Capacitance Properties and Durability of Various Single-Walled Carbon Nanotube Electrodes for Electric Double Layer Capacitor

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ABSTRACT

Recently, the single-walled carbon nanotube (SWCNT) has been the focus as a durable electrode with a high rate performance for the electric double layer capacitor (EDLC). However, it has not yet been clarified whether these reported outstanding properties are universal for all SWCNTs. The authors compared various self-standing SWCNT membranes (buckypapers) as the EDLC electrode to evaluate their stability to a floating high-voltage charge. Some SWCNTs exhibited an excellent rate performance even after the floating durability test, but other electrodes were degraded and showed a lower capacitance-retention. This variability in the durability for the SWCNTs can be attributed to the presence of residual metal impurities. Thus, it should be noted that the purity is a significant factor when using SWCNTs as the EDLC electrode, in addition to the nano-structure design from the viewpoint of operation stability.

Keywords : Single-walled Carbon Nanotube, Electric Double Layer Capacitor, Durability, Impurity

1. Introduction

The electric double layer capacitor (EDLC) is an electric energy storage device using the electric double layer formed on the interface between the electrolyte and nanoporous carbon electrode such as activated carbon. The charge-discharge mechanism of the EDLC is a non-faradaic process (physical process) by adsorption/desorption of electrolyte ions at the electrode surface. Thus, the EDLC exhibits excellent properties for power density and long cycle-life. However, the energy density of the EDLC is much lower than that of rechargeable batteries based on a faradaic process (electrochemical reaction). The electric energy stored in the EDLC is expressed by Eq. (1).

$$E = \frac{CV^2}{2}$$

Where, $E$ is the stored energy of the EDLC, $C$ is the electric double layer capacitance, and $V$ is the operating voltage. This equation indicates that the capacitance and the operating voltage of the EDLC should be improved in order to increase the energy density. In most previous studies, many researchers have investigated the correlation between the capacitance and the pore structures, such as the specific surface area and the pore size distribution of the activated carbon electrode. For example, the gravimetric capacitance almost increases with the increasing specific surface area, but the volumetric capacitance, which is significant for practical use, is not proportional to the surface area. This suggests the difficulty in improving the volumetric capacitance and energy density only by optimizing the pore structure of the nanoporous carbon electrode.

Nanocarbons, such as the carbon nanotube, carbon nanohorn, and graphene, are the focus as active materials for the EDLC since they have properties superior to the conventional activated carbons. The specific capacitance per surface area (areal capacitance) of the single-walled carbon nanotube (SWCNT) electrode in an organic electrolyte is relatively higher than that of activated carbons. It is also reported that the operating voltage range of the EDLC is widened by using the carbon nanotube or graphene electrode. For example, the capacitance-retention of the EDLC using the SWCNT electrodes prepared by the super-growth method is 96.4% after the charge/discharge cycle test of 2000 cycles at the operating cell voltage of 0–4 V. The high durability for the SWCNT electrode is considered to be due to a small number of electrochemically active sites for electrochemical decomposition between the carbon surface and electrolyte. The decomposition reaction causes a capacitance decline that decreases the energy density. Therefore, the SWCNT is a promising electrode material for the EDLC, however, it has not yet been clarified that these superior properties are universal for all SWCNTs.

Based on this background information, the authors evaluated the capacitance and the durability against high voltage charge of the EDLC using various SWCNTs to confirm the universal properties as the electrode active material for the EDLC. The SWCNTs prepared by the HiPco method, super-growth method, and enhanced direct injection pyrolytic synthesis (dIPS) method were used for this research. They are suitable for this research purpose since all of them have few carbon particles as an impurity to fabricate a paper-like self-standing membrane (bucky-paper). It is very important to cancel any influence of the carbon impurity, conductive additive, and electrode binder and to evaluate the electrode performance by comparison to the typical activated carbon electrode for the EDLC. Thus, this paper addresses the capacitance and the durability for five types of SWCNT self-standing paper electrodes in an organic electrolyte using the data of the typical activated carbon electrode for the EDLC under the same experimental evaluation conditions.
2. Experimental

