Electrochemical characterization of carbon nanotubes as electrode in electrochemical double-layer capacitors


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Abstract

Carbon nanotubes uniformly 50 nm in diameter were directly grown on graphite foil. Cyclic voltammetry (CV) shows that the carbon nanotube/graphite foil electrode has a high specific capacitance (115.7 F/g at a scan rate of 100 mV/s) and exhibits typical double-layer behavior. A rectangular-shaped CV curve persists even at a scan rate of 100 mV/s in 1.0 M H₂SO₄ aqueous solution, which suggests that the carbon nanotube electrode could be an excellent candidate as the electrode in electrochemical double-layer capacitors. In addition, the influence of the potential scan rate, aging, and the electrolyte solution on the specific capacitance of nanotube electrodes was also studied. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: A. Carbon nanotubes, Electrodes; B. Chemical vapor deposition; C. Scanning electron microscopy (SEM), Sputtering

1. Introduction

Electrochemical capacitors are unique energy storage devices that exhibit high power density and long cycle life. According to the energy storage mechanism, electrochemical capacitors can be divided into two types: electrochemical double-layer and redox supercapacitors. In the former, energy storage arises mainly from the separation of electronic and ionic charges at the interface between high-specific-area electrode materials and the electrolyte solution. Principally, it is electrostatic [1]. In the latter, fast Faradic reactions take place at the electrode materials at characteristic potentials like in batteries, and give rise to what is called pseudo-capacitance [2]. Recently, electrochemical double-layer capacitors (EDLC) have shown new promising applications in the capacitive deionization of water [3] and as pulse power sources for digital communication devices and electric vehicles [4]. The popularity of these devices is derived from their higher energy density relative to conventional capacitors, and their longer cycle life and higher power density relative to batteries.

Carbon nanotubes were discovered in 1991 [5]. Due to their nanometer size and interesting properties, including electrical conductivity and mechanical strength, carbon nanotubes are of great interest for many applications—for example, batteries [6], storage of hydrogen [7], flat panel displays [8,9], chemical sensors [10], etc. Furthermore, their high accessible surface area, low resistance and high stability [11–13] suggest that carbon nanotubes are suitable materials for electrodes in electrochemical double-layer capacitors, which are being studied extensively [14–17]. Currently, two kinds of carbon nanotube electrodes have been developed: binder-free [14] and binder-enriched [15]. Generally, the preparation of carbon nanotube electrodes is very complicated. The following steps are necessary [14]: (1) harvest the nanotubes and introduce chemical functional groups on the surface of the nanotubes; (2) disperse the functionalized hydrophilic nanotubes in solvent; (3) assemble the individualized carbon nanotubes into an interconnected, entangled and free-standing structure. In the binder-free electrode, carbon nanotubes are mechanically and electrically loose. When a binder is used [15], it brings impurities into the electrode and degrades the electrochemical performance. Furthermore, both methods result in a high contact resistance between the active material (carbon nanotubes) and current collectors (graphite foil or metallic substrates). However, many studies and applications demand nanotubes to be directly grown on the substrate to minimize the contact resistance between nanotubes and substrate, especially on graphite.
substrate, which is still a challenge. This paper reports the direct growth of carbon nanotubes on bare graphite foil, which is usually used as a current collector in electrochemical double-layer capacitors. This simplifies the preparation of carbon nanotube electrodes. The electrochemical characterization of the carbon nanotube electrodes was investigated by cyclic voltammetry, and a high specific capacitance was obtained. This kind of carbon nanotube electrode has several advantages: sufficient mechanical strength, binder-free, and minimum contact resistance between activated materials (carbon nanotubes) and current collector (graphite foil).

