

# Morphology-stable alloy/C composites for lithium insertion

Y. Liu\*, J.Y. Xie, J. Yang

*Energy Science and Technology Laboratory, Shanghai Institute of Microsystem and Information Technology,  
Chinese Academy of Sciences, Shanghai 200050, China*

## Abstract

Composite materials, obtained by depositing sub-micron size particles of  $\text{SnCu}_x$  and  $\text{SnSb}_x$  on the surface of carbonaceous mesophase spherules (CMS), can endure the large volume effect of alloy host for lithium insertion and extraction. The alloy/C composites deliver large reversible capacities ( $430 \text{ mAh g}^{-1}$  for  $\text{SnSb}_x/\text{CMS}$ ,  $390 \text{ mAh g}^{-1}$  for  $\text{SnCu}_x/\text{CMS}$ ); the capacity retention at the 30th cycle is 90% for  $\text{SnSb}_x/\text{CMS}$  and 95.2% for  $\text{SnCu}_x/\text{CMS}$ , respectively. They are promising anode materials for lithium-ion batteries.

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## 1. Introduction

Lithium-ion batteries have been widely used in our daily life. The most popular anodes are based on intercalative carbonaceous materials [1]. Although these anode materials have excellent cycling stability, the reversible capacity is normally below  $370 \text{ mAh g}^{-1}$ . As alternatives, lithium storage metals, such as Al, Sn, Si and Sb have been researched because of the much larger capacity. High-capacity lithium-ion batteries with alloy anodes, however, have not penetrated into commercial markets so far. The major problem is a large volume change that accompanies lithium insertion and extraction, which causes rapid mechanical disintegration of the metallic host and subsequent degradation of electrode performance [2,3]. It is especially serious under high lithium utilization. In order to minimize the mechanical stress and volume effect, multi-phase composite structures and small particle alloy systems have been proposed [4–6].

On the other hand, carbonaceous materials demonstrate small volume expansion for lithium accommodation (ca. 9% for graphite) and have soft and flexible characteristics. Lithium storage metals and alloys in combination with carbon could endure the volume change and reduce the mechanical stress within the electrode, and thereby prevent the disintegration. Sn/KS6 (synthetic graphite) composite by chemically reductive precipitation in aqueous solution, pyrolyzed polysiloxanes, highly dispersed silver on carbon and nano-SnSb/carbon composite are the representatives of this

class of anode materials [7–11]. Such composite materials can support large volume change of alloy host and generally provide a larger capacity than graphite matrices. However, most of the metal/carbon composites are still inferior to carbonaceous materials in the cycleability, especially if metallic host with large insertion capacity is used as a component.

As we reported previously, ultrafine tin particles were finely deposited on the surface of CMS by the reduction of organic tin salt at high temperature [12]. The good cycleability was attribute to the homogenous particle distribution and high contacting strength between two active materials. In this paper, we try to deposit SnSb and  $\text{Sn}_5\text{Cu}_6$  alloys on the surface of CMS to obtain alloy/C composites for anodes in lithium-ion batteries.

## 2. Experimental

Carbonaceous mesophase spherules (CMS, BET surface area =  $1.92 \text{ m}^2 \text{ g}^{-1}$ , typical particle size:  $15 \mu\text{m}$ ) was commercially available from Shanghai Shanshan Ltd., dibutyltin dilaurate from Shanghai Reagent Ltd., Cu(II) 2-ethylhexanoate and antimony oxide from Aldrich. For preparing  $\text{SnSb}_x/\text{CMS}$  composite material, dibutyltin dilaurate and antimony oxide were chosen as precursors. For  $\text{SnCu}_x/\text{CMS}$  composite material, Cu(II) 2-ethylhexanoate was used. By the decomposition and reduction of metallic salt at high temperature, alloy particles were deposited on the surface of CMS. The complete reaction steps were described elsewhere [12]. The reactions were carried at  $450\text{--}500 \text{ }^\circ\text{C}$  for 30 min under protected atmosphere (96% Ar and 4%  $\text{H}_2$ ).

\* Corresponding author. Tel.: +86-21-62511070;

fax: +86-21-32200534.

E-mail address: liuyu@mail.sim.ac.cn (Y. Liu).

Electrochemical performance of composite materials was investigated via coin cells containing 1 M LiPF<sub>6</sub>/EC + DEC (1:1, v/v) from Mitsubishi Chemical Company. All mentioned electrodes contained 4 wt.% acetylene black, 8 wt.% PVdF and 88 wt.% active material. Active powder and acetylene black were added into PVdF/1-methyl-2-pyrrolidone solution and stirred to form slurry, which was then coated onto 20 μm-thick copper foils. After solvent evaporation, the obtained film was cut into disc-form electrode (Ø: 14 mm) and further dried at 130 °C under vacuum for 2 h. Finally, electrodes were compacted at 3 MPa. The cells were assembled in Ar atmosphere using lithium counter electrode and microporous polypropylene separator. Unless stated otherwise, charging and discharging test was carried out under a controlled cut-off voltage from 0 to 1.5 V and at a constant current density of 0.2 mA cm<sup>-2</sup>.

