Supporting Information

Chemical synthesis of porous hierarchical Ge-Sn binary composite by metathesis reaction for rechargeable Li-ion batteries

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Experimental section

Synthesis of Ge-Sn

In a typical procedure, the Mg$_2$Ge was first prepared by annealing commercial Ge and metallic Mg powder with a mole ratio of 1/2 at 700 °C for 20 hours under Ar atmosphere. Then, the metathesis reaction between the pre-synthesized Mg$_2$Ge and SnCl$_4$ with a mole ratio of 1/1 was carried out in a stainless steel autoclave at 250 °C for 6 h. After cooling to room temperature naturally, the solid product was collected and washed with a small quantity of diluted hydrochloric acid, distilled water and ethanol several times, and then dried in vacuum oven at 50 °C for further characterization. The synthesis of Si-Sn and Si-C are similar to the above procedure, which is realized by reacting Mg$_2$Si with SnCl$_4$ and CCl$_4$, respectively, at 230 °C.

Synthesis of Si-Sn and Si-C

In a typical procedure, the Mg$_2$Si was first prepared by annealing commercial Si and metallic Mg powder with a mole ratio of 1/2 at 700 °C for 20 hours under Ar atmosphere, as previous
report described. Then, the metathesis reaction between the pre-synthesized Mg$_2$Si and SnCl$_4$ or CCl$_4$ with a mole ratio of 1/1 was carried out in a stainless steel autoclave at 230 °C for 6 h, producing Si-Sn and Si-C, respectively. After cooling to room temperature naturally, the solid product was collected and washed with a small quantity of diluted hydrochloric acid, distilled water and ethanol several times, and then dried in vacuum oven at 50 °C for further characterization.

**Characterization**

The structure and morphology of the product were characterized by X-ray diffractometer (Philips X’ Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å)), Raman spectrometer (Lab-RAM HR UV/VIS/NIR), X-ray photoelectron spectroscopy (XPS) (ESCA-Lab MKII X-ray photoelectron spectrometer), scanning electron microscopy (SEM, JEOL-JSM-6700F), and transmission electron microscopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). The measurement of tap density and the electrochemical performance in half/full coin-type cells are exhibited in supporting information.

**Measurement of tap density**

The tap density of the Ge-Sn sample was measured with a Powder Autotap Density Meter (JT-1, Chengdu Jingxin Powder Analyse Instrument Co., LTD). First, a stainless steel cylinder is filled with the as prepared Ge-Sn sample of known weight (marked as m) and mounted onto the Autotap instrument. The Autotap is then programmed to automate 1000 taps with the rate of one tap per second. Then, the volume of the powder (marked as V) is recorded and the tap density (marked as TD) is calculated based on the formula of TD=m/V and expressed in g cm$^{-3}$. The tap density of the Ge-Sn sample are averaged based on three repeated experiments.

**Electrochemical Measurement**
The electrochemical properties of the prepared Ge-Sn composite were evaluated through coin-type cells (2016 R-type) which were assembled under an argon-filled glove box (H₂O, O₂ < 1 ppm). Metallic Li sheet was used as counter and reference electrode. 1 M LiPF₆ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by volume) was served as the electrolyte (Zhuhai Smoothway Electronic Materials Co., Ltd (china)). For preparing working electrode, the slurry mixed with as-prepared active material, carbon black (super P) and sodium alginate (SA) binder in a weight ratio of 6:2:2 in water solvent was pasted onto a Cu foil and then dried in a vacuum oven at 80 °C for 10 h. The active material density of each electrode was determined to be about 1.5 mg cm⁻². Galvanostatic measurements were conducted using a LAND-CT2001A instrument at room temperature with a fixed voltage range of 0.005–1.5 V (vs. Li/Li⁺). Cyclic voltammetry (CV) was performed on electrochemistry workstation (CHI660D), with a scanning rate of 0.2 mV s⁻¹ at room temperature.

For assembling the full cells, the commercial available LiCoO₂ (Ningbo Veken Battery Company) is employed as cathode. The LiCoO₂ cathode electrode was prepared by mixing the commercial LCO material, carbon black, and poly(vinyl difluoride) (PVDF) binder in a weight ratio of 8:1:1. N-Methyl-2-pyrrolidone (NMP) was used as the solvent to form slurry. The resulted slurry was coated onto the Al foil and dried at 120 °C for 12h for further use. A pre-lithiation treatment of Ge-Sn anodes was performed in half-cells which is discharged at cut-off voltage of 0.1 V vs. Li/Li⁺ at 0.2 A g⁻¹. For Ge-Sn/LiCoO₂ full cell assembly, the anode capacity is limited and the excess capacity of cathode is controlled at about 10%. The reversible capacity and energy density of the full cells were calculated based on the weight of Ge-Sn anode. Galvanostatic measurements of the full cells were conducted using a LAND-CT2001A instrument at room temperature with a voltage range of 2.5-4.2 V.

(1)
Figure S1 shows the XRD patterns of the pre-synthesized Mg$_2$Ge, all peaks could be indexed to be the cubic phase Mg$_2$Ge (JCPDS No. 86-1028).

