VOLUME AND NUMBER DISTRIBUTION OF MESOPHASE MICROBEADS PREPARED IN PRESENCE OF SULFUR

Xiu-Jun Liu [1], Cheng-Yang Wang [2], Tong-Qi Li[3], Bing Pan[1]
1. School of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin, 300160, China
2. School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
3.National Key Laboratory of Advanced Functional Composite Materials, Aerospace Research Institute of Materials and Processing Technology, Beijing, 100076, China

Abstract

Mesophase microbeads were prepared by the way of thermal condensation between sulfur with different concentration and coal-tar pitch from different system. Morphologies and sizes of mesophase microbeads are characterized by scanning electronic microcopy (SEM), polarized light optical microphotography (PLOM) and laser particle size analyzer. SEM and PLOM results exhibit that mesophase microbeads have a narrow size distribution and many large particle in heterogeneous system. In homogeneous system, there are a great deal of smaller mesophase microbeads and a very little of larger mesophase microbeads. The laser particle size analysis results show that size distribution of mesophase microbeads in heterogeneous system is quite different from that in homogeneous system. There are multi-peaks on volume distribution curve in heterogeneous system. Larger mesophase microbeads are mainly in tens micron peak of size distribution curve. They can be used to Li-ion secondary battery as electrode materials after removing smaller fragments. In homogeneous system, particle size of mesophase microbeads has a wide distribution and only single peak on size distribution curve. They will be better used in high density and intensity materials. Moreover, sulfur concentration in reaction system makes the size of mesophase microbeads increase and the size distribution curve move to larger particle diameter. But sulfur concentration can not affect the curve pattern of size distribution.

Keywords: sulfur; mesophase microbeads; size distribution; average diameter

1. Introduction

Mesophase microbeads have particular microstructure and properties. They are widely used in Lithium ion secondary batteries [1], column packing for high performance liquid chromatography [2], supporter of catalysts [3], and high density strength materials [4]. The mesophase microbeads that have different microstructure, sizes, and morphologies provide different electrochemical properties [5]. The technical difficulty, complicacy of process and the application field depends on their size distributions. The more narrow size distribution, the more homogeneous on electrochemical properties, and the more complex in screen technology. In some occasions, the reasonable allocation of granularities can bring an excellent geometrical surface and higher density of materials. Sulfur can affect thermal condensation of coal-tar pitch, meso-phase morphologies [6] and so on. In this paper, we discussed the size distribution and their characteristics of mesophase microbeads from different nucleation systems in presence of sulfur.

2. Experimental

2.1 Preparation of mesophase microbeads

In this experiment, two kinds of coal tar pitch are from Jining Coal Co. of Shan Dong Province (China). Their softening points are 78ºC and 27ºC, quinoline insolubles (QI) are 4.7% and 0.3%.

Coal tar pitch (softening points 78ºC, QI 4.7%) reacted with sulfur (1%, 5%) at 420ºC for 7h formed mesophase pitch. Mesophase microbeads P50, P69 were obtained when the mesophase pitches were extraction, washed, and dried. And another coal tar pitch (softening points 27ºC, QI0.3%) reacted with sulfur (1%) at 440ºC for 2h prepared another mesophase pitch. Mesophase microbeads M100 were obtained when the former production were purified, washed, and dried.

