

Short communication

Lithium insertion into CuO/carbon nanotubes

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Abstract

Carbon nanotubes are coated with a layer of copper by an electroless plating method. To prepare CuO/carbon nanotubes, Cu/carbon nanotubes are oxidized by heating to 160°C in air for 12 h. The lithium insertion properties of carbon and CuO/carbon nanotubes are tested by an electrochemical method. Carbon nanotubes can reversibly store 700 mA h Li g⁻¹ carbon, while CuO in CuO/carbon nanotubes can reversibly store 268 mA h Li g⁻¹ CuO. Li can insert into the CuO lattice at 1.7 to ~ 1.0 V and be released at 2.3 to ~ 2.5 V vs. Li according to $\text{CuO} + xe + x\text{Li} \leftrightarrow \text{CuOLi}_x$. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The discovery of carbon nanotube [1] has led to an extensive study of this new form of carbon which is obtained by means of arc discharge [2] or catalytic decomposition [3,4]. Most carbonaceous materials can react reversibly with lithium to some extent. Therefore, they can be used as negative electrodes in lithium-ion batteries [5]. Nevertheless, there has been little investigation of the electrochemical performance of Li insertion into catalytic carbon nanotubes [6,7]. One of our objectives is to study the insertion of Li into catalytic carbon nanotube by means of an electrochemical method.

Carbon nanotubes can be used as a support matrix to prepare one-dimensional, nanoscale, composite structures, such as carbon nanotubes coated with nickel [8]. The second of our objectives is to prepare CuO/carbon nanotube composite materials for use as cathodes in Li/CuO cells. Carbon nanotubes provide a pathway for Li diffusion into the crystal lattice of CuO while it remains available to intercalate Li reversibly. Li/CuO cells have been examined in detail by many authors [9–13] due to their high specific capacity for unit weight and volume and the fact that the discharge voltage is close to that of commonly used dry cells. There are, however, practically no pub-

lished data on the electrochemical charge performance of Li/CuO cells. In this study, the discharge and charge performance of a Li/(CuO/carbon nanotube) cell is examined, which is very helpful in understanding the electrochemical reaction mechanism of the CuO electrode.

2. Experimental

2.1. Catalytic synthesis and purification of carbon nanotubes

The procedures for catalytic synthesis and purification of carbon nanotubes were similar to those described by Hernadi et al. [14]. The carbon nanotubes used in this work were synthesized by catalytic decomposition of acetylene with iron nanoparticles. A ceramic boat containing 20 mg of iron nanoparticles was placed in a quartz tube. A reaction mixture of 5% acetylene in hydrogen was passed through the quartz tube at a rate of 200 ml min⁻¹. The reaction was carried out for 40 min at 700°C. The resulting carbon nanotubes were kept in diluted HNO₃ for 4 h to dissolve the iron catalyst. Then, they were filtered, washed with distilled water, and dried at 150°C under vacuum.

2.2. Preparation of CuO/carbon nanotubes

At first, carbon nanotubes were coated with a layer of copper by means of an electroless plating method. The

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Table 1
Composition of plating solution and reaction conditions

Chemical	
HCHO (37 wt.%)	10 ml l ⁻¹
NaOH	20 g l ⁻¹
NaKC ₄ O ₆ ·4H ₂ O	50 g l ⁻¹
CuSO ₄ ·5H ₂ O	10 g l ⁻¹
Reaction time	10 min
Reaction temperature	25°C

carbon nanotubes were activated in a solution of 0.1 M SnCl₂/0.1 M HCl for 30 min, and in a solution of 0.0014 M PdCl₂/0.25 M HCl for a further 30 min. The activated carbon nanotubes were then introduced into the electroless plating bath. The composition of the plating solution and the reaction conditions are given in Table 1. After electroless plating, the Cu-coated carbon nanotubes were washed, dried, and oxidized in air at 160°C for 12 h to prepare CuO/carbon nanotubes. The CuO content of the CuO/carbon nanotubes was determined by chemical analysis [15]. The weight ratio of carbon to CuO is 1:1.5.

2.3. TEM and HRTEM observations

A JEOL 100 CX was used for the observation of the morphology of carbon nanotubes. The microstructure observation and high resolution images were taken in a side-entry JEOL2010 transmission electron microscope with a point-to-point resolution of 0.19 nm and operated at 200 kV. To prepare transmission electron microscope specimens, carbon nanotubes were dispersed in acetone by an ultrasonic method for 10 min and then dropped on carbon grids.