### 3. Results and discussion

A Sn/CMS composite we prepared preciously showed an interesting result concerning both cycleability and reversible capacity [12]. SnSb<sub>x</sub> and SnCu<sub>x</sub> are chosen for depositing on the surface of CMS follow the same preparation. Under controlled reaction condition, reduced Sb deposited on the surface of CMS firstly, followed by Sn deposition and alloying with Sb. Fig. 1 exhibits XRD patterns of SnSb<sub>x</sub>/CMS composite powder containing 35 wt.% SnSb<sub>x</sub>, from which peak of metallic Sn and SnSb alloy can be observed. There is a similar reduction and alloying process for the formation of SnCu<sub>x</sub>/CMS composite. Fig. 2 shows the presence of metallic Sn, Cu and Sn<sub>5</sub>Cu<sub>6</sub> in composite powder.

Reduced metallic particles are finely dispersed and deposited on the surface of CMS particles. The typical particle size is below 0.8 μm. Fig. 3 illustrates a SEM photograph of SnSb<sub>x</sub>/CMS composite. The SnCu<sub>x</sub>/CMS composite has a

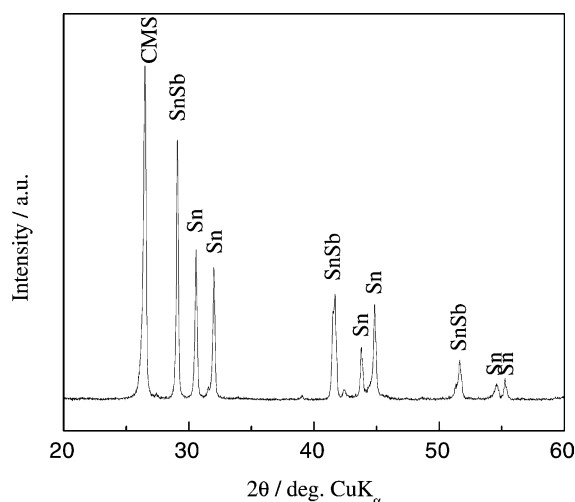


Fig. 1. XRD pattern of SnSb<sub>x</sub>/CMS composite powder.

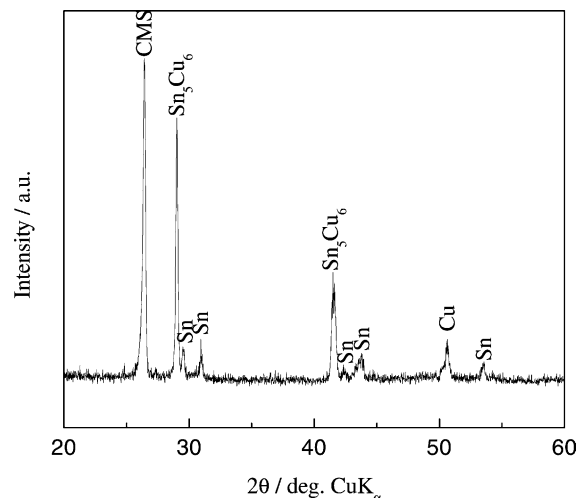


Fig. 2. XRD pattern of SnCu<sub>x</sub>/CMS composite powder.

quite similar morphology. By the decomposition of multi-carbon organic metallic salt, part of carbon may be also deposited on the surface of CMS with metallic particles together and encircle them. This may enhance the connecting strength between metallic particles and carbon matrix. In addition, the distance between two metallic particles is far enough to prevent the particle contact after the volume expansion. Such a configuration seems able to reduce the mechanical stress caused by the volume effect and improve the morphological and conducting stability of the composite.

