Competitive effect of carbon nanotubes oxidation on aqueous EDLC performance: Balancing hydrophilicity and conductivity

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Abstract

We have investigated the oxidation effect of multi-walled carbon nanotubes (MWNT) as electrode materials on the performance of an aqueous electrochemical double layer capacitor (EDLC). Carboxyl groups showing hydrophilic properties were mainly introduced on the MWNT surface by oxidation with an extremely aggressive oxidizing agent such as mixed acid H_2SO_4/HNO_3. The hydrophilicity of MWNT increased with oxidation time, promising increased capacitance due to a good wettability to the aqueous electrolyte. In contrast, the surface structure disruption resulting from excessive treatment leads to the simultaneous decrease in the conductivity of the MWNT electrode, causing deterioration in EDLC performance. The balance between hydrophilicity and conductivity is therefore a key factor when designing improved electrode materials for EDLC. In this study, we found that specific capacitance was increased with oxidation times within 60 min (dominant region of hydrophilicity increase), but decreased with times of more than 60 min (dominant region of conductivity decrease). These results were identified with several analyses, such as Fourier transform-infrared (FT-IR) spectrometry, Boehm titration, N_2 adsorption, water vapor adsorption, transmission electron microscopy (TEM), Fourier transform-Raman (FT-Raman), 4-probe IV measurement, and cyclic voltammetry (CV).
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1. Introduction

Electrochemical double layer capacitors (EDLC) have actively been researched to meet the needs of new energy storage devices that require high power ($10 \, kW \, kg^{-1}$) and long durability (over 10^6 cycles), for hybrid power sources in electric vehicles or backup sources for various electrical devices, and so on [1]. EDLC accumulate electrical energy generated by the formation of the electrochemical double layer suggested by Helmholtz in 1879, at the interface of electrode and electrolyte (non-Faradaic process), unlike secondary batteries such as the lithium ion battery and nickel metal hydride battery which use a redox reaction (Faradaic process). This energy storage system by a non-Faradaic process promises very fast charge and discharge, making the EDLC the best candidate to fulfill the demand for high power and long durability. Carbon has been studied extensively as an electrode material for EDLC, because

of its unique physico-chemical nature, such as large specific surface area, good electrical conductivity, and chemically stable properties [2,3]. In order to improve the performance of aqueous type EDLC, numerous attempts have been made to increase the wettability to aqueous electrolytes, i.e., hydrophilicity, using various surface oxidation methods for carbon materials, such as the gas-phase activation [4–9] in static air or plasma, and the liquid-phase activation or oxidation treatment [10–21] with strong oxidants including hydrogen peroxide, potassium permanganate, potassium hydroxide, and nitric and/or sulfuric acid. When carbon materials were oxidized with extremely aggressive agents, their hydrophilicity was increased by the introduction of oxygen-containing functional groups, such as carboxyl, carbonyl, and phenol groups. On the other hand, this process causes some damages or structural changes on carbon surfaces by disrupting their graphene sheet structure. Especially, in the case of carbon nanotubes, some unique phenomena, such as cap opening, length shortening, and diameter thinning occur through this process, in addition to the general phenomena mentioned above. This structure changes result in the decrease of electrical conductivity which is negative in terms of the application to the

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electrode materials for EDLC. Hence, the oxidation treatment with extremely aggressive agents provides both the positive hydrophilicity increase and negative conductivity decrease to the performance of aqueous type EDLC.

