

Preparation of MCMB-Sn composite as anode material for lithium-ion batteries

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1. Introduction

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. 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 1-40 μm 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]. 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, Pb, 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, MCMB-Sn composites with different content of tin were prepared by pyrolysis of the mixture of MCMB, organotin compound and pitch. The physical properties and microstructure of the MCMB-Sn composites were characterized by X-ray diffraction (XRD) and Scanning electron micrograph (SEM). The anodic performance of the composites was examined using lithium test cells.

2. Experimental

MCMB, purchased dibutyltin dilaurate (AR) and petroleum pitch were used as starting materials. MCMB was formed by liquid carbonization of petroleum residue with 2% N_{110} carbon black at 410°C for 4.5h and extracted by Pyridine, and then graphitized at 2900°C . The characteristics of the petroleum residue are listed in Table 1. Dibutyltin dilaurate and pitch were dissolved in THF. MCMB was added into the solution and homogeneously mixed. After evaporating the THF solvent, the mixture was heated at 1000°C for 1h under inert atmosphere. Obtained MCMB-Sn composite sample was ground and sieved (-200 mesh). To study the structure of MCMB-Sn composite, X-ray Powder diffraction (XRD) was carried out on a D/max 2500VB2+/PC X-ray diffractometer

with Cu-K α radiation. Scanning electron micrograph (SEM) was carried out on a stereoscin 250 MK3 (CAMBRIDGE COMPANY). Sn contents in the composite were measured by an IPC emission spectroscopy (E-8000).

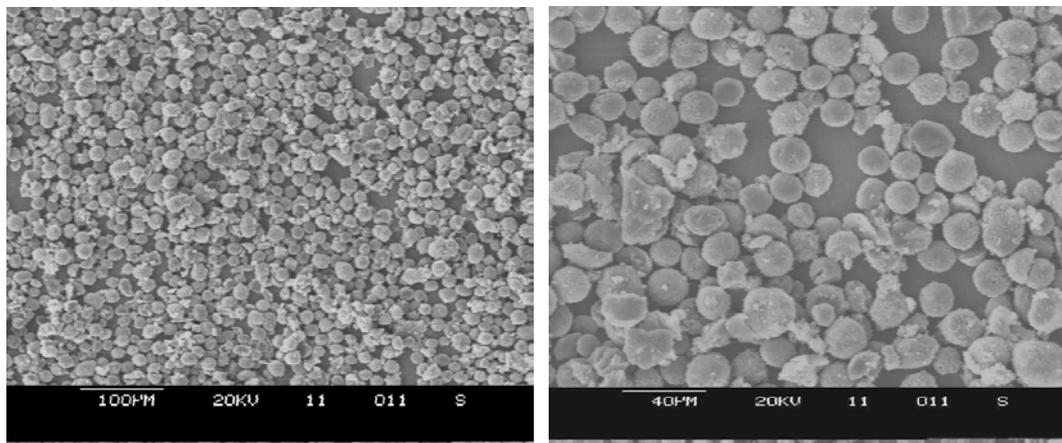


Fig.1 SEM images of MCMB heated at 2900°C

Table 1. Characteristics of petroleum residue

Ash (%)	Fixed carbon (%)	Pyridine insolubles (%)	Toluene insolubles (%)
0.05	89.49	1.4	16.0

CR2025 coin cells were fabricated to test the electrochemical properties of MCMB-Sn composites. The MCMB-Sn composite electrodes were made by dispersing 90 wt% active materials, 5wt% carbon black and 5wt% polyvinylidene fluoride (PVdF) binder in N-methylpyrrolidone (NMP) solvent to form a slurry, which was then spread on to the steel mesh and dried under vacuum at 120°C. Lithium sheet acted as the counter electrode and the electrolyte was 1 M LiPF₆/EC+DC+DMC (1:1:1 in volume). The cells were assembled in argon filled glove-box (MB LABMASTER). The cells were galvanostatically charged and discharged with current density of 0.2mA/cm² in the voltage range of 0.001/2.8V versus Li/Li⁺.

