

Preparation and Characterization of Co-mesocarbon Composite Microbeads

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1. Introduction

Recently, there have been immense interests in researching the Cobalt/carbon composites due to their remarkable properties and their promises for applications. It have been found that ferromagnetic nanoclusters, such as Iron, cobalt and nickel, have much better magnetic properties than bulk metals due to their single domain nature [1-2]. However, poor oxidation resistance of the bare metal nanoparticles sets a great barricade for further exploring their application. The best way to protect metallic nanoclusters from air-oxidation is to encapsulate them with carbon materials. So the recent scientific literature contains many reports on the cobalt nanoparticles/carbon composites [1-5]. Moreover, the outstanding catalytic and electrical properties of cobalt and its oxide have attracted researches to combine the properties of cobalt metal and carbon materials by their composites [6, 7].

Mesocarbon microbeads (MCMB) isolated from the heat-treated pitch containing mesophase spherules have been used as a precursor for high-density carbon artifact [8], column packing material [9], and super active carbon [10,11]. Especially, MCMB have been applied as a Li-ion secondary battery anode material and have revealed promising behavior. In this paper, we describe the synthesis of Co-mesocarbon composite microbeads by pyrolysis of the mixture of coal tar pitch and cobalt acetate and then extraction with Pyridine. The structure of composite microbeads and distribution of Co metal particle within the microbeads have been investigated. The resulting materials may be promising applied as electrode and magnetic material.

2. Experimental

Coal tar pitch was used as starting material and its some properties are summarized in Table 1. Cobalt acetate (AR) was purchased and used as additives in present study. Cobalt acetate was added to the coal tar pitch in a autoclave in an nitrogen atmosphere and stirred for 30 min at 200C so that well-proportioned mixture can be obtained. The mixture was heat-treated up to 410C or 420C 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 cobalt acetate were varied in the range of 5, 12.5, 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 Co-mesophase carbon composite microbeads (Co-MCMB) can be obtained. Co-MCMB was carbonized at 1000C and 1800C under nitrogen flow and then further graphitized at 2500C under argon atmosphere.

To study the structure of Co-MCMB, X-ray Powder diffraction (XRD) was carried out on a D/max 2500VB2+/PC X-ray diffractometer with Cu-K α radiation. Co 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 (C)	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

^aHS, Hexane solubles; HI, Hexane insolubles; TS, toluene solubles; TI, toluene insolubles; PS, pyridine solubles; PI, pyridine insolubles.

3. Results and discussion

3.1. Pyrolysis of coal tar pitch with cobalt acetate and solvent extraction

Table 2 summarizes the pyrolysis conditions of coal tar pitch with cobalt acetate and the yields of pyrolysis products and Co-MCMB. The yield of pyrolysis product decreases with the increase of the CoAc content. After the heat-treatment, CoAc decomposed and produced metal Co and organic compounds, which trend to polymerize into the mesogens of larger component of pitch or escape with the smaller molecular weight component produced by pyrolysis of pitch. The remarkable decrease of pyrolysis yield with the CoAc content increasing indicates that most of organic compounds produced by decomposition of CoAc escape from mixture by volatilization. The effects of pyrolysis temperature in this study show the same trend as pyrolysis of coal tar pitch alone. When increasing pyrolysis temperature, more the smaller molecular weight components escape and more the mesogens of larger component can be produced by polymerization because of the severe reaction conditions. Therefore, higher pyrolysis brings on lower pyrolysis and higher content of mesophase carbon, which result in the content of Co in Co-MCMB decrease.

Table 2. Pyrolysis conditions and yields.

Pyrolysis conditions		CoAc, wt. %	Pyrolysis yield, wt. %	Co-MCMB	
Temperature, C	Time, h			Yield, wt. %	Resulted beads
410	0.5	5	93.0	40	Co-MCMB1
410	0.5	12.5	84.6	39	Co-MCMB2
410	0.5	50	66.7	37	Co-MCMB3
420	0.5	50	63.3	42	Co-MCMB4

Fig.1 shows the content of element Co in the resulted Co-MCMB. It can be found adding more CoAc can produce the Co-MCMB with higher content of Co and higher reaction temperature result in lower content of Co in Co-MCMB. Based on the data of Table 2 and Fig. 2, it can be reckoned that most of Co element in the raw material has grown into the Co-MCMB.