![XRD pattern of Mg$_2$Ge](image1)

**Figure S1.** The XRD patterns of the pre-synthesized Mg$_2$Ge sample.

(2)

![Raman spectrum of Ge](image2)

**Figure S2.** The Raman spectrum of the commercial Ge powder.
Figure S3. (a) The typical nitrogen adsorption–desorption isotherms, and (b) the corresponding BJH pore size distribution curve. The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore distribution plots were measured on a Micromeritics ASAP 2020 accelerated surface area and porosimetry system.

Figure S4. The EDX mapping of the prepared Ge-Sn binary composite.
Figure S5. The XPS plots of (a) Ge and (b) Sn contents.

Figure S6 demonstrates that the Si-Sn and Si-C composite are produced through reacting Mg$_2$Si with SnCl$_4$ and CCl$_4$ at 230 °C, respectively. The Si-Sn sample consists of cubic Si and tetragonal phase β-Sn, as determined by XRD patterns (Figure S6a). The SEM image (Figure S6b) shows that the product consists of aggregated particles. As for Si-C composite, the XRD pattern (Figure S6a) and the Raman spectrum (Figure S6c) confirms that well-crystallized Si and amorphous carbon are formed in the reaction system. Similarly, the sample also exhibit aggregated micro-sized particles (Figure S6d). Besides group IV elements, this reaction may be applicable in preparing binary anode including other alloy type materials such as Sb, Te, and Bi.
Figure S6. (a) XRD patterns of the prepared Si-C and Si-Sn composite. SEM pictures of (b) Si-Sn and (d) Si-C composite. (c) Raman spectrum of the Si-C composite.

Table S1. Cycling performance Ge-Sn electrode compared with those in previously reported Ge-Sn composite.

<table>
<thead>
<tr>
<th>anode materials</th>
<th>cycling performance</th>
<th>synthetic routes</th>
<th>references</th>
</tr>
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<tbody>
<tr>
<td>Sn_{78}Ge_{22}@Carbon</td>
<td>1040 mA h/g after 45 cycles</td>
<td>Reduction of SnCl₄ and GeCl₂ with Sodium naphthalide and annealing treatment</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>at 0.3 A/g</td>
<td></td>
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<tr>
<td>Sn_{78}Ge_{22}@Carbon</td>
<td>1020 mA h/g after 40 cycles</td>
<td>Reduction SnCl₄ and GeCl₄ with sodium naphthalide and subsequent annealing</td>
<td>[14]</td>
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<tr>
<td></td>
<td>at 0.3 A/g</td>
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<td></td>
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<tr>
<td>Sn–Ge alloy</td>
<td>1000 mA h/g</td>
<td>Melton spinning of tin and germanium precursors</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>are maintained over 60 cycles at 143 mA/g</td>
<td></td>
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<tr>
<td>Ge_{0.95}Sn_{0.05} nanocrystals</td>
<td>1010 mA h/g after 50 cycles at 160 mA/g</td>
<td>Gas-phase laser photolysis reaction of tetramethyl germanium and tetramethyl tin</td>
<td>[3]</td>
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<tr>
<td>Sn-Ge Nanorods</td>
<td>1000 mAh/g after 100 cycles at 1 A/g</td>
<td>Solution-liquid-solid growth catalyzed by pre-synthesized Sn</td>
<td>[2]</td>
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</tbody>
</table>
Figure S7. The cycling performance at 500 mA g\(^{-1}\) of the full cell consists of a Ge-Sn anode and a LiCoO\(_2\) cathode.

The Figure S8 exhibits the SEM images of the electrodes. Before cycling, as shown in Figure S8a, b, the un-cycled electrodes exhibit a uniform mixture of the micro-sized active materials, binder, and carbon black, showing relatively flat surface. After 10 discharge/charge cycles, the surface of the electrode becomes smoother, which may result from the formation of solid state interface membrane. As we can see, some protuberance on the electrode surface is formed, which may be caused by the volume change of the alloy-type Ge and Sn components, as exhibited in Figure S8c, d. It should be also mentioned that the electrode are maintained integrity well. After 1000 discharge/charge cycles (Figure S8e, f), the electrode still keeps well,
and the generated protuberance becomes to be more obvious. After a long-term cycling, the origin structure may disappear, but still connect with binder and carbon black tightly.

![Figure S8.](image)

**Figure S8.** The SEM and enlarged SEM images of as-prepared Ge-Sn composite electrode, (a) and (b) before cycling; (c) and (d) after 10 cycles; (e) and (f) after 1000 cycles.

Figure S9a shows the XRD patterns of the Ge-Sn based electrodes before and after cycling. As one can see, the Ge-Sn active materials becomes from crystalline to amorphous after 150 cycles, which results from the repeated charge/discharge cycling. The EDX mapping pictures (Figure S9b) indicates that the Ge and Sn components are still distributed uniformly after cycling. It is important to take advantage of the synergistic effect between Ge and Sn.
Figure S9. (a) The XRD patterns of the Ge-Sn electrodes before cycled, and after 150 cycles. (b) The EDX mapping picture of Sn and Ge elements of the cycled Ge-Sn composite after 150 cycles.