The Influence of Graphitic Structure of Carbon Electrode on Aging Behavior of Electric Double Layer Capacitor

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ABSTRACT

The double-layer capacitors and their degradation after aging process for nano-fibrous carbon electrodes with various graphitic structures have been compared. The nano-fibrous carbon with amorphous structure has successfully been prepared from biomass precursor. The nano-fibrous carbons with graphitic and amorphous structures exhibit similar specific surface area and double-layer capacitance. However, the change of the capacitances of the cells consisting of both carbons by the aging process under high temperature and high voltage condition are different. The amorphous nano-fibrous carbon electrode provides capacitance decrease by the deposit on electrode, while the graphitic nano-fiber provides capacitance increased likely due to the gas evolution.

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1. Introduction

Electric double layer capacitors (EDLCs) are rechargeable electrical energy storage devices based on the capacitance of electric double layer without charge transfer reaction. Therefore, EDLCs have been expected to have long cycle life compared with batteries.^{1–3} However, practical EDLCs frequently show severe capacitance degradation at shorter time than expected. Many attempts have been made to understand the degradation mechanism for EDLCs. Such parasitic reactions as the decomposition of electrolyte or deformation of electrode have been proposed as the cause of the degradation. The existences of moisture impurity in non-aqueous or surface oxygen-containing functional groups can also promote the decomposition of electrolyte.^{4–10}

For most carbonaceous materials, surface functional groups exist on the edge of graphitic planes. Therefore, the graphitic structure of carbon electrode is expected to give significant influence on the aging behavior for EDLCs. However, the detail of such influence is still unclear. The difficulty of revealing the degradation mechanism is arisen by the closed pore structure of activate carbon (AC) electrodes used in conventional EDLCs devices.^{11–13} In the present study, fibrous nano-carbons having an exposed outer surface were applied in order to elucidate the effects of graphitic structure of carbon surface. Vapor-grown carbon fiber (VGCF) has been well known as fibrous nano-carbon with exposed graphene surface. Here alternative fibrous nano-carbon with amorphous carbon structure has been prepared by the carbonization of cellulose fiber derived from biomass, and its electrochemical behavior, in particular concerning on aging, is compared with VGCF.

2. Experimental

2.1 Preparation of fibrous nano-carbon derived from biomass

An edible gel consisting of nano-fibrous cellulose named as ‘Nata-de-Coco’ has used as a carbon precursor.¹⁴ The ‘Nata-de-Coco’ gel was milled and dispersed in de-ionized water, with ultrasonic treatment for the removal of impurity contained. Then, the suspension was filtrated, washed with de-ionized water several times, and dried to remove entrapped water. The obtained cellulose

nano-fiber was carbonized at 1273 K under the argon flow, with heating rate of 10 K min^{−1}. The content of impurity in the product was confirmed by X-ray diffraction (XRD; Ultima IV Protectus, RIGAKU, Japan) and the elemental analyses. The obtained biomass-derived carbon nano-fiber, here-after denoted as BCNF, was characterized by transmitted electron microscope (TEM; JEM-6320F, JEOL, Japan). Surface area and pore structure of BCNF was estimated from nitrogen adsorption (NOVA2000, Quantachrome) isotherm. VGCF was purchased from Showa Denko Co.