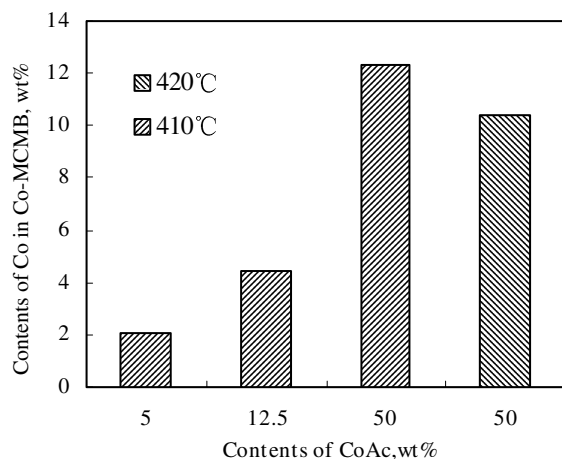


Fig.1. The relationship between Co content in Co-MCMB and addition content of CoAc.

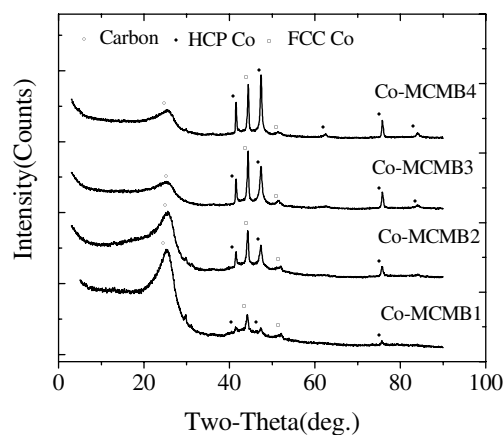


Fig.2. The XRD patterns of Co-MCMB.

The XRD patterns in Fig. 2 reveal the structures of the Co-MCMB, indicating the existence of cubic and hexagonal cobalt phases, together with carbon. Furthermore, it can be seen from Fig.2 that, with the content of Co increasing, the relative height of diffraction peak of carbon (002) decreases and the relative height of diffraction peaks of cobalt increase. When the content of Co is small, the diffraction peaks of cubic cobalt phase are clearer than that of hexagonal cobalt phase. However, with the content of Co increase, the diffraction peaks associated with hexagonal cobalt phase are more and more clear. When the content of Co is up to 12.3 wt% (Co-MCMB3), the highest peak is associated with hexagonal cobalt rather than cubic cobalt phase. These results suggest that the structures of carbon and cobalt are affected by each other in the formation of Co-MCMB.

3.2. Carbonization and graphitization of the Co-MCMB

Fig.3 shows the XRD patterns of carbonized Co-MCMB. As can be seen in Fig.3, peaks of f.c.c. Co become very sharper than peak of carbon with the content of Co increasing. Compared with the diffraction patterns of untreated samples, the XRD patterns of carbonized Co-MCMB do not display any peaks associated with h.c.p. cobalt. The results indicate that the h.c.p. cobalt phase transformed into f.c.c. cobalt phase during the carbonization of the Co-MCMB.

Table 3. The XRD parameters of Co-MCMBs carbonized at 1000C.

Sample	Heat-treatment temperature(□)	2θ(°) Carbon (002)	d ₀₀₂ (nm)
Co-MCMB-2	1000	24.865	0.3578
Co-MCMB-4	1000	25.120	0.3542
Co-MCMB-3 ^a	1000	24.731	0.3597
		26.575	0.3352

^aTwo d₀₀₂ values correspond to two peaks at two diffraction angle, respectively, because of thermal and catalytic graphitization in the presence of Co.