In this paper, we study the competitive effects on aqueous EDLC performance of hydrophilicity increase and a simultaneous conductivity decrease resulting from the oxidation of carbon materials, using both qualitative and quantitative approaches. In order to evaluate the effect more clearly, we adopted carbon nanotubes as electrode materials for the following reasons. First, they were suitable for studying the effect of increased hydrophilicity after oxidation on EDLC performance, because they are known to have a quite inert surface nature before oxidation [22]. Second, their perfect graphene sheet structure before oxidation gives them an advantage for evaluating the conductivity decrease with an increase of oxidation time from the highest conductivity. We were also encouraged in our selection by the fact that they could become the most popular materials for EDLC electrodes, based on their superior physico-chemical properties to common active carbon, if their moderate specific capacitance could be increased with a surface oxidation treatment [23,24]. This study shows which is a dominant factor and what is the best balance between hydrophilicity and conductivity in order to improve aqueous EDLC performance, using analytical tools such as Fourier transform-infrared (FT-IR) spectrometry, Boehm titration, N_2 adsorption, water vapor adsorption, transmission electron microscopy (TEM), Fourier transform-Raman (FT-Raman), 4-probe IV measurement, and cyclic voltammetry (CV).

2. Experimental

2.1. Oxidation treatment of MWNT

Multi-walled carbon nanotubes (MWNT, purity: 95%, diameter: 10–20 nm, length: 0.5–40 μm, Helix Material Solutions, TX, USA) used were commercial products prepared by a conventional CVD method. Raw soot containing MWNT was purified by heating for 2 h at 400 °C in static air followed by treatment with 6 M hydrochloric acid at 70 °C for 12 h. Subsequently, these purified MWNT were oxidized by simply stirring in a concentrated H_2SO_4/HNO_3 (3:1 volume ratio, 98% and 70% gravimetric concentration, respectively, Kanto Chemical) mixture at 70 °C for various oxidation times (OT: 15 min, 30 min, 60 min, and 120 min).

2.2. Hydrophilicity test

Fourier transform-infrared spectrometry (AVATAR-360, Nicolet) was employed to qualitatively evaluate the introduced functional groups on the MWNT surfaces. The pellet for FT-IR measurement was composed of diluted MWNT in KBr. For quantitative assay of introduced functional groups, especially carboxyl groups, we adopted the titration method reported by Boehm [25] and a water vapor adsorption test. Titration was conducted in the following order. Oxidized MWNT (50 mg) was placed in 25 ml of 0.01 M NaOH and suspended by a strong ultra-

sonic homogenizer for 10 min. This suspension solution was stirred for 24 h at room temperature in a closed vessel and then filtered. Subsequently, 20 ml of this filtrate was reacted with the same amount of 0.01 M HCl for 24 h and then this solution was back-titrated with 0.01 M NaOH. Hydrophilicity was also analyzed quantitatively through evaluation of water vapor adsorption amount. The oxidized MWNT samples obtained at various times were placed and adsorbed with water vapor in a closed vessel adjusted to saturated vapor pressure corresponding to room temperature for 48 h; the amount of adsorbed water vapor was then measured with thermo gravimetric analysis (TGA, EXSTAR6000, SEIKO). Brunauer–Emmett–Teller (BET) specific surface area was calculated from the N_2 adsorption isotherms at 77 K by using an adsorption system (BELSORP28SA, BEL, Japan).

2.3. Conductivity test

Conductivity was measured by a conventional 4-probe DC method with a pellet of oxidized MWNT prepared in the pressure of 200 kgf cm^{-2}. Fourier transform-Raman (LABRAM, ISA) spectrometry equipped with He–Ne laser ($\lambda = 632.8$ nm) and transmission electron microscopy (H-7100, Hitachi) with an accelerating voltage of 100 kV were employed to observe the disruption of the MWNT structure.

2.4. Aqueous EDLC performance test

Finally, the performance of aqueous type EDLC was measured with cyclic voltammetry (608A, ALS). A working electrode was formed with MWNT as the active material, acetylene black as the conductor, and polyvinylidene fluoride (PVdF) solution in N-methyl-2-pyrollidone (NMP) as the binder in weight ratio of 80%, 10%, and 10%, respectively. The reference and counter electrodes were a saturated calomel electrode (SCE) and a Pt wire, respectively. The voltammograms were recorded in 1 M H_2SO_4 aqueous electrolyte with a sweep rate of 100 mV s^{-1} after N_2 purging for 1 min.

