



Short communication

Preparation and electrochemical characterization of tin/graphite/silver composite as anode materials for lithium-ion batteries

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ABSTRACT

The tin/graphite/silver (Sn/G/Ag) composite was prepared by high-energy mechanical milling (HEMM) for the first time. The composite powders consisted of electrochemically active Sn, Ag₄Sn phases which were uniformly distributed on the surface of the graphite particles. The formation of Ag₄Sn alloy phase and the uniform distribution of the active particles could accommodate the large volume changes during cycling. X-ray diffraction (XRD), high-resolution transmission electron microscope (HRTEM) and scanning electron microscopy (SEM) were used to determine the phases obtained and to observe the microstructure and dispersion of particles. In addition, cyclic voltammetry (CV) and galvanostatic discharge/charge tests were carried out to characterize the electrochemical properties of the composite. The composite electrodes exhibited an initial capacity of 1154 mAh g⁻¹ and maintained a reversible capacity of above 380 mAh g⁻¹ for more than 100 cycles.

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1. Introduction

In recent years, research on lithium-ion batteries with high energy density and long cycle life is indispensable with the development of portable devices and electric vehicles. However, it is difficult to enhance the electrochemical performance of commercial lithium rechargeable batteries only by improving their assembly technology due to the low theoretical capacity of the traditional anode materials. In order to improve the capacity of lithium-ion batteries, various new anode materials have been proposed, such as Si, Sn, Al and Sb-based materials which can electrochemically alloy with lithium at room temperature and show reversible lithium-storage capacities. Metallic Sn is of special interest because of its potentially large theoretical specific capacity (992 mAh g⁻¹) which is much higher than that of the already commercialized graphite (372 mAh g⁻¹) [1–3]. One of the critical problems encountered with this anode is the severe volume change during the alloying and dealloying reaction with lithium ions. Due to the repeated volume change upon cycling, Sn particles are pulverized and lose their Li⁺ storage ability [4]. To overcome this problem, a great amount of work has been done. For example, Wolfenstine et al. [5] synthesized the Cu₆Sn₅ by chemical deposition which improved the capacity maintaining ability. Ahn et al.

[6] dispersed the tin, tin oxide and NiSn-based nanocomposites into Al₂O₃ powders by ball milling, but the initial cycling efficiency was only 20% for the Sn–Al₂O₃ electrode. It was also reported that the Ag–Sn alloys electrodes consisting of β-Sn and Ag₃Sn phases exhibit an initial capacity of 800 mAh g⁻¹ and maintain a reversible capacity of above 350 mAh g⁻¹ for more than 50 cycles [7]. Further study was pursued through partial substitution of Fe or Sb for Ag to form Ag–Sn–Fe or Ag–Sn–Sb ternary composites [8,9]. The results showed that the ternary Ag–M–Sn composites got better cycling performance than the Ag–Sn alloys.

Recently, a new nanostructured Sn–Co–C ternary composite used as an anode material has been given much report [10–13]. Although Sn₃₀Co₃₀C₄₀ composite prepared by co-sputtering demonstrated a reversible specific capacity of 700 mAh g⁻¹ [10], it was not suitable for commercial use due to the high cost of the electrical power needed to sputter bulk quantities of material. In literature [13], the authors synthesized the Sn₃₀Co₃₀C₄₀ composite using mechanochemical techniques. But the reversible specific capacity was not as high as the same composite prepared by co-sputtering.

In spite of a lot of laborious work, however, the performances of the Sn-based alloy anodes have not been sufficient for practical use in Li-ion batteries. The improvement of cyclability is usually realized at the expense of capacity or increase the manufacture cost.

In this work, we prepared a new ternary tin/graphite/silver composite by high-energy mechanical milling (HEMM). The

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composite powders consisted of electrochemically active Sn and Ag_4Sn phases which were distributed uniformly on the surface of the graphite. Although all the ingredients of the composite were active toward Li, the main effect of Ag and C was to buffer the large volume change of Sn during cycling. The composite electrodes revealed a rechargeable capacity of above 380 mAh g^{-1} for more than 100 cycles. Compared with the literature about the Sn–Ag alloy composite [7], we introduced much less amount of element Ag particles (6.59 wt.%) using AgNO_3 as the precursor which could reduce the cost to some extent and get better cycling performances.

