Iodine Encapsulation in CNTs and Its Application for Electrochemical Capacitor

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Abstract. We report the experimental results for new type electrochemical capacitor using iodine redox reaction in single-walled carbon nanotubes (SWCNTs). It was found that the energy density of the present redox capacitor using SWCNTs is almost three times larger than that of the normal electric double layer capacitor.

INTRODUCTION

Owing to their unique structural features, carbon nanotubes (CNTs) have attracted much interest. One of their structural features is the hollow core in which diverse molecules (e.g. C_{60}, β-carotene, H_2O, 1,4-bis(dicyanomethylene)cyclohexadiene (TCNQ)) [1,2,3,4] can be encapsulated. Encapsulation of some kinds of molecules improves the electric conductivity of CNTs, due to the charge transfer between the encapsulated molecules and CNTs. Among such molecules, iodine molecules are known to be very effective for the improvement of CNTs conductivity. Therefore, many papers have been reported on the encapsulation of iodine molecule. However, since most of the previous works used gas phase reaction to encapsulate iodine molecules, it was not very easy to control the encapsulation amount. Recently, we developed new encapsulation technique for iodine molecules using an electrochemical method [5]. By electrochemical oxidation of iodine ions on CNT electrode, iodine ions are oxidized to neutral iodine molecules and encapsulated in hollow cores of CNTs. This method is very simple and can control the encapsulation level very easily. So far, we reported the unique dispersion properties and the electric conductivities of iodine-encapsulated CNTs prepared by this method. In this paper, we discuss the possibility of a new type of electrochemical capacitor using the redox reactions of iodine molecules encapsulated in CNTs [6,7].

EXPERIMENTAL

We used mainly single-walled carbon nanotubes (SWCNTs) in the present work. The SWCNT sample (Meijo NanoCarbon Co. Ltd., e-DiPS 2.0 type) was produced by CVD method. The sample showed very high crystallinity and high purity which were confirmed by Raman and TEM measurements. The mean tube diameter is about 2.0 nm. We fabricated a paper-form SWCNTs (bucky-paper) by filtration of SWCNT dispersed water on a membrane filter and used it as a working electrode. A mixture of activated carbon, carbon black, and PTFE was used as a counter electrode. These two electrodes were immersed in 1M NaI aqueous electrolyte in a H-type cell having a membrane filter as separator. To monitor each electrode potential, Ag/AgCl reference electrode was also used. Raman measurements were performed using a micro-Raman spectroscopy system equipped with CCD detector (Acton SP2300) to examine iodine molecule encapsulation level. Nd:YAG laser (533 nm) was used as an excitation source.

RESULTS & DISCUSSION

Figure 1 shows the observed Raman spectra before and after the encapsulation treatment. A new peak appeared at around 173 cm^{-1} by the iodine encapsulation treatment. The peak can be assigned as a Raman band of poly-iodine molecule (I_n). It indicates that poly-iodine molecules are formed by recombination of diatomic iodine I_2 molecules produced by electrochemical oxidation of iodine ions I^-. The poly-iodine molecules should be slightly negatively charged because the G-band of SWCNTs showed blue shift from 1589 cm^{-1} to 1607 cm^{-1} which corresponds to hole-doping in SWCNTs. We also confirmed that the peak that appeared disappeared by applying negative potential to SWCNT electrode. It means that the iodine molecules encapsulated in SWCNTs can be reversely reduced to iodine ions.