2.4. Electrochemical testing

The Li insertion properties of carbon and CuO/carbon nanotubes were tested in coin-type cells. Cathodes were prepared using 92 wt.% CuO/carbon or carbon nanotubes, and 8 wt.% polytetrafluoroethylene (PTFE) diluted in anhydrous alcohol. Excess anhydrous alcohol was added to make a slurry. The slurry then was spread uniformly on pre-weighed foam nickel. Once the cathode stock was dried, it was compressed between flat plates to ~30 bar pressure, dried at 150°C under vacuum overnight, and then weighed to determine the active mass of carbon and CuO. The anode was Li metal foil. A microporous separator wetted with 1 M LiClO₄ dissolved in a 50/50 (v/o) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was sandwiched between the cathode and a Li anode. Cells were assembled in an argon-filled glove box. During the first three discharge–charge cycles, Li/(CuO/carbon nanotube) cells were tested by using a constant current of 0.24 mA cm⁻² between 0.005 and ~2.8 V at 30°C. To determine cycle life, a higher current,

viz., 0.72 mA cm⁻², was adopted after the first three discharge–charge cycles.

3. Results and discussion

3.1. Morphology and microstructure of carbon nanotubes

TEM and HRTEM images of carbon nanotubes are shown in Fig. 1(a) and (b), respectively. The TEM image shows that the diameter of the tubes is around 30 nm. The yield of carbon nanotubes is above 95% (v/o) as estimated from Fig. 1(a). The HRTEM image (Fig. 1(b)) shows that the carbon nanotubes are poorly graphitized and, therefore, the Li is able to insert into their edge planes. In lattice images of [002] reflections, the fringes of the graphite sheets are wrinkled, discontinuous, and not parallel to the axis of the carbon nanotube, which is different from that reported in the literature [1–4]. The detailed growth mechanism of the carbon nanotubes prepared here will be presented elsewhere.

3.2. Charge and discharge of Li/carbon nanotube cell

Fig. 2 shows the discharge and charge behaviour of a Li/carbon nanotube cell at a current density of 20 mA g⁻¹ carbon nanotube during the first three cycles. The first discharge curve shows a plateau at about 0.8 V. This may be associated with electrolyte decomposition and causes the formation of a passivate film or a solid electrolyte interphase on the carbon surface [16]. In subsequent cycles, Li can insert into the carbon nanotubes reversibly. The reversible capacity is 700 mA h g⁻¹ in the first charge, 592 mA h g⁻¹ in the second charge, and 577 mA h g⁻¹ in the third charge. The discharge–the charge coulombic efficiency during the first three cycles was 43, 82 and 88%, respectively. In the experiments, an amount of Li significantly higher than LiC₆ (372 mA h g⁻¹) has electrochemically inserted into carbon nanotubes. Nevertheless, this reversible capacity displays a large hysteresis (Li is inserted near 0 V and removed near 1 V vs. Li). Dahn et al. [5] claimed that Li can bind near hydrogen atoms in carbonaceous materials containing substantial hydrogen; voltage profiles with large hysteresis for carbonaceous materials is related to the hydrogen in these samples. Carbon nanotubes produced by the catalytic decomposition of hydrocarbon contain substantial hydrogen [17]. Thus, Li binding near hydrogen atoms may cause the hysteresis.

3.3. Charge and discharge of Li/(CuO/carbon nanotube) cell

The first three discharge–charge cycles of a Li/(CuO/carbon nanotube) cell at a current density of 7