3. Results and discussion

3.1. Effect of hydrophilicity increase

Fig. 1 shows the FT-IR spectra change with oxidation time. Before oxidation, there are peaks only around 1570 cm^{-1}, corresponding to C=C stretching, and around 1630 cm^{-1} to C=O stretching of carbonyl groups which might be introduced in purification process. However, a marked increase of the peak around 1720 cm^{-1}, corresponding to C=O stretching of carboxyl groups, appears with longer oxidation time, indicating the successful introduction of carboxyl groups on the MWNT surfaces, in accordance with previous studies [2,26]. Indeed, this peak is somewhat broad, because some other oxygen containing groups like lactone in addition to carboxyl groups might also be introduced on the surfaces. Notably, it should be noted that this peak is drastically increased during the first 15 min oxidation treatment and gradual increases are observed with continued treatment
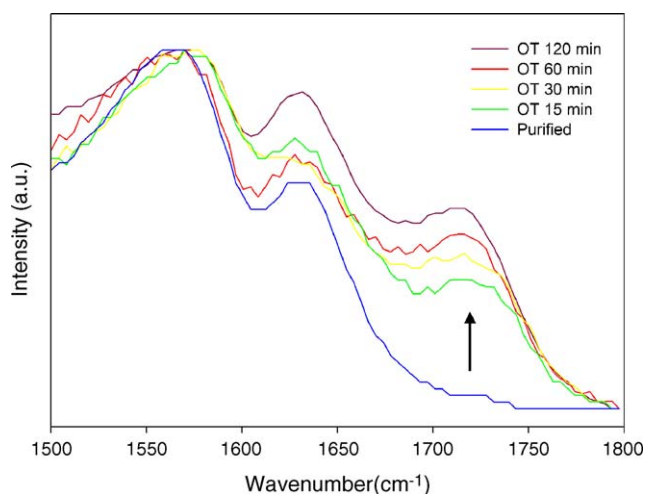
Fig. 1. FT-IR spectra change as a function of oxidation time.

above 15 min. This phenomenon could be explained by a very intensive attack on the C=C bond of the graphene structure at an early stage by very electrophilic groups, NO_2^+ formed by the mixing of concentrated sulfuric and nitric acid, followed by an ordinary attack resulting in the gradual peak increases with oxidation time.

It is possible to estimate the amount of introduced carboxyl groups using a titration method reported by Boehm [25]. Fig. 2 shows the quantitative change of carboxyl groups with oxidation time. The shape of the graph seems to be not linear but rather a logarithmic increase, meaning that the oxidizing process is very violent in the early stages, rather than a gradual reaction over time as mentioned above.

The quantitative evaluation of hydrophilicity was performed with water vapor wettability test. Indeed, in order to evaluate the wettability more exactly, the effect of surface morphology should be considered as well as that of hydrophilicity due to introduced surface carboxyl groups. However, in the case of MWNT, such effect can be negligible because little change of their flat surface textures was observed with oxidation treatment. As shown in Fig. 3, nitrogen adsorption properties are almost
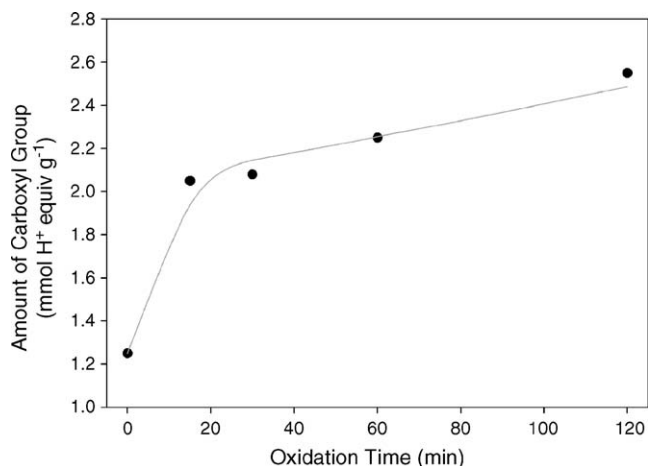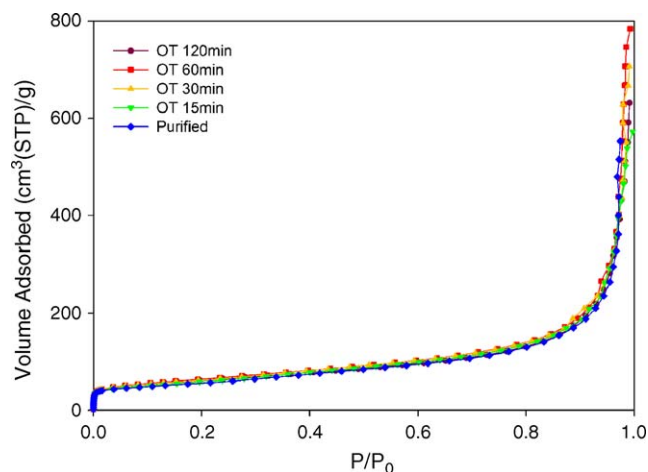