Table3 summarizes the XRD of the Co-MCMB carbonized at 1000C. Compared with Co-MCMB-2 and Co-MCMB-4, the content of Co increase from 4.45% to 10.44%, accordingly, for their carbonized samples, the diffraction angle of carbon (002) increase from 24.865° to 25.120° and the interlayer spacing, d₀₀₂, decrease from 0.3578 to 0.3542. As for Co-MCMB-3, which contain 12.34% Co, after carbonization at 1000□, its diffraction profile give two peaks at 24.731° and 26.575° of 2θ, although the double peaks is not very clear. The above results indicate that there exist thermal and catalytic graphitization processes in the carbonization of Co-MCMB and metal Co have catalysis effect on graphitization of carbon even at 1000C.

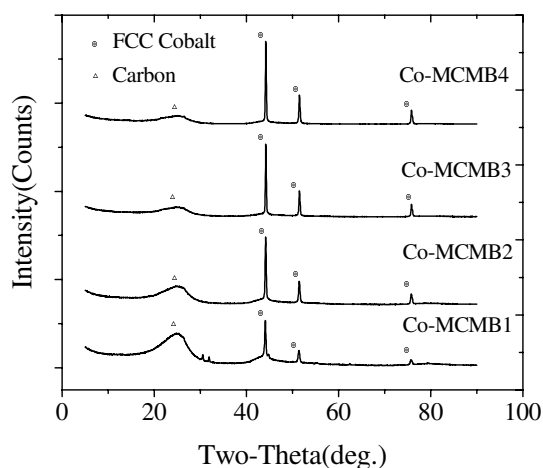


Fig.3. The XRD patterns of Co-MCMB carbonized at 1000°C.

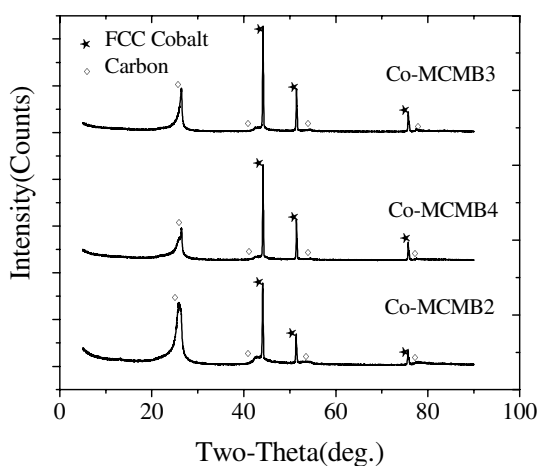


Fig.4. The XRD patterns of Co-MCMB carbonized at 1800°C.

Table 4. The XRD parameters of Co-MCMBs carbonized at 1800C.

Sample	Heat-treatment temperature(C)	2 θ (°) Carbon (002)	d ₀₀₂ (nm)
Co-MCMB-2 ^a	1800	25.761	0.3456
		26.319	0.3383
Co-MCMB-4 ^a	1800	25.740	0.3458
		26.421	0.3371
Co-MCMB-3	1800	26.479	0.3363

^aTwo d₀₀₂ values correspond to two peaks at two diffraction angle, respectively, because of thermal and catalytic graphitization in the presence of Co.

The XRD patterns in Fig.4 reveal the structures of the Co-MCMB carbonized at 1800C, also indicating the existence of f.c.c. cobalt and carbon. It is noticed in Fig. 4 that the diffraction peaks associated with (100), (004) and (110) profiles of graphite appear, which indicate the graphitic crystal structure in Co-MCMB has developed more regular in carbonization at 1800C. Fig.5 and Table 4 show the XRD diffraction of carbon (002) of the Co-MCMB carbonized at 1800C in detail. As for Co-MCMB-2, the interlayer space distances calculated from the diffraction peaks were 0.3456 and 0.3383 nm, respectively. Two peaks at higher and lower angles appear to reflect the catalytic and thermal graphitization, respectively. More Co content in Co-MCMB increases the higher diffraction angles and the intensity of its peak. Co-MCMB-3 have highest Co content of 12.34%, so its sample carbonized at 1800C gave only one single peak at 26.479° of d₀₀₂ diffraction and the smallest interlayer spacing of 0.3363 nm. It can be inferred that there exist catalytic and thermal graphitization in carbonization at 1800C and the effect of catalysis change more prominent with the increase of Co content in Co-MCMB.