2.2 Electrochemical studies of fibrous nano-carbon electrodes

Powder of BCNF or VGCF was molded with 10 wt% of poly(tetrafluoroethylene) (PTFE; Mitsui Fluorotech Co., Japan) binder, cut into disk shape with 7 or 12 mm in diameter and 0.30 mm of thickness. The masses of BCNF electrodes are approximately 7.0 or 24 mg, and those of VGCF are 4.0 or 13 mg, respectively. PTFE-lined sealed cells, 3-electrode configuration with a carbon/PTFE disk as working electrode, a platinum plate as counter electrode, and silver wire as quasi-reference electrode for cyclic voltammetry (CV) and 2-electrode configuration with two carbon/PTFE disks with similar diameter placed at both side of glass fiber separation for the constant-current tests, were assembled, respectively. The solution, 1 mol dm^{−3} tetraethyl ammonium tetrafluoroborate (TEABF₄; Kishida Chemicals Co., Japan) dissolved into propylene carbonate (PC; Kishida Chemicals Co., Japan) was used as electrolyte. Each cell was assembled in a glove box filled with argon, and placed in a sealed vessel for measurements outside of the glove box. Cyclic voltammetry was measured by using a potentiostat (Versastat4, Princeton Applied Research Inc.) between −1.0 and 1.0 V at the scan rate of 50 mV s^{−1}. The constant current charge-discharge experimental was conducted under such conditions the cut-off voltage of 0 to 2 V, and the prescribed current, using a cycler (BTS-2004 Nagano Co., Japan).

The aging behavior of each electrode was monitored by the following sequence; the constant-voltage storage was conducted at 3.5 V for 100 h under the constant temperature of 333 K controlled by a temperature chamber (SU-241, Espec Co., Japan). The cell capacitances were estimated from the discharge profiles on the constant current charge-discharge test was conducted at 0.1 mA per

Figure 1. TEM images of nano-fibrous carbons. (a) BCNF, (b) VGCF.

square geometric area of electrode under the cut-off voltage of 0 to 2 V on 2-electrode cell at room temperature, using a cyclic (BTS-2004 Nagano Co., Japan). The cell resistance of the BCNF and VGCF cells electrode after these discharging processes was confirmed by AC impedance measurements using the same apparatus as frequency response analyzer. The frequency region and AC amplitude applied in these measurements were from 10^6 to 10^{-2} Hz, and 10 mV from OCV. The morphology of each carbon electrode after aging was observed by using scanning electron microscope (SEM; VE-8800, Keyence Co., Japan).

3. Results and Discussion

3.1 The structure of BCNF

The TEM image of BCNF and VGCF are shown in Fig. 1. Both carbons have similar fibrous feature with tens of nanometer in diameter. VGCF shows the microstructure with graphitic planes along fiber direction. In contrast, BCNF shows confirmed amorphous micro-texture. From elemental analysis, BCNF consists of 90 wt% carbon, 2 wt% hydrogen, and 7 wt% oxygen, while VGCF consists of 99 wt% carbon. The ash contents in BCNF are less than 1 wt%. The oxygen content on BCNF suggests the existence of many functional groups on its surface. The surface areas of VGCF and BCNF calculated from nitrogen adsorption isotherm are 20 and $28 \text{ m}^2 \text{ g}^{-1}$, respectively. In addition, the pore size distributions of both fibrous nano-carbons show no characteristic peaks, indicating smooth surface structures of these fibrous nano-carbons.

3.2 Electrode properties of fibrous nano-carbon

The cyclic voltammograms of VGCF and BCNF under the scan rate of 50 mV s^{-1} are shown in Fig. 2. Both carbon electrodes exhibit typical rectangular voltammograms of double-layer capacitor electrode without redox current. The specific capacitance values calculated from the voltammograms are 1.2 and 0.8 F g^{-1} for BCNF and VGCF, respectively. The specific capacitance values divided by their specific surface area for BCNF and VGCF are 4.3 and 4.0 F cm^{-2} , respectively. The capacitance per unit surface area of BCNF is similar to that of VGCF, regardless of the graphitic structure.

3.3 Aging behavior of each carbon electrode

The charge-discharge profiles under constant-current 0.1 mA cm^{-2} before and after aging experience are shown in Figs. 3(a) and 3(b) for the BCNF and the VGCF cells, respectively. Both fresh cells exhibit typical EDLC charge-discharge profiles with good efficiency. The difference of capacitance for both fresh cells is caused by the difference in the mass of electrode. After the aging process, the charging profiles of both cells show plateau above 1.75 V. The capacitance of BCNF decreases significantly by aging. In contrast, the capacitance of VGCF increases. The capacitance

Figure 2. Cyclic voltammograms of nano-fibrous carbon electrodes. Scan rate: 50 mV s^{-1} .