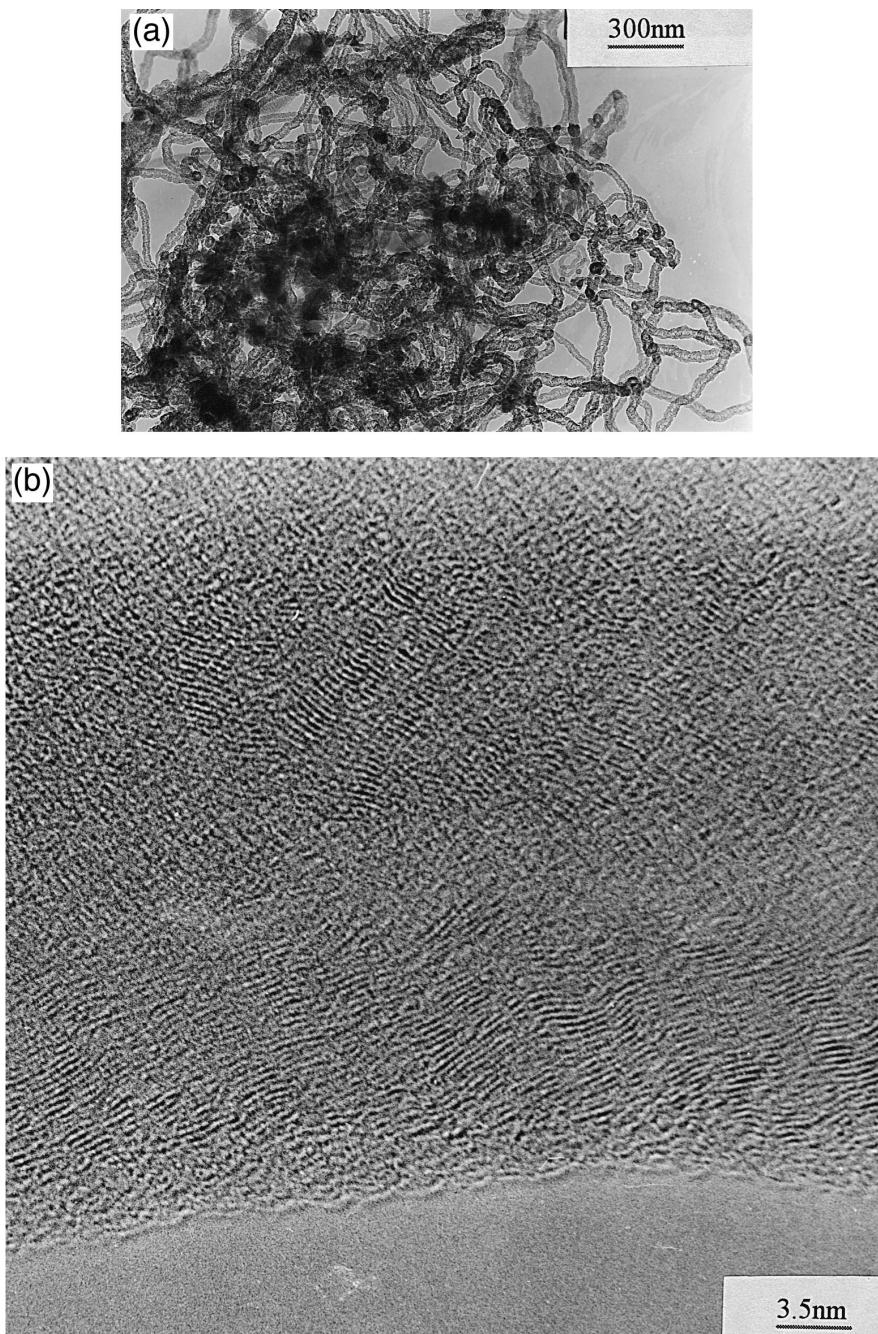


Fig. 1. (a) TEM and (b) HRTEM images for carbon nanotubes.

mA g^{-1} CuO/carbon nanotube are given in Fig. 3. A comparison of the curves in Figs. 2 and 3 reveals the difference between the discharge–charge behaviour of a Li/(CuO/carbon nanotube) cell and that of a Li/carbon nanotube cell. The first discharge curve in Fig. 3 shows two additional plateaus at 2.2 V and as 1.7 to 1.0 V. The plateau close to 2.2 V is due to the reduction of O_2 and H_2O [10]. The participation of O_2 and H_2O cannot be excluded, since these species are known to be strongly absorbed on the CuO surface. After the first charge, the

plateau close to 2.2 V disappears because O_2 and H_2O absorbed on the CuO surface reduce completely. The plateau from 1.7 to 1.0 V corresponds to Li insertion into the crystal lattice of CuO [9–13]. The first charge curve in Fig. 3 shows an additional plateau at 2.3 to 2.5 V. Since the open-circuit voltage of a Li/CuO cell is 2.4 V [13], we believe that this plateau corresponds to Li extraction from the crystal lattice of CuO. In subsequent cycles, the discharge plateau from 1.7 to 1.0 V and the charge plateau from 2.3 to 2.5 V remain, which confirms that Li can

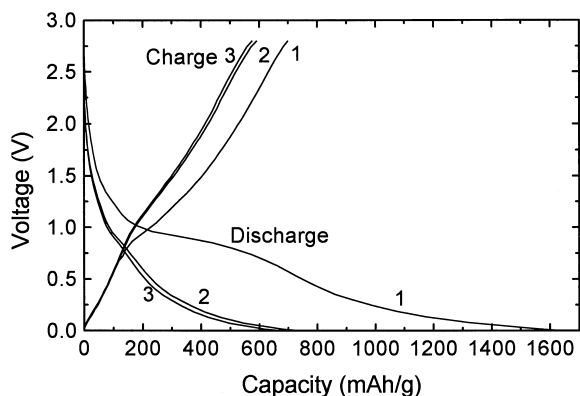


Fig. 2. Discharge and charge curves for a Li/carbon nanotube cell during the first three cycles (discharge and charge at a current density of 20 mA g^{-1} carbon nanotube).

