Germanium nanoparticles supported by 3D ordered macroporous nickel frameworks as high-performance free-standing anodes for Li-ion batteries

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HIGHLIGHTS

- Self-supporting binder-free Ge nanoparticle electrode is fabricated on 3DOM Ni.
- Excellent lithium-ion storage property is achieved for the Ge electrode.
- The three-dimensional porous network improves the electrode mass transport kinetics.
- Possible Ge-Ni alloy interface helps to maintain the good electronic contact.

ABSTRACT

Germanium-based materials are gaining increasing attention as promising anodes for Li-ion batteries (LIBs) due to their high specific capacity, good cycling stability and excellent rate performance. Similarly to Si, Ge-based anodes undergo a huge volume expansion and contraction during Li intercalation and deintercalation, causing a rapid and irreversible capacity decay. In this work, Ge nanoparticles are uniformly attached to a 3D ordered macroporous (3DOM) Ni framework (Ge/3DOM-Ni) via a facile drop-coating technique in order to address the volume expansion and stability issues plaguing Ge anodes. The 3D ordered macroporous Ni frameworks with high porosity act not only as highly conductive current collectors but also as a robust porous support for the formation of a thin layer of Ge nanoparticles. The three-dimensional porous network facilitates the penetration of the electrolyte and lithium ions. The possible alloy interface generated among the Ge nanoparticles and Ni framework during the calcination process ensures good electric contact among the nanoparticles and the 3D ordered macroporous Ni framework. When used as self-supporting binder-free anodes for lithium ion batteries, the Ge/3DOM-Ni electrode shows high rate performance and excellent structural and cycling stability. This work provides a facile and effective strategy for improving the electrochemical performance of Ge-based anodes.

1. Introduction

Germanium-based materials with high energy density and reasonable power density have been regarded as promising anodes for Li-ion batteries (LIBs). Ge has a very high theoretical specific capacity (1624 mA h g^{-1} for Li$_{22}$Ge$_5$ and 1384 mA h g^{-1} for Li$_{15}$Ge$_4$) [1,2]. Ge-based anodes have many attractive features which make them preferable to Si including, a larger volumetric capacity (7366 A h L^{-1} for Li$_{15}$Ge$_4$), faster Li-ion diffusivity (400 times faster than that of Si), higher electrical conductivity (10^4 times than those of Si [3]), increased resistance to surface oxidation [4], and improved structural integrity due to the weak anisotropy of lithiation insertion strains [5,6]. However, Ge-based anodes usually suffer from huge volume expansion and

contraction upon Li intercalation and deintercalation, leading to rapid and irreversible capacity decay. In order to promote the practical application of Ge materials in LIBs, this issue has to be addressed.

Several strategies have been proposed to improve the structural and cycling stability of electrode materials, such as decreasing the particle size [7–11] or dimension [12–14], alloying with other active/inactive elements [15], introducing a porous structure [16–19], surface and interface modification [20]. Among them, the introduction of a porous structure has proven to be an established and very efficient way to suppress the volume expansion during lithiation. The large void space in a porous structure can accommodate the huge volume expansion. The bicontinuous porous network can provide fast pathways for both ion diffusion and electrolyte transportation. Recently examples of

mesoporous [21–23] and macroporous [24–30] Ge materials have been reported, and they showed improved rate capabilities and cycling stability [31,32]. However, these porous structures are not fully stabilized and will collapse after lithiation/delithiation [33]. Additionally using porous powders as electrode materials means polymer binders and conductive substances have to be involved in the electrode generation process. Although strides have been taken, it is still challenging and highly desirable to improve the structural stability of Ge anodes.

Herein, self-supporting porous Ge electrodes (Ge/3DOM-Ni electrodes) were fabricated by attaching Ge nanoparticles onto the 3D ordered macroporous Ni (3DOM-Ni) framework fabricated via an electrodeposition method by using polystyrene (PS) coated on Ni foil as templates. The small particle size of Ge reduces the diffusion distance of Li ions, ensuring high rate capability. The porous 3DOM-Ni framework offers solid support for the Ge nanoparticles and functions as an effective electron collector. The high porosity accommodates the volume expansion of the Ge nanoparticles occurring upon cycling, and the readily accessible macroporous channels provide efficient transport pathways for both electrolyte and lithium ions. These porous Ge anodes on 3DOM-Ni frameworks can avoid the involvement of polymer binders and conductive substances, which usually accounts for 20 wt% of the electrode. As expected, high specific capacity and good cycling stability are achieved for the self-supporting porous Ge anodes on 3DOM-Ni framework.

2. Experimental section

2.1. Preparation of PS opals and 3D ordered macroporous Ni

The 3DOM-Ni frameworks were prepared via the template-assisted potentiostatic electrodeposition method by using PS colloidal crystals deposited on Ni foil as hard templates. The PS templates were prepared by submerging Ni foil into a latex containing 0.15 vol% PS spheres. After the complete evaporation of water, well-ordered PS templates formed on the Ni foil through the self-assembly of PS spheres. Then, The PS-coated Ni foil worked as the working electrode and Ni foil as the counter electrode were immersed into an electrolyte containing 300 g/L $NiCl_2 \cdot 6H_2O$ and 28 g/L boric acid to form a two-electrode system. The pH value of the electrolyte was adjusted to 3.5–4.0 using an HCl solution [34–37]. The electrodeposition was carried out at 60 °C for 10 min with a potential of −0.95 V and a current density of 10 mA cm^{-2}. Finally, in order to form the 3DOM-Ni framework the PS template was thoroughly removed by immersing it in tetrahydrofuran or toluene for 30 min.