3. Results and discussion

The XRD patterns in Fig. 2 reveal the structures of the MCMB-Sn composites, indicating the existence of clear carbon and synthesized tin phase. The results suggest that, during pyrolysis, dibutyltin dilaurate decomposed and mostly converted to the metallic Sn. Fig.3 illustrates the content of Sn in the composite. It can be seen from Fig.2 and Fig.3 that, with the content of Sn increasing, the relative height of diffraction peaks of Sn increase.

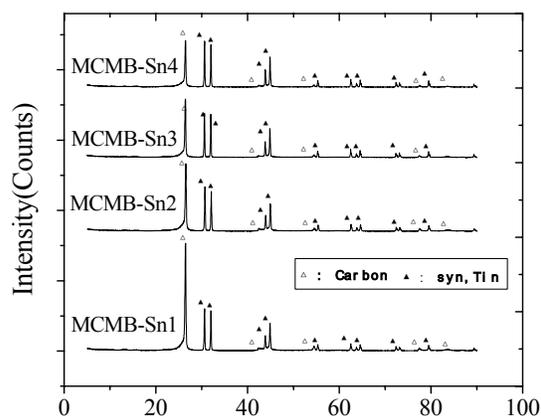


Fig.2 XRD patterns of the MCMB-Sn composites

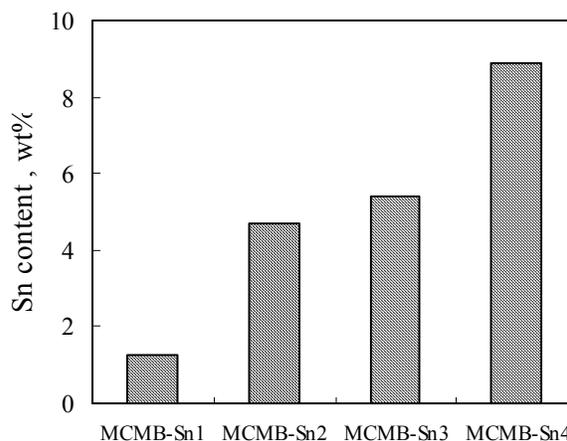


Fig.3 Sn content of the MCMB-Sn composites

Morphology of MCMB-Sn composites is illustrated in Fig.4. The microsphere in the micrograph is not as round and regular as the starting material and its smooth surface is coated with pyrolytic carbons. It can also be found in Fig.4 that the circular shaped particles are dispersed on the surface of the microsphere. It can be inferred that the metallic Sn particles are dispersed in the pyrolytic carbons and then pyrolytic carbons together with Sn particles deposit on the surface of mesocarbon microbeads during pyrolysis.

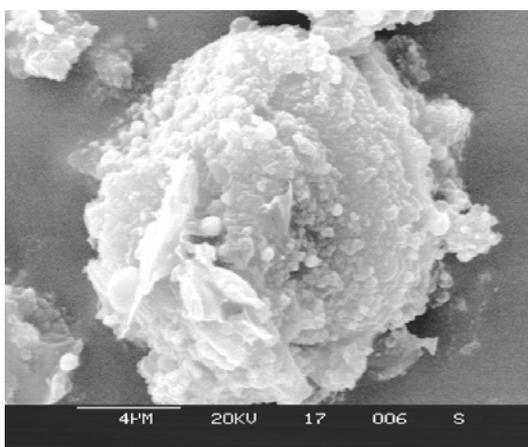


Fig.4. SEM images of MCMB-Sn3 composite

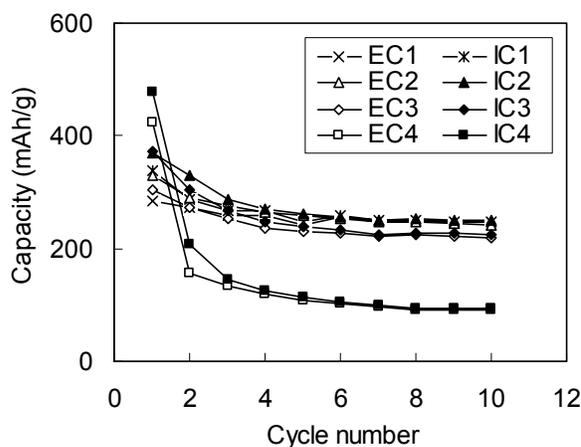


Fig.5. The capacities vs. cycle number for MCMB-Sn composites electrode. (IC: Insertion Capacity; EC: Extraction Capacity; the number corresponding to the number of samples)

