A study of activated carbon nanotubes as electrochemical super capacitors electrode materials

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Abstract

Activated carbon nanotubes (CNTs) were produced by KOH. The activated CNTs and the normal CNTs were both used as the electrochemical super capacitors (ESCs) electrode materials. The electrochemical capacitance of the activated CNTs was 2 times that of the normal CNTs. Moreover, the activated CNTs had 3 times BET specific surface area and 1.5 times pore volume than those of the normal CNTs. The activated CNTs and the normal CNTs were both examined by transmission electron microscopy (TEM), scanning electric microscopy (SEM) and X-ray diffraction (XRD).

Keywords: Activated carbon nanotubes; Electrode materials; Electrochemical super capacitors

1. Introduction

In recent years, electrochemical super capacitors (ESCs) have been focused on for their practical applications as high power devices since they have large capacitance, have long cycling life and are free from toxic materials [1,2]. Many materials, such as RuO₂ [3] and activated carbon [4], have been used as the ESCs electrode materials.

Carbon nanotubes (CNTs) have come to be one of the most interesting materials since Iijima [5] first found them in 1991. Lots of studies about the applications of CNTs were carried out for the CNTs’ novel hollow-tube structure, nanometer dimensions, high specific surface area and excellent electronic semi-conductivity and conductivity. Studies on the CNTs’ application as ESCs electrode materials were also performed [6,7], and the results showed that the CNTs were a promising candidate electrode material of ESCs. However, from those literatures, we found the specific capacitance of the ESCs based on CNTs were not very high. Especially for those CNTs’ ESCs using organic electrolyte, their specific capacitance was only about 30 F/g [8]. In order to enhance specific capacitance of the ESCs based on CNTs using organic electrolyte, we pretreated the CNTs with KOH to activate before using as the ESCs electrode materials and had 2 times capacitance than that of the CNTs without pretreatment.

2. Experimental procedure

CNTs were produced by chemical vapor deposition method using CH₄ and La₂NiO₄ as the carbon source and catalyst. First, the catalyst precursor, La₂NiO₄, was reduced to La–Ni mixture by H₂ at 1073 K for an hour.
Then, the temperature was dropped to 953 K under the N₂ protection, at the same time; the CH₄ was introduced in to grow CNTs for an hour. Finally, the temperature was naturally cooled to ambient one under the N₂ protection [9]. Nitric acid treatment was employed to remove the catalyst particles. The CNTs without being activated were called the normal CNTs. The CNTs being activated by KOH were called the activated CNTs.

The activated CNTs were directly produced by KOH at 1123 K as the proportion \( \frac{m_{\text{KOH}}}{m_{\text{CNTs}}} = 4:1 \). The activated process was performed under the N₂ flow (240 ml/min). The activated CNTs were purified by distilled water. The normal CNTs and the activated CNTs were both characterized by transmission electron microscopy (TEM), scanning electric microscopy (SEM), X-ray diffraction (XRD) and N₂-adsorption.

In order to fabricate ESCs, the two kinds of CNTs were first made into electrodes. The electrodes were prepared in the form of pellets with 80 wt.% content of CNTs, 10 wt.% of acetylene black and 10 wt.% of binding substance (polyvinylidene fluoride). A microporous separator (celgard 2400) was sandwiched between the two CNTs electrodes. The two CNTs electrodes and the microporous separator were both entirely wetted by 1.0 mol/l lithium perchlorate (LiClO₄) dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The ESCs were fabricated in an argon-filled glove box.

The performances of the ESCs were operated with constant current 3.3 A/m² charge–discharge model between 0.0 and 3.0 V at 298 K on the battery-testing instrument. The capacitances of the ESCs were calculated by the discharging curve with the equation:

\[ C = \frac{It}{U} \]

In this equation, the products of the discharge time \( t \) (s) and current \( I \) (A) were the discharge coulomb capacitances, the quotients of the coulomb capacitances and discharge voltage \( U \) (V) were equal to the capacitances \( C \) (F) of the materials.

### 3. Results and discussions

The results of the electrochemical capacitance experiment were listed in Table 1. The electrochemical capacitance of the normal CNTs was 25.0 F/g and the activated CNTs’ electrochemical capacitance was 50.0 F/g. The reasons that the capacitance of the activated CNTs was 2 times that of normal CNTs owed to the CNTs’ different structure we considered, so we studied their structures by means of N₂-adsorption, TEM, SEM and XRD.

The data of the N₂ adsorption at 77 K were listed in Tables 1 and 2. The pore volume and the BET specific surface area of the normal CNTs were about 194.1 m²/g and 0.66 cm³/g, respectively, whereas the activated CNTs’ pore volume and BET specific surface area were about 510.5 m²/g and 0.91 cm³/g. The BET specific surface area of the activated CNTs was greatly increased, about 3 times that of the normal CNTs. In addition, the pore volume of the activated CNTs was also increased, about 1.5 times that of the normal CNTs. Moreover, the data of the pore diameter distribution showed that though the pore diameter distribution of the activated CNTs had a trend of micropore compared with that of the normal CNTs, both were in the range of mesopore (2–50 nm), which was the valid pore to ESCs electrode materials [1,2].