2. Experimental

Tin powder (200 meshes), graphite powder (C.P.) and silver nitrate (A.R) which were used as the starting materials with a weight ratio of 6:3:1 were transferred to a steel vial inside an argon-filled glove box (VAC) for mechanical milling. The ball-milling was carried out in a planetary ball mill (Shenyang New Technology Scientific Instruments Co., Ltd.) at a rotation rate of 475 rpm. The mass ratio of milling balls to the reactants was 10:1. After milling for 25 h, the final product was obtained without any grinding and sieving.

The sample was characterized by X-ray diffraction (XRD, Rigaku RINT-2000) with $\text{Cu K}\alpha$ radiation to identify the phases formed. Field emission scanning electron microscope (FESEM JSM-6700) and transmission electron microscope (TEM, JEM-2010) were applied to observe the morphology and particle size of the synthesized composite materials.

Electrodes containing 60 wt.% active materials, 20 wt.% polyvinylidene fluoride (PVDF) binder and 20 wt.% carbon black were made by coating the slurry of the electrode ingredients in *N*-methyl pyrrolidinone (NMP) onto copper foil and dried at 100°C under vacuum for 10 h. The thickness of the electrodes was about $28 \mu\text{m}$. The working electrodes were assembled in 2025 coin cells using Celgard 2400 as the separator and lithium foils as the counter and reference electrodes. A solution of 1 M LiPF_6 in EC:DMC (1:1 weight) was employed as the electrolyte. The assembly of cells was processed in an argon-filled glove box with oxygen and water contents less than 1 ppm. The galvanostatic charge/discharge tests were conducted on a LAND CT2001A battery test system in a voltage range of 0.02–1.5 V (vs. Li/Li^+) at a current density of 0.1 mA cm^{-2} . The cyclic voltammetry experiments were

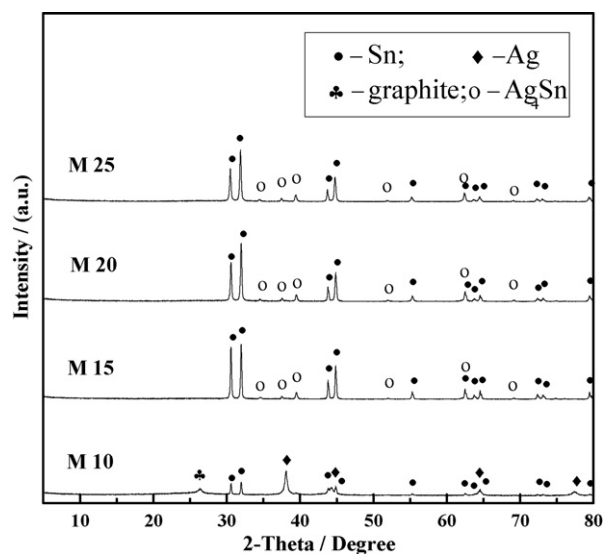


Fig. 1. X-ray diffraction patterns of Sn/G/Ag composite milled for different periods.

performed on a CHI440 Electrochemical Workstation at a scan rate of 0.05 mV s^{-1} .

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the X-ray diffraction patterns of the composite milled for different periods. As seen after 10 h of milling, the narrow peaks of elemental Ag were observed obviously, implying the successful decomposition of AgNO_3 assumed as the reaction $2\text{AgNO}_3 = 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$ during the HEMM process. One peak of graphite at about 26.4° was also found. When further milled for 5 h, the composite displayed the peaks of Ag_4Sn but the peaks of Ag vanished, which was different from the literature [7]. But the intensity of the peaks were very weak which were due to the low content of Ag (6.59 wt.%). The peak of graphite also disappeared, indicating its complete change into amorphous structure. When the milling time increased to 25 h, no any further change of the XRD pattern was observed.

3.2. Morphological feature

The morphology of the synthesized powders was observed by SEM. Fig. 2 shows the secondary electron image of the composite. It was seen that the as-prepared composite consisted of clusters