Fig. 3. Nitrogen adsorption isotherms at 77 K.

same in all samples and a very small increase of specific surface area is only shown with oxidation time ($201 \, m^2 \, g^{-1}$ for purified MWNT into $208 \, m^2 \, g^{-1}$ for oxidized MWNT for 120 min). Hence, the hydrophilicity due to surface carboxyl groups is a dominant factor to determine the wettability and it is reasonable to quantitatively evaluate the hydrophilicity with wettability test. The increase in hydrophilicity was consistent with the amount of introduced carboxyl groups. As shown in Fig. 4, it has almost the same shape as Fig. 2 in logarithmic increase, so that hydrophilicity can be understood to have a direct relationship with the introduced carboxyl groups. Actually, only purified MWNT are perfectly non-dispersible in water due to their very inert surface nature, however, all oxidized samples are dispersible and make a black ink. Indeed, such inert surface nature of MWNT hinders displaying their maximum value of obtainable capacitance, because a wetting in electrolyte is the most essential condition for the formation of electrochemical double layer. Therefore, improving the hydrophilicity of MWNT is very important for enhancing the capacitance of aqueous EDLC. Furthermore, it is possible for introduced oxygen containing functional groups, mainly carboxyl groups and additionally carbonyl and phenol

Fig. 2. Quantitative analysis of surface carboxyl groups by titration based on the Boehm method.
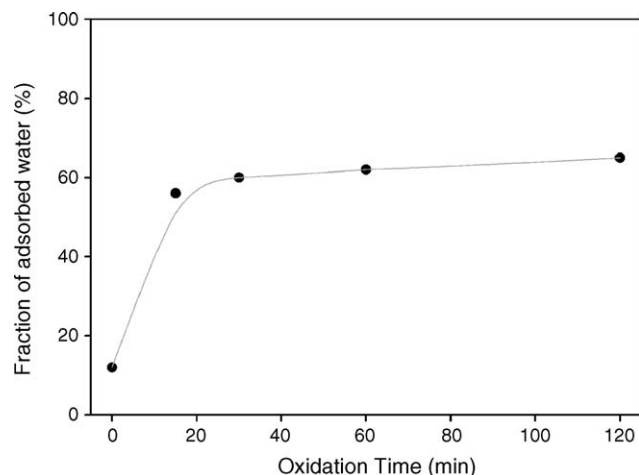

