CAPACITOR PROPERTIES OF PURE SINGLE-WALLED CARBON NANOTUBE ELECTRODES

Hiroaki Hatori, Osamu Tanaike, Junya Yamashita, Tatsuki Hiraoka, Don N. Futaba, Kenji Hata, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, Japan
Osamu Kimizuka, Susumu Saeki and Yoshio Yamada, 3-9-1 Bunkyo, Fukui 910-8507, Japan

Introduction

Electric double layer capacitors (EDLCs) have excellent properties in power density and durability compared with secondary batteries. Recently, development of advanced capacitors with high energy density is active because the storage devices with high power density have huge market in the fields of hybrid vehicles, mobile instruments and so on. The single-walled carbon nanotubes (SWNTs) have high surface area theoretically up to 2600 m^2/g inside and outside of the tubes. The material is considered to be ideal for capacitor electrodes and hence many authors have reported the EDLC properties (Niu 1997 and Shiraishi 2002). However, the SWNTs used in the previous attempts contain considerable amounts of impurities and defects and have low surface area.

Hata et al. (2004) have reported a highly efficient synthesis method of impurity-free SWNTs. The "*Super growth"* method named gives vertically aligned SWNT forests with millimeter-scale height (SG-SWNTs). The SG-SWNTs can be easily separated from the catalyst, providing nanotube material with carbon purity above 99.98%. The excellent capacitor performance of SG-SWNTs has already been reported. The capacitance per unit surface area was 1.5 times higher than that of commercially available activated carbons for EDLC at the potential of 3V in two electrode cell system (Tanaike 2006). Densely packed SG-SWNTs prepared by controlling the fabrication process showed excellent energy density and power density as capacitor electrodes (Futaba 2006a). In the present study, electrochemical behaviors of the SG-SWNTs were studied and the characteristic mechanism of energy storage as capacitor electrodes was revealed.

Experimental

Samples

The preparation method of impurity-free SWNTs used is in the references (Hata 2004, Futaba 2005 and 2006b). A stand-alone SWNT sheet with BET surface area more than 1100 m^2/g can be easily pealed from the substrate used for CVD growth. The analysis of nitrogen adsorption isotherm revealed that the surface area of SG-SWNTs is attributable to the outer surface, that is, the nanotubes are closed. It is noteworthy that more than 80% of the theoretical value (1300 m^2/g) of the outer surface area is "isolated" from the surface of the other tubes, that is to say, SG-SWNTs have less bundle structure. Pure SG-SWNT sheets with high density and without any additives were used in the present study. The BET surface area was 1090 m^2/g even after a process for densification.

Characterization

In situ measurement of conductivity of SG-SWNT electrodes was conducted by the method in the reference (Claye 2000). A SG-SWNT sheet was held against four Pt wires, two voltage leads and two current leads. The ac impedance measurements were made by using the four leads at various potentials which was controlled by dc current. One of the current lead, connected to activated carbon as a counter electrode and an Ag/Ag^+ reference, was shared to control the potential of the SG-SWNT electrode. Electron conductivity of the SG-SWNT electrode was given as an inverse of the impedance measured at 10 kHz.

In situ Raman spectra of SG-SWNT were measured through ITO glass as a current collector by using specially assembled three-electrode cell. Activated carbon electrodes were used as counter and reference electrodes.

Results and Discussion

The properties of SG-SWNTs as electrodes for supercapacitors were evaluated in 1M tetraethylammonium tetrafluoroborate ($TEABF_4$) in propylene carbonate (PC), the most popular electrolyte used for commercial capacitors. Cyclic voltammograms (CVs) measured by three electrode cell system are shown in Figure 1. Unlike the typical rectangular CV shape of activated carbon electrodes by electrostatic capacitance, the SG-SWNTs gives a profile of butterfly shape. As reported previously (Tanaike 2006), the capacitance of SG-SWNTs is higher at higher charging potentials because of the potential dependence. The potential dependence of specific capacitance suggests the capacity by some electrochemical process in addition to the electrostatic capacitance. Nyquist plots given from impedance spectroscopy also showed the potential dependence, decrease of internal resistance of the cell circuit at higher potentials (Figure 1, right). In Figure 2, the result of *in situ* measurement of electron conductivity is shown for a pure SG-SWNT sheet with bulk density of 0.64 g/cm^3. The conductivity is lowest around -0.3 V, where the current is lowest in CV profile in Figure 1. The conductivity increased symmetrically both at the higher and lower potentials than -0.3V, and the maximum conductivity became more than ten times as high as the minimum value. The results clearly showed that the potential dependence of the Nyquist plot in Figure 1

