Influence of the Heating Temperature on the Electrochemical Performance of Coal-Based Needle Coke Anode for Lithium Ion Batteries

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Abstract. In this study, the effect of the heating temperature on the initial coulombic efficiency, capacity and cycle stability of the coal-based needle coke was examined. The needle cokes were heated to different temperatures, and their microstructures were characterized by the scanning electron microscope, the X-ray diffraction and Raman spectroscopy. The results indicated that the defect and the degree of disorder were reduced with increasing the heating temperature. Moreover, the electrochemical properties of these needle cokes were tested. A decrease of the capacity from 368.3 to 257.3 mAh/g, while an increase of the initial coulombic efficiency was observed, when the heating temperature was improved to 1100 oC. This is because fewer defects and more ordered crystal structures reduce active sites for the storage of Li ions and decrease the irreversible consumption of Li ions, as the heating temperature was higher.

1. Introduction

To solve the problems of environmental pollution and energy crisis, flexible technological solutions including energy supply and storage have been developed rapidly [1,2]. The lithium ion battery, an environmentally friendly secondary battery with high capacity, could contribute strongly to the energy storage picture [3-5]. The anode material, one of the most critical factors to improve the electrochemical performances, has always been a hot topic in lithium ion batteries [6-8]. Carbon materials, such as mesocarbon microbead, graphite and needle coke, are the main anode materials for lithium ion batteries [9,10]. Coal-based needle cokes with a variety of sources and low price, have attracted increasing attention of researchers, recently. However, due to their complex components, the method to improve their electrochemical performances has been a problem. In this research, the influence of heating temperatures on the electrochemical performances of coal-based needle cokes were revealed, through analyzing the microstructures, capacities, initial coulombic efficiency and cycle stability of coal-based needle cokes fabricated at different temperatures. It affords clues to improve electrochemical properties of coal-based needle cokes.

2. Experimental

2.1 Materials

The coal-based needle coke, fabricated at 600 oC, was purchased from Ansteel Group CO., LTD. Its volatile, ash content, density and sulfur residue value were shown in table 1.

<p>| Tabel 1. The properties of the coal-based needle coke. |</p>
<table>
<thead>
<tr>
<th>Volatile (%)</th>
<th>Ash (%)</th>
<th>Density (g/cm³)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Needle Coke</td>
<td>5.2</td>
<td>0.01</td>
<td>1.41</td>
</tr>
</tbody>
</table>

2.2 Heat Treatment of the Needle Coke

The pristine needle coke (Nc) was heated to 850 oC at a rate of 10 °C/min under the protection of nitrogen, and kept at this temperature for 6 h. The product was named as Nc850. The sample Nc1100 was produced at the same condition but the heating temperature was changed to 1100 °C.
2.3 Characterization
The microstructure of the sample was observed by the field emission scanning electron microscope (FESEM, Gemini 560), and the X-ray diffraction (XRD, Bruker D8 Advance) spectroscopy with a Cu Kα radiation source (1.5405 Å) was employed to analyze the crystalline structures of samples. The Raman spectra were recorded by a Horiba (JY-HR800 micro-Raman) spectrometer. All the electrochemical tests were conducted using coin cells (CR2025). The working electrodes were prepared by spreading the mixed slurry of active material, Super P and sodium alginate in water with a weight ratio of 7:2:1 onto copper foil. Then they were dried at 120 °C in vacuum for 12 h. The electrolyte was a solution of 1 M LiPF$_6$ in ethylene (EC) and dimethyl carbonate (DMC) (v:v=1:1). A lithium foil was used as the counter electrode. All the operations were performed in a glove box under argon atmosphere. The discharge/charge tests were carried out on a Land BT2000 battery test system at room temperature. The voltage ranged from 0.01 to 2 V with a current density of 100 mA/g.

3. Results and Discussion

![Typical SEM images of needle cokes heated at different temperatures.](image1)

Figure 1. The morphologies of the pristine needle coke, needle cokes heated at 850 °C and 1100 °C were presented in Fig. 1. The sizes of these needle cokes were 2-20 μm. The XRD patterns of needle cokes prepared at different temperatures were shown in Fig. 2. The needle cokes Nc, Nc850 and Nc1100 have broad peaks of (002) at approximately 25.2°, 25.6° and 25.8°, respectively. It confirms that these samples have amorphous structure. However, as the increase of heating temperature, the peaks of (002) are sharper, the intensities are stronger, and the 2θ is closer to the graphite. These results indicate a more ordered structure of the needle coke with the improvement of heating temperature.