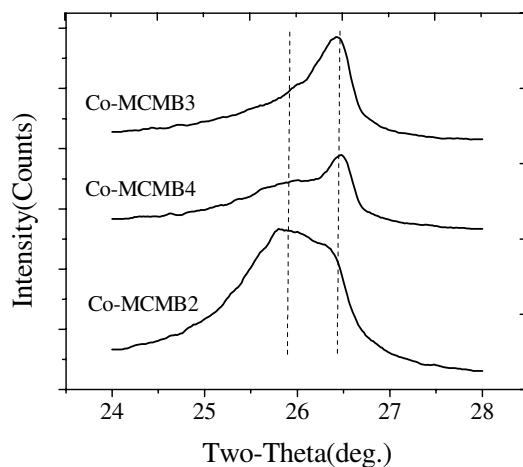


Fig.5. The XRD patterns of the carbon (002) of the Co-MCMB carbonized at 1800°C.

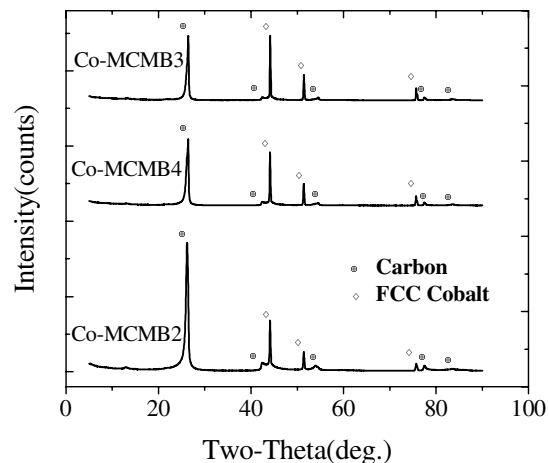


Fig.6. The XRD patterns of Co-MCMB carbonized at 2500°C.

The XRD patterns of the Co-MCMB graphitized at 2500C in Fig. 6 show there exist

developed graphite crystal and f.c.c. cobalt in Co-MCMB graphitized at 2500C. Table 5 summarizes the carbon d_{002} diffraction of the Co-MCMB graphitized at 2500C. From Table 5, it can also be seen more Co content in Co-MCMB increases the diffraction angle and decrease the interlayer spacing. But the carbon interlayer spacing of Co-MCMB-3 is ca. 0.3368 nm, which is bigger than d_{002} of graphite, 0.3354 nm and even bigger than d_{002} of Co-MCMB-3 carbonized at 1800C. In the carbon/cobalt composite, a few of metal Co can possibly diffuse into the interlayer of carbon, which can affect the interlayer spacing of carbon and induce d_{002} , as an average value, to be biggish.

Table 5. The XRD parameters of Co-MCMBs graphitized at 2500C.

Sample	Heat-treatment temperature(C)	$2\theta(^{\circ})$ Carbon (002)	d_{002} (nm)
Co-MCMB-2	2500	26.180	0.34011
Co-MCMB-4	2500	26.439	0.33684
Co-MCMB-3	2500	26.440	0.33682

3.3 The morphology and composition distribution of the Co-MCMB

The sizes of Co crystals and their distribution in carbon/cobalt composite are important for the characteristics of Co-MCMB as magnetic material or precursor of electrode. Fig.7 shows the TEM photographs of Co-MCMB3 graphitized at 2500C. It can be seen that the cobalt metal particle with particle size of 10~20nm well dispersed in the carbon matrix.