Fig. 4. Evaluation of hydrophilicity by the measurement of water vapor adsorption.
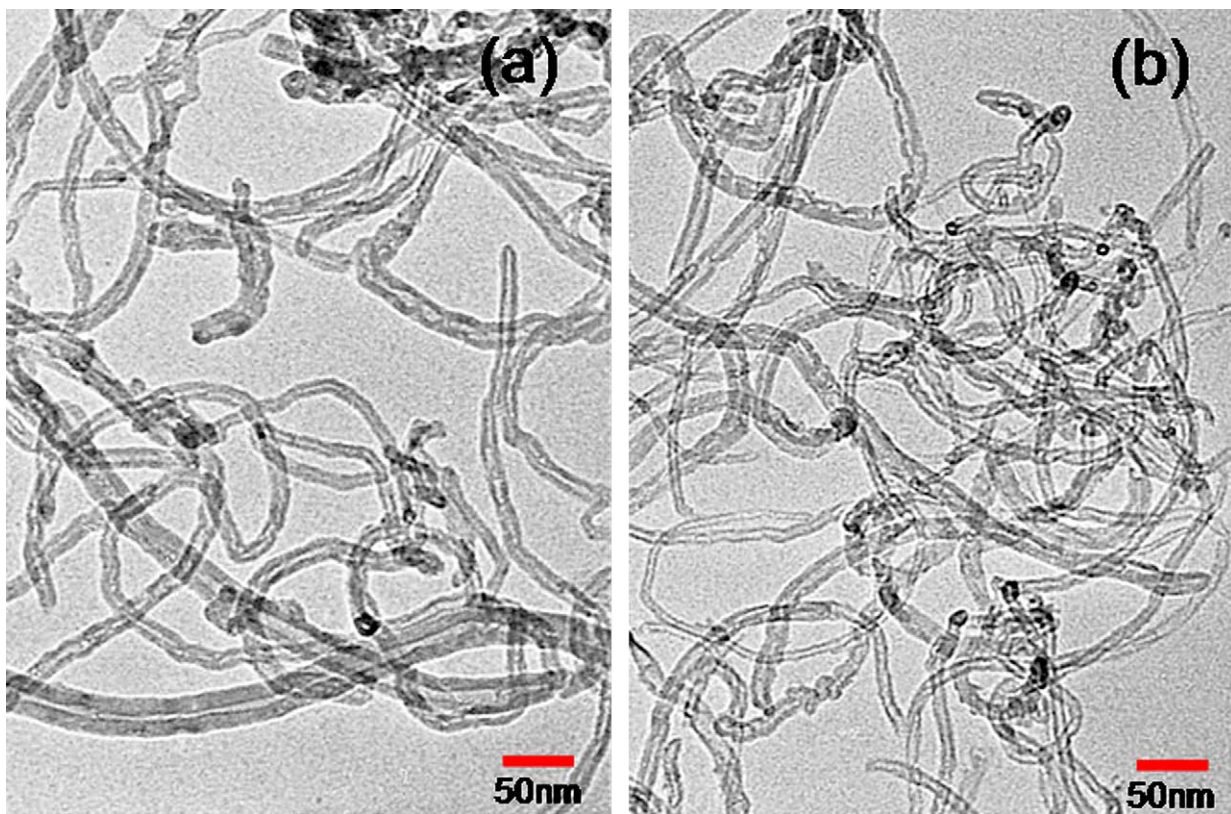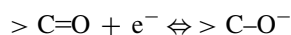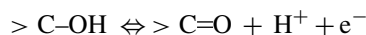
Fig. 5. TEM images of (a) purified MWNT and (b) MWNT oxidized for 120 min.

groups to directly provide increased capacitance through a redox reaction with protons, as follows [3]:

$$-COOH \Leftrightarrow -COO + H^+ + e^-$$

$$> C\text{-}OH \Leftrightarrow > C\text{=}O + H^+ + e^-$$

$$> C\text{=}O + e^- \Leftrightarrow > C\text{-}O^-$$

Hence, oxidation for as long a time as possible seems to be a perfectly advantageous process in terms of enhanced aqueous EDLC performance. However, against such expectations, excessive oxidation actually resulted in decreased capacitance, as explained below.