2.2 Characterization of mesophase microbeads

2.2.1 Scanning Electronic Microscopy (SEM): PHILIPS(XL30 ESEM).

2.2.2 Polarized Light Optical Microphotography (PLOM): Olympus (BX51M).

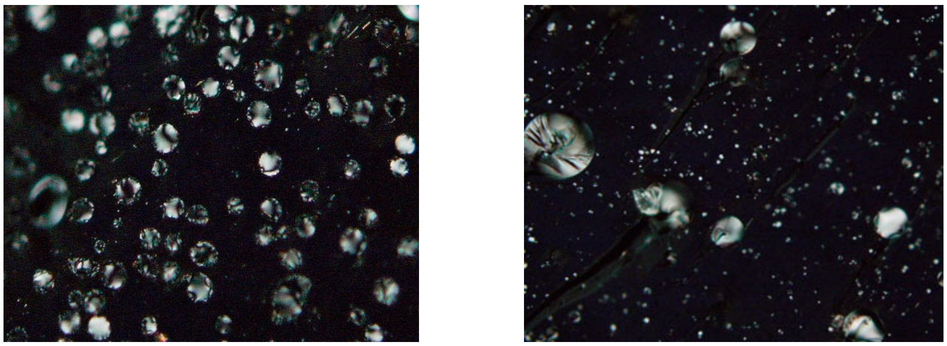
2.2.3 Laser Particle Size Analyzer: LA-300(Japanese), ethanol as dispersant.

3. Results and discussion

3.1 Electronic Microscopic and Polarized Microscopic Imagines

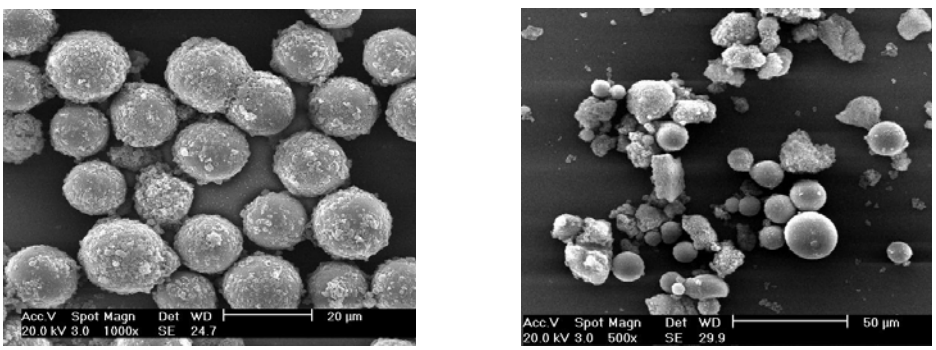
Size distributions of mesophase microbeads in homogeneous and heterogeneous systems had obvious differences. Fig.1 shows polarized light optical microscopic micrographs. It could be seen that the P50 spheres generated from the heterogeneous system had larger number and a narrow distribution, while M100 spheres generated in the homogeneous system had a wider distribution.

Figure 2 gives the SEM micrographs of mesophase microbeads out of mesophase pitch. Spheres of P50 have rough surfaces, M100 have smooth surfaces and agglomerated particles.



(a)P50 (b) M100

Fig.1 Photographs of mesophase pitch under cross polarization



(a)P50 (b) M100

Fig.2 Morphologies of mesophase microbeads

3.2Volume Statistic Characteristics

Volume distribution curve (Fig.3) from the volume analysis data of the spheres. Volume analysis results of P50 are as follows: average volume (weight) diameter D (4, 3) is 19.52μm, cumulative volume diameter D10 is 4.3μm, D50 is 19.98μm, and D90 is 28.97μm. Volume distribution of D (4, 3) and D50 are comparative symmetrical in their numerical value. The three peaks in the volume distribution curve display there are three classes of spheres. The characteristics are shown in the Figure 2. The mesophase microbeads which are relative uniform are obtained by screening. The mesophase microbeads after removing smaller fragments could be used in lithium ion batteries. The rightmost peak in the volume distribution curve makes the largest contribution to volume, that is to say the larger spheres are the main contributor. Small fragments are more in number but contributed to average volume diameter less. Volume distribution results of M100 are as follows: average volume (weight) diameter D (4, 3) is 5.78μm, cumulative volume diameter D10 is 0.62μm, D50 is 3.15μm, and D90 is 14.43μm. The distinction between volume distribution of D (4, 3) and D50 is considerable bigger in view of their numerical value. A small side-peak is emerged 0.1μm to 1μm, but volume distribution is from little to big as a whole. Their contribution to volume exhibits a steady trend. As can be seen in Fig.1 and Fig.2, spheres have a high dispersion degree, which are used to prepared high-density, high intensity carbonaceous materials.