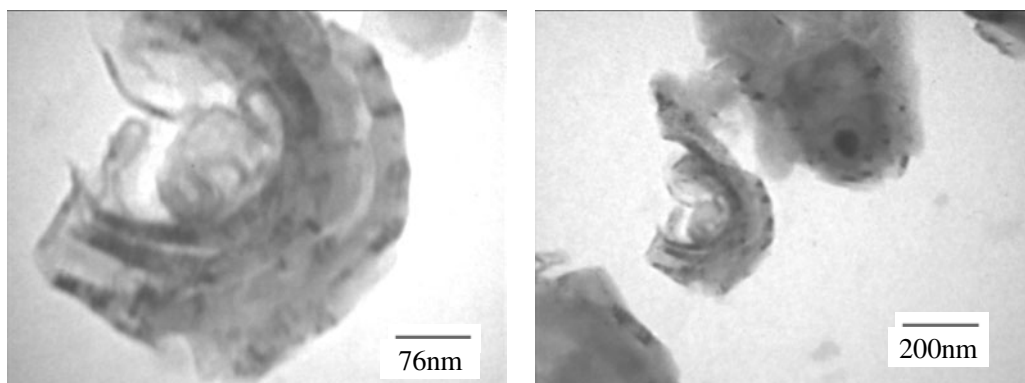


Fig.7 TEM photograph of Co-MCMB3 graphitized at 2500°C.

4. Conclusions

Co-mesocarbon composite microbeads are prepared by pyrolysis of the mixture of coal tar pitch and cobalt acetate and then extraction with Pyridine. The structures of resulted composite microbeads heat-treated at different temperature have been studied. It can be found that the content of Co metal in composite microbeads increase with the increasing

of the ratio of cobalt acetate to coal tar pitch in raw material and nano-size Co particles are dispersed in carbon matrix. The X-ray diffraction patterns of composite microbeads indicate obvious diffraction peaks associated with graphitic carbon and Co metal even for the composite microbeads heated at 2500C. The X-ray diffraction patterns of composite microbeads heated at 1800C show double diffraction peaks at ca. 26°, which can be attributed to the catalysis of Co particle on the forming and ordering stacking of graphene layers in composite microbeads.

References

- [1]G. H. Lee, S. H. Huha, J. W. Jeong, H.-C. Ri, Excellent magnetic properties of fullerene encapsulated ferromagnetic nanoclusters, *Journal of Magnetism and Magnetic Materials* 2002; 246: 404-411.
- [2]Hong Bi, Shandong Li, Xiqun Jiang, Youwei Du, Changzheng Yang, Magnetic anisotropy in carbon encapsulated Co/CoO “lines” with large exchange bias, *Physics Letters A*, 2003; 307: 69-75.
- [3]Z. H. Wang, C. J. Choi, B. K. Kim, J. C. Kim, Z. D. Zhang, Characterization and magnetic properties of carbon-coated cobalt nanocapsules synthesized by the chemical vapor-condensation process, *Carbon* 2003; 41: 1751-1758.
- [4]B. H. Liu, J. Ding, Z. Y. Zhong, et al., Large-scale preparation of carbon-encapsulated cobalt nanoparticles by the catalytic method, *Chemical Physics Letters* 2002; 358: 96-102.
- [5]Xicheng Ma, Yuanhua Cai, Xia Li, Shulin Wen, Growth and microstructure of Co-filled carbon nanotubes, *Materials Science and Engineering A*, 2003; 357: 308-313.
- [6]Ruowen Fu, Mildred S. Dresselhaus, et al., The growth of carbon nanostructures on cobalt-doped carbon aerogels, *Journal of Non-Crystalline Solids*, 2003; 318:223-232.
- [7]A. Weidenkaff, S. G. Ebbinghaus, et al., Metal nanoparticles for the production of carbon nanotube composite materials by decomposition of different carbon sources, *Materials Science and Engineering C* 2002; 19: 119-123.
- [8] Lu Yonggen, Ling Licheng, Wu Dong , Liu Lang, Zhang Bijiang, Mochida, Isao, Preparation of mesocarbon microbeads from coal tar, *Journal of Materials Science* 2000; 34 (16): 4043-4050
- [9] Honda, Hidemasa, Carbonaceous mesophase: history and prospects, *Carbon* 1988; 26(2): 139-156
- [10] Zengmin Shen, Ruishengxue, Preparation of activated mesocarbon microbeads with high mesopore content, *Fuel Processing technology* 2003; 84: 95-103.
- [11]Ruisheng Xue, Zengmin Shen, Formation of graphite-potassium intercalation during activated of MCMB with KOH, *Carbon* 2003; 41: 1862-1864.