insert into the crystal lattice of CuO reversibly. According to the length of the plateau of Li extraction from the crystal lattice of CuO, the current density and the CuO content, we conclude that the CuO in CuO/carbon nanotubes can reversibly store 268 mA h g^{-1} CuO. Our results are very helpful towards understanding the electrochemical reaction mechanism of Li/CuO cells. From studying the discharge performance of the cathode of Li/CuO cells, Novak [9] asserted that the discharge reaction involves intercalation of Li ions into the CuO lattice according to $\text{CuO} + xe + x\text{Li}^+ \rightarrow \text{CuOLi}_x$. Based on the above findings, it seems probable that Li can insert into the CuO lattice at 1.7 to $\sim 1.0 \text{ V}$ and desorb at 2.3 to $\sim 2.5 \text{ V}$ vs. Li, according to $\text{CuO} + xe + x\text{Li} \leftrightarrow \text{CuOLi}_x$.

3.4. Cycle life of Li/(CuO/carbon nanotube) cell

The discharge–charge curves of a Li/(CuO/carbon nanotube) cell at the 4th, 10th and 20th cycles are shown in Fig. 4. The cycle life appears to be limited, as shown in Fig. 4. The limited cycle life, on the one hand, may be due

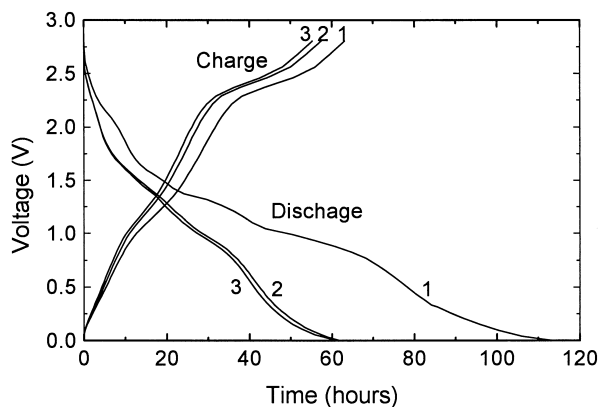


Fig. 3. Discharge and charge curves for a Li/(CuO/carbon nanotube) cell during the first three cycles (discharge and charge at a current density of 0.24 mA cm^{-2}).

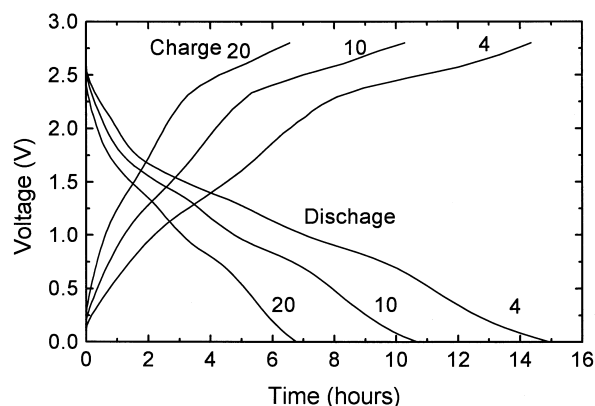


Fig. 4. Discharge and charge curves for a Li/(CuO/carbon nanotube) cell at 4th, 10th and 20th cycles. (Discharge and charge at a current density of 0.72 mA cm^{-2}).

to CuOLi_x decomposing to Cu, Cu_2O and Li_2O during the Li insertion and release process [9], which results in degradation of the capacity of Li insertion into CuO. On the other hand, when Li inserts into carbon nanotubes, the lattice of the carbon will expand. Part of the graphite sheets of the carbon nanotubes may be exfoliated [16] due to their weak connection since the coulombic efficiency after 10 cycles is still about 0.98, which results in a decline in the capacity of Li insertion into carbon nanotube.

4. Conclusions

A study has been made of the microstructure and morphology of carbon nanotubes and their electrochemical performance during Li insertion and release. The results show that the reversibly capacity of carbon nanotubes is 700 mA h g^{-1} corresponding to 1.88Li for 6C, but the high capacity exhibits a larger potential hysteresis. Carbon nanotubes have been used as a support matrix to prepare nanoscale composite materials such as CuO/carbon nanotubes. The Li insertion properties of CuO/carbon nanotubes have also been examined. It is found that CuO in CuO/carbon nanotubes can reversibly store 268 mA h g^{-1} CuO. It is concluded that Li can insert into the CuO lattice at 1.7 to $\sim 1.0 \text{ V}$ and be released at 2.3 to $\sim 2.5 \text{ V}$ vs. Li, according to $\text{CuO} + xe + x\text{Li} \leftrightarrow \text{CuOLi}_x$. The cycle life of a Li/(CuO/carbon nanotube) cell is limited due to CuOLi_x decomposing to Cu, Cu_2O and Li_2O and the microstructure of carbon nanotube being destroyed during Li insertion and release.

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