Supporting Information

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

Ning Lin, Jie Zhou, Ying Han, Kailong Zhang, Yongchun Zhu,* and Yitai Qian*

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: ychzhu@ustc.edu.cn; ytqian@ustc.edu.cn

Experimental section

Synthesis of Ge-Sn

In a typical procedure, the Mg₂Ge 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 Mg₂Ge and SnCl₄ 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 Mg₂Si with SnCl₄ and CCl₄, respectively, at 230 °C.

Synthesis of Si-Sn and Si-C

In a typical procedure, the Mg_2Si 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 Mg₂Si and SnCl₄ or CCl₄ 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 K α radiation (λ =1.54178 Å)), Raman spectrometer (Lab-RAM HR UV/VIS/NIR), X-rayphotoelectron 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

2

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.

Figure S1 shows the XRD patterns of the pre-synthesized Mg_2Ge , all peaks could be indexed to be the cubic phase Mg_2Ge (JCPDS No. 86-1028).



Figure S1. The XRD patterns of the pre-synthesized Mg_2Ge sample.

(2)



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.

(4)



Figure S4. The EDX mapping of the prepared Ge-Sn binary composite.



Figure S5. The XPS plots of (a) Ge and (b) Sn contents.

(6)

(5)

Figure S6 demonstrates that the Si-Sn and Si-C composite are produced through reacting Mg_2Si 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.

(7)

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

anode materials	cycling performance	synthetic routes	references
Sn ₇₈ Ge ₂₂ @Carbon	1040 mA h/g after 45 cycles	Reduction of $SnCl_4$ and $GeCl_2$ with	[13]
	at 0.3 A/g	Sodium naphthalide and annealing	
		treatment	
Sn ₇₈ Ge ₂₂ @Carbon	1020 mA h/g after 40 cycles	Reduction $SnCl_4$ and $GeCl_4$ with	[14]
	at 0.3 A/g	sodium naphthalide and subsequent	
		annealing	
Sn–Ge alloy	1000 mA h/g	Melton spinning of tin	[17]
	are maintained over 60	and germanium precursors	
	cycles at 143 mA/g		
$Ge_{0.95}Sn_{0.05}$ nanocrystals	1010 mA h/g after50 cycles	Gas-phase laser photolysis reaction	[3]
	at 160 mA/g	of tetramethyl germanium and	
		tetramethyl tin	
Sn-Ge Nanorods	1000 mAh/g after 100	Solution-liquid-solid growth	[2]
	cycles at 1 A/g	catalyzed by pre-synthesized Sn	

nanoparticles (8) 1000 Specific capacity (mAh g^{-1} 800 600 500 mA g⁻¹ 400 200 Charge Discharge 0 20 40 0 60 80 100 120

Figure S7. The cycling performance at 500 mA g^{-1} of the full cell consists of a Ge-Sn anode and a LiCoO₂ cathode.

Cycle number

(9)

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. 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.