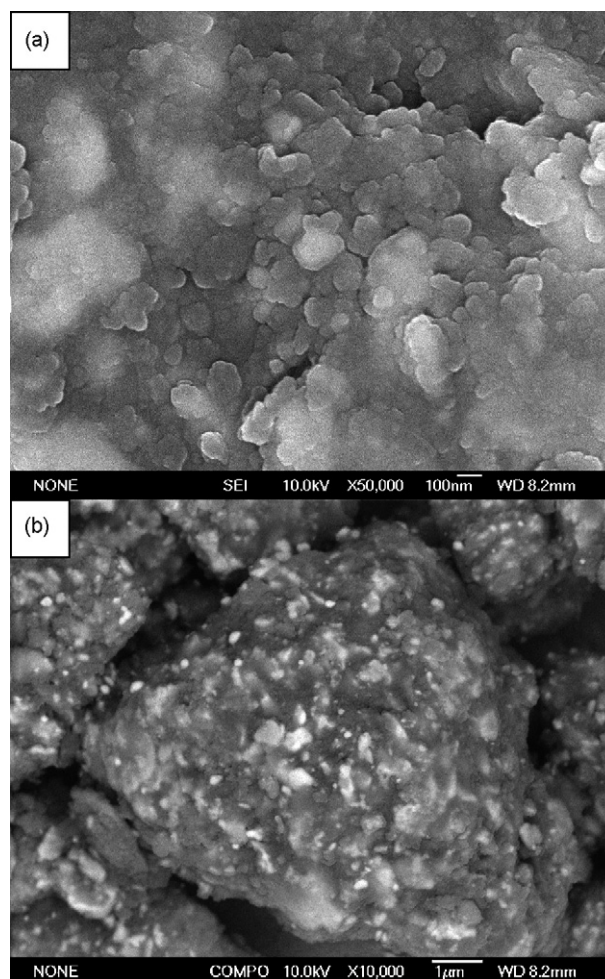


Fig. 2. SEM morphology of the as-prepared composite: (a) the secondary electron image, (b) the BSED image.

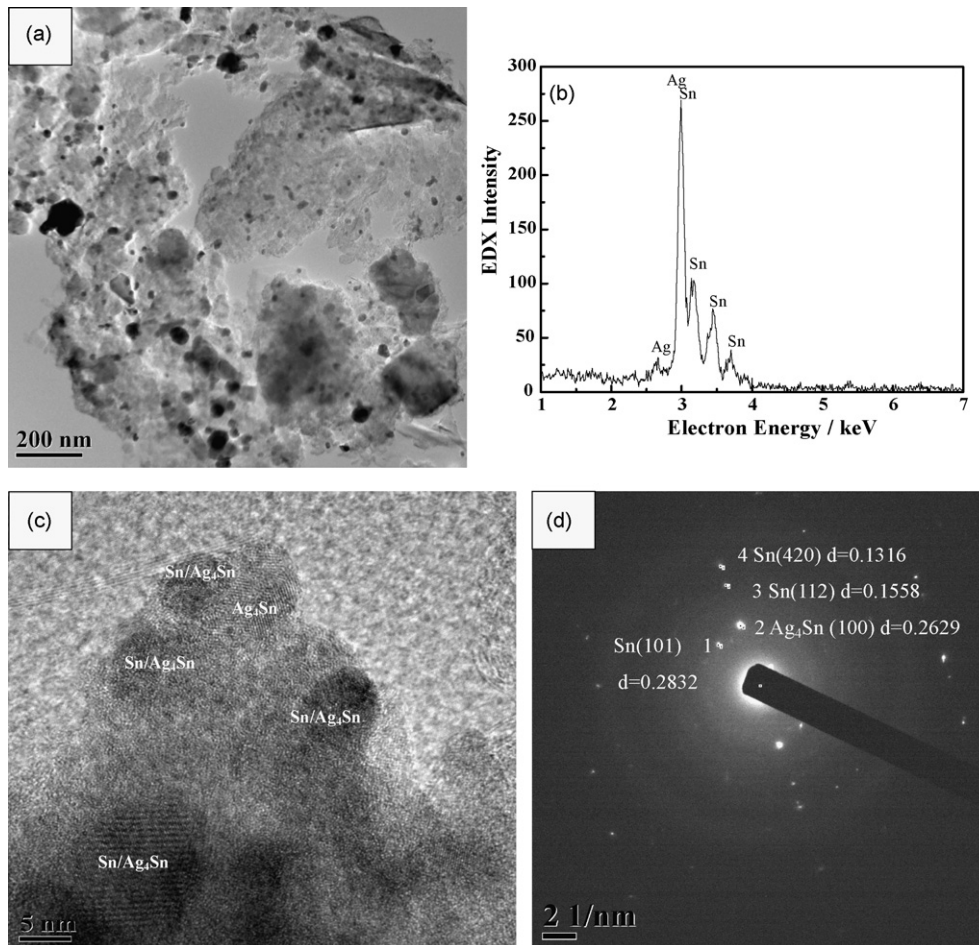


Fig. 3. (a) The TEM image of the composite powder, (b) the XEDS pattern of the black particle in Fig. 3a, (c) the HRTEM image of the composite powder and (d) the SAED image of the composite powder.

with size of several micrometers which were agglomerated by the primary particles with size of dozens of nanometers. The main feature of element Sn was soft and ductile and it could be easily agglomerated with other phases during the HEMM process.

