Preparation of multi-walled carbon nanotube array electrodes and its electrochemical intercalation behavior of Li ions

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Abstract

In this work, multi-walled carbon nanotube array electrodes were prepared by chemical vapor decomposition (CVD) in nano-sized porous alumina membranes (the diameter of the pore is about 55 nm). The intercalation behavior of Li⁺ in the array electrodes was also primarily investigated. The importance of selection of current collectors for the study of Li⁺-intercalation processes in carbon nanotube array electrodes was stressed. Since carbon nanotube array electrodes can give high current density due to its high surface area and ordered electrode configuration, which may be used in some fields such as chemical sensors and micro-battery. © 2002 Published by Elsevier Science B.V.

1. Introduction

The carbon nanotubes, discovered by Iijima in 1991 [1], have novel structure, high surface area, low resistance and high stability [2–4], thus opened up different ways of its applications in different fields. Recent progress in template synthesis of nano-structured materials has made it possible to investigate the carbon nanotubes and other one dimensional (1D) materials prepared in alumina template [5–7], thus carbon nanotube array electrodes should be prepared by using this technique and its electrochemical performance can be determined. The 1D carbon nanotube array electrode is shown to have very high specific area, relatively ordered structure and has been proposed to have potential technical applications in molecular electronic devices such as electron filed emission and energy storage [8–10]. Because of the special character of carbon nanotube array, it should be a potential material for chemical sensors and lithium ion micro-battery. The electrochemical intercalation of lithium in multi-wall and single-wall carbon nanotubes has been studied in recent years [11–13]. It was also reported that the multi-wall nanotubes (MWNT) are composed of concentric and graphene tubules and the lithium atoms can inserted into the inter-shell spaces, moreover the structural defect also provides some interstitial sites [14,15] for lithium ion intercalation. However, detailed mechanism of electrochemical lithium atom intercalation in MWNT are still not be accurately
described, array electrode will be a useful model system for the study because of its particular structural nature. Alumina template has been widely utilized to prepare various nano-structured array for some time, and the MWNT arrays were also prepared in this template, but its electrochemical property especially the electrochemical intercalation behavior of lithium ions into MWNT array electrodes has not been reported in the literature to our knowledge.

In this Letter, we not only show the preparation procedures of carbon nanotube array electrodes by alumina template, but also discuss the electrochemical performance of array electrode in 1 M LiPF$_6$/EC + DMC by cyclic voltammetric technique. Furthermore, vacuum spattered Pt and Ni film employed as current collectors of carbon nanotube array anodes and their electrochemical performance are compared.

2. Experimental

Before anodization, an Al sheet was electro-polished in phosphoric/glycerol solution at 13–15 V for 10 min at 70–80 °C until a mirror-finish was obtained. Then the pretreated Al sheet was anodized in 0.3 M oxalic acid solutions for about 1 h under 40 V at 25 °C, thereafter anodized Al substrate was immersed in 5% H$_3$PO$_4$ for some time to remove partial alumina template, and then anodized again under the same condition. By this two-step anodization process, a regular pore structure of membrane is obtained [16,17]. After that, 50 Hz alternative current sources was used to deposit Co metal in the pores, then the alumina membrane was removed from substrate by being immersed in the saturated HgCl$_2$ solution.

The template membranes with metal Co in the holes were used as reaction vessels and catalyst, which were put into furnace and thermally treated by programmed heating-process. In short, carbon monoxide was first used for reducing possible oxides on cobalt for about 5 h at 600 °C, then the temperature was increased from 600 to 650 °C in 20 min. Thereafter a mixture of acetylene and N$_2$ flowed into the furnace to produce carbon nanotubes within the holes of the membrane. In order to dissolve the alumina surrounding the carbon nanotubes, the whole membrane was immersed in 40% w/w HF solution for several minutes to disperse carbon in the solution before transmission electron microscopic (TEM) measurement. On the upper surface of template with MWNT, a thin Pt or Ni film was deposited by Magnestron ion-sputtering method. In order to study electrochemical character of MWNT array, the membrane was put into 5% H$_3$PO$_4$ for several hours to dissolve the barrier layer of alumina template, then the electrode was installed in a three-electrode cell. All of those steps described above are summarized in a scheme shown in Fig. 1.

