Preparation and Characterization of Sn-mesocarbon Composite Microbeads

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1. Introduction

Many kinds of carbon materials are now widely used for the negative electrode of lithium ion batteries. Particularly, mesocarbon microbeads (MCMB) have revealed promising behaviors [1-4]. This material consists of roughly spherical structures with 1-40μm in diameter and, consequently, low specific surface area. That means a high packing density that avoids extended side reactions with the electrolyte during the processes of charge and discharge of lithium-ion cells [5]. Recently, the demand for lithium ion batteries as a power supply for portable electric devices has steadily increased, and their capacity requirement has become larger. However, the capacity of graphite has already approached the theoretical limit of C_6Li ($372mAhg^{-1}$). In order to enhance the energy density of lithium ion batteries, some metals such as Ag, Ph, Al and Sn, with larger specific capacity than graphite, have recently attracted worldwide attention. Tin and its oxides with a theoretical capacity of 990mAh/g may be a promising anodic materials, however, the main shortcoming for their commercialization is the volume expansion during the process of alloying with Li, which causes crumbling and cracking of the electrode, inducing a very short cycle life. To overcome this problem, many researchers have tried to prepare the fine tin metal-graphite composite [6-10].

In this paper, we describe the in-situ synthesis of tin-mesocarbon composite microbead (Sn-MCMB) by pyrolysis of the mixture of coal tar pitch and dibutyltin dilaurate. The objective of this investigation is to combine the high lithium storage capacity of the element Sn and the stable cyclability of mesocarbon.

2. Experimental

Coal tar pitch was used as starting material and its some properties are summarized in Table 1. Dibutyltin dilaurate (AR) was purchased and used as additives in present study. Dibutyltin dilaurate was added to the coal tar pitch in an autoclave in a nitrogen atmosphere and stirred for 30 min at 200C so that well-proportioned mixture can be obtained. The mixture was heat-treated up to 430C for 0.5 hour at a heating rate of 2C/min under nitrogen atmosphere. The pressure of reaction was controlled at the range of atmospheric pressure to 2 MPa. Amounts of dibutyltin dilaurate were varied in the range of 5.5, 10, 50 wt. %, respectively.

The resulted mesophase pitch was ground and extracted by pyridine at 100C, and the

pyridine insoluble was washed by acetone and dried under vacuum. And then the Sn-mesophase carbon composite microbeads (Sn-MCMB) can be obtained. Sn-MCMB was carbonized at 1000C and 1800C under nitrogen flow.

To study the structure of Sn-MCMB, X-ray Powder diffraction (XRD) was carried out on a D/max 2500VB2+/PC X-ray diffractometer with Cu-Kα radiation. Sn contents in the composite microbeads were measured by an IPC emission spectroscopy (E-8000). Transmission electron microscopy (TEM, JEOL, 1200EX) was used to observe the microscopic structure.

Table1. Some properties of coal tar pitch

Softening point (□)	Solubility[a] (wt.%)			
	HS	HI-TS	TI-PS	PI
78	9.6	68.7	12.1	9.6
Ash (wt.%)	Elemental analyses (wt.%)			
	C	H	N	C/H
0.14	92.87	4.37	0.83	0.56

[a]HS, Hexane solubles; HI, Hexane insolubles; TS, toluene solubles; TI, toluene insolubles; PS, pyridine solubles; PI, pyridine insulubles.

2. Results and discussion

Fig.1 shows the dependence of element Sn content on the content of dibutyltin dilaurate in the raw material mixture. It can be found adding more dibutyltin dilaurate can produce the Sn-MCMB with higher Sn content. In the present paper, Sn-MCMB samples with Sn content of 0.43%, 1.38% and 5.65% are named as Sn-MCMB1, Sn-MCMB2 and Sn-MCMB3, respectively.