Fig. 5 shows the dependence of the capacity of MCMB-Sn composite electrode on cycle number. It can be found that, with the increase of Sn content, the initial capacity of composite electrode increases, but the capacity degrading with cycling becomes more quickly at the same time. For the MCMB-Sn₄ composite electrode, the capacities were only about 100 mAh/g after 10 times cycling, although its first insertion capacity can be up to 470 mAh/g. The electrochemical performance of MCMB-Sn composite electrode suggests that the insertion capacity produced by Sn particles fades rapidly on cycling and Sn particles become inactive after several cycles. The pyrolytic carbon matrix and MCMB cannot restrain effectively Sn from structure deterioration. The main reason for it may be attributed to that the Sn particles in the composite exist as a crystal phase. As for metallic hosts, the favorable structure for the long-term cycle performance is a stable amorphous structure rather than a crystal structure [11]. So, to control the phase of Sn particles in the composite would be a feasible way to overcome this disadvantage.

4. Conclusions

MCMB-Sn composite can be prepared by pyrolysis of the mixture of MCMB, organotin compound and pitch. Sn particles exist as a crystal phase and are dispersed in the pyrolytic carbon matrix. MCMBs are coated with the pyrolytic carbons together with Sn particles. The electrochemical performance of MCMB-Sn composite electrode shows that the resulted composites have a large lithium storage capacity at the first cycle, but their poor cyclability still needs to be improved by the next work.

References

- [1] Akihiro Mabuchi, Katsuhisa Tokumitsu et al., Charge-discharge characteristics of the mesocarbon microbeads heat-treated at different temperatures, *J. Electrochem. Soc.*, v142n4, p1041-1046
- [2] Kim, C., Fujino, T., Miyashita, K., Hayashi, T., Endo, M., Dresselhaus, M.S., Microstructure and electrochemical properties of boron-doped mesocarbon microbeads, *Journal of the Electrochemical Society*, 147(4), 2000, p 1257-1264
- [3] Ishiyama, Shintaro, Asano, Masaharu, Anode performance of electron irradiated mesocarbon microbeads for secondary lithium batteries, *Journal of Nuclear Science and Technology*, 37(12), 2000, p 1056-1062
- [4] Mabuchi, Akihiro, Fujimoto, Hiroyuki, Tokumitsu, Katsuhisa, Kasuh, Takahiro, Charge-discharge mechanism of graphitized mesocarbon microbeads, *Journal of the Electrochemical Society*, 142(9), 1995, p 3049-3051
- [5] R. Alcántara, F. J. Fernández Madrigal, et al., Characterisation of mesocarbon microbeads (MCMB) as active electrode material in lithium and sodium cells, *Carbon* 2000; 38:1031-1041.
- [6] G. X. Wang, Jung-Ho Ahn, M. J. Lindsay, L. Sun et al., Graphite-Tin composites as anode materials for lithium-ion batteries, *Journal of power sources*, v97-98, 2001,

211-215.

[7] Jim Yang Lee, Ruifen Zhang, Zhaolin Liu, Dispersion of Sn and SnO on carbon anodes, *Journal of Power Sources*, v90, 2000, 70-75

[8] J. Read, D. Foster, J. Wolfenstine, W. Behl, SnO₂-carbon composites for lithium-ion battery anodes, *Journal of power sources*, v96, 2001, 277-281.

[9] Minato Egashira, Hideyasu Takatsuji, Shigeto Okada, Jun-ichi Yamaki, Properties of containing Sn nanoparticles activated carbon fiber for a negative electrode in lithium batteries, *Journal of Power Sources*, v107, 2002, 56–60.

[10] Hisashi Tamai, Shinji Matsuoka, Masashi Ishihara, Hajime Yasuda, New carbon materials from pitch containing organotin compounds for anode of lithium ion batteries, *Carbon*, v39, 2001, 1515–1523.

[11] Z. S. Wen, J. Yang, B. F. Wang, K. Wang, Y. Liu, High capacity silicon/carbon composite anode materials for lithium ion batteries, *Electrochemistry Communications* 2003; 5: 165-168.