3. Fabrication of the Ge/3DOM-Ni electrodes

First, Ge nanoparticles were prepared through the reduction of germinate ions synthesized via the reaction of GeO_2 with NaOH by $NaBH_4$ [38,39]. Typically, 8.0 g of GeO_2 (99.999%, Aldrich) was added to 144 mL of distilled water, followed by the addition of 16 mL of 1 M NaOH solution to dissolve GeO_2. Then a fresh $NaBH_4$ solution (28.9 g in 80 mL of water) was added to the above solution. After continuous stirring for 24 h, Ge nanoparticles were collected by filtration, washed with distilled water, and dried under vacuum. 5 g of Ge nanoparticles were dispersed in 10 mL of ethanol using ultrasonication. The resulting suspension was slowly drop-coated onto the 3DOM-Ni framework heated on a hotplate. Finally, the self-supporting porous Ge/3DOM-Ni electrodes were obtained by annealing the 3DOM-Ni framework with the Ge nanoparticles in a tube furnace at 500 °C for 2 h in Ar.

4. Cell assembly and electrochemical measurement

The coin-type half cells (2025R size) were assembled in a glove box filled with ultra-high pure argon by using a microporous polyethylene as the separator, Li metal as counter/reference electrode, and 1 M $LiPF_6$

in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 vol%) as the electrolyte. For comparison, the slurry-cast method was also adopted to fabricate the battery electrodes with Ge nanoparticles, denoted as Ge-NP electrodes. The slurry contained Ge nanoparticles, carbon black, and poly (vinyl difluoride) (PVDF) with a weight ratio of 80:10:10 respectively and was spread on Cu foil. The cyclic voltammetry performance test was conducted at a scanning rate of 0.1 mV s^{-1} in a potential range of 0.02 V to 1.5 V (vs Li/Li$^+$), and electrochemical impedance spectroscopy (EIS) test was carried out in the range of 0.01–10^{5}Hz with an AC amplitude of 5 mV (PARSTAT 2273, AMETCH). The galvanostatic charge and discharge experiment was performed with a battery tester (LAND CT2001A) in the potential range of 0.01–2.0 V at room temperature. The cells were equilibrated at open circuit for 24 h before testing.

4.1. Characterization

The morphological characterization was performed with a Hitachi S-4800 scanning electron microscope (SEM) operating at 20 kV. Transmission electron microscopy (TEM) was performed by FEI Tecnai G2F30 operated at 300 kV. Elemental and structural analyses were also achieved by X-ray diffraction (XRD, Bruker D8 advance), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. XPS spectrum was collected on a Perkin-Elmer PHI5700 ESCA system with an Al Kα source. The Raman spectrum was measured on a modified micro Raman confocal spectrometer (JY-Horiba, JY HR-800) using the 458 nm Ar$^+$ laser.

5. Results and discussion

The typical fabrication procedure of the self-supporting porous Ge/3DOM-Ni electrodes is shown in Scheme 1. Highly ordered colloidal crystals were first formed by the hexagonally close packing of PS spheres of approximately 500 nm in diameter. The electrodeposition method was adopted to fill the interstices of the PS colloidal crystal with Ni. After the subsequent removal of PS spheres with tetrahydrofuran, porous 3DOM-Ni framework, an accurate replication of the ordered colloidal crystal structures was obtained. Then Ge nanoparticles prepared by the reduction of GeO_2 with $NaBH_4$ were dispersed in ethanol. A certain amount of the ethanoic suspension of Ge nanoparticles was slowly drop-coated onto the 3DOM-Ni framework which was heated on a hotplate at 80 °C. The self-supporting porous Ge/3DOM-Ni electrodes were obtained by annealing in an Ar atmosphere at 500 °C.

The top and cross-section scanning electron microscope (SEM) images of the PS colloidal crystal formed on Ni foil is shown in Fig. 1a, b and Fig. S1† with lower magnifications. The thickness of the colloidal crystal is tunable by changing the concentration of the PS colloidal suspension. A thickness of approximately 10 μm, equal to more than 20 stacking layers of PS spheres is achieved with a suspension containing 0.15 vol% of PS spheres (Fig. 1b). The porous 3DOM-Ni framework has
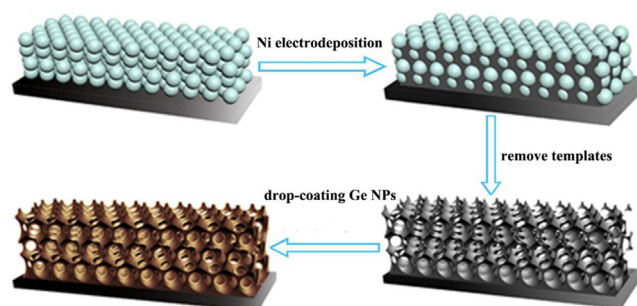
Scheme 1. Schematic illustration of the preparation of Ge/3DOM-Ni electrodes.