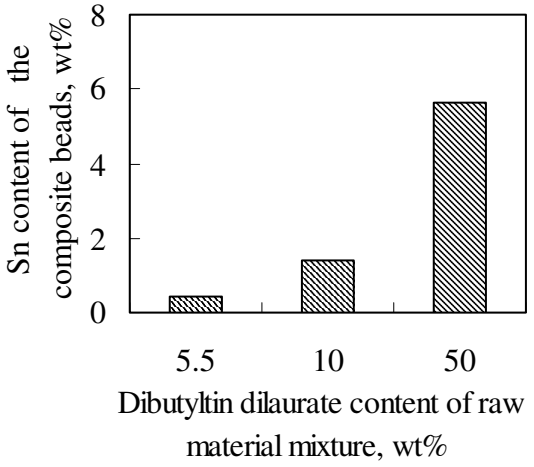

Fig.1 Sn content of composite microbeads changes as a function of dibutyltin dilaurate content of raw material

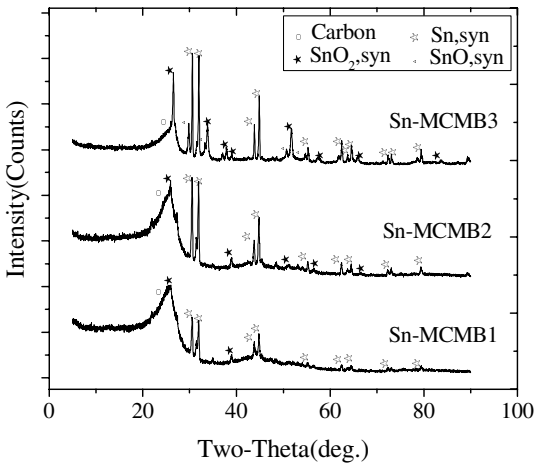

Fig.2 The XRD patterns of Sn-MCMB

The XRD patterns in Fig. 2 reveal the structures of the Sn-MCMB, indicating the existence of clear carbon and synthesized tin phase, together with some diffraction peaks corresponded to synthesized SnO_2 and SnO. Furthermore, it can be seen from Fig.2 that, with the content of Sn increasing, the relative height of diffraction peak of carbon (002) decreases and the relative height of diffraction peaks of Sn increase. The increase of Sn content also induces the diffraction peaks of tin oxide to become clearer. These results suggest that, during pyrolysis, dibutyltin dilaurate decomposed and mostly produced metal Sn and organic compounds, together with producing a few amounts of tin oxides.

Fig.3 shows the XRD patterns of carbonized Sn-MCMB. As can be seen in Fig.3, peaks of tin become very sharper than peak of carbon with the content of Sn increasing. Compared with the diffraction patters of untreated samples, the XRD patterns of carbonized Sn-MCMB do not display any peaks associated with tin oxides. The results indicate that the tin oxides decomposed and produced metal tin during carbonization.