The composite electrodes have an obvious charge and discharge character of pure CMS and pure alloy. Fig. 4 shows the first charge and discharge profile of obtained composite and pure CMS. The capacity above 0.25 V is mainly attributed to alloying and de-alloying. This part provides a lithium insertion capacity increment for composite electrodes, in comparison with pure CMS. With increasing alloy content, the reversible capacity rises, however, the cycling performance becomes deteriorate. Considering both

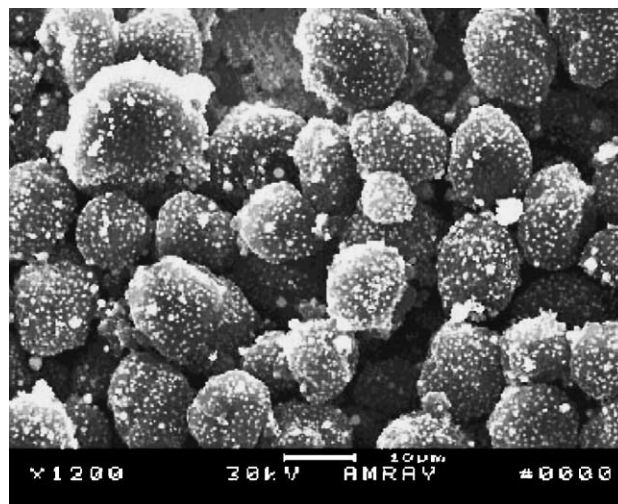


Fig. 3. SEM image of SnSb<sub>x</sub>/CMS composite powder.

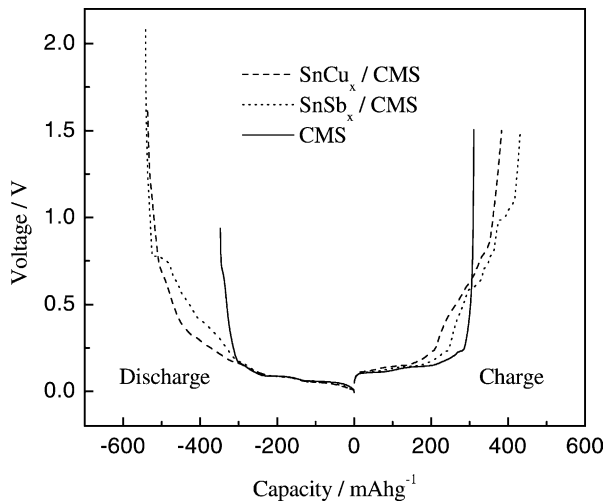


Fig. 4. The first cycle profiles for SnSb<sub>x</sub>/CMS, SnCu<sub>x</sub>/CMS composite and CMS electrodes.

capacity and cycleability, the 35 wt.% SnSb<sub>x</sub> and 42 wt.% SnCu<sub>x</sub> in composites are suitable. As shown in Table 1, the composite electrodes deliver high reversible capacity, 430 mAh g<sup>-1</sup> for SnSb<sub>x</sub>/CMS and 390 mAh g<sup>-1</sup> for SnCu<sub>x</sub>/CMS, much higher than pure CMS, 310 mAh g<sup>-1</sup>. If the reversible capacity of CMS in the composite electrodes is regarded as the same as that of pure CMS electrode, the SnSb<sub>x</sub> and SnCu<sub>x</sub> in the electrodes can provide a reversible capacity of about 650 and 500 mAh g<sup>-1</sup>.

The composite electrodes present good cycling stability. The capacity retention at the 30th cycle is 90% for SnSb<sub>x</sub>/CMS and 95.2% for SnCu<sub>x</sub>/CMS, as shown in Fig. 5. With its small volume expansion for lithium accommodation and elastic structure, CMS can endure the volume effect of metallic host and reduce the mechanical stress within the electrode. Lithium insertion and extraction at different voltage stage corresponds to different active part in composites. All of these alleviate the whole volume effect and prevent the electrode disintegration, leading to a better cycling performance.

The first coulombic efficiency drops when active alloy is added in composites (see Fig. 6). Although the charge and discharge efficiency of composite electrodes rises rapidly and closes to that of CMS electrode after the initial cycle, the

Table 1  
The electrochemical performance of different electrodes

	CMS	SnSb <sub>x</sub> / CMS	SnCu <sub>x</sub> / CMS	SnSb <sub>x</sub> / graphite
The first Li-insertion capacity (mAh g <sup>-1</sup> )	347	542	536	520
The first Li-extraction capacity (mAh g <sup>-1</sup> )	310	431	390	296
Coulombic efficiency at the first cycle (%)	89.3	79.5	72.8	56.9
The 30th Li-extraction capacity (mAh g <sup>-1</sup> )	310	390	375	165