2. Experimental

2.1. Preparation of carbon nanotube electrodes

Carbon nanotubes were directly grown on graphite foil (thickness 0.067 mm) by the chemical vapor deposition (CVD) technique in a tube furnace. Nickel (Ni) catalyst particles were deposited on the graphite foil by magnetron sputtering. Carbon nanotubes were grown in a pressure of 5–9 Torr maintained by flowing acetylene and nitrogen gases with a total flow rate of 110 sccm for 1 h at 660°C [18]. The acetylene-to-nitrogen volume ratio was 1:10. A scanning electron microscope (SEM, JEOL JSM-6340F) was employed to examine the packing density, purity and diameter of the carbon nanotubes. Energy disperse X-ray spectra (EDX) were recorded by SiLi detectors attached to the SEM, to analyze the chemical composition of the carbon nanotube samples.

2.2. Electrochemical measurements

The electrochemical properties of the carbon nanotube electrodes were investigated by cyclic voltammetry in the standard three-electrode cell. A PC4 Potentiostat/Galvanostat (Gamary Instruments, Warminster, PA, USA) was employed for the cyclic voltammetric (CV) measurements. A platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. Before measurement of the cyclic voltammogram, samples were immersed in 15 wt.% HNO₃ aqueous solution for 30 min to remove metallic Ni particles (catalyst) and also to increase the electrochemical activity of the surface of the carbon nanotubes in the solution [14]. All measurements were made under ambient atmospheric conditions.

3. Results and discussion

Fig. 1 shows SEM images of carbon nanotubes that were grown directly on graphite foil. The diameter of the nanotubes is uniformly about 50 nm, as shown in Fig. 1b. The packing density and purity of the carbon nanotubes are high, as shown in Fig. 1a.

To ensure that the carbon nanotubes grow directly on the graphite foil, EDX was employed to examine the position of the Ni catalyst on as-grown and acid-treated (in 15 wt.% HNO₃ aqueous solution for 6 h) samples. For comparison, EDX spectra were recorded for the bottom and tip areas of the carbon nanotubes. The results are presented in Table 1. It can clearly be seen that, both before and after acid treatment, the Ni content is much higher at the bottom area of the nanotubes than at the tip area, which indicates that the growth of carbon nanotubes was initiated from the bottom. After the sample was treated in 15 wt.% HNO₃ aqueous solution for 6 h, the Ni content was still as high as 3.23 at%, which means that the remaining Ni is enclosed inside the nanotubes, otherwise it would have been removed by HNO₃. More importantly, the nanotubes did not come off the graphite foil, which
Table 1  
EDX-determined chemical composition at the bottom and top of carbon nanotubes grown on graphite foil

<table>
<thead>
<tr>
<th>EDX area</th>
<th>Chemical composition (at%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>Bottom $^a$</td>
<td>Before acid treatment 89.58 10.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top $^b$</td>
<td>Before acid treatment 99.69 0.31</td>
<td></td>
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$^a$ Bottom area of carbon nanotubes, SEM magnification 1000.
$^b$ Samples were acid-treated in 15 wt.% HNO$_3$ aqueous solution for 6 h, and then immersed in double distilled water. When the pH of the double distilled water (with samples) was about 6.5, the samples were taken out and dried in an oven overnight (at 130°C).
$^c$ Top area of carbon nanotubes, SEM magnification 3000.

means that the nanotubes are not grown on Ni, but directly on the graphite foil. The higher Ni content (about 10.42 at%) measured before acid treatment is due to the Ni particles that sit on the graphite surface in the gap between the nanotubes. Obviously, these exposed Ni particles outside the nanotubes are easily removed by HNO$_3$ during acid treatment. At the tip area, there were also some Ni particles, which may be the catalyst maintaining the growth of the nanotubes.

