Preparation of Si-MCMB 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. The presently used active anode material is graphite, whose maximum capacity of Li insertion is 372mAh.g. However, the required capacity for the new active material should be over 1100mA/g [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. Among the attractive materials, the likeliest candidate is metallic Si whose maximum capacity of Li insertion is as high as 4200mAh/g. Moreover, the discharge curve of Si during the electrochemical extraction of Li is sufficiently flat, very similar to that of graphite, making it very attractive [1-3]. The cycleability of Si, however, is too poor to be utilized for the anode of actual Li-ion batteries. In order to avoid this problem, many research works have so far been performed, such as using metal silicide alloys [4, 5] and producing many kinds of carbon /silicon composite by mechanical milling or CVD method [6-8]. Although the anodic performance of silisic materials have been improved to different extent by the above methods, the satisfying results have not been achieved. In this paper, we prepared silicon- graphitized mesocarbon microbeads (Si-MCMB) composite materials by heat-treatment of the mixture of MCMB, silicon powders and petroleum pitch at 1000℃ and try to combine the high lithium storage capacity of the element Si and the stable cyclability of MCMB.

2. Experimental

MCMB, silicon 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℃ for 4.5h and extracted by Pyridine, and then graphitized at 2900℃. The average diameter of MCMB is about 20μm.The characteristics of the petroleum residue are listed in Table 1. Silicon (-500mesh, 99.8%) was purchased. The petroleum residue was dissolved in THF. MCMB and silicon powders were added into the pitch solution and homogeneously mixed. After evaporating the THF solvent, the solid mixture was heated at 1000℃ for 1h under inert atmosphere. Obtained Si-MCMB composite sample was ground and sieved (-200 mesh). To study the structure of Si-MCMB composite, X-ray Powder diffraction

(XRD) was carried out on a D/max 2500VB2+/PC X-ray diffractometer with Cu-Kα radiation. Scanning electron micrograph (SEM) was carried out on a stereoscin 250 MK3 (CAMBRIDGE COMPANY).

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 Si-MCMB composites. The Si-MCMB composite electrodes were made by dispersing 90 wt% active materials, 5wt%a 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℃. Lithium sheet acted as the counter electrode and the electrolyte was 1 M $LiPF_6$/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/cm^2 in the voltage range of 0.001/2.8V versus Li/Li^+.

3. Results and discussion

The XRD patterns of Si-MCMB composites are shown in Fig. 1. It can be seen that the Si particles exist in the composite as crystal phase and diffraction peaks of Si become sharper with more content of Si in the composite. Fig. 2 shows the SEM photographs of Si-MCMB composite. It can be seen from Fig.2 that both MCMB and Si particles are embedded in the pyrolysis carbon. The pits in the SEM image probably resulted from brushed off of the MCMB or Si particles by grinding.