2.1 Materials

In this study, five types of SWCNTs derived from the chemical-vapor deposition (CVD) process were used as samples. An unpurified (tube diameter: 0.8–1.2 nm, Lot. No. Hp-86, 10518-53156) or purified type (Lot. No. Hp-93s17) of the SWCNTs prepared by the HiPco method was purchased from Carbon Naotechnologies, Inc. An SWCNT manufactured by the super-growth method (ZEONANO® SG101, tube diameter: 3–5 nm, Lot. No. T66220) was obtained from Zeon Nano Technology Co., Ltd. An SWCNT prepared by eDIPS was purchased as dispersion ink (EC-DH, tube diameter: about 1.5 nm, Lot. No. 92001) from Meijo Nano Carbon Co., Ltd. These SWCNTs by the HiPco (unpurified and purified), super-growth, and eDIPS methods were hereafter referred to as HP, P-HP, SG, and ED, respectively.

2.2 CO2-activated SWCNT

The SG was activated by CO2 to increase the specific surface area in accordance with the following procedure. ZEONANO® SG101 was heated to 800 °C at the rate of 5 °C min⁻¹ and held at 800 °C for 2 h in a nitrogen gas flow. The activated yield was 87%.

2.3 Characterization

The SWCNTs were characterized by scanning electron microscopy (SEM) observations and energy dispersive X-ray spectroscopy (EDS) using a JSM-6510A (JEOL Ltd.). Nitrogen gas adsorption/desorption measurements were also carried out at 77 K using a BELSORP28SA (MicrotracBEL Co.) to characterize the pore structure. The specific surface area (SSA) was obtained by the BET method according to the literature. The volume of mesopores (Vmeso), volume of micropores (Vmicro), and mean micropore width (wmicro) were calculated by the Dollimore-Heal (DH) and Dubinin-Radushkevich (DR) analyses of the adsorption isotherms, respectively.

2.4 Electrode preparation

Each SWCNT (40 mg) was dispersed in methanol (100 mL) by ultrasonic irradiation for 40 min to prepare the SWCNT suspension. The self-standing SWCNT sheets were fabricated by filtering the SWCNT dispersions through a poly(tetrafluoroethylene)-based porous membrane. The SWCNT disks (ca. 6–9 mg, 15.5 mm in diameter) were punched out from the SWCNT sheet and attached to an etched Al foil current collector and dried for 12 h at 80 °C to prepare the activated SWCNT electrode. The activated yield was 87%.

2.5 Capacitance performance evaluation

The SWCNT and YP50F electrode were prepared by the following steps. In this study, YP50F (Kuraray Co., Ltd.) was used as the typical activated carbon for the EDLC. YP50F (1 g), acetylene black (Denka black, Denka Co., Ltd.) and poly(vinylidene fluoride)-based binder (L9305, KUREHA Co.) were mixed in the mass ratio of 80:10:10, then an appropriate amount of N-methyl-2-pyrrolidone was added to prepare the slurry paste. This slurry was coated on the etched Al foil current collector and dried for 12 h at 80 °C to fabricate the YP50F electrode sheet. The YP50F test electrode (ca. 8 mg, 15.5 mm in diameter, bulk density of 0.5 g cm⁻³) was punched out from the sheet. The weight, thickness, and bulk density of each electrode were summarized in Table S-1.

3. Results and Discussion

3.1 Electrode surface morphology and chemical composition

Figure 1 and Fig. S1 show the SEM images for the five SWCNT electrodes. The elemental compositions of the electrodes are summarized in Table 1. All the electrodes had the typical bundle structure for the SWCNT. For the SG and A-SG, the bundle was wider than those of the original SWCNTs. According to the data from the suppliers as shown in the experimental section, the tube diameter (3–5 nm) of the SG was much larger than those of the others (ex. 0.8–1.2 nm, 1.5 nm). Thus, this suggested that the width of the bundle is related to the tube diameter of the SWCNT. The A-SG had a narrower bundle than the original SG, which is possibly due to the partial destructive process of the tubes by the activation treatment.

The EDLC test cell was assembled using the test electrodes (for negative and positive electrodes), the electrolyte, a sealed Al-body two-electrode cell (Hosen Co.), and a cellulose-based separator in an argon glove box.