Fig. 2b shows the backscattering electron diffraction (BSED) image of the Sn/G/Ag composite. The bright clusters containing Sn and Ag_4Sn phases could be observed which were distributed uniformly on the surface of the graphite. This was proved further in the TEM image.

In order to observe the primary particles of the composite and to further confirm its phases, the transmission electron microscope (TEM) with X-ray energy-dispersive spectrometry (XEDS) and high-resolution transmission electron microscope (HRTEM) with selected area electron diffraction (SAED) were used and the results were shown in Fig. 3. Fig. 3b shows the XEDS image of the black point in Fig. 3a. It was clear that the black particles consisted of Sn and Ag. According to the interplanar distance (d -spacing) as shown in Fig. 3d we could confirm the existence of Sn and Ag_4Sn . It was clear that the nanosized Sn and Ag_4Sn particles were dispersed in the amorphous graphite matrix (Fig. 3c).

3.3. Cyclic voltammograms

Fig. 4 shows the cyclic voltammograms of the as-prepared composite electrodes from the 1st to 5th cycles in the potential window

from 0 to 1.5 V (vs. Li^+/Li) at the scan rate of 0.05 mV s^{-1} . During the first cycle, it experienced two broad reduction peaks in the range of 0.8–1.4 V and 0.05–0.4 V. The former peak was attributed to the formation of a solid electrolyte interface (SEI) film on the

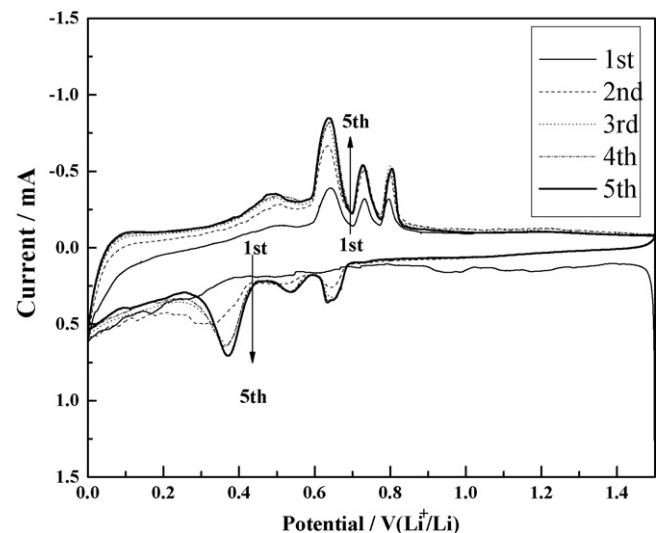


Fig. 4. Cyclic voltammogram of the as-prepared composite electrode in the potential window from 0 to 1.5 V (vs. Li^+/Li) at the scan rate of 0.05 V s^{-1} .