3.2. Effect of conductivity decrease

It is well known that excessive oxidation of carbon nanotubes leads to the formation of short-cut pipes and the exfoliation of graphene sheets [27,28]. In our experiment, the length-shortening phenomenon was very slight in the oxidized samples, even after 120 min, as can be seen in Fig. 5. The shape and length of the cut MWNT may appear to be fairly different from those of single-walled carbon nanotubes (SWNT), i.e., the fullerene pipes reported previously [28]. This is attributable to their different structure disruption and shortening mechanisms. Zhang et al. suggested that SWNT is shortened via a two-step, defect-generating, and defect-consuming step [26]. In the defect-generating step, the graphene structure of SWNT is attacked by

very aggressive NO_2^+ derived from nitric acid in concentrated sulfuric acid and generates active sites, i.e., functional groups that include oxygen, such as hydroxyl and/or carbonyl groups. Thereupon, in the defect-consuming step they are cut and shortened, along with the introduction of carboxyl groups in their ends, by more oxidation of the active sites under the presence of strong oxidants. However, MWNT are constituted with multiple rolled graphene sheets, not single ones, so they exhibit some different aspects in the cutting and shortening process. They are attacked by strong oxidants in the same way, but in the defect-consuming step, they do not show cutting and shortening, but only defect deepening and gradual thinning by exfoliation. Hence, hydrophilic functional groups introduced on both the sidewalls and open ends of the MWNT, not only the open ends. Certainly, this is essential for the increase of hydrophilicity with oxidation time, without marked length shortening.

This surface structure disruption could be pointed out with FT-Raman measurements. In Fig. 6, a strong G-band peak around $1580\,cm^{-1}$, corresponding to perfect graphene structure, is shown accompanied by a strong D-band peak around $1350\,cm^{-1}$. This D-band peak corresponds to a structural defect, such as a dangling bond, which is inevitable in the case of MWNT prepared by the CVD method, a relatively mild synthetic condition. With oxidation time, the D-band peak is increased showing the defect deepening. It is interesting that the increasing aspect of the D-band peak is consistent with that of hydrophilicity (drastic change at the early stage of oxidation treatment). This means that for aqueous EDLC performance, an advantageous
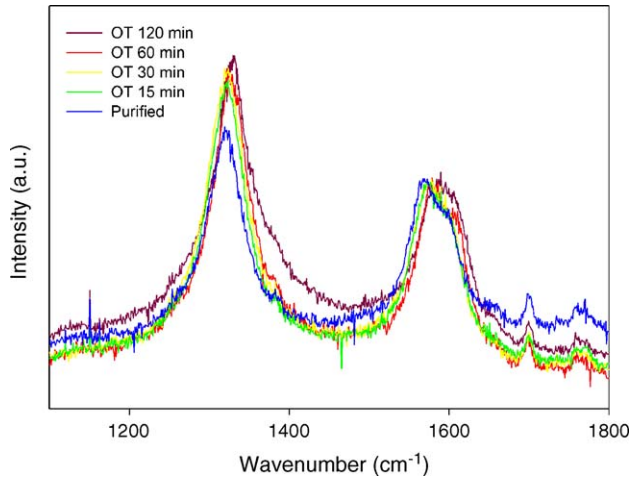
Fig. 6. FT-Raman spectra change as a function of oxidation time.
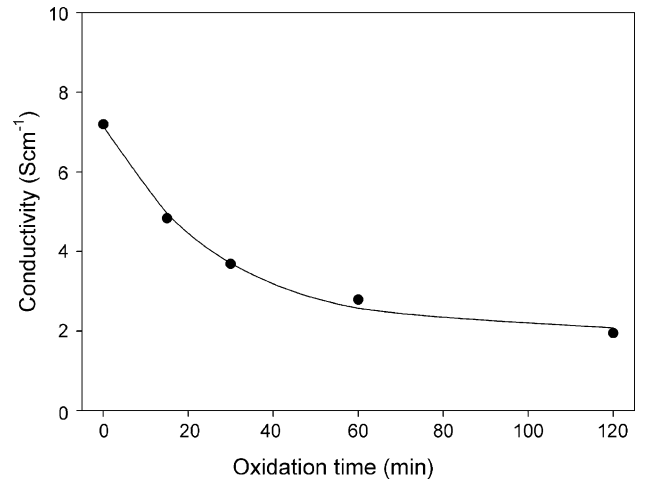

Fig. 8. Conductivity change as a function of oxidation time.

hydrophilicity increase inevitably accompanies a disadvantageous defect deepening.