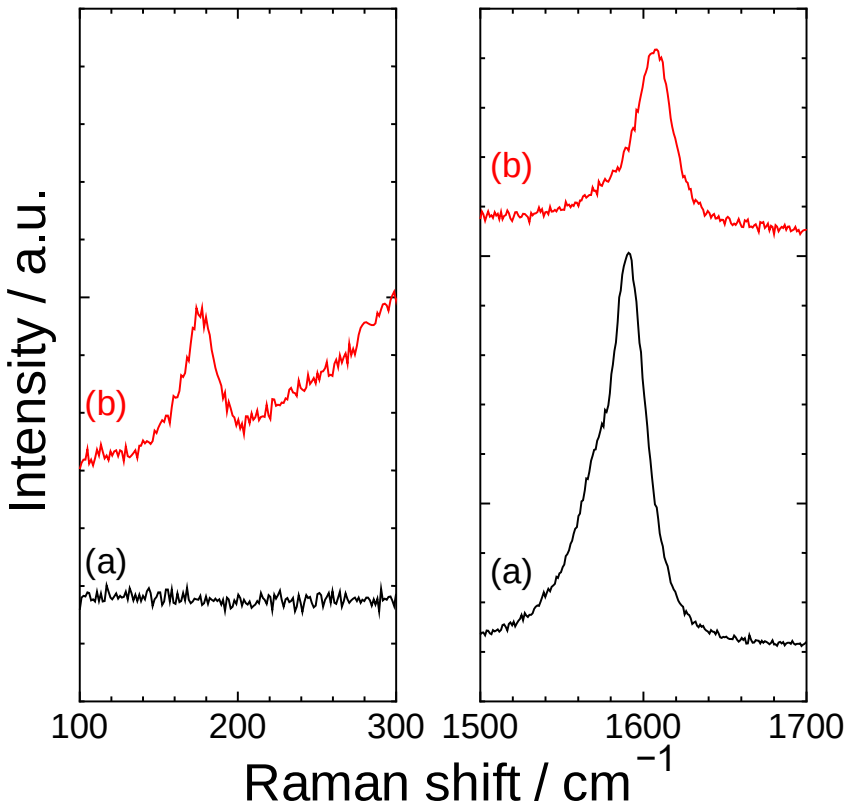

FIGURE 1.Raman spectra of SWCNTs (a) before and (b) after iodine encapsulation treatment.

As mentioned above, it was confirmed that it is possible to insert and extract iodine molecules into and from SWCNTs. In the next step, we checked that self-discharge of the redox capacitor should not occur. For this purpose, we performed time-resolved Raman measurements after the iodine encapsulation treatment. During the Raman measurements, we did not apply potential to SWCNT electrode (the circuit was open). If self-discharge occurred, the G-band peak position should return to 1589 cm^{-1} of pristine SWCNTs. As shown in Fig. 2, the G-band peak shifted toward lower wavenumber in the first 30 minutes. However, the amount of shift was very small and the G-band peak position maintained much higher value (ca. 1605 cm^{-1}) than that of pristine SWCNT for long time. It indicates that most of the encapsulated iodine molecules remained in SWCNTs in the absence of external voltage. We also observed that the open-circuit voltage did not change so much during the Raman measurements.

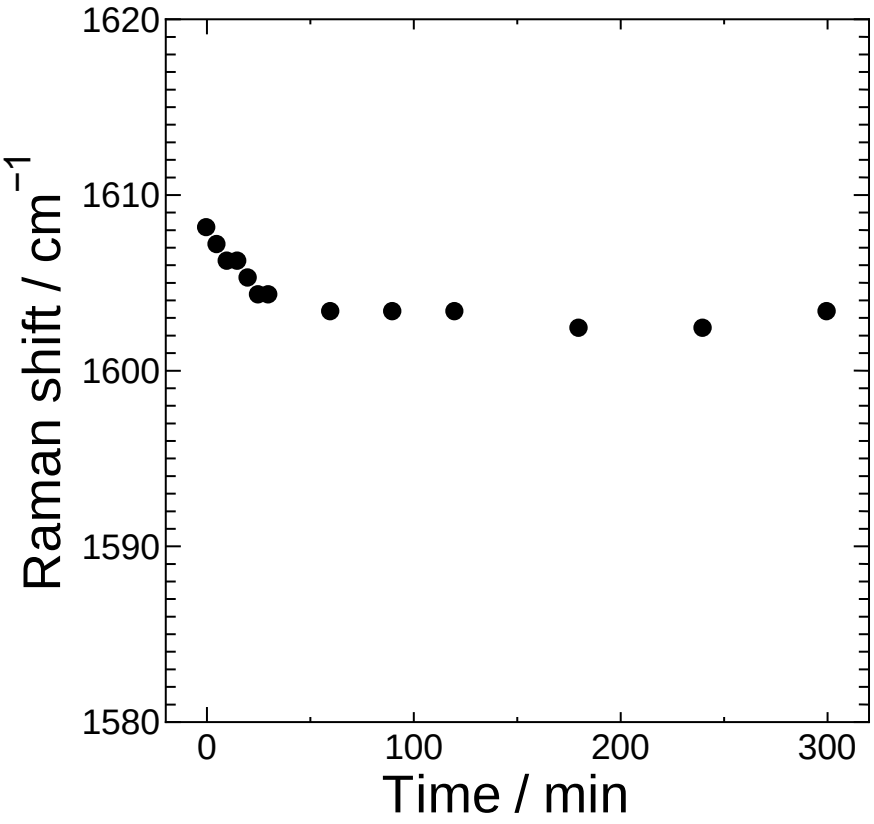

FIGURE 2.Raman G-band peak positions of SWCNTs encapsulating iodine molecules as a function of time after the EDLC circuit was open.

