Electrochemical Lithium Insertion Properties of Carbon Nanotubes Produced by Catalytic Pyrolysis of Acetylene*

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Abstract—Carbon nanotubes are synthesized in catalytic pyrolysis of acetylene over Co/SiO$_2$ at 650, 700, and 750°C. The first-charge capacities are 436, 303, and 205 mA h/g for samples produced at 650, 700, and 750°C. The capacity of the 650°C sample shows is higher than that of LiC$_6$ (372 mA h/g), but the voltage profile shows a large hysteresis (lithium is inserted below 0.25 V and removed above 1 V). The capacity below 1 V may be related to lithium intercalated into the interlayer of graphite planes, and that above 1 V, to accommodation of lithium at vacancies and nanoscopic cavities. With increasing preparation temperature, the cavities and vacancies are annihilated and the first-charge capacity above 1 V decreases.

Key words: carbon nanotube, catalytic pyrolysis, charge capacity, vacancy, nanoscopic cavity

INTRODUCTION

Since the discovery of carbon nanotubes (CNT) [1], catalytic pyrolysis of hydrocarbons has been developed to produce carbon nanotubes [2, 3]. Carbon nanotubes have many potential applications, such as electrochemical storage of energy [4]. Single-walled nanotubes [5], multiwalled nanotubes produced by the arc discharge [6], and multiwalled nanotubes produced by pyrolyzing hydrocarbons [7, 8], have been used as negative electrodes in lithium-ion batteries for this application. The results showed that the structures of CNT play major roles in electrochemical lithium insertion [8]. The slightly graphitized CNT shows a higher capacity than the theoretical capacity of graphite (372 mA h/g), but the potential profile shows large hysteresis. Depending on the chemical nature and geometry of catalyst particles and the reaction conditions, carbon nanotubes with various morphologies and structures can be produced. It can be predicted that the electrochemical performance of CNT is obviously different.

In this paper, CNT were prepared by catalytic pyrolysis of acetylene over Co/SiO$_2$ at 650–750°C. Electrochemical lithium insertion properties of these samples used as negative electrodes in lithium-ion batteries were evaluated.

EXPERIMENTAL

Catalytic synthesis of carbon nanotube and nanofibers. Carbon nanotubes were prepared by catalytic pyrolysis of acetylene over Co/SiO$_2$ catalysts at 650–750°C [2, 3]. The catalysts were obtained by porous impregnation of silica gel with an aqueous solution of Co nitrates in appropriate amounts. A quartz tube (diameter 5 cm, length 140 cm) reactor with ~100 mg of catalysts was placed in a horizontal oven, the temperature of which could be adjusted by a program temperature controller. A mixture of 5% acetylene in N$_2$ was introduced into the quartz tube at different temperatures at a rate of 200 ml/min for 30 min during the reactions. As-formed carbon nanotubes were held in HF solution for 12 h and in diluted HNO$_3$ for 12 h to dissolve the catalyst, then they were filtered, washed with distilled water, and dried at 150°C under vacuum.

Structure characterization of carbon nanotubes. Carbon nanotubes and nanofibers were observed by JEOL 100 CX transmission electron microscope. The specimens for TEM were dispersed in dehydrated ethanol by ultrasound and then dropped on Cu grids or holey carbon grids. X-ray diffraction (XRD) measurements were performed using Rigaku D/MAX-C diffractometer operated at 40 kV and 30 mA with CuK$_{α}$ radiation (0.15406 nm). Raman spectra were excited with 30 mW of 514.5-nm radiation from an Ar-ion laser at room temperature using a confocal microprobe Raman system (LabRam I) equipped with a charge-coupled device (CCD) multichannel detector.

Electrochemical measurements. Electrochemical measurements were performed using a three-electrodes test cell made of glass. A mixture of 95 wt % carbon
nanotubes and 5 wt % PTFE was rolled onto a plate. The plate was pressed thinly onto a nickel mesh at 10 MPa and then dried in vacuum for 24 h at 423 K and then used as the working electrode. Lithium foils were used as the counterelectrode and the reference electrode. The electrolyte was 1 M LiPF$_6$ dissolved in a 50/50 (vol) mixture of ethylene carbonate and diethyl carbonate. The discharge/charge measurements were performed at Arbin BT-2043 in the range 0.005–3.0 V at the discharge/charge rate of 40 mA/g. All cell assembly operations were carried out in a glove box filled with argon gas, where water and oxygen concentrations were less than 3 ppm.

RESULTS AND DISCUSSION

The TEM image in Fig. 1 shows that morphologies of CNT prepared by catalytic pyrolysis of acetylene are central hollow cylinders with diameters ca. a few tens of nanometers. With the increase of reaction temperature, the outer diameter of CNT produced by Co/SiO$_2$ catalyst has no apparent change.

Fig. 1. TEM image of carbon nanotubes.

The results of X-ray diffraction measurement are shown in Fig. 2. The sharp and high 002 carbon Bragg peak can be seen in XRD patterns of all samples. The crystallite size $d_{002}$ and lattice constant $L_c$ are determined from the 002 carbon Bragg peak using the Bragg–Scherrer formulas, $d_{002} = \lambda/2\sin\theta$, $L_c = K\lambda/\beta\cos\theta$, where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg angle, $\beta$ is the real half-peak width, the form factor $K$ is 0.9 for $L_c$. The crystallite size $d_{002}$ and $L_c$ of CNT are given in Table 1. With increasing preparation temperature, the $d_{002}$ values of samples decrease, indicating an increase in the samples’ crystallinity.

Raman spectroscopy is now routinely used to study the structure of carbonaceous materials. Figure 3 shows the Raman spectra of CNT measured at room temperature in the frequency range 1100–1800 cm$^{-1}$. The spectra clearly show strong peaks at 1580 cm$^{-1}$ ($G$ band), indicating the formation of graphitized CNTs. This is in good agreement with previous observations that the CNTs synthesized using CVD methods are in most cases multivalled. The peak at 1326 cm$^{-1}$ ($D$ band) is also observed for CNT walls, and defective pentagonal and heptagonal structures in the graphitized walls exist due to low growth temperatures.

Those features, including the wavenumbers and relative integrated intensities, are close to those of graph-

<table>
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<td>$L_c$, nm</td>
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Fig. 2. XRD patterns of carbon nanotubes obtained at (1) 650; (2) 700; and (3) 750°C.