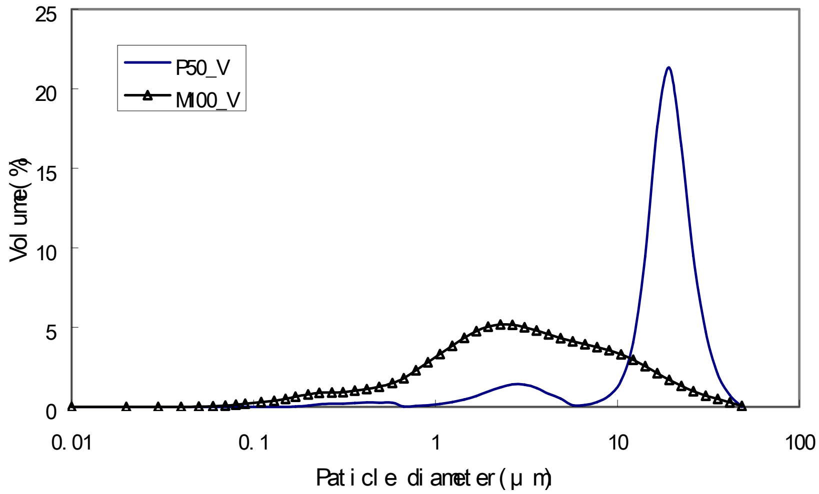


Fig.3 Volume distribution of mesophase microbeads

3.3 Number Statistic Characteristics

Number distribution curves (Fig.4) are obtained from the results of number statistical data of spheres. Number analysis results of P50 are as follows: average volume (weight) diameter (4, 3) is 19.52μm, cumulative number diameter D10 is 0.17μm, D50 is0.26μm, and D90 is 0.45μm. Two peaks were present in the number distribution curve. It is believed that the smaller particles made the largest contribution to number, but their contribution to average volume (weight) diameter less. Second peak is very small, that is the number of spheres is very less. But it is important for volume (weight), so it is also the major contributor to average volume diameter. Number analysis results of M100 are as follows: average volume (weight) diameter D (4, 3) is 5.78μm, cumulative number diameter D10 is 0.06μm, D50 is 0.10μm, and D90 is 0.23μm. Its distribution curve was relative regular, having only one apex. Number statistic was discrete as a result of tailed peaks.

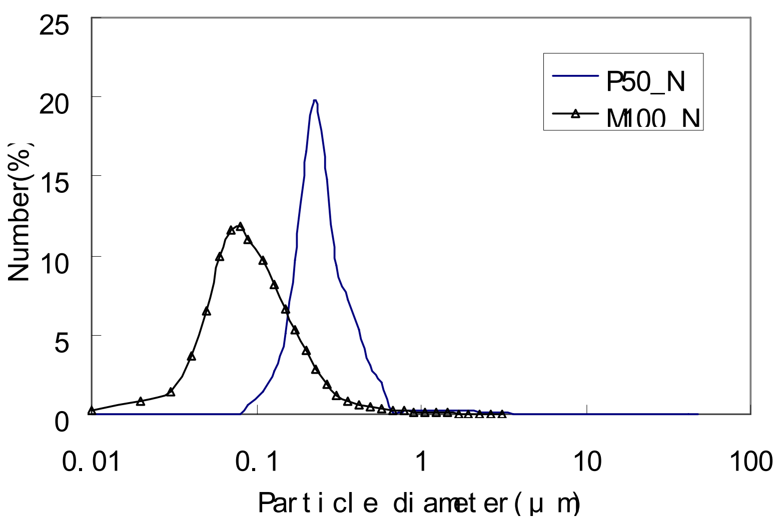
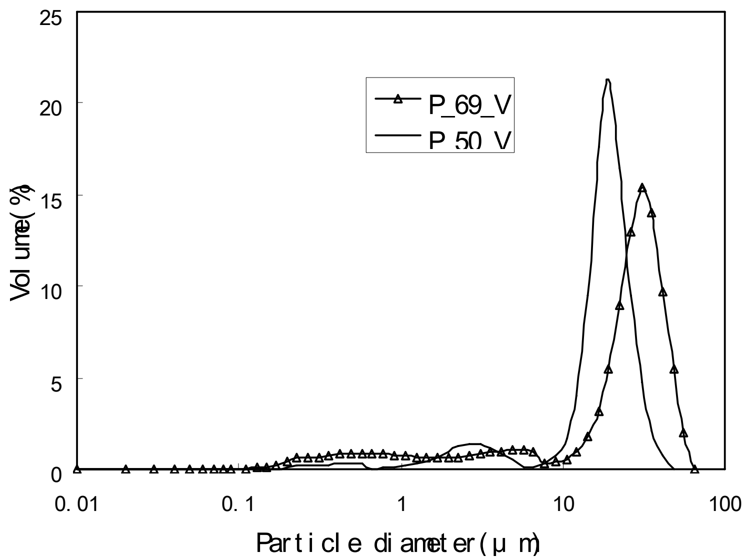


