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Scalable synthesis of hierarchical porous Ge/rGO microspheres with an ultra-long cycling life for lithium storage

Bangrun Wang[a,b], Jun Jin[a], Kun Rui[a], Chenxi Zhu[a], Zhaoyin Wen[a,*]

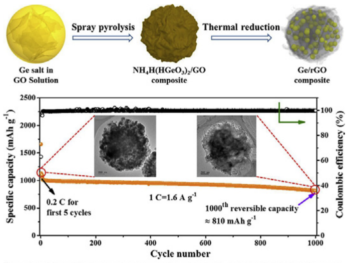
[a] *CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, 200050, PR China*
[b] *University of Chinese Academy of Science, Beijing, 100049, PR China*

HIGHLIGHTS

- Ge/rGO microspheres were prepared via spray drying combined with heat reduction method.
- The commercial GeO_2 was selected for prepare $NH_4H(HGeO_3)_2$ precursor.
- The hierarchical porous Ge/rGO hybrid with high structural integrity.
- The Ge/rGO electrodes with excellent electrochemical performance.

GRAPHICAL ABSTRACT

The unique hierarchical porous structure endows the excellent electrochemical performance of Ge/rGO microspheres.



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ABSTRACT

The hierarchical porous germanium/reduced graphene oxide (Ge/rGO) microspheres are synthesized through an industrially scalable spray drying technique using commercial germanium dioxide (GeO_2) as raw material. The Ge/rGO microspheres architecture with Ge nanoparticles homogeneously embedded in the three-dimensional (3D) interconnected conductive rGO network. When employed as anode for lithium ion batteries (LIBs), the as-obtained Ge/rGO microspheres exhibit excellent electrochemical performance with a high reversible capacity (811 $mAh\ g^{-1}$ after 1000 cycles), ultra-long cycling life (over 80% capacity retention from the 6th to 1000th cycles at 1 C), and high rate capability (380 $mAh\ g^{-1}$ at 20 C). In addition, the full cell consisting of Ge/rGO-2 anode and $LiFePO_4$ cathode also delivers good cycling stability with high energy density. The 3D conductive rGO network provides the pathway for electron transportation and promotes to form stable solid electrolyte interphase (SEI) layer. Furthermore, the void space deduced from the porous structure can effectively accommodate volume changes and enhance the structural integrity of Ge/rGO microspheres. This facile and scalable synthetic strategy is beneficial for large-scale production of Ge-based electrode materials for further application in high energy and power density LIBs.

1. Introduction

The development of electric vehicles, smart grid, and renewable power stations creates tremendous demand for advanced lithium ion batteries (LIBs) with long cycling life, high energy density, and low cost. Nevertheless, the current commercial LIBs still suffer from the lack of high-capacity electrodes for the ever-growing demand of large-scale energy storage systems. Therefore, it is urgent to develop novel electrode materials with high gravimetric and volumetric capacity to increase the energy density of LIBs [1–3]. In terms of anode materials, the

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[*] Corresponding author.
E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

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key solutions is to replace the graphite anode (372 mAh g^{-1}) by high capacity electrode materials [4]. Recently, alloy-type anode (e.g., Si, Ge, and Sn) materials have attract great attention due to their high theoretical capacity and reasonable anodic potential. Among them, germanium (Ge) is a prospective anode material owing to its relatively high theoretical capacity (1600 mAh g^{-1}, for $Li_{4.4}Ge$), outstanding lithium-ion diffusivity (about 100 times than Si), and high electronic conductivity (about 400 times than Si) [5–7]. However, similar to other alloy-type anodes (like Si and Sn), Ge also undergoes large volume changes (~300%) and low intrinsic electronic conductivity during cycling [8]. The repeated volume expansions and contractions cause pulverization of active materials and generate unstable thick solid electrolyte interphase (SEI) layer, leading to loss of electrical contact between active materials and current collector which depress the performance of the battery [9–11]. To tackle these problems, several efforts have been devoted to enhance the electrochemical performance of Ge-based anode materials. Among the efficient strategies, fabrication of nanostructured Ge (e.g., nanoparticles, nanotubes, nanowires) with the use of highly conductive matrix is an effective way to improve the cycling performance of Ge anodes [12–16]. Moreover, an electrode with three-dimensional (3D) porosity and enough void space could weaken the volume variations of the active materials [17,18]. It is obvious that the carbon-supported Ge composite with an optimized structure and composition can enhance the electrochemical performance efficiently [19,20].

Graphene is often selected as a carbon matrix to synthesize graphene-based composite anodes for LIBs due to its unique high surface area, excellent electronic conductivity, and strong chemical and structural stability [21,22]. In recent years, considerable strategies have been made to synthesize Ge/graphene composites to boost the cyclability of Ge anodes, such as carbon thermal reduction [6], microwave-assisted solvothermal [23], and thermal evaporation methods [24]. It is noteworthy that in most of the above cases, expensive Ge precursors (e.g., $GeCl_4$ and GeI_2) were used as Ge source with the multistep synthetic method, resulting in high-cost of the products. In addition, Ge/graphene composites without rational structure that constructed by 2D graphene sheets can't maintain high structural stability and reversible capacity after long cycles. Thus, there are still many challenges for facile and effective synthesis of Ge/graphene composites with superior electrochemical performance. For practical application, the suitable manufacturing strategy should meet several critical criteria, including low cost, simple operation, and high yield.

