Synthesis of dual porous structured germanium anodes with exceptional lithium-ion storage performance

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HIGHLIGHTS

- A two-step method for tunable porous nanostructures of Ge is proposed.
- Selective Zn reduction and subsequent etching process provides dual-porous structures.
- Dual-porous Ge anodes have a structural integrity over the prolonged cycles.

GRAPHICAL ABSTRACT
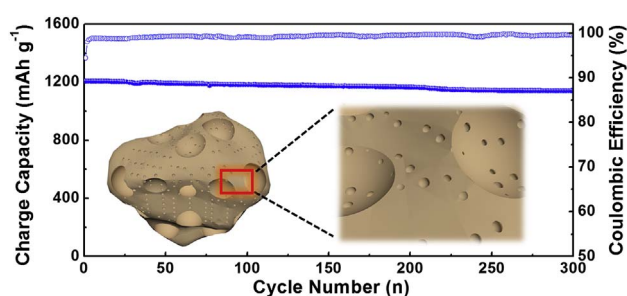
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ABSTRACT

Dual-porous Ge nanostructures are synthesized *via* two straightforward steps. Compared with conventional approaches related to porous Ge materials, different types of pores can be readily generated by adjusting the relative ratio of the precursor amounts for GeO_2 and SiO_2. Unlike using hard templates with different sizes for introducing secondary pores, this system makes a uniformly blended structure of porogen and active sites in the nanoscale range. When GeO_2 is subjected to zincothermic reduction, it is selectively converted to pure Ge still connected to unreacted SiO_2. During the reduction process, primary pores (larger than 50 nm) are formed by eliminating zinc oxide by-products, while inactive SiO_2 with respect to zinc metal could contribute to retaining the overall structure. Finally, the HF treatment completely leaches remaining SiO_2 and formed secondary pores (micro/mesopores) to complete the dual-porous Ge structure. The resulting Ge structure is tested as an anode material for lithium-ion batteries. The Ge electrode exhibits an outstanding reversibility and an exceptional cycling stability corresponding to a capacity retention of 100% after 100 cycles at C/5 and of 94.4% after 300 cycles at C/2. Furthermore, multi-scale pores facilitate a facile Li-ion accessibility, resulting in an excellent rate capability delivering ~740 mAh g^{-1} at 5C.

1. Introduction

Alloy-type materials primarily comprise group IV elements and are considered as the most promising anodes for next-generation lithium-ion batteries (LIBs) owing to their exceptionally high gravimetric capacities. For example, Si delivers a specific capacity of approximately

3579 mAh g^{-1} (Li$_{15}$Si$_4$ at room temperature) and possesses a low working potential (< 0.4 V *vs.* Li/Li$^+$). However, it exhibits a large volume expansion that exceeds 300% with respect to Li-ion uptake, and this causes mechanical failure with severe pulverization of electrodes [1–3]. Additionally, poor Li-ion diffusivity and low electronic conductivity cannot be easily resolved by well-known strategies such as down-scaling, surface engineering, and composites with conductive materials, which placed a limitation on a variety of applications [4–6]. Compared to Si-based anodes, Ge exhibits higher Li-ion diffusivity (400 times faster than Si at room temperature) as well as excellent electronic conductivity (10^4 times greater than that of Si), which can facilitate improved rate capability and cycling stability with a comparable specific volumetric energy of 7366 Ah L^{-1}. However, Ge-based anodes have not drawn great attention owing to their cost issues. Similar problems were also observed like in the case of Si, such as isolation of active materials from a conductive network and pulverization originating from the large volume expansion [7–12].

Various approaches for addressing these issues include porous nanostructures that have extensively explored due to their large surface area that can tolerate lithiation-induced strains [13–29]. A conventional method to realize a porous structure involves template-assisted synthesis. For example, Park et al. utilized a SiO$_2$ template to produce three-dimensional porous Ge/C composites and showed stable cycling properties for 100 cycles as a robust anode material [22]. However, this process required an elaborate experimental setup and expensive reagents. Another approach employed a dealloying process from alloy materials by the selective dissolution of impurities, resulting in the formation of a bicontinuous structure [15]. An alternative method to prepare porous Ge involves the reduction of germanium oxide (GeO$_2$) in a molten salt system using Mg reductant [30]. These methods generally operate at temperatures of > 650 °C. Liang et al. presented a hydrothermal reduction process for synthesizing macroporous Ge microparticles at low temperatures [16]. Recently, a study reported a new method to lower the reaction temperature below 450 °C by zincothermic reduction [26]. To date, simple and controllable synthetic methods continue to pose significant challenges.

Herein, we demonstrate a straightforward synthetic protocol to synthesize a dual-porous Ge nanostructure by co-precipitation and subsequent selective chemical reduction process. Two different precursors are simultaneously precipitated in a coagulation bath to form a uniform dispersion of amorphous SiO$_x$/GeO$_x$ in the nanoscale range. When the mixture is subjected to zincothermic reduction, GeO$_2$ preferentially reacts with Zn vapors to make porous Ge. Afterwards, inactive SiO$_2$ with respect to Zn vapors is etched out to introduce additional controllable pores based on their portions. The as-prepared porous Ge nanostructures deliver a high specific capacity of approximately 1200 mAh g^{-1} over 300 cycles at a rate of C/2 and an improved rate performance compared to those of non-porous nano-Ge anodes.

