC) is commonly used for the EDLC electrode because of its large specific surface area [11–15]. AC is a main material which is used for all of commercially available EDLC electrodes. These EDLCs can be used in HEVs and EVs. However, the specific capacitance of AC is decreased in rapid charge/discharge use because its conductivity is low. Therefore, researches study carbon nanomaterials including carbon nanotube and graphene which can be replaced with AC [16,17]. In our previous study, we improved both of the specific capacitance and conductivity of EDLCs by using a mixture of arc black (AcB) and carbon nanoballoon (CNB) [18]. AcB was synthesized by arc discharge [19]. CNB was produced by heating AcB at

2400 °C [20]. In this study, oxidized carbon nanoballoon (Ox-CNB) was prepared by oxidizing CNB. Ox-CNB has a larger specific surface area than CNB and has conductivity as high as CNB. We intended to improve the performance of EDLCs in rapid charge/discharge use using Ox-CNB.

2. Experimental

2.1. Synthesis of carbon nanomaterials

Arc black (AcB) was prepared using a twin-torch arc discharge apparatus [18]. AcB is synthesized by arc discharge between graphite electrodes in N_2 gas. This apparatus can synthesize AcB continuously by pushing out the electrodes using a motor. AcB is mainly composed of cocoon-shaped carbon nanoparticles with a lot of amorphous ingredients [21–25].

Carbon nanoballoon (CNB) was obtained by heating AcB in a Tammann oven in Ar gas above 2000 °C for 2 h. CNB has a high electrical conductivity and consists of hollow particles. The number of graphitic layers of CNB increases and its shell becomes thick with increasing the heating temperature [19]. In this research, CNB was prepared at 2600 °C.

Oxidized CNB (Ox-CNB) was prepared by heat treatment of CNB in the air using an electrical furnace. The treatment temperature was raised to 625 °C in an hour and kept at 625 °C for an hour.

The prepared AcB, CNB and Ox-CNB were observed using transmission electron microscopy (TEM; JEOL JEM-2100F). Thermogravimetric analysis (TGA; Shimadzu DTG-60/60H) with two kinds of ambient was carried out under the conditions: the ambient, dry air and N_2; the temperature increment, 10 °C/min. Laser Raman spectroscopy (JASCO NRS-1000, excitation wavelength: 532 nm) was used to evaluate the crystallinity of the materials.

2.2. Preparation of EDLC electrodes

In this study, we used a typical two-electrode cell with two symmetric coin-type electrodes for the electrochemical measurement of the EDLCs. Activated carbon (AC; YP80F, provided by Kuraray Co. Ltd.) was used as a comparison material. First, 10 mg of polytetrafluoroethylene (PTFE) dispersion liquid was dropped onto 90 mg of AcB, CNB, and Ox-CNB. AC was mixed with Ketjen black (KB) and PTFE by weight ratio of 80:10:10. Then each of them was mixed for 15 min by an automatic mortar (Nitto Kagaku ANM-1000). 100 mg of the mixed material was put into the jig (inner diameter: 15 mm). The jig was pressed by 14 MPa for 30 min at room temperature.

The materials were put into a two-electrode cell in the following order: collector electrode (Nilaco SUS 304 foil), prepared electrode, separator (Nippon Kodoshi MPF0830), prepared electrode, and collector electrode. 1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) in propylene carbonates (PC) were used as electrolysis solution. All these cells were assembled in a glove box filled with pure N_2 gas. We also prepared EDLCs with 1 M H_2SO_4 solution in order to compare the EDLCs in organic electrolyte with those in aqueous electrolyte.

2.3. Electrochemical measurement

An electrochemical measurement system (Hokuto Denko HZ-5000) was used for the electrochemical measurement. The electrochemical measurements were performed using Et_4NBF_4 and H_2SO_4 electrolytes. Cyclic voltammetry, galvanostatic charge/discharge tests and electrochemical impedance measurement, which are general techniques for the electrochemical measurement of EDLC, were used. The result obtained by cyclic voltammetry is called a cyclic

Table 1
Characteristics of carbon nanomaterials.

	Crystal structure	G/D ratio	Particle size (nm)	BET specific surface area (m²/g)
AcB	Amorphous sphere	0.77	20-50	152
CNB	Graphitic hollow sphere	3.05	20-50	35
Ox-CNB	Graphitic wrinkle	1.22	20-50	153
AC	Porous sphere	0.75	5000-20000	2165

voltammogram (CV). From CV, the specific capacitance C [F/g] of EDLCs was calculated by eq. (1) [26].

$$C = \frac{2\int I \cdot dV}{\Delta V} \cdot \frac{1}{m} \tag{1}$$

Here, m [g] is the weight of the active material, I [A] is the current, V [V] is a potential window (2.5 V) for Et_4NBF_4, and ΔV [V/s] is the voltage scan rate. CVs were also performed in H_2SO_4 electrolyte under a potential window from 0 to 1 V, and compared with those in Et_4NBF_4 electrolyte.

Galvanostatic charge/discharge tests were performed under a potential window from 0 to 2.5 V and various current densities: 0.1, 0.5, 1, 1.5, 2 A/g (Et_4NBF_4). Power density P [W/kg] and energy density E [Wh/kg] of EDLCs were calculated using eq. (2) and (3).

$$P = \frac{I(V_1 - V_2)}{2} \cdot \frac{1000}{m} \tag{2}$$

$$E = \frac{I \Delta t \Delta V}{2} \cdot \frac{1000}{m} = \frac{C(\Delta V)^2}{2} \cdot \frac{1000}{m} \tag{3}$$

Here, V_1 [V] and V_2 [V] are voltages at 80% and 40% of the potential window ΔV, respectively, and Δt [s] is the discharge time. Then, the EDLC composed of Ox-CNB was discharged 10000 times in Et_4NBF_4 by a current density of 1 A/g in order to verify the cycle stability of the Ox-CNB electrodes.

The electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 10 mHz to 100 kHz and at an amplitude of 10 mV [27]. The double layer capacitance C_{dl} [F/g] from Nyquest plots were given by following eq. (4).

$$C_{dl} = -\frac{1}{2\pi f(ImZ)} \cdot \frac{1}{m} \tag{4}$$

Here f [Hz] is the frequency of applied voltage and Im Z [Ω] is an imaginary part of the impedance of a certain frequency.

3. Results and Discussion

3.1. Characterization of synthesized carbon nanomaterials

The characteristics of AcB, CNB, Ox-CNB and AC are summarized in Table 1. Fig. 1 shows their TEM images. There is little difference between the sizes of AcB, CNB and Ox-CNB, and their diameters are approximately 20 - 50 nm. The TEM image contrast of CNB between its surface and inside is larger than that of AcB. This shows that CNB has a hollow structure. The thickness of the outer shell of CNB is approximately 5 nm, and the number of graphite layers is from several to ten. CNB contains some five-membered rings in the graphite layers. This is the reason for that the graphite shell of CNB makes an angle and CNB forms spherical shape [19]. The chemical compositions of AcB and CNB were measured by an X-ray photoelectron spectroscopy and their oxygen contents showed almost no difference. (See Supplementary data, Fig. S1.) The number of graphite layers of Ox-CNB is as many as that of CNB. However, it was observed that the outer shell of Ox-CNB is partly broken and has a wrinkle shape (Fig. 1(f)). The parts enclosed with red circles in