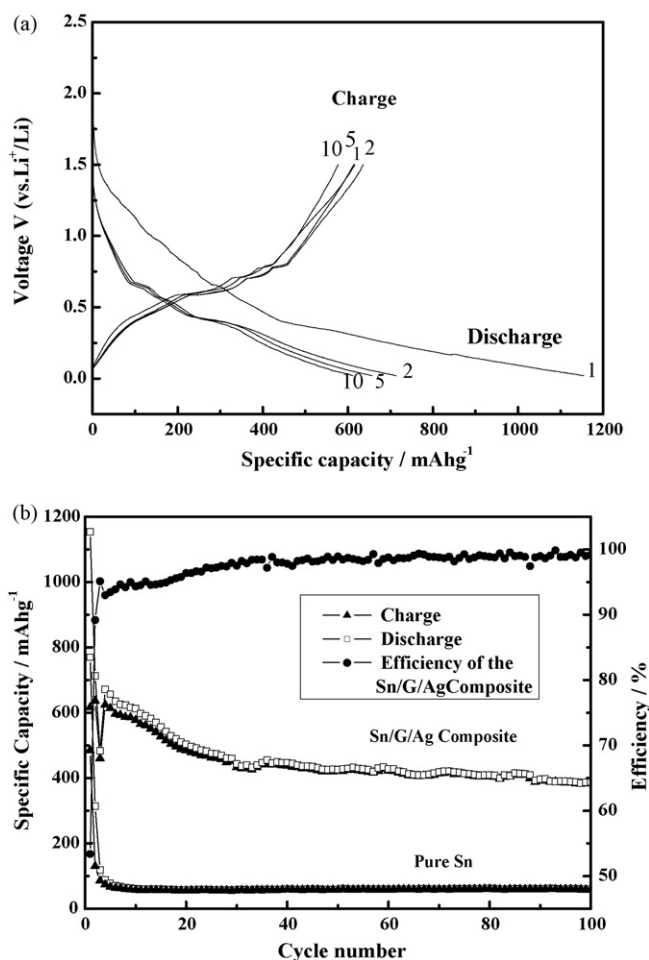


Fig. 5. (a) The discharge and charge curves for the as-prepared composite electrodes at 0.1 mA cm^{-2} and (b) the cycling performance of the as-prepared composite electrodes and the pure tin electrodes.

surface of active particles; the latter would be corresponding to the formation of Li_xSn and Li_xC [3,14,15]. During the first extraction process there were two very weak peaks in the range of 0.05–0.2 V and 0.4–0.55 V, and then three sharp peaks at about 0.63, 0.72 and 0.8 V were observed. In the subsequent cycles, the oxidation peaks were almost the same as the first scan, while the reduction peaks were very different. Three new peaks were observed at 0.37 (during the second cycle at about 0.32 V), 0.54 and 0.65 V, respectively, while the broad peak between 0.8 and 1.4 V vanished. The redox peaks confirmed the reaction between Li and crystalline Sn, as well as Li and amorphous graphite [14] during electrochemical cycling.

In addition, the current of the redox reactions increased with cycling, implying a possible activation process during the insertion/extraction process.

3.4. Cycling performance

Fig. 5a shows the 1st, 2nd, 5th and 10th discharge and charge curves of the as-prepared composite electrodes in the voltage range of 0.02–1.5 V (vs. Li^+/Li) at the current density of 0.1 mA cm^{-2} . The first cycle began with discharging process, corresponding to the lithium insertion of the electrodes. From the figure, we could see the charge and discharge platforms clearly, which were coinci-

dent with the cyclic voltammograms (as shown in Fig. 4). Fig. 5b shows the cycling performance of the as-prepared composite electrodes and the pure tin electrodes. It was obvious that the cycling performance of the as-prepared composite electrodes was much better than that of the pure tin electrodes. For the tin electrodes, the capacity loss was very fast in the first few cycles and the reversible capacity was less than 100 mAh g^{-1} . For the composite electrodes, after the first cycle, the capacity fade became less and the coulombic efficiency was over 95%. The composite electrodes revealed a rechargeable capacity of above 380 mAh g^{-1} for more than 100 cycles, which might be ascribed to the formation of Ag_4Sn alloy particles and the uniform distribution of the active particles on the surface of the graphite matrix [7,15]. Comparing with the literature [7], we introduced much lower content of element Ag particles (6.59 wt.%) using AgNO_3 as the precursor which could reduce the cost to some extent and got better cycling performances.

However, the first efficiency of the composite electrodes during the first cycle was still low, which was due to the formation of the solid electrolyte interface (SEI) films and the particle pulverization. In addition, according to the literature [7], a considerable amount of Ag–Li–Sn ternary lithiated phases remained in the structure upon Li extraction, which should also be responsible for the low first efficiency. In the early cycles, the gradual formation of the Ag–Li–Sn ternary lithiated phases and the shrinkage of Sn and Ag_4Sn phases might be an important reason for capacity fading. In addition, the particle size might also be a factor [13]. The Sn was soft and ductile and it could be easily agglomerated, so it was difficult to reduce its particle size only by increasing the milling time. The optimization of the composite ingredients and the influence of the particle size should be further investigated.

4. Conclusions

The tin/graphite/silver composite (containing 6.59 wt.% of Ag) was prepared by high-energy mechanical milling for the first time. The composite powders consisted of electrochemically active Sn and Ag_4Sn phases which were distributed uniformly on the surface of the graphite matrix. The composite electrodes revealed a rechargeable capacity of above 380 mAh g^{-1} for more than 100 cycles. The agglomeration of the composite during the HEMM process and the low first efficiency remains to be improved.

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