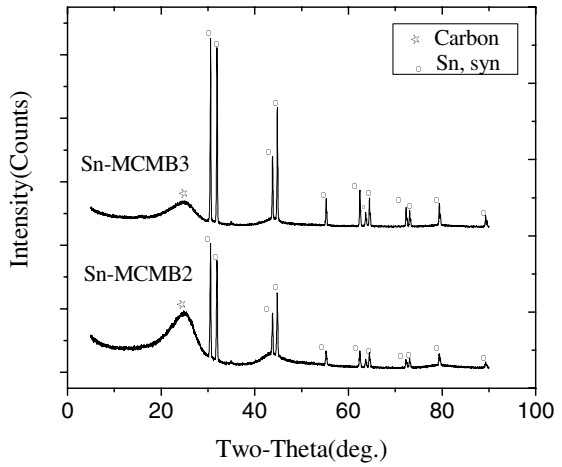

Fig.3 The The XRD patterns of Sn-MCMB carbonized at 1000℃

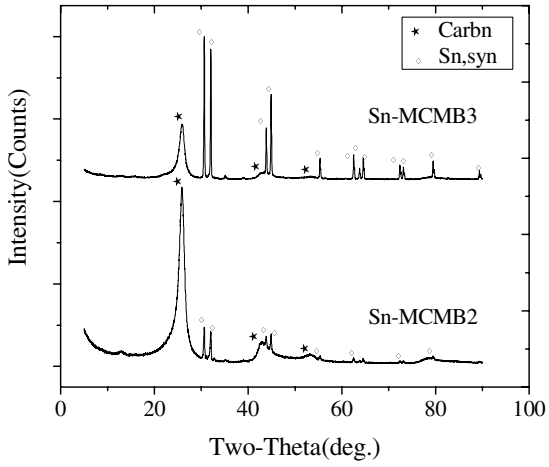

Fig.4 The The XRD patterns of Sn-MCMB carbonized at 1800℃

The XRD patterns in Fig. 4 reveal the structures of theSn-MCMB carbonized at 1800C, also indicating the existence of tin and carbon. It is noticed in Fig. 4 that the diffraction peaks associated with (100) and (004) profiles of graphite appear, which indicate the graphitic crystal structure in Sn-MCMB has developed more regular in carbonization at 1800C. In addition, compared with XRD patterns of Sn-MCMB3, the XRD patterns of Sn-MCMB2 exhibit the carbon diffraction is very sharper and Sn diffraction is weaker. It can be inferred that there maybe exist the volatilization of Sn with the increasing of carbonization temperature; furthermore, Sn particle within composite microbeads may possibly restrain the graphitization of mesocarbon.

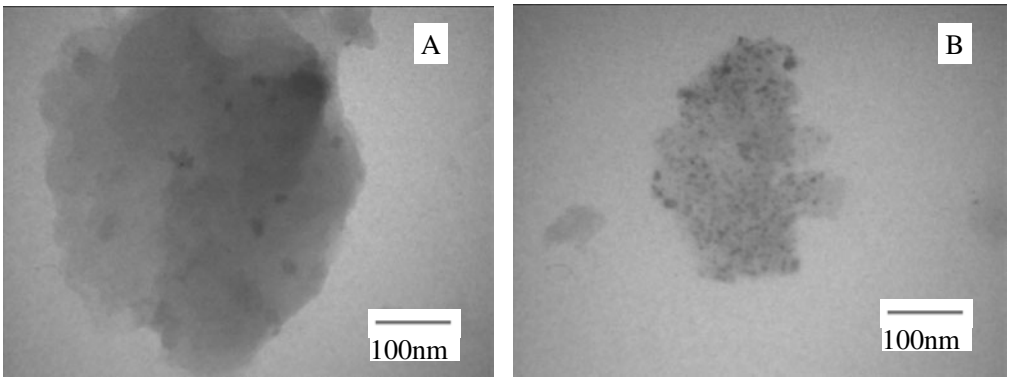

Fig.5 TEM photographs of Sn-MCMB2(A) and Sn-MCMB3(B).

The sizes of Sn crystals and their distribution in carbon/tin composite are important for the characteristics of Sn-MCMB as electrode. Fig.5 shows the TEM photographs of Sn-MCMB2 and Sn-MCMB3. It can be seen that the tin metal particle with particle size of 10~20nm well dispersed in the carbon matrix.

3.Conclusions

Sn-mesocarbon composite microbeads are prepared by pyrolysis of the mixture of coal tar pitch and dibutyltin dilaurate and then extraction with Pyridine. The structure and composition of Sn-mesocarbon composite microbeads have been studied. It can be found that the content of Sn metal in composite microbeads increase with the increasing of the ratio of dibutyltin dilaurate to coal tar pitch in raw material and nano-size Sn particles are dispersed in mesophase carbon matrix. The X-ray diffraction patterns of composite microbeads indicate obvious diffraction peaks associated with graphitic carbon, synthesized Sn metal and synthesized SnO_2, SnO. When the heat-treatment temperature is up to 1000C, the diffraction peaks associated with tin oxides disappear. With the increasing treated temperature, the crystallinity of the carbons increase and the diffraction peaks of Sn metal weaken, which can be inferred that more Sn metal has been evaporated with increasing heat treatment temperature.

References

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