caused by the change of electron conductivity of the SG-SWNT electrode.

It is well known that SWNTs are naturally the mixture of conductive and semi-conductive tubes varying with their chirality. The characteristic CV profiles with butterfly shape are explainable by the combination of electrostatic capacitance on conductive tubes and electrochemical doping on semi-conductive tubes. The potential with lowest current in Figure 1, -0.3V against Ag/Ag^+, is considered to be the flat band potential of semi-conductive tubes. The increase of the electron conductivity both at higher and lower potentials than the flat band potential suggests a doping mechanism; electrochemical doping such like conductive polymers occurs and the amphoteric nature of SWNTs as electron donor and acceptor caused the symmetrical increase.

Change of Raman spectra by the potential in the direction of hole doping is shown in Figure 3. The behaviors of tangential mode peaks, so-called G band, were similar to that of chemical or electrochemical doping of alkali metals or halogens (Chen 2005 and Kim 2006); a) peak intensity decreases with doping, b) peak intensity of G^- line around 1580 cm^{-1} decreases much faster than that of G^+ line at 1596 cm^{-1} and c) G^+ line shifts upward (e.g. +9 cm^{-1} at 0.75 V in Figure 3) both for electron and hole doping though the relation between the direction of peak shift and doping species is not necessarily consistent with references. In case of the SG-SWNT electrodes, the nanotubes have less bundle structure considering from the high surface area. In addition, the butterfly CV shape and the symmetrical change of electron conductivity deny some doping reactions into nanotube bundles. In conclusion, doping reactions are considered to be occurred on the "isolated" semi-conductor nanotubes without bundles.

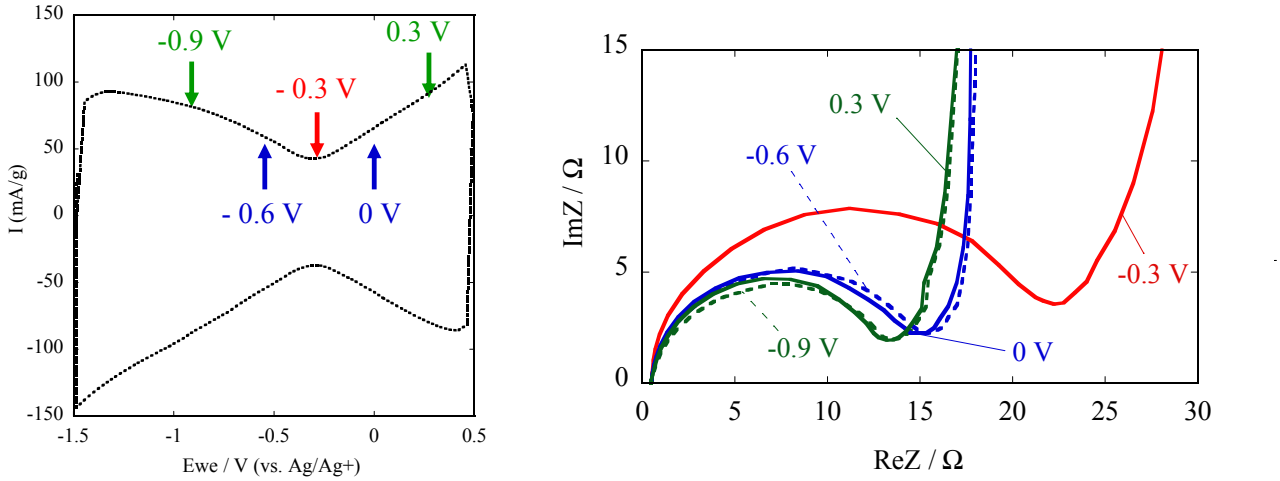

Figure 1. Cyclic voltamograms of SG-SWNTs in $TEABF_4$/PC with three electrode cell system (scan rate: 1mV/s) and Nyquist plots at the potentials against Ag/Ag^+ reference.

