



# A novel nano-structured interpenetrating phase composite of silicon/graphite–tin for lithium-ion rechargeable batteries anode materials



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## ABSTRACT

A novel nano-structured interpenetrating phase composite (NSIPC) of silicon/graphite–tin (SGM) anode material for lithium-ion rechargeable batteries is synthesized by high energy mechanical milling (HEMM). The structural and morphological characterizations have been carried out through X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical performances have been analyzed with reference to  $\text{Li}^+/\text{Li}$  and the results are compared with silicon/graphite composites. The SGM NSIPC electrode exhibits the better cyclability than the SG composite electrodes. The initial discharge specific capacity of the as-prepared SGM NSIPC is relatively high around  $1790 \text{ mA h g}^{-1}$  with  $1592 \text{ mA h g}^{-1}$  reversible capacity retention in the following cycle at a current density of  $237 \text{ mA g}^{-1}$  in the voltage from 0.03 V to 1.5 V. In addition, the SGM NSIPC electrode shows the good rate capability and possesses the stable cycling performance even charging and discharging at the large current density. Consequently, SGM NSIPC can be the promising anode material for the next generation lithium ion rechargeable batteries.

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## 1. Introduction

Li-ion batteries (LIBs) are now considered to be applied as energy storage system for the electric vehicle (EV) and plug-in hybrid electric vehicle (HEV) due to their unique features, such as long cycle life, high operation voltage, low self-discharge, and environmental friendliness [1–5]. However, the present commercial LIBs using the carbonaceous materials, e.g. carbon and natural graphite as the anode materials that have low specific capacity, cannot meet the high energy density requirements [6,7]. In order to fulfill the automobile and military industrial demands, silicon is investigated as the candidate for anode material and has attracted the most interest due to its high theoretical specific capacity ( $4200 \text{ mA h g}^{-1}$  for  $\text{Li}_2\text{Si}_5$ ) [8–10].

Unfortunately, the practical application of the pure silicon has been hindered because of the drastic volume ( $\sim 300\%$  volume changes) and structure changes during the  $\text{Li}^+$  insertion and extraction, which causes mechanical fracture and pulverization and results in rapid decrease in the capacity [11,12].

Recently, there has been intense interests focus on the silicon/graphite (SG) composites [13–19]. The carbonaceous material matrix is expected to function as the structure buffer layer and accommodates the volume change during the charging and discharging process of the anode materials.

In normal SG composites, the graphite has low deformation capacity ( $\sim 10\%$ ), so large amount of graphite is added as buffer in order to accommodate the large scale volume change of the anode material during the process of charge and discharge. However, it heavily discounts the specific capacity of the electrode. Additionally, normal SG composites fail to form stable electric contact between active silicon and copper current collector which leads to polarization and capacity fading.

To promote the utilization of the silicon and improve the electrochemical performance of the anodes, some metal has been added into silicon/graphite composite. However, the specific capacity remained to be too low [6,13,20]. Tin shall be incorporated into the SG nano-composite due to the following advantages. The theoretical specific capacity of tin is considerably high, indicating that the addition of tin does not heavily reduce the theoretical specific capacity of anodes. The fairly good ductility of metallic tin relaxes the stress mutation caused by the volume and structural changes and improves the fatigue property of the electrode during the repeating charge–discharge process, which is helpful to the

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improvement of the cycle life of the anode. With compared to the graphite (parallel to the planes  $3 \times 10^6$  S/m), tin has the higher electrical conductivity ( $9 \times 10^6$  S/m), which improves the electrical conductivity of the composite anode, and mitigate the polarization of the electrode, leading to increasing the cyclability of the anodes. Furthermore, the discharge potential (versus Li/Li<sup>+</sup>) of the tin is different from the silicon during the discharge process, while charging at the potential of silicon, tin can act as buffer. On the contrary, silicon acts as buffer while charging at the potential of tin. In this way, it will enhance the electrochemical performance of the composite electrodes. However, whether the aforementioned advantages are achieved or not lies on the microstructure of the composite, i.e., the correlation between silicon and tin in the composite.

In this work, a novel nano-structured interpenetrating phase composite (NSIPC) of SGM was synthesized using HEMM method. In the composite, silicon and tin continuously extend in microstructure of material to form a completely homogeneously distribution. This novel structure ensures the well electric contact and mechanical integrity, leading to the better electrochemical performance than the present silicon/graphite anode composite [14,21,22].

## 2. Experimental

The commercial silicon powder ( $\geq 99.99\%$ ,  $\sim 300$  mesh) and tin powder ( $\geq 99.5\%$ ,  $\sim 300$  mesh) and graphite ( $\geq 99.85\%$ ,  $\sim 30$   $\mu\text{m}$ ) were used as starting materials. The powders were mixed according to the predetermined nominal composition (listed in Table 1) and sealed into a 250 mL tempered steel bowl with 10 mm, 8 mm, 5 mm diameter bearing steel balls. The ball to powder mass ratio was 16:1. Mechanical milling was carried out in a Fritsch P5 planetary mill under argon atmosphere for 20 h with 30 min break every hour to remove the possible thermal effect. Milling time should not be longer than 20 h, because milling exceeds 20 h will cause contamination. The rotation speed of the milling is 250 rpm.