3. Results and discussion

A typical scanning electron microscopic (SEM) image of outer surface of the template is shown in Fig. 2a, the pore diameters can be evaluated from such an image. i.e. about 55 nm in this study. The cross section of the membrane is also shown in Fig. 2b. It can be seen that a uniform and straight pores were formed in the alumina substrates. The importance of template method are its reproducible ability and predictable by controlling both the diameter, length and its ratio of the pores. Furthermore, the pores are completely vertically oriented in the same direction which will contribute greatly to the special nature of carbon nanotube
array electrodes developed by us. As indicated in the experimental sections, carbon nanotubes were catalytically produced with Co particles in aluminum membrane, and HF acid treatment is employed to remove the catalyst and excess membrane before TEM measurement. A typical TEM image of carbon nanotubes is shown in Fig. 3a, which indicates that outer diameter of carbon nanotube is about 55 nm with a hollow core of 40 nm. The image also approved that unwanted barrier layer of alumina membrane and cobalt catalysts are almost completely dissolved by using 40% w/w HF acid under ultrasonic treatment. Raman spectroscopic characterization of carbon nanotubes which shows that MWNT has both amorphous carbon (1398 cm\(^{-1}\)) and graphite (1598 cm\(^{-1}\)) structural character, however we did not observe that low frequency modes originating from the RBM of SWMN, it implies the co-existence of some disorder carbon in our system and a combined contribution of two different structural nature (i.e. amorphous carbon and graphite-ring carbon) to the electrochemical behavior of MWNT can be expected. The individual contribution of above two types of carbon to the Li\(^+\) insertion needs further investigations.

Figs. 3b and c show images of upper surface and cross section of the array electrode after treatment of H\(_3\)PO\(_4\), respectively. Although the dissolution of alumina template, there exists some defects in the array electrode. It still can be approximately viewed as a regular array of carbon nanotube. We believed that the array electrode is a good model system for our mechanism study of lithium interaction in carbon nanotubes, i.e. lithium ions can diffuse either through the exposed part into the graphene or inner core of nanotubes. From the images, it is thought that lithium ions diffusion route include outer surface and upper tips of the carbon nanotubes, but it may be expected that the later part may contribute much more to the lithium intercalation processes because of its easier route in diffusion process.

It has been reported that Pt, Cu, and Ni film can be used as current collector of anode under certain conditions, and Cu current collector plays the most important role in commercial process [18,19]. But literature results indicate that Pt sheet, Cu film may form alloys at lower voltage window, and our study also approved that vacuum sputtered Pt film on carbon nanotubes show obvious evidence of alloy forming. Figs. 4a and b are typical voltammetric curves of Pt sheet and vacuum sputtered Pt film electrodes in cyclic voltammetric curve in 1 M LiPF\(_6\)/EC + DMC electrolytes, and the CV curves also show an
Fig. 3. TEM and SEM images of carbon nanotubes (CNs) and its array electrode membranes prepared by alumina template (a) TEM image of CNs prepared by alumina template. (b) and (c) are SEM images of carbon nanotube array electrodes membranes: (b) cross section, (c) upper surface of the carbon nanotube array membrane.

Fig. 4. Cyclic voltammetric curves of different metal electrodes in 1 M LiPF$_6$/EC + DMC: (a) Pt sheet; (b) vacuum sputtered Pt film; (c) sputtered Ni film. The scan rate is 1 mV/s.
apparent hysteresis circle at lower voltage. Our cyclic voltammetric results of carbon nanotube array electrodes with Pt current collectors also shows the electrochemical performance of carbon nanotubes/Pt system were interfered and concealed by Pt/Li alloy formation process. Thus Pt current collector is not one of suitable options for study of carbon nanotube anodes. Fig. 4c is a CV curve of vacuum sputtered Ni film in same electrolytes, it did not show hysteresis cycle and there just shows current peaks for reduction and oxidation of the electrolytes. In addition, to our knowledge, the nickel alloy formed with lithium is not ever reported in the literature. Thus Ni can be considered as a good current collector for the study of Li\(^+\) intercalation behavior of carbon nanotube array electrodes.

Fig. 5 shows CV curves of carbon nanotube array electrodes and carbon nanotube sheet electrodes with Ni current collectors in first potential cycle. Compared with that typical CV curves of carbon nanotube sheet electrode at about in 1.1 V or slightly lower potential, some solvents in electrolytes were reduced and a solid electrolyte interface (SEI) on the carbon nanotube electrode was formed in the first cycle. However when the potential is negative than 0.5 V, lithium ions were inserted into the carbon nanotubes, but the de-intercalation reaction cannot be clearly distinguished from the CV curves in the reversing scanning process due to the reason of higher potential scanning rate in CV experiments. Because quantity of carbon nanotubes in the array electrodes is very small (e.g. < 0.1 mg supposing the electrode area is 0.2 cm\(^2\)), the current originated from lithium ion intercalation reaction should be smaller than sheet electrode, but current density is apparently much higher (i.e. 100 mA/g or 500 mA/cm\(^2\) can be estimated). Thus we anticipated, the array electrodes have very high specific area, and it can endure higher current density, thus array electrode may have utilization in micro-battery system and electrochemical sensor.

4. Conclusions

Our results indicate that lithium ion can diffuse through the outer surface and upper tips into the inner graphene without any interference of binder and conductors in an ordered carbon nanotube array electrodes. In order to get rid of the interfering effects from current collector, different current collector were prepared and compared. It is demonstrated that vacuum sputtered Ni film is a good choice. The sputtered Pt film is proved to be not suitable for lithium battery anode. Furthermore, the array electrode may tolerate high current density, thus its potential application in micro-battery and electrochemical sensors should be anticipated.

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