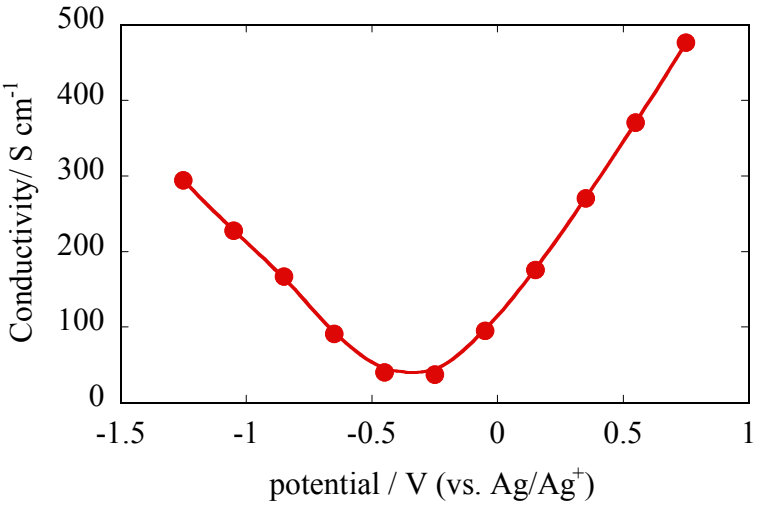

Figure 2. Change of electron conductivity of SG-SWNT electrodes by the potentials against Ag/Ag^+ reference.

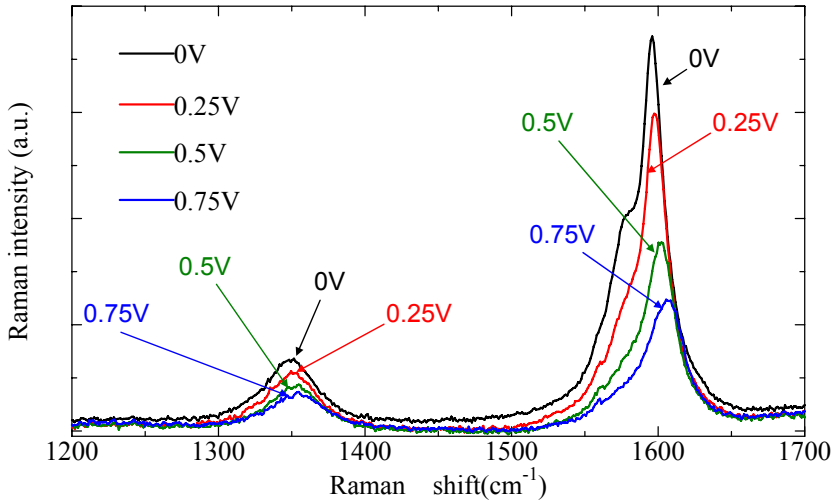

Figure 3. Raman spectra of the SG-SWNT electrodes by *in situ* measurement at the potentials against activated carbon electrode as a reference. The flat band potential was at -0.15 V against the reference electrode.

Conclusions

The characteristic behaviors of the SG-SWNT electrodes were studied. The dependence of electron conductivity and Raman profiles on the charging potentials indicates doping reactions on the "isolated" semi-conductor nanotubes without bundles. The characteristic CV profiles with butterfly shape are explainable by the combination of electrostatic capacitance on conductive tubes and electrochemical doping on semi-conductive tubes. The excellent performance as capacitor electrodes, the high specific capacitance per unit surface area, is considered to be due to the doping mechanism on the semi-conductor tubes.

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