Fig. 2 shows CV curves measured from a carbon nanotube electrode in 1.0 M H$_2$SO$_4$ aqueous solution at potential scan rates of 100 and 25 mV/s. Typical double-layer behavior is observed. A similar result has also been observed for single wall carbon nanotubes at a potential scan rate of 50 mV/s [16]. The featureless CV probably results from the distribution of the nanotubes [16]. The electronic properties of carbon nanotubes are sensitive to structural variations, such as the length, diameter, and helicity of the arrangement of carbon hexagon rings in their walls [19–21]. Indeed, in both single wall nanotubes [22] and multi-wall nanotubes [23], a different chirality of the nanotube structure (Armchair and Zigzag), which is related to the different electronic properties (metallic and semiconducting), has been observed. Therefore, the featureless CV might be an average of many closely spaced peaks representing electron transfer into each tube [13]. Another possibility is that the current which is used to charge the double-layer capacitor between the nanotube electrode and the electrolyte solution is much more than the Faradic current due to the very high specific surface area of the carbon nanotube electrode.

As we know, the achievement of rectangular-shaped cyclic voltammograms over a wide range of scan rates is the ultimate goal in electrochemical double-layer capacitors. This behavior is very important for practical applications. First, a higher energy density is expected, because the usable potential range is wide. Second, a higher power density is expected as the critical scan rate increases. As shown in Fig. 2, the carbon nanotube electrode can retain the rectangular-shaped CV up to a high scan rate (100 mV/s). By contrast, MSC-25 carbon, the most popularly applied activated carbon, has a deformed cyclic voltammogram at a scan rate of 10 mV/s and a completely collapsed one at a scan rate of 20 mV/s [24]. The featureless and rectangular-shaped CVs suggest that the carbon nanotube electrode is an excellent candidate for electrochemical double-layer capacitors.

To obtain a quantitative estimate of the amount of charge stored per unit mass of carbon nanotubes, the capacitance can be obtained from CV curves using the equation $c = i/v$, where $i$ and $v$ are the current and the potential scan rate, respectively. The average specific capacitance can be obtained by integrating oxidation currents in the CV curve. Note that the specific capacitance is as high as 115.7 and 146.6 F/g at potential scan rates of 100 and 25 mV/s, respectively.

In order to investigate the stability of the carbon nanotube electrodes, we measured the electrochemical properties again after the samples had been aged in air for 1 month. The corresponding cyclic voltammograms are shown in Fig. 3. Compared to the CV curve shown in Fig. 2, there were large background currents observed. This current increases with increasing scan rate, suggesting that it is capacitive in nature. Furthermore, a pair of broad redox peaks (A and A’) is also observed in Fig. 3. To test the hypothesis that the A/A’ peaks are due to a Faradic process occurring on the surface of the carbon nanotubes, the response peak height was measured as a function of scan rate. The linearity of the curve obtained (Fig. 4) indicates that the process in question is not diffusion controlled in this scan rate range, which is consistent with
Table 2 shows the influence of scan rate, aging and electrolyte solution on the specific capacitance of the carbon nanotube electrode. In all cases, capacitance increases with decreasing scan rate. Furthermore, no significant change of the specific capacitance is observed after 1-month aging. However, the specific capacitance is much lower in 0.1 M LiClO₄ propylene carbonate (PC) solution than in 1.0 M H₂SO₄ aqueous solution, although featureless cyclic voltammograms are also observed. Additionally, comparing the capacitance obtained at 2 and 100 mV/s, which are denoted $C_2$ and $C_{100}$, $(C_2 - C_{100})/C_{100}$ in PC solution (514.1%) is much larger than that in aqueous solution (21.7%). This indicates that slow charging–discharging processes are present in non-aqueous solutions. Low specific capacitance and slow charging–discharging processes suggest that carbon nanotubes may not be suitable for electrode materials in electrochemical double-layer capacitors in non-aqueous solutions.

4. Conclusion

Carbon nanotube electrodes are obtained simply by growing carbon nanotubes directly onto graphite foil to minimize the contact resistance between the active material and the current collector and also to simplify the electrode fabrication process. The electrochemical properties of the carbon nanotube electrodes were investigated by cyclic voltammetry. A high specific capacitance (115.7 F/g) and rectangular-shaped CV curves were obtained up to a high potential scan rate (100 mV/s) in 1.0 M H₂SO₄ aqueous solution. These results show that the carbon nanotube electrode could be an excellent candidate in electrochemical double-layer capacitors.

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References


