



Elastic Reduced Graphene Oxide Nanosheets Embedded in Germanium Nanofiber Matrix as Anode Material for High-Performance Li-Ion Battery



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ABSTRACT

Germanium, as a semiconductor material, has a poor electrical conductivity, but the high theoretical capacity of 1600 mA h g^{-1} makes it as a promising high-capacity anode material for lithium-ion batteries (LIBs). The huge volume variation during charge and discharge leads to a poor cycling stability. In this paper, Ge with reduced graphene oxide nanofibers (Ge@RGO NFs) are firstly prepared by electrospinning. The nanofibers with a uniform diameter of 50 nm combined RGO delivered a high specific capacity of $1727.0 \text{ mA h g}^{-1}$ in the first discharging and $1205.1 \text{ mA h g}^{-1}$ after 100 cycles at the constant current density of 200 mA g^{-1} . RGO in the composites has two important roles: (i) as a conductive agent to improve electrical conductivity; (ii) as a buffer to protect Ge nanostructure from pulverization during charge and discharge processes. Electrochemical testing results show that the Ge@RGO nanofibers anode has a high specific capacity of $661.6 \text{ mA h g}^{-1}$ at the current density of 5000 mA g^{-1} , suggesting the Ge@RGO electrodes can be used to high current and high-power electronic equipments.

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1. Introduction

Energy and environment, as two major problems in today's social development, are two key factors for social progress and the long-term survival of human beings, which result in searching for efficient and clean energy has become one of the biggest challenges facing currently [1–3]. Lithium-ion batteries (LIBs), a secondary battery (rechargeable batteries) with many advantages, such as high specific capacity, high working voltage (about 3.6 V, 3 times higher than Ni–Cd battery), long cycle life, pollution-free, no memory effect and so on, mainly rely on lithium ions move between the positive and negative during charge and discharge [4–6]. Powered by LIBs, such as zero-emission electric vehicles (EVs) or low-emission hybrid electric vehicles (HEVs), smartphone and tablet computer, requiring high power density and long cycle-life is indispensable in our daily