Figure 3. Charge-discharge profiles of the EDLC cells consisting of nano-fibrous carbon electrodes. Current density: 0.1 mA cm^{-2} . (a) BCNF cell, (b) VGCF cell.

Figure 4. Charge-discharge profiles for the EDLC cells consisting of nano-fibrous carbon electrodes. Current density: 0.1 mA cm^{-2} . (a) BCNF cell, (b) VGCF cell.

values of the BCNF and the VGCF cells are 0.23 and 0.15 F g^{-1} , and those of after aging are 0.18 and 0.25 F g^{-1} , respectively.

The potential changes of positive and negative electrode on 2-electrode cell for BCNF and VGCF are estimated by applying silver reference electrode. The potential profiles are shown in Figs. 4(a) and 4(b) for the BCNF and VGCF cells, respectively. The capacitances appear to be limited by the negative electrode for the cells regardless of aging. In addition, negative electrode of the BCNF cell on fresh cell, a plateau potential change is observed likely due to the side reaction. After aging, a plateau is observed at the profiles of both positive and negative electrodes for the BCNF cell, while in case of VGCF it appears only negative side.

The Nyquist plots of fresh cells and after aging are shown in Figs. 5(a) and 5(b) for the BCNF and VGCF cells, respectively. The Nyquist plots of BCNF show only 45° slope, indicating diffusion-limited process, and vertical rise, indicating ideal capacitor behavior, without semicircle. After aging, 45° slope regions become extended with increase of Z' intercept of high frequency region, indicating series resistance component. In constant, those of VGCF show a vertical rise with the small semicircle and on fresh cells, and show increase of the semicircle resistance after aging.

Figure 5. Nyquist plots for fresh EDLC cells and the cells after aging in the immersion voltage. (a) BCNF cell, (b) VGCF cell.

Figure 6. SEM images of the electrodes after the aging test. (a) BCNF positive electrode, (b) BCNF negative electrode, (c) VGCF positive electrode, (d) VGCF negative electrode.

The morphologies of electrodes after aging observed by SEM are shown in Fig. 6. The negative electrode of the BCNF cell in Fig. 6(b) shows some coverage with deposits. In contrast, the positive and negative electrodes of the VGCF cell rather show fibrous textures, similar to the fresh situation. The change TEM images of VGCF before and after aging are indicated in Fig. 7. The electrode after aging shown in Fig. 7(b) has somewhat amorphous surface, while the fresh VGCF shows graphitic surface structure. Such the change of surface graphitic structure is related to the increase of specific capacitance.

From SEM and TEM observation, the products on aging process are different between BCNF and VGCF. Therefore, the capacitance degradation of BCNF is due to the decrease of the effective surface area of carbon electrode, while, etching of graphene edges by evolved gas may increase the surface area of VGCF and then increase its capacitance. The difference of aging behavior is conjectured due to the difference of structure between the carbon electrodes. However, presently it is still unclear which factors dominantly contribute the reaction. Based on these results, as electrode materials for EDLC with high durability, the carbon

Figure 7. (Color online) TEM images of fresh VGCF and the positive electrode after aging. (a) Fresh VGCF, (b) After aging.

materials with rich graphitic basal plane on its surface are advantageous compared with amorphous carbons.

4. Conclusion

Amorphous fibrous nano-carbon, BCNF was prepared from biomass cellulose. BCNF has specific surface area of $28 \text{ m}^2 \text{ g}^{-1}$, and oxygen-containing functional groups. The influence of graphitic structure of carbon electrode on the aging process can be elucidated by comparing the aging behavior of the cell consisting of between BCNF and VGCF. Amorphous BCNF provides similar capacitance per unit surface area to VGCF, regardless of the different graphitic structure. On accelerating aging test by the constant voltage of 3.5 V and high temperature, BCNF provides the degradation of cell capacitance because of decreasing effective surface area of carbon electrode by deposit. In contrast, VGCF provides the increase of capacitance by surface etching.

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