STRUCTURE CHARACTERISTICS AND FORMATION MECHANISM OF MCMB HEAT-TREATED AT DIFFERENT TEMPERATURES

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Abstract

Mesocarbon microbeads (MCMB) is an excellent anode material for rechargeable lithium ion batteries (LIB) for its high charge/discharge capacity and long cycle life. The electrochemical performance of MCMB is closely related to its structure. In this paper, structures of MCMB heat-treated at different temperatures were characterized after peeling their surface layers by ablation. It has found that the crystallite size of MCMB doesn’t increase linearly with the heat-treatment temperature increasing but decrease firstly to 500 oC and then increase slowly up to 1100 oC. However, for MCMBs heat-treated at different temperatures, all the crystallite sizes of them increase when the surface layers were gradually ablated, i.e., cores of MCMB have more ordered carbon layers than the surface layers. From the structure characteristics of MCMBs and their cores, formation mechanism of MCMB was discussed.

Keywords: Mesocarbon microbeads (MCMB), structure, heat-treatment, ablation

1 Introduction

Mesocarbon microbeads (MCMB) is regarded as an excellent electrode material of rechargeable lithium ion batteries (LIB) with high reversible capacity and long cycle life. It was reported that the structure of MCMB was an important factor that influences the electrochemical performance of LIB. Although the structures of MCMBs derived from different precursors or from one precursor but under different heat-treatment conditions were different as been investigated systematically in previous reports, no literature can be found to study the structure of MCMB spheres in different depths, especially the structures in different depths of MCMBs heat-treated at different temperatures.

To fulfill this objective, an industrial MCMB was heat-treated at different temperatures and then ablated in oxidative environment. By investigating the structures of the ablated MCMBs, formation mechanism of MCMBs was delivered.

2 Experimental

Green MCMB was offered by Tiecheng Electrode Material Co., Ltd., China, which was generated in a coal tar pitch and then separated out by solvent extraction method. The original MCMB will be referred to gMCB later.

To study the structure evolution of MCMB during carbonization, gMCB was respectively heat-treated at 500°C, 700°C, 900°C or 1100°C for 1h in a quartz tube oven with flowing nitrogen protection of 0.02m³/h. The obtained MCMB was marked 500MCB, 700MCB, 900MCB and 1100MCB. Here the number refers to the heat-treatment temperature (HTT).

MCMBs, including gMCB, 500MCB, 700MCB, 900MCB or 1100MCB, were oxidized in 550 °C muffle oven for different times and their cores in different depths were obtained.

The morphologies of MCMBs and their cores were observed under a scanning electron microscope (SEM, PHILIPS XL30).

X-ray diffraction (XRD) analysis was carried out using Rigaku D/max-7500 based diffractometer with a generator voltage of 40 kV and a current of 100mA. The scans were made over a range of 20 values of 5-80° with data acquisition occurring for 1.0 s, at intervals of 0.04°.

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3 Results and discussion

3.1 Morphologies and microstructures of MCMBs before ablation

The morphology of gMCB is given in Fig.1. It can be seen that the size of gMCB falls in the range of 7-14μm. On the surface of MCB, there are many small particles. With the increase of HTT these small particles become projecting. Two typical micrographs in Fig.2 show the surface morphologies of gMCB and 1100MCB. It should be noted that with increasing HTT MCMB tends to reduce its size slightly.

![Overview of gMCB under SEM](image1)

**Figure 1.** Overview of gMCB under SEM

![SEM micrographs of surface morphology of (a) gMCB and (b) 1100MCB.](image2)

**Figure 2.** SEM micrographs of surface morphology of (a) gMCB and (b) 1100MCB.

Fig.3 gives the XRD patterns of MCMBs heat-treated at different temperatures and Table 1 lists the microstructure parameters of them. It can be seen from Fig.3 that, with the increase of HTT, 002 peak broadens and shifts to small diffraction angle until HTT is above 900°C, which means interlayer distance (d_{002}) of crystallite enlarges and stacking height of graphene layers (Lc) decreases as proven by the data in Table 1. Stacking number of graphene layers in crystallite (N) also decreases before HTT increases to 1100°C. Crystallite size (La) of MCBM has a small decrease when HTT increases to 500°C and then increases gradually when HTT exceeds this value.

![XRD patterns of MCMBs heat-treated at different temperatures](image3)

**Figure 3.** XRD patterns of MCMBs heat-treated at different temperatures
Table 1. Microstructure parameters of MCMB heat-treated at different temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d_{002}/\text{nm})</th>
<th>(L_c/\text{nm})</th>
<th>(L_a/\text{nm})</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gMCB</td>
<td>0.3486</td>
<td>5.69</td>
<td>2.63</td>
<td>17.3</td>
</tr>
<tr>
<td>500MCB</td>
<td>0.3496</td>
<td>5.65</td>
<td>1.93</td>
<td>17.2</td>
</tr>
<tr>
<td>700MCB</td>
<td>0.3570</td>
<td>3.21</td>
<td>2.03</td>
<td>10.0</td>
</tr>
<tr>
<td>900MCB</td>
<td>0.3599</td>
<td>2.80</td>
<td>2.64</td>
<td>8.8</td>
</tr>
<tr>
<td>1100MCB</td>
<td>0.3596</td>
<td>2.93</td>
<td>2.71</td>
<td>9.1</td>
</tr>
</tbody>
</table>