![XRD patterns of needle cokes heated at different temperatures.](image2)

Figure 2. XRD patterns of needle cokes heated at different temperatures.

![Raman spectra of a) Nc, b) Nc850 and c) Nc1100. d) The ratios of the I_G/I_D.](image3)

Figure 3. The structure of needle cokes fabricated at different temperatures was further investigated by Raman spectroscopy, as shown in Fig. 3. The samples Nc, Nc850 and Nc1100 all exhibited a defect-induced band at about 1343 cm$^{-1}$ (D-band) and a crystalline graphite band at approximately 1589 cm$^{-1}$ (G band) (Fig. 3a-c). The intensity ratios of G-band and D-band (I_G/I_D) for Nc, Nc850 and Nc1100 were 1.06, 1.12 and 1.21, respectively (Fig. 3d). It demonstrated that the disorder degree decreased as the increasing of heating temperature, which was consistent with the XRD patterns.

The electrochemical performances of needle cokes heated at different temperatures were analyzed in half cells using Li foil as the counter electrode. As presented in the Fig. 4a, the pristine needle coke Nc showed a reversible capacity of 368.3 mAh/g and a coulombic efficiency of 44.9% in the first cycle at a current density of 100 mA/g. After heating at 850 °C and 1100 °C, the needle cokes Nc850 and Nc1100 delivered a reversible capacity of 306.7 mAh/g and 257.3 mAh/g in the first cycle, respectively (Fig. 4b,c). However, the initial coulombic efficiency increased to 53.7% and 65.0% as the improvement of the heating temperature to 850 °C and 1100 °C, respectively (Fig. 4b,c). Table 2 summarized the crystal structure data and electrochemical performances of needle cokes heated at different temperatures. As discussed above, increasing heating temperature led to less defects and more ordered crystal structure, which reduced active sites for the storage of Li ions and...
decreased the irreversible consumption of Li ions. Thus, a higher heating temperature caused less capacity and higher initial coulombic efficiency [11].

After 50 cycles, the Nc, Nc850 and Nc1100 showed a good cycling stability, and the reversible capacities were 352.3 mAh/g, 341.4 mAh/g and 267.4 mAh/g, respectively (Fig. 4a-c). Fig. 4d showed the first discharge-charge profiles of the Nc, Nc850 and Nc1100. All the samples presented sloping charging curves, also demonstrating their amorphous structures (consistent with the XRD patterns).

![Figure 4](image)

**Figure 4.** Cycle performance and the corresponding coulombic efficiency of a) Nc, b) Nc850 and c) Nc1100 at the current density of 100 mA/g. d) Voltage profiles of Nc, Nc850 and Nc1100 at the current density of 100 mA/g in the first cycle.

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ (002)</th>
<th>Ic/I0</th>
<th>Capacity (mAh/g)</th>
<th>Initial Coulombic Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nc</td>
<td>25.2°</td>
<td>1.06</td>
<td>368.3</td>
<td>44.9%</td>
</tr>
<tr>
<td>Nc850</td>
<td>25.6°</td>
<td>1.12</td>
<td>306.7</td>
<td>53.7%</td>
</tr>
<tr>
<td>Nc1100</td>
<td>25.8°</td>
<td>1.21</td>
<td>257.3</td>
<td>65.0%</td>
</tr>
</tbody>
</table>

**4. Conclusion**

In this research, the coal-based needle cokes were heated at different temperatures to prepare anode materials of the lithium ion battery. SEM, XRD and Raman spectroscopy were utilized to characterize the microstructures of these needle cokes. Also, their capacity, initial coulombic efficiency and cycling stability were analyzed in coin cells. The results demonstrated that the capacity decreased from 368.3 to 257.3 mAh/g, but the initial coulombic efficiency increased from 44.9% to 65.0%, as the improvement of heating temperature to 1100 °C. Since less defects and more ordered crystal structures were formed at a higher temperature, which reduced active sites for the storage of Li ions and decreased the irreversible consumption of Li ions. This work revealed the influence of the heating temperature on the electrochemical performances of coal-based needle cokes, providing clues to adjust coal-based needle cokes for the application in the lithium ion battery.

**Acknowledgments**

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**References**

10. N. Ohta, K. Nagaoka, and K. Hoshi, Carbon-coated graphite for anode of lithium ion rechargeable batteries:Graphite substrates for carbon coating,
11. D. J. Wang, Y. L. Wang, L. Zhan, and X. Y. Zhang, 
Graphitization mechanisms and electrochemical 
performance of needle coke anode for Li-ion battery, 
Journal of Inorganic Materials, vol. 26, pp. 619-624, 
2011.