Fig.4 Number distribution of mesophase microbeads

3.4 Effect of sulfur on volume/number distribution

Fig.5 shows the volume and number distribution. Size distributions of mesophase microbeads are quite different from homogeneous and heterogeneous systems in presence of sulfur. Volume/number distribution of spheres obtained from the same system is similar pattern even if sulfur had different concentrations. But their statistic varies. With sulfur increasing, average volume (weight) diameter D(4,3) increases from 19.52μm to 27.38μm, cumulative volume diameter D10 varies from 4.3μm to 1.49μm, D50 varies from 19.98μm to 29.46μm, and D90 varies from 28.97μm to 45.95μm. Cumulative number diameter D10 varies from 0.17μm to 0.10μm, D50 varies from 0.26μm to 0.21μm, and D90 varies from 0.45μm to 0.39μm.



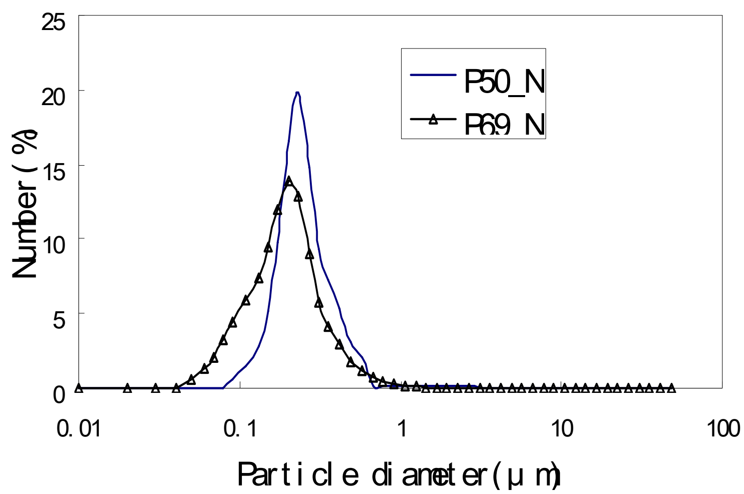


Fig.5 Effect of sulfur concentration on particle size and distribution of mesophase microbeads

4. Conclusions

There are multi-peaks on volume distribution curve of mesophase microbeads obtained from heterogeneous system. Li-ion electrode materials, which have narrow size distribution and uniform electrochemical properties, could be obtained after simple screening. In homogeneous system, particle size of mesophase microbeads has a wide distribution and high dispersion degree. They will be better used in high-density, high-intensity materials. Moreover, in the same system, the increase of sulfur concentration in reaction system makes the size of mesophase microbeads increase and the size distribution curve move to larger particle diameter.

References

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