The galvanostatic charge/discharge tests (current density: 80 mA g⁻¹, 0–2.5 V at 40 °C) of the EDLC cell were carried out by a HJ1001SM8 auto charge-discharge unit (Hokuto Denko Co.). The observed capacitance (the quantity of discharged electricity divided by 2.5 V) was normalized by the total weight of the SWCNT or YP50F in the positive and negative electrodes to obtain the gravimetric capacitance. The internal-resistance of the cell was calculated from the ohmic drop observed at the switch point from the charge process to the discharge process. The durability test was conducted under the floating charge condition (3.4 V, 100 h at 70 °C). For the EDLC, the floating charge at high voltage is more aggressive than the galvanostatic charge-discharge cycle. The capacitance-retention after the durability test corresponds to the ratio of the capacitance before and after the durability test. In addition, the rate performance of the EDLC cell over the wide current density range of 40–5000 mA g⁻¹ at 40 °C was evaluated before and after the durability test.
The SG and A-SG were mainly composed of elemental carbon (ca. 99 wt\%) with a small amount of elemental oxygen (ca. 1 wt\%) as oxygen surface functionalities. The ED had a small amount of elemental sulfur (ca. 2 wt\%) in addition to elemental carbon and oxygen, but no other impurities were detected. The HP had a non-negligible amount (ca. 25 wt\%) of elemental iron as an impurity, which is derived from the HiPco\textsuperscript{6} process catalyst. A small amount of elemental iron was still detected in the purified type (P-HP). The residual metal catalyst can influence the capacitance performance. Therefore, the presence of iron impurities should be noted for the HP, P-HP, and ED has type II isotherms, so it can be said that they do not have a lot of micropores due to the disintegration of the bundles. For the A-SG, it is suggested that the mesopores produced by the activation also contribute to a large amount of adsorbed nitrogen in the middle relative pressure region.

The pore structures calculated from the isotherms are summarized in Table 2. The specific surface areas of all the SWCNTs are lower than that of YP50F. Especially, for the HP, P-HP, and ED, the specific surface areas are much lower than the theoretical value (ca. 1300 m\textsuperscript{2} g\textsuperscript{-1}) of the ideal cap-closed SWCNT, therefore, a large part of the external surface for each tube is not accessible due to the bundle structure. Most of the mesopore volume for the SWCNTs, except for the A-SG, comes from the interspace between the bundles as previously discussed. The A-SG had a higher specific surface area and mesopore volume than the original SG, which suggests that the inside tube surface and space (3–5 nm, corresponding to mesopore) can be exposed through the open-end of the tube or some defects on the tube side-wall by the activation treatment. Yamada et al. also reported the role of the inner space as a mesopore for the oxidized or activated super-growth SWCNTs.\textsuperscript{23} However, the specific surface area of the A-SG is still lower than the theoretical specific surface area (ca. 2600 m\textsuperscript{2} g\textsuperscript{-1}) of the ideal cap-opened SWCNT, so most of A-SG tubes can be considered to maintain the bundle structure.

The above characterizations revealed that these five CVD-derived SWCNTs used in this study have different chemical compositions and pore structures. Thus, a general tendency for the capacitance properties of the SWCNTs as the EDLC electrode should be qualitatively confirmed by using these SWCNTs.

### 3.3 Capacitance and durability

Figure 3 shows the charge-discharge curves of the EDLC using the SWCNTs and YP50F electrodes before and after the durability tests. The SWCNTs and YP50F showed typical capacitive charge/discharge curves before the durability test (Fig. 3(a)). The slope of the curve implies the gravimetric capacitance for these samples as follows: YP50F > A-SG > SG > P-HP > ED ≈ HP. The calculated gravimetric capacitance based on the discharge curve was correlated with the specific surface area as shown in Fig. 4. The gravimetric capacitance is almost proportional to the specific surface area of the active material in the electrode. The capacitance of the SG, A-SG, or HP in Fig. 4 is roughly consistent with the result obtained with three-electrode system.\textsuperscript{8,23} The capacitance of the A-SG was the highest for those of the SWCNTs, but it was still lower than that of the YP50F. This indicated for application as the EDLC electrode that the surface area is basically significant for the SWCNTs as well as microporous carbons such as activated carbon. Focusing on the capacitance per unit specific surface area (areal capacitance), the HP had a relatively higher areal capacitance (ca. 2.2 µF cm\textsuperscript{-2}) than the other samples (e.g., SG series and YP50F: ca. 1.6 µF cm\textsuperscript{-2}), which has been discussed in a previous paper.\textsuperscript{8} The ED and HP with similar surface areas also had high areal capacitances. Thus, the high areal capacitance of the HP and ED can be related to the large curvature that originated from the small tube diameter.