Finally, we performed charge-discharge experiments (Fig. 3). As shown in Fig. 3, the SWCNT electrode maintained almost constant potential value (ca. 0.3 V vs Ag/AgCl), while the counter electrode potential changed with the value of electric current. Since iodine redox reactions occurred at the SWCNT electrode, the electrode showed constant potential. On the other hand, the counter electrode shows pure capacitive behavior , which means that only physisorption of electrolyte ions occurred at the counter electrode. The cell voltage is of course determined by the difference of the two electrodes. It should be noted that the capacitance of the present redox capacitor is almost twice as that of normal EDLC because the maximum voltage is determined by the voltage window of the electrolyte. Furthermore, the amount of SWCNTs used in redox capacitor can be reduced compared to the normal EDLC case. Taking these into account, it is estimated that the energy density (7.58 Wh/kg) of the present redox capacitor is almost three times bigger than that of the normal EDLC using NaCl electrolyte (2.38 Wh/kg).

We also tried to perform similar experiments for multi-walled carbon nanotubes (MWCNTs). It was confirmed that the present iodine doping method is also applicable for some kinds of MWCNTs.

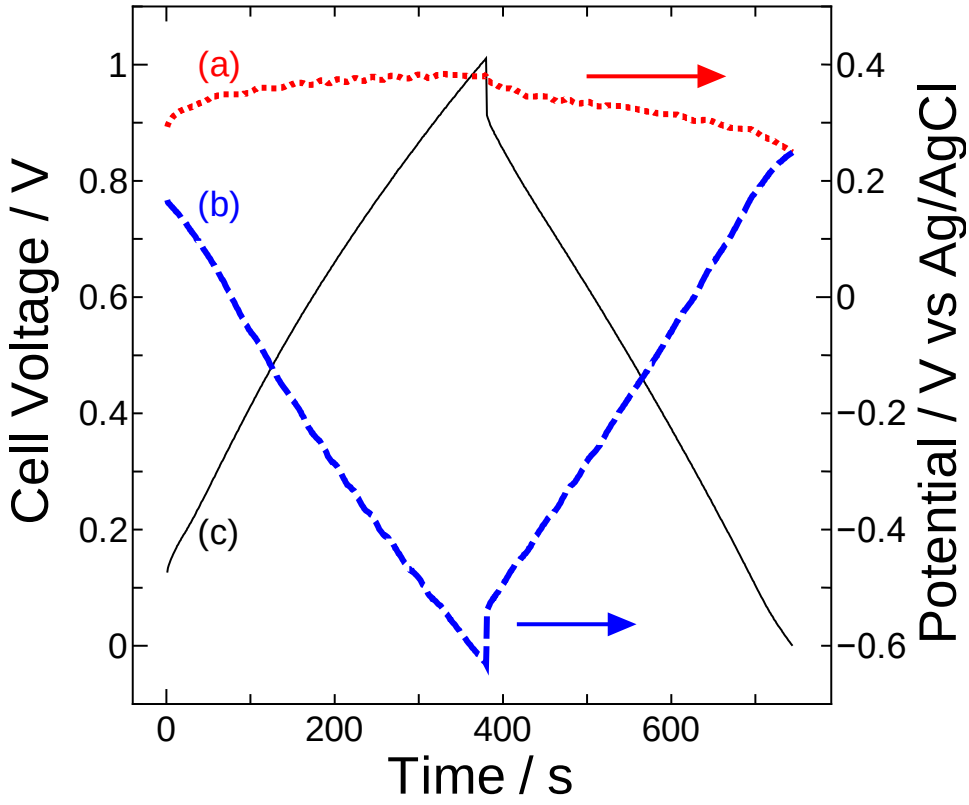

FIGURE 3.Charge and dis charge curves of redox capacitor consisting of SWCNT positive electrode and activated carbon negative electrode. (a) positive electrode potential , (b) negative electrode potential , (c) cell voltage.

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