PREPARATION OF CARBON MICROSPHERE ON THE SURFACE OF CARBON FILM

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1. Introduction

Spherical carbons such as carbon black and mesocarbon microbeads(MCMB) have been developed as a filer for composite materials and the electrodes for secondary buttery and electric double layer capacitor(EDLC) [1]. On the other hand, we have already reported that carbon microsphere(CMS) with ca. 1 μm in diameter were prepared from the mixture of coal tar pitch based COPNA resin and polyethylene glycol(PEG) [2]. CMS was obtained by carbonization of polymer microsphere. Polymer microsphere produced on the COPNA resin based film at 130℃. Spherical shape of the polymer sphere was not distorted during the period of carbonization to 1000℃. Here we will report the conditions for formation of the polymer and carbon microspheres. Carbonization and graphitization behavior of those microspheres, a large scale preparation and electrochemical properties of CMS will be also reported.

2. Experimental

2.1. Materials.

Pyrene based COPNA resin(Py-COPNA) and additives were used for the formation of polymer microspheres. Py-COPNA was prepared by heating the mixture of pyrene and 1,4-benzene dimethanol with acid catalyst at 130℃ for 30 min. PEG, polypropylene glycol, polyethylene, polyvinylalcohol etc. were used as additives without purification.

2.2. Instrumentation.

Surface of the samples was observed with a scanning electron microscope (SEM). Crystal structure was measured with an X-ray powder diffractometer. Electrochemical properties were measured by cyclic voltammetry(CV) and galvanostatic charge/discharge cycling.

2.3. Preparation of polymer and carbon microspheres.

Polymer microspheres were prepared on COPNA resin based films. The mixture of PEG and Py-COPNA(PEG:20 wt%) was dissolved into chloroform. The solution was poured to cast a film into the alminium mold and then it was cured at 200 ℃ for 20 h under inert atmosphere. The cured film after peeled from aluminium mold was carbonized at 1000 ℃ for 1 h. Other additives were also used with the same procedure stated above.

A large scale preparation of polymer microsphere was carried out as follows. The mixture of PEG and Py-COPNA (PEG:90 wt%) was heated at 200 ℃ with stirring rate of 80 to 640 rpm for 3 h. The resulting polymer microsphere was immersed to cure the surface of the sphere into 95 wt% of conc. H_2SO_4 with stirring for 3 to 20 min. The cured sample was heated at 1000℃ for 1 h.

2.4. Graphitization of the carbonized film containing CMS.

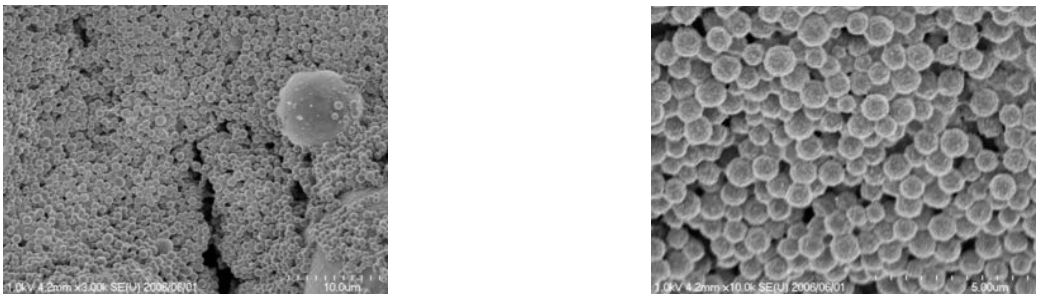
The carbonized film containing CMS was graphitized at 1500, 2000, 2500, 2800℃.

3. Results and Discussion

3.1. Formation and Graphitization behavior of CMS.

Polymer microsphere was formed on PEG or polypropylene glycol. Other additives did not contribute the

formation of microsphere. As a result, additives containing ether linkage in main chain of molecule were effective to the formation of microsphere. Microsphere formed with PEG was the small size before and after 1 μm than that with polypropylene glycol. Figure 1 shows typical SEM images of CMS formed with PEG.



(a) Low magnification image ———:10 μm (b) High magnification image ———: 5 μm

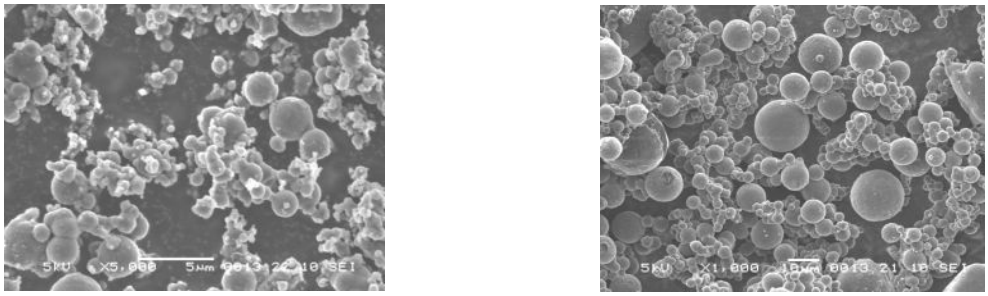
Figure 1. SEM images of CMS on the surface of carbon film with PEG.

X-ray diffraction profiles of CMS and Py-COPNA with graphitization treatment showed different behavior. The difference appeared over 2500℃. Crystallinity of CMS increased over 2500℃, compared with that of Py-COPNA and d_{002} diffraction line of the sample heated at 2800℃ turned sharply with narrow half peak width at 26° .

Electrostatic capacitance from the carbonized film containing CMS was 86 F/g (at 10mA/g).

3.2. Large scale preparation

Polymer microsphere was also obtained by large scale preparation. Yield after carbonization was 30-40 % in this condition and this value was one digit larger than that of CMS formed on carbon film. The particle size basically depends on stirring rate and content of Py-COPNA in the mixture. Particle size showed a general tendency to turn large from 1 to a couple of ten μm. Carbonization was successful in the case of cured polymer microsphere immersed into conc. H_2SO_4. Figure 2 shows a typical SEM image of CMS formed from large scale preparation.



(a) Stirring rate: 80 rpm (b) Stirring rate: 640 rpm

Figure 2. SEM images of CMS formed from large scale preparation.

4. Conclusion.

Polymer microsphere was obtained from additives consisted of ether linkage in main chain of molecule. Crystallinity of CMS formed on carbon film increased over 2500℃. Large scale preparation of CMS was successful in the case of polymer microsphere cured with conc. H_2SO_4. Particle size showed a general tendency to turn large.

5. References.

[1] Yi Zheng Jin, Chao Gao, Wen Kuang Hsu, *et al.,* Large-scale synthesis and characterization of carbon spheres prepared by direct pyrolysis of hydrocarbons, Carbon 43 1944-1953(2005).

[2] Ota M., Kametani J., Kogure T., Tago T., Tomosaka H., S. Otani, Pyrolytic preparation of carbon microsphere and and nanosphere from coal tar pitch-based COPNA resin film, Pacifichem 2005 Congress, abstract MATL0643(2005).