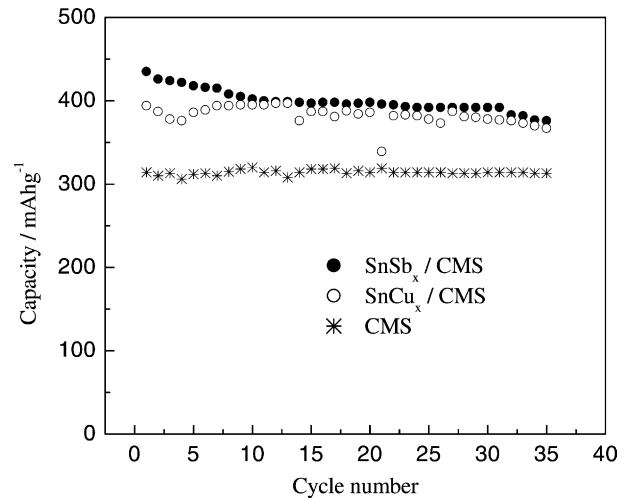


Fig. 5. Cycling performance of SnSb<sub>x</sub>/CMS, SnCu<sub>x</sub>/CMS composites and CMS electrodes.

efficiency of composite electrodes is always below that of CMS. This result may be related to incomplete SEI film formation on the composite electrodes or gradual pulverization and detachment of alloys from CMS. For this reason, it is difficult for this type of composite materials to achieve a long-term cycling stability.

For a comparison, SnSb<sub>x</sub> alloy was also deposited on small graphite particles (1–2 μm). A small alloy particles distribution like SnSb<sub>x</sub>/CMS composite is not obtainable, in spite of similar alloy content in the composites. There are many large particles (>0.8 μm) in the SnSb<sub>x</sub>/graphite composite. As shown in Fig. 7, such a composite materials exhibits poor cycling performance. It appears that there are two reasons for the very low efficiency at the first cycle. Firstly, small particle graphite powder has a large surface area and more charge is consumed for surface filming. Secondly, coarse alloy particles cause dramatic local volume change and great degradation of the electronic contact.

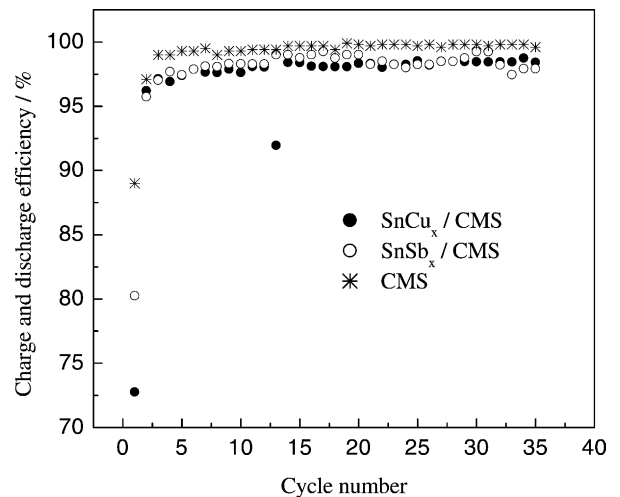


Fig. 6. Coulombic efficiency of SnSb<sub>x</sub>/CMS, SnCu<sub>x</sub>/CMS and CMS electrodes during cycling.

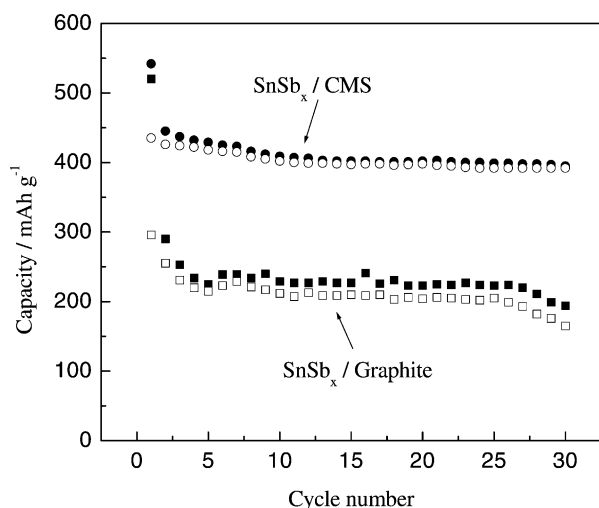


Fig. 7. Cycling performance of SnSb<sub>x</sub>/CMS, SnSb<sub>x</sub>/graphite composites electrodes (solid symbols: Li-insertion; hollow symbols: Li-extraction).

#### 4. Conclusions

Sub-micron particles of alloy were deposited on the surface of CMS by high temperature reduction. As anode materials, the alloy/CMS composites deliver high reversible capacities (430 mAh g<sup>-1</sup> for SnSb<sub>x</sub>/CMS and 390 mAh g<sup>-1</sup> for SnCu<sub>x</sub>/CMS); the capacity retention is 90% for SnSb<sub>x</sub>/

CMS and 95.2% for SnCu<sub>x</sub>/CMS after the 30th cycles. The composite morphology and cycling performance are strongly dependent on the particle size of carbon matrix for alloy deposition. Fine carbon powder (particle size: <5 μm) is not a suitable precursor for the composite preparation by this way.

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