This accompanying disadvantage can be represented by the decrease of conductivity. It is well known that electron conduction in carbon materials has an unusual anisotropic nature due to the very large difference of effective mass between the in-plane and through-thicknesses [29], so that the disruption of the surface graphene structure directly causes the decrease of conductivity. A change in conductivity with oxidation time was observed using a common 4-probe DC method; the pellet of oxidized MWNT was deposited with aluminum thin layer electrode as shown in Fig. 7. Indeed, this method for determining the bulk conductivity has some disadvantages for understanding the relationship between surface structure and intrinsic conductivity, because the estimated value reflects not only the effect of

surface structure, but also some other factors, such as the contact resistance between MWNT. Hence, we employed this method to measure not an intrinsic but a bulk conductivity change by oxidation treatment. This bulk conductivity measurement could be more reasonable to investigate the effect of conductivity change on capacitance, because an actual capacitance value is determined with the electrode composed of bulk MWNT in electrochemical cell. As can be seen in Fig. 8, the bulk conductivity is decreased with oxidation time, according to expectation. Hence, for enhanced performance of aqueous EDLC, it is vital to establish correct oxidation conditions in order to achieve a proper balance between hydrophilicity increase and conductivity decrease.

3.3. Balancing hydrophilicity and conductivity

The best balance can easily be derived from the relationship between specific capacitance and oxidation time. Fig. 9 shows cyclic voltammograms of oxidized samples for various times, and Fig. 10 is their specific capacitance change as a function of oxidation time. Specific capacitance tends to increase with
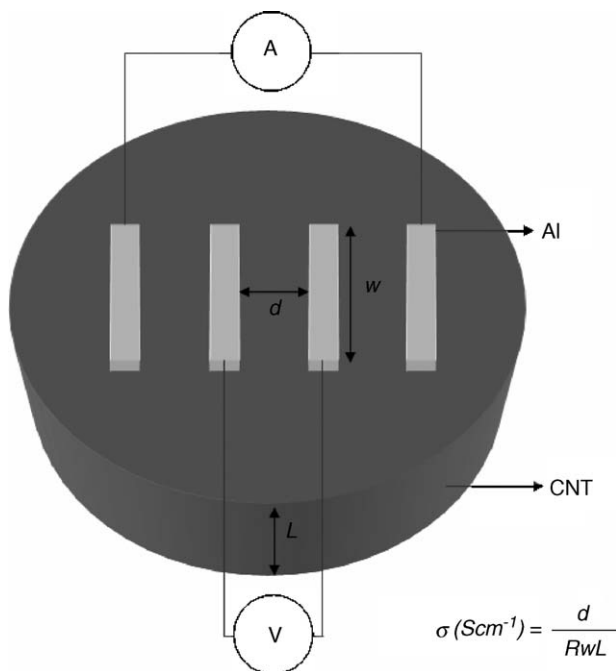

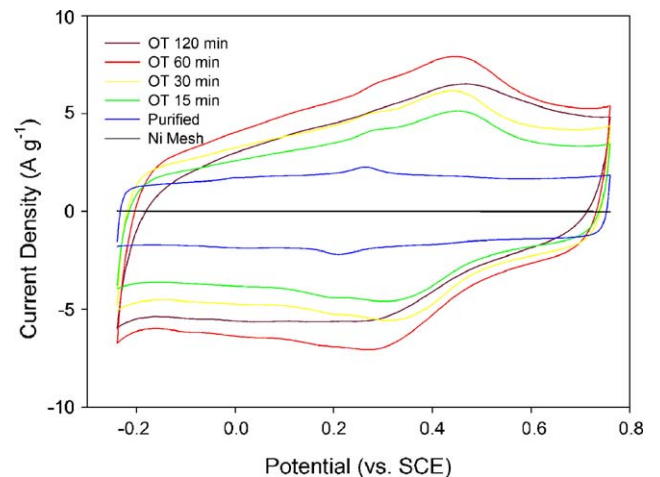Fig. 7. MWNT pellet deposited with aluminum thin layer electrode for 4-probe DC method.

