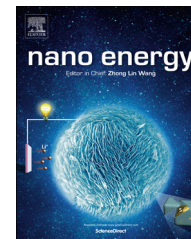


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RAPID COMMUNICATION

Nanoporous germanium as high-capacity lithium-ion battery anode



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Abstract

For the first time nanoporous germanium (np-Ge) was prepared by chemical dealloying allowing for mass production of electrodes for LIBs. Nanoporous structure can accommodate volume changes during the lithiation/de-lithiation progress and promote high-rate capability. The np-Ge shows a promising electrochemical performance as an advanced anode materials for LIBs with a specific capacity of 1191 mA h g^{-1} after 160 cycles at a rate of 160 mA g^{-1} and good rate capability.

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Introduction

Li-ion battery has become the dominated energy storage device of choice for electromobile and portable electronic devices such as smart phones and laptop computers due to its high energy density and environment protection [1]. Nowadays more and more attention has been paid on higher-capacity

alternatives for graphite anode (theoretical specific capacity 372 mA h g^{-1}) because of the fast growing demand for highly efficient Li-ion battery to power diverse electric devices. The alternative materials should have higher specific capacity, energy density, cycle life and lower cost, which also could be mass produced. From the viewpoint of capacity, group IVA elements are the most promising materials, especially silicon and germanium which show theoretical capacities of 4200 and 1600 mA h g^{-1} , respectively [2,3]. Germanium has also been in the spotlight because it exhibits a lower specific volume change during the Li insertion/extraction process and a faster room temperature Li diffusivity (400 times faster) than Si

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[4-9]. Additionally, anisotropic lithiation in crystalline Si leads to anisotropic swelling and surface fracture, in contrast to isotropic lithiation, isotropic swelling, and tough behavior in crystalline Ge [10,11]. The tough Ge nanoparticles offer substantial potential for the development of durable, high-capacity, and high-rate anodes for advanced lithium-ion batteries [12]. However, Ge also exhibits rapid capacity loss accompanied by a huge irreversible capacity similar to Si [7]. The main reason is that during the Li insertion and extraction process there is still a drastic volume change of the active material resulting in the pulverization of bulky particles, which electrically isolates the particles from the current collector, leading to poor cycleability [13-15]. To solve these problems, there has recently been significant attention devoted to creating germanium nanostructures that can accommodate the lithiation-induced strain and thus exhibit high coulombic efficiency and long cycle life [2,6-8,14,16-19]. Additionally, the nanoporous germanium (np-Ge) could also be produced using surfactant-driven self-organization of soluble Zintl clusters [20]. Germanium negative electrodes with porous structures have exhibited improved cyclic performance because the pores in such structures act as ideal volume expansion buffers. Despite its superior properties, the lack of inexpensive and simple methods to mass produce np-Ge limits its use.

Nanoporous metals can be fabricated by the process called dealloying, which refers to the selective dissolution of one or more components out of an alloy [21]. The dealloying process can also result in the formation of a bicontinuous structure of metal-and-void with an average metal ligament diameter (or pore diameter) as small as 3 nm [22]. We have successfully fabricated monolithic nanoporous Cu ribbons by chemical dealloying [23]. To date, there have been no reports on the synthesis of np-Ge by chemical dealloying. Herein, we report the synthesis and electrochemical properties of nanoporous germanium prepared by chemical dealloying of Al-Ge alloys with a composition of 28.4 at% Ge (eutectic point as shown in Figure S1) performed in a 5 wt% HCl aqueous solution at 60 °C. The np-Ge exhibits high retention capacity of 1191 mA h g⁻¹ after 160 cycles at a rate of 160 mA g⁻¹ and good rate capability for the electrodes.

Experimental section

Material preparation

Al_{71.6}Ge_{28.4} eutectic alloys were prepared from pure Al (99.99 wt%) and pure Ge (99.99 wt%). High-frequency induction heating was employed to melt the Al and Ge in a quartz crucible (at a temperature of 800 °C for 5 min), and then the melt was cast into ingots in an iron chill mold. By use of a single roller melt spinning apparatus (Model number: SP009A) (as shown in Figure S2), the Al-Ge ingots were remelted in a quartz tube by high-frequency induction heating and melt-spun onto a copper roller at a circumferential speed of about 27 m s⁻¹. The Al-Ge ribbons obtained were typically 20-50 μm in thickness, 2-4 mm in width, and several centimeters in length. The dealloying of the melt-spun Al-Ge ribbons was performed in a 5 wt% HCl aqueous solution with water bath at 60 °C for 10 h. The magnetic

stirring (Model number: JJ-I) was at the rate of 600 r/min. At the beginning of the reaction, abundant gas bubbles generated on the surface of ribbons. The dealloying reactions finished when no bubbles emerged in the solution. After dealloying, the precipitation was filtered with filter paper and rinsed with distilled water for several times, followed by vacuum drying for 24 h at 80 °C. The as-dealloyed samples were kept in a vacuum chamber to avoid oxidation.

Materials characterization

The structure was characterized using X-ray diffraction (XRD, Rigaku Dmax-rc diffractometer) and LabRAM HR800 spectrometer for Raman spectra. The microstructures of the as-prepared materials were characterized by scanning emission microscope (SEM, Zeiss SUPRA 55), transmission electron microscope (TEM, JEOL JEM-1011) and HRTEM (JEOL JEM-2100). Element was analyzed on X-ray photo-electron spectroscopy (XPS, ESCALAB 250).

Electrochemical characterization

Electrochemical performance was measured in 2016 coin-type cells. The slurry of active materials (np-Ge/Ge powder (larger than several micrometers, purchased from Aladdin Industrial Co., Ltd.) (80 wt%), carbon black (10 wt%), and polyvinylidene fluoride (PVDF) (10 wt%) were dissolved uniformly in N-methyl-2-pyrrolidone (NMP), which were then coated onto a Cu foil and dried in a vacuum oven at 120 °C for 24 h to form the electrodes. Li sheet was used as counter electrode, and Celgard 2400 as the separator, and a mixture of 1 M LiPF₆ in ethylene carbonate, dimethyl carbonate, diethyl carbonate (1:1:1 by volume) as electrolyte. Half-cells were assembled in a glovebox full of argon at room temperature. Galvanostatic discharge/charge cycles were performed between 0.05 and 0.9 V on a lithium battery cycler (LAND CT-2001A, Wuhan, China). The EIS performance was measured by half coin cell on a CHI 660E (Shanghai China) in the frequency range of 0.01-100 kHz.

Results and discussion

According to the binary phase diagrams (Figure S1), Al and Ge exist as simple substance in Al-Ge alloy at room temperature [24,25]. Additionally, Al is soluble in hydrochloric acid, whereas Ge cannot dissolve in it. Therefore, we used Al-Ge-hydrochloric acid system, with Ge acting as the porous-structure-forming element, Al acting as sacrificial element and hydrochloric acid acting as the dealloying melt medium. By immersing an Al-Ge alloy precursor in hydrochloric acid, Al should selectively dissolve from the Al-Ge alloy into the hydrochloric acid, as suggested by our previous work on other porous metals [23]. Figure 1a shows a schematic of the evolution of the np-Ge structure by dealloying. Initially, the Al-Ge alloy precursor has an atomically mixed structure (i). When the precursor is immersed in 5 wt% HCl aqueous solution at 60 °C, only the Al atoms dissolve into the hydrochloric acid (ii). More and more Al atoms dissolve into the hydrochloric acid; the Ge atoms left at the solid/liquid interface cohere, growing Ge islands in

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