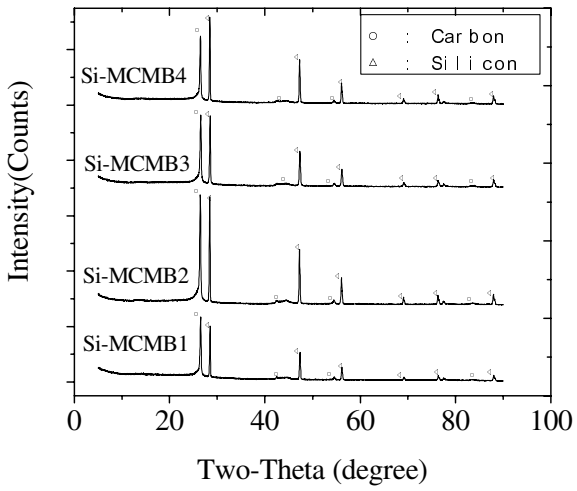

Fig.1. The XRD patterns of Si-MCMB composites

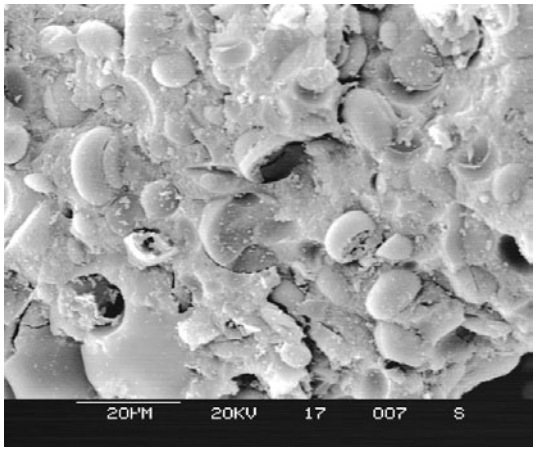

Fig.2. The SEM image of Si-MCMB3 composites

Table 2 summarized the first cycle results of Si-MCMB composites with different Si content. The data in Table 2 show that the insertion capacity increase and coulombic efficiency decrease with the increasing of Si content. Moreover, it can be also seen that the pitch content in composite affects the anodic performance of Si-MCMB. The performances of Si-MCMB3 and Si-MCMB2 show that lower content of pitch result declining of both insertion capacity and coulombic efficiency, which may be attributed to the Si and MCMB particles can not be effectively adhered to each other with lower content of pitch.

Table 2. The raw compositions of Si-MCMB composites and their first cycle data

Composition of precursor (wt%)			Resulted sample	The first cycle data		
				Capacity (mAh/g)		Coulombic efficiency
MCMB	Si	Pitch		Insertion	Extraction	(%)
3	1	1	Si-MCMB4	1210.5	841.8	69.5
5	1	3	Si-MCMB3	1087.8	851.2	78.3
5	1	1	Si-MCMB2	1017.5	777.6	76.4
8	1	3	Si-MCMB1	976.0	749.6	76.8

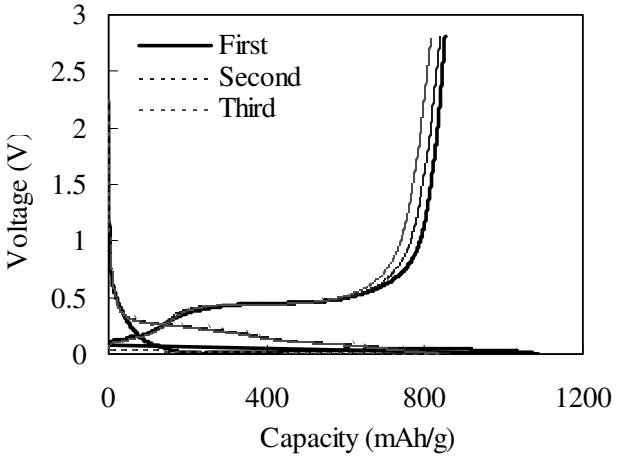

Fig.2. The discharge and charge curves of Si-MCMB3 composites

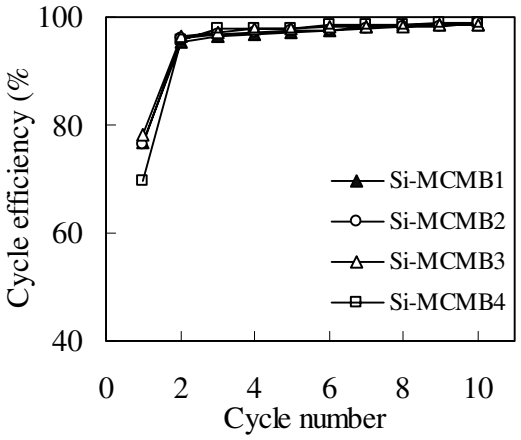

Fig.4. The cycle performance of Si-MCMB composites

The discharge and charge curves of Si-MCMB3 are presented in Fig.3. The voltage profile for the first insertion of Si-MCMB3 is similar to that of MCMB and shows a long flat at about 0.05v. After the first cycle, the lithium insertion voltage is obviously enhanced and the voltage trend becomes stable in the following cycles, which maybe result from converting of Si phase structure from crystalline to amorphous state after the first cycle [6]. The cycle performance of Si-MCMB composites shown in Fig.4 indicate that, after

first cycle, all the composite electrodes can keep a high coulombic efficiency of about 98%.

4. Conclusions

Si-MCMB composites were prepared by heat-treatment of the mixture of MCMB, silicon powders and petroleum pitch at 1000□. Pitch, as an adhesive, can facilitate the Si and MCMB particles adhering to each other. The resulting composites shown good anodic performances and the results revealed that the insertion capacity increase and coulombic efficiency decrease with the increasing of Si content. The initial insertion capacities and coulombic efficiencies obtained for the produced composites were 976~1210mAh/g and 69.5~78.3%, respectively.

References

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