X-ray diffraction (XRD) patterns of the as-synthesized composites were obtained using a Rigaku D/max-2500pc diffractometer (reflection 2 theta geometry, Cu K $\alpha$  radiation). The morphologies and microstructures of the composites were observed by Supra 35 field emission scanning electron microscope (FESEM) and High-resolution transmission electron microscope (HR-TEM, FEI Tecnai F20 Super Twin FEG TEM).

Electrochemical performances were evaluated using a CR2025-type coin half cell. The composite materials working electrodes were prepared by coating the slurries onto the copper foil ( $\sim 25$   $\mu\text{m}$ ). The slurry was fabricated by mixing 60% composite materials, 20% carbon black (Super P) and 20% polyvinylidene fluoride (PVDF). After coating, the film was dried at 120 °C for 24 h under vacuum, then cut into sheets with 12 mm in diameter and compressed under a pressure of  $2 \times 10^5$  Pa between two stainless steel plates. Lithium metal was used as the Li<sup>+</sup> source, counter and reference electrode. 1 M LiPF<sub>6</sub> (dissolved in ethylene carbonate and dimethyl carbonate with a 1:1 volume ratio) was applied as the electrolyte. A sheet with 16 mm in diameter Celgard 2400 membrane was utilized as the separator. The coin cell was assembled in an argon-filled glove box with the content of oxygen and moisture below 1 ppm. All the charging and discharging test were performed under different current density using a LAND-CT2001A battery test system (Jinnuo Wuhan Corp., China).

Cyclic voltammetric measurements were performed in the voltage range from 2.5 to 0 V (versus Li/Li<sup>+</sup>) at a sweep rate of 0.001 V s<sup>-1</sup> by an electrochemical station (CHI 770 CH Instruments, Shanghai).

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the SGM and SG composites synthesized by HEMM method. JCPDS #04-0673 for tin, JCPDS

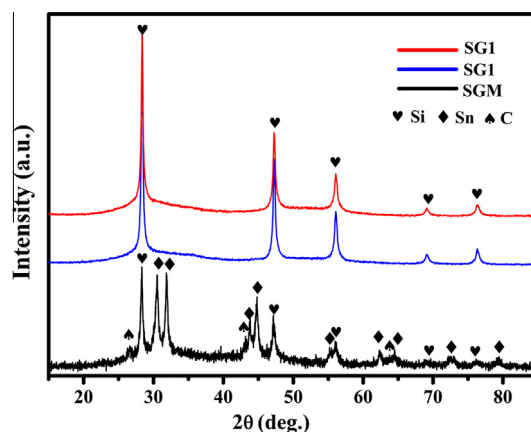


Fig. 1. XRD patterns of the SGM composite and SG composites with different silicon/graphite ratios.

#80-0018 for silicon and JCPDS #261079 for graphite are used to confirm that the XRD pattern of the SGM composite material is composed of the diffraction peaks of the element state silicon, tin and graphite. Additionally, the XRD pattern of the SGM shows very low intensities of broad reflections, which are associated with the amorphization of Si. This is caused by the high energy impact during the HEMM, which leads to deformation of the silicon particles and increases the crystal defects. These crystal defects help enhance the diffusion of the elements and form amorphous structure.

However, the diffraction patterns of the SG composites with different weight ratios are indexed as just single silicon substance. High energy mechanical milling is an outstanding approach to obtain well-distribution silicon, tin and graphite. No silicon carbide and steel peaks can be seen on all the three patterns, indicating that HEMM do not induce silicon carbide compounds and metallic contamination. It is good for the achievement of the high specific capacity properties of the studied system without inactive carbide phase and metallic contamination.

SEM micrographs of the as-synthesized composites are shown in Fig. 2. It can be seen from Fig. 2(a) and (b) that the SG composite consisted of large agglomerates in a shape of grape, which is typically found in the products prepared by HEMM. Actually, these agglomerates are composed of nano-particles. Because of the high energy impact results in cold welding and fracturing, the particles aggregate together. Similar morphology for SGM samples are observed via SEM shown in Fig. 2(c), the large chunks of 10  $\mu\text{m}$  and more are carbon particles coated with silicon particles and tin particles. In order to get a further understanding about the distribution of the elements after adding tin, mapping analysis was done. It can be seen from Fig. 2(d) that, silicon and tin form a continuous net work. In fact, both of constituent silicon and tin in their standalone state have an open-cellular microstructure. Because of the fairly good plasticity, the additive tin shows large deformation when under high energy ball milling. The silicon nano-particles are entangled by the ductile tin and cold-welded together. After milling of 20 h, lots of silicon nano-particles and tin interpenetrate into each other and form clusters. Each of these clusters is confirmed to NSIPC. TEM and HR-TEM micrograph are shown in Fig. 3 to fully recognize the morphological features and microstructure of the SGM composite. Aggregates are shown in Fig. 3(a), which have no difference with the results observed by SEM. From the HR-TEM micrograph Fig. 3(b), two kinds of lattice fringes with distance of 0.311 nm and 0.279 nm can be visualized, which correspond to the (111) plane of cubic silicon (JCPDS#80-0018) and the (101) plane of tetragonal tin (JCPDS#04-0673), respectively. It indicates that Sn has no influence in the lattice

Table 1  
Composition of the as-prepared composites.

| Composites | Nominal composition (At%) |          |     |
|------------|---------------------------|----------|-----|
|            | Silicon                   | Graphite | Tin |
| SGM        | 70                        | 20       | 10  |
| SG1        | 80                        | 20       |     |
| SG2        | 70                        | 30       |     |

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