Spray drying technique is one of the most common processes to produce dry powders from liquid solution, it has been successfully used for mass synthesis of various electrode materials due to its simple apparatus and easy scale-up [25–29]. Nevertheless, the use of spray drying technique to synthesize the Ge/graphene composite has never been reported. In this work, we report the hierarchical porous Ge/rGO microspheres by a facile spray drying combined with a calcination process using commercial germanium dioxide (GeO_2) as raw material. The Ge/rGO microspheres with uniformly dispersed Ge nanoparticles embedded in a 3D interconnected conductive rGO framework. As a result, the as-obtained Ge/rGO microspheres exhibit excellent electrochemical performance with a high reversible capacity (811 mAh g^{-1} after 1000 cycles), long cycling stability (over 80% specific capacity retention from the 6th to 1000th cycles at 1 C), and ultra-high rate capability (380 mAh g^{-1} at 20 C) as anode for LIBs. Furthermore, the full cell consisting of Ge/rGO anode and $LiFePO_4$ cathode shows a reversible capacity of 135 mAh g^{-1} at 1 C rate with high energy density of ~338 Wh kg^{-1}. This work paves a way to develop porous Ge-based anodes with high-capacity and long cycle life for high-energy LIBs.

2. Experimental section

2.1. Materials

In this work, all chemical reagents were of analytical purity and were used without further purification. Germanium dioxide (GeO_2, 99.9999%) powder was purchased from Germanium Co., Ltd. (China). Graphite powder was provided by Aladdin Chemistry Co., Ltd. (China). Commercial $LiFePO_4$ electrode materials were provided by Tianjin STL Energy Technology Co., Ltd. (China).

2.2. Synthesis of Ge/rGO microspheres

Graphite oxide (GO) was synthesized through a modified Hummer's method starting from graphite powder [30]. The graphite oxide was exfoliated into deionized water by sonication to form a GO suspension. A certain amount of GeO_2 was dispersed in aqueous ammonia with magnetic stirring to form a transparent solution [11,31]. Then the as-synthesized GO suspension (20 mg mL^{-1}) was added into the above solution with a weight ratio of GeO_2:GO of 3:1 to form a good aqueous dispersion by sonication. Subsequently, the mixture was pumped into a spray dying apparatus to form aerosol droplets. The inlet air temperature at spray drying process was maintained at 120 °C and the fine droplets were dried in the cylinder. GO sheets can spontaneously assemble on the surface of the droplets owing to their amphiphilicity and subsequently shrink and encapsulate $NH_4H(HGeO_3)_2$ to form $NH_4H(HGeO_3)_2$/GO precursor [32]. The product was collected at the vessel and calcinated under 15% H_2/85% Ar flow at 650 °C for 4 h to form Ge/rGO hybrid, denoted as Ge/rGO-1. The Ge/rGO-2 was synthesized by the same method, except that the weight ratio of GeO_2:GO was 3:2.

2.3. Material characterization

X-ray diffraction (XRD) patterns were conducted on a Rigaku Ultima with Cu Kα ($\lambda = 1.542$ Å). Raman spectrum was measured by a DXR Raman with a laser wavelength of 532 nm. SEM and TEM images were carried out a field-emission scanning electron microscope (FESEM, FEI-Magellan 400, 10.0 KV) and a transmission electron microscope (TEM, JEM-2100F, 200.0 KV), respectively. The XPS measurement of the sample was carried out on ESCALAB 250Xi spectrometer (Thermo Fisher) with Al Kα radiation ($h\nu = 1486.6$ eV). Unless specified otherwise, the X-ray anode was run at 150 W with the spot size of about 500 μm. The pass energy was fixed at 50 eV to ensure sufficient sensitivity. Binding energies were calibrated by using the containment carbon (C 1s = 285.0 eV). The spectrum decomposition was performed using the XPS Peak 41 program with Gaussian functions after subtraction of a Shirley background. Nitrogen adsorption/desorption and pore size distribution curves were measured on Micromeritic TristarII 3020. TG was measured on a TGA 409 PC thermogravimetric analyzer (Netzsch STA) in air atmosphere at a heating rate of 10 °C min^{-1} from room temperature to 900 °C.

2.4. Electrochemical measurements of Ge/rGO

The electrochemical performance of Ge/rGO was investigated using CR2025-type coin cells. The working electrodes were prepared by pasting a slurry of active material, super-P carbon black, lithium polyacrylate (Li-PAA) as binder at a weight ratio of 8:1:1 onto a copper foil and dried in a vacuum at 80 °C overnight. The mass loading of active material in the anode was adjusted in the range of 0.8–2.5 mg cm^{-2}. All the cells were assembled in an argon-filled glove box with water/oxygen contents lower than 0.1 ppm and tested at room temperature. 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, by volume), 5 wt% fluoride ethylene carbonate (FEC) was used as the electrolyte additive. Glass fiber membranes and lithium metal foil were used as separators and counter

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