2. Experimental

2.1. Synthesis of Ge nanostructures

SiO$_2$/GeO$_2$ mixtures (SGO) were prepared *via* a modified Stöber method. First, 9 mL of NH$_4$OH (aqueous ammonia), 16.25 mL of ethanol, and 24.75 mL of deionized (DI) water were pre-mixed at room temperature with stirring at 1100 rpm to form a uniform solution A. Next, solution B was prepared by adding certain amount of tetraethyl orthosilicate (TEOS) and germanium tetraethoxide (TEOG) to 10 mL of ethanol. Solution B was slowly added into the solution A using a syringe pump with stirring at 450 rpm and the final mixture kept stirring for 2 h. The final products were washed with a mixture of water and ethanol repeatedly and collected by filtration and subsequent drying. The samples were calcined at 500 °C in air to completely remove organic compounds. Calcined SGO was mixed with a zinc powder (Zn 99.9%, Alfa Aesar) in a mortar. The mixture was placed in a stainless

steel vessel. The furnace was heated to 600 °C in argon at a rate of 5 °C min^{-1} and kept at the target temperature for 1 h. The obtained samples were immersed in a 0.5 M HCl solution for 1 h to remove ZnO byproducts. And then, the product was etched to remove SiO$_2$ at room temperature by 0.5 M HF for 1 h. To clarify the name of each sample, we summarized notations for each sample (see Table S1 in Supplementary data).

2.2. Material characterization

Surface morphologies of SGO (composite of crystalline GeO$_2$ and amorphous SiO$_2$), SG (composite of crystalline Ge and SiO$_2$ after Zn reduction and subsequent HCl treatment) and NG (dual-porous Ge nanostructures after HF treatment) composites were characterized using a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), which was performed at an acceleration voltage of 10 keV. Transmission electron microscopy (TEM, JEM-1400) was used to investigate the morphologies of NG and NG-based composites before and after cycling. The microstructures of NG and NG-based composites were investigated using X-ray diffractormeter (XRD, Bruker D8-Advance), which were performed at 3 kW using Cu Kα radiation. The NG and NG-based composites were characterized by Raman spectroscopy (Alpha 300s, WLTec GmbH) operating with a laser excitation wavelength of 532 nm. The nitrogen adsorption and desorption isotherms were measured with a VELSORP-mini II (BET, Japan, Inc.) at 77 K in the relative pressure range of P/P$_0$ from 0.05 to 0.3 to determine the BET surface areas and pore size distribution. Bonding states (stretching, vibration, and so on) of prepared samples were analyzed by Fourier-transform infrared spectroscopy (FT-IR, Varian-620).

2.3. Electrochemical measurements

Electrochemical properties of the series of NG samples were evaluated using coin-type half cell (2016 type) at 25 °C. The NG samples comprised of active material, super-P carbon black, and poly (acrylic acid)/sodium carboxymethyl cellulose (1:1, w/w) as binder in a weight ratio of 70:15:15. The loading level of active materials are 1.2–2.1 mg cm^{-2} (detailed loading levels of each electrode are shown in Table S2). The coin cell comprised of lithium metal as the counter electrode, a polyethylene separator, and 1.3 M LiPF$_6$ containing ethylene carbonate/diethyl carbonate (PANAX starlyte, Korea, 3/7 (v/v)) with 10 wt% fluoroethylene carbonate additive as the electrolytes. The half cells were tested galvanostatically in the range of 0.005–2.0 V for precycle and 0.01–1.5 V for subsequent cycles (versus Li/Li$^+$) at 0.05–5 C rates. The cell performance was examined using a cycle tester (WBCS 3000 battery systems, Wonatech). For impedance measurement, AC complex impedance analysis with an IVIUM frequency response analyzer was used over a frequency range of 10 mHz–1 MHz. Cyclic voltammetry (CV) measurements were performed at a scan rate of 0.2 mV s^{-1} in the rage of 0.01–2.5 V at 25 °C for the assembled half cells with NG-21, SG-21, NG-10 electrodes.

3. Results and discussion

Novel Ge nanostructures are realized through three simple steps, as depicted in Fig. 1a. First, a uniformly mixed precursor solution containing two different metal alkoxides (TEOG and TEOS) with specific weight ratios (4:1, 2:1, 1:1, and 1:0) was rapidly loaded in a syringe pump to avoid continuous exposure to moisture because this could cause an undesirable gelation of the solution. The solution was slowly fed into a basic coagulation bath [31], and the mixture was precipitated quickly at the bottom of the bath to form an amorphous SiO$_x$–GeO$_x$ composite (see Figure S1 in Supplementary data). During this synthesis process, hydroxyl anions produced from aqueous ammonia solutions could readily lead to a hydrolysis reaction as a catalyst and subsequent condensation reactions very quickly (see Figure S2 in Supplementary