3.2 Morphologies and microstructures of MCMBs after ablation

Fig.4 shows the SEM micrographs of MCMBs heat-treated at different temperatures and then ablated to different degrees. It can be seen from Fig.4 that after heat-treatment at different temperatures MCMB shows different ablation features. For gMCB, 500MCB and 700MCB, with the increase of weight loss (\(R_{ss}\)) up to above 70%, MCMB continuously reduces its size and all the ablated surfaces rich in small particles similar to those on the original surface. On the surfaces of 500MCB- \(R_{ss}=71.8\%\) and 700MCB-\(R_{ss}=83.7\%\), compact MCMB cores can be observed under several small particles. It can be concluded from these phenomena that green MCMB is completely built up by small particles, whereas heat-treated MCMBs are made up of compact cores and small particles-built outer layers, which means during carbonization small particles in cores preferentially amalgamate together forming larger graphene layers. For 900MCB and 1100MCB, the compact cores enlarged and small particles in outer layers even sintered together as shown in Fig.4 (d) and (e). With the weight loss increasing, many pores appeared on their surfaces with only slight reduction of size, indicating that due to the amalgamation of small particles during heat-treatment the anti-oxidation performance of MCMB is greatly enhanced, but in the large graphene layers there are still many poor structures which are more oxidable than others. During ablation, some spheres in 1100MCB split into pieces, which can be attributed to the formation of large graphene layers and also to the lacking of protection from outer layers and bonding structures as mentioned above.

Fig.5 gives the microstructure parameter as the functions of weight loss. It can be seen from Fig.5 (a) that during ablation \(d_{002}\) of gMCB and 500MCB increase suddenly and then decrease gradually with the increase of weight loss. However when heat-treatment temperature is as high as 700°C, the \(d_{002}\) of MCMB decreases monotonously except for a slight increase for 1100MCB-\(R_{ss}=72.1\%\). During ablation, \(L_c\) of gMCB and 500MCB decrease sharply at the beginning stage and then slowly to the end. Although \(L_c\) of 700MCB also decreases monotonously, its decrement is small. The decrease of \(L_c\) indicates graphene layers in the cores of MCMB have poorer arrangement than those in the outer layers. After heat-treatment at 700°C, this difference becomes small. For 900MCB and 1100MCB, \(L_c\) increases slowly before weight loss is above 40% and beyond this point \(L_c\) decreases slightly as shown in Fig.5 (d). From Fig.5 (b) it can be seen that stacking number of graphene layers has the similar tendency to that of \(L_c\). For crystallite size \(L_a\), all of the MCMB cores have larger \(L_a\) than their outer layers except for the small decrease for 900MCB and 1100MCB when weight loss is beyond 40%.

3.3 Discussion

As-mentioned above, green MCMB is built up by small particles, which confirms the formation mechanism of Building from Granular Basic Units (BGBU) delivered by the present authors. During carbonization, small particles constructing MCMB spheres amalgamate preferentially in their cores and then in outer layers.

For gMCB and 500MCB, the small particles in outer layers have larger \(L_c\) and smaller \(L_a\) than the inner ones; especially the surface particles have far larger \(L_c\) than the inner ones. However, for 700MCB no large difference in \(L_c\) exists between surface layers and inner cores, although the small particles in outer layers still have larger \(L_c\). During formation of green MCMB in pitches small particles stacked early tend to amalgamate causing polyaromatic molecules in them to polymerize into large ones, which can increase \(L_a\) but decrease \(L_c\). However, for the small particles in outer layers, they have stacked together for short times and thus have larger \(L_c\) but smaller \(L_a\). During carbonization up to high temperatures, polyaromatic molecules continue to polymerize causing the decrease of \(L_c\) and increase of \(L_a\) with increasing temperature and also the changes of both two parameters for MCMBs from surface layers to inner cores. When HTT is high, say above 700°C, the rearrangement of graphene layers become frequent and thus improve the ordered stacking of graphene layers, which explains the slight increase of \(L_c\) for 1100MCB and large increase of \(L_c\) for the cores of 900MCB and 1100MCB. For 900MCB and 1100MCB, when weigh loss is above 40wt\%, many pores appear in MCMB spheres and oxidation can be proceeded in these pores, which can impair the carbon crystallites in cores. Therefore the \(L_c\) and \(L_a\) of 900MCB and 1100MCB have slight decreases after serious ablation.

It is worthy to be noted that the growth and rearrangement of graphene layers and escape of light
components companied during carbonization can form many poor bonding structures in MCMB spheres, which are easily oxidized and can be observed as pores in 900MCB and 1100MCB after serious ablation.

**Figure 4.** SEM micrographs of MCMBs heat-treated at different temperatures and then ablated to different degrees in 550°C oxidative oven.
4 Conclusions

By investigating the structures of MCMBs after carbonization and the structures of these MCMBs after ablation, some conclusions can be drawn as follows.

(1) Green MCMB is formed by stacking small particles together as BGBU theory given and small particles in the outer layers of MCMB have larger Lc but smaller La than those in cores due to their different contact times in different depths.

(2) During carbonization small particles in MCMB cores preferentially amalgamate into compact structures with large graphene layers, whereas Lc continues to decrease until HTT is above 900°C. For MCMBs heat-treated at low temperatures, they have cores with small Lc and La. When HTT is above 700°C, microcrystallite sizes (Lc and La) of MCMB cores exceed the ones of their outer layers.

References