Comparing the charge-discharge curves before and after the durability test (Fig. 3(a) and Fig. 3(b)) clarifies the stability to the high voltage charge. For the P-HP and YP, the curves after the durability test were distorted and the curve slope became steeper. The EDLC with the HP was not working after the durability test (data not shown in Fig. 3(b)), which means complete degradation. The results of the durability tests are summarized in Table 3. The capacitance-retention and the internal-resistance of the YP are 75\% and 20 Ω, respectively.

For the SG and A-SG, the capacitance-retentions were 99 and 98\% and the internal-resistance increases were only 1 Ω and 2 Ω, respectively.
respectively. They have a much better durability than the YP50F. This result agrees with the literature. The capacitance of the A-SG is higher than that of the SG, so it can be seen that the activation for the SG is a good modification along with maintaining the durability against the high voltage charge. On the surface of the SWCNT or graphene, catalytically active-sites promoting electrochemical decomposition can be considered to be less than that of the activated carbons. However, the integrated leakage-current during the floating charge for the SG series, which is a measure of the electrochemical decomposition, was not less than that of the YP50F, so the excellent stability observed in this study can be attributed to the self-standing structure (binder and conducive-additive free) rather than the surface condition of the electrochemically active sites.

As previously mentioned, the floating charge at high voltage resulted in a significant deterioration of the HP. In fact, the capacitance-retention and internal-resistance increase could not be evaluated after the durability test because of too large internal-resistance. Figure 5 shows the galvanostatic charge-discharge curves for the cell using the SG and HP at the operating voltage of 0–3.4 V at 70°C. The SG had stable charge-discharge cycles while plateaus of the cell-voltage around 3–3.2 V were observed during the charge process for the HP, which suggests an electrochemical decomposition or short circuit. Origins of the degradation can be related to the presence of a significant amount of the residual iron catalyst (25 wt.%). The P-HP exhibited a better durability than the YP50F, but the capacitance-retention (85%) and the internal-resistance increment (225 Ω) were not as good as those of the SG series. The integrated leakage-current was 35 mAh, which was higher than those of the others. The significant electrochemical decomposition can be due to electrochemically active sites such as the residual Fe catalyst and structural defects induced by the purification process.

The ED also exhibited an excellent durability as the high capacitance-retention (116%) and the low internal-resistance...
increase (1 Ω) were observed. This unusual higher retention greater than 100% suggests an increase in the ion-accessible surface area during the floating charge at 3.4 V, which can be caused by expansion of the inter-space of the SWCNTs in the bundle. A similar phenomenon is well known as electrochemical activation for expanded graphite and KOH-activated carbons.

3.4 Rate performance

Figure 6 shows the rate-performance of the EDLC using the SWCNTs and YP50F. All systems originally had a good rate-performance, but the reduction in the performance depended on the SWCNTs and YP50F. All systems originally had a good rate-performance, but the reduction in the performance depended on the

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Figure 6. Dependence of capacitance (0–2.5 V, 40 °C) of SWCNTs and YP50F on current density (a) before and (b) after the durability test (3.4 V, 100 h, 70 °C).

4. Conclusion

In this study, various self-standing SWCNT membranes were evaluated as the electrode for the EDLC and compared to the conventional activated carbon electrode under the same measurement conditions. The SWCNTs prepared by the super-growth or eDIPS method exhibited an excellent capacitance-retention and the rate-performance after the floating charge at high voltage (3.4 V, 100 h, 70 °C). The CO₂-activation was effective for improving the capacitance without sacrificing the durability for the super-growth SWCNT. The durability of the SWCNTs prepared by the HiPco method was not as good as those of the super-growth or eDIPS method. Therefore, a well-controlled structure and purification are very significant for the use of an SWCNT as the electrode of the EDLC.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-64059.

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