As we knew, the data of the BET specific surface area, pore volume and pore diameter distribution were the crucial parameters to ESCs electrode materials. The activated CNTs had 3 times BET specific surface area, 1.5 times pore volume than those of the normal CNT, we considered, which was the main reasons that the activated CNTs had 2 times capacitance that of the normal CNTs.

### Table 1

The characteristics of normal and activated CNTs

<table>
<thead>
<tr>
<th>CNTs</th>
<th>Yield (%)</th>
<th>C (F/g)</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( V_{\text{tot}} ) (cm³/g)</th>
<th>( V_{\text{mi}} ) (cm³/g)</th>
<th>( V_{\text{me}} ) (cm³/g)</th>
<th>( D_{\text{mean}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>–</td>
<td>25.0</td>
<td>194.1</td>
<td>0.66</td>
<td>0.0</td>
<td>0.66</td>
<td>14.64</td>
</tr>
<tr>
<td>Activated</td>
<td>85</td>
<td>50.0</td>
<td>510.5</td>
<td>0.91</td>
<td>0.0</td>
<td>0.91</td>
<td>8.16</td>
</tr>
</tbody>
</table>

\( C \): capacitance; \( S_{\text{BET}} \): specific BET surface area; \( V_{\text{tot}} \): total volume; \( V_{\text{mi}} \): micropore volume; \( V_{\text{me}} \): mesopore volume; \( D_{\text{mean}} \): mean pore diameter.
Table 2
The pore diameter distributions of normal and activated CNTs

<table>
<thead>
<tr>
<th>Pore diameters (nm)</th>
<th>Pore distribution in total pore volume (%)</th>
<th>Normal CNTs</th>
<th>Activated CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0–2.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.0–3.0</td>
<td>0.33</td>
<td>3.44</td>
<td></td>
</tr>
<tr>
<td>3.0–4.0</td>
<td>2.15</td>
<td>11.86</td>
<td></td>
</tr>
<tr>
<td>4.0–6.0</td>
<td>1.63</td>
<td>4.16</td>
<td></td>
</tr>
<tr>
<td>6.0–8.0</td>
<td>2.04</td>
<td>11.03</td>
<td></td>
</tr>
<tr>
<td>8.0–10.0</td>
<td>4.67</td>
<td>11.19</td>
<td></td>
</tr>
<tr>
<td>10.0–20.0</td>
<td>44.87</td>
<td>45.56</td>
<td></td>
</tr>
<tr>
<td>20.0–30.0</td>
<td>30.68</td>
<td>12.05</td>
<td></td>
</tr>
<tr>
<td>30.0–40.0</td>
<td>13.24</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>40.0–50.0</td>
<td>0.39</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>50.0–60.0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1a,b is the TEM images of the normal CNTs and the activated CNTs, respectively. They were both multi-walled CNTs, randomly entangled and a good interior-empty structure. The normal CNTs had a diameter of about 20 nm and they were about 20,000 nm in length, while the activated CNTs have a diameter of about 20 nm and they were about 2000 nm in length. Comparing the two TEM images, we would find that the diameters of the normal CNTs and the activated CNTs were both about 20 nm just based on the TEM images, whereas the length of the activated CNTs were shorter than that of the normal CNTs, which was good to the enlargement of the BET specific surface area and pore volume.

Fig. 2a,b shows the SEM images of the normal CNTs and the activated CNTs, respectively. The outer layers well of the normal CNTs was very smooth, while the outer layers well of the activated CNTs was not so smooth and there were some disfigurements on it. Moreover, comparing the two images carefully, we could also find that the diameter of the activated...
CNTS was a bit smaller than that of the normal CNTs. The activated process damaged some outer layers of the CNTs we considered and resulted in some disfigurements on the outer layers well of the activated CNTs. These disfigurements on the outer layers well of the activated CNTs were of help to the enlargement of the BET specific surface area and pore volume. Fig. 3a,b is the XRD pattern of the two CNTs. The XRD pattern of the activated CNTs was very similar to that of the normal CNTs. They both had a strong peak and a two-weak peak. Thus, we considered the crystal structure of the activated CNTs was the same as that of the normal CNTs. The activated process did not damage the novel structure of the normal CNTs.

4. Conclusions

ESCs based on the activated CNTs had better electrochemical capacitance than those based on the normal CNTs. The reasons that the activated CNTs had better electrochemical capacitance than the normal CNTs owed to the changes of the CNTs’ structure during the activated process. In a word, the experiments had shown that the activated CNTs excelled the normal CNTs in the ESCs electrode materials and the activated CNTs were a kind of promising novel materials.

References