$$\sigma\,(Scm^{-1}) = \frac{d}{RwL}$$

Fig. 9. Cyclic voltammograms in $1\,M\,H_2SO_4$ electrolyte with a scan rate of $100\,mV\,s^{-1}$.
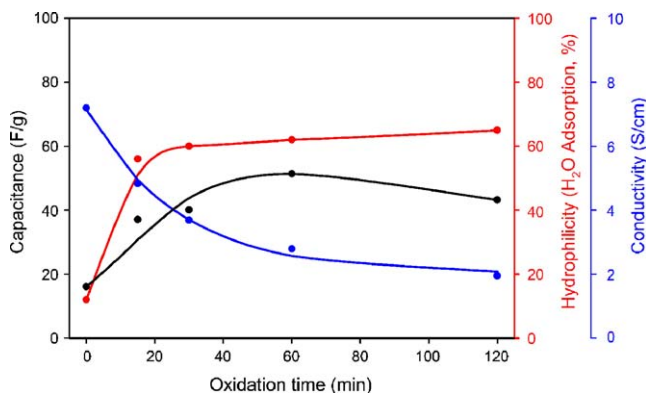
Fig. 10. Summarized changes of specific capacitance, hydrophilicity, and conductivity as a function of oxidation time.

oxidation time, but the oxidized samples for 120 min show a rather decreased value from that at 60 min, showing not a linear shape but a volcano curve. This means that excessive oxidation over 60 min causes a severe surface structure disruption without a corresponding increase of hydrophilicity, so that effect on performance from the slight increase in hydrophilicity is canceled by the decrease in conductivity. In other words, it is possible to say that the oxidation effect is dominated by a hydrophilicity increase before 60 min and a conductivity decrease after 60 min. With oxidation time, the pseudocapacitance of oxygen containing functional groups, such as carbonyl and carboxyl groups can also be observed at around 0.25 V and 0.45 V (versus SCE), respectively, in the voltammograms. The contribution of these functional groups to total capacitance could be quantitatively elucidated by the proportion of peak area to total area. Furthermore, conductivity decrease is also shown in the shape change of the voltammograms, from a rectangular type into a parallelogram, indicating a larger ohmic loss. Consequently, in our study, it is considered that the oxidation for 60 min of purified MWNT is the best condition for enhancing the performance of aqueous EDLC, showing about 3.2 times larger specific capacitance ($51.3 \, \mathrm{F \, g^{-1}}$) than purified MWNT ($16.1 \, \mathrm{F \, g^{-1}}$).

4. Conclusions

We have studied the competitive effect on aqueous EDLC performance between hydrophilicity increase and conductivity decrease through oxidation of carbon nanotubes. Proper oxidation resulted in the enhancement of aqueous EDLC performance via increased hydrophilicity, ignoring a slight conductivity decrease. Moreover, the pseudocapacitance obtained from the redox reaction of introduced oxygen containing functional groups somewhat contributed to the increase of total capacitance. However, excessive treatment resulted in a specific capacitance decrease through a severe conductivity drop, canceling the effect of the small hydrophilicity increase. In this study, the oxidation for 60 min of purified MWNT in H_2SO_4/HNO_3

mixture at 70 °C was the optimum condition, showing about 3.2 times larger specific capacitance than purified MWNT alone. Proper determination of oxidation condition is, therefore, a key factor in the enhancement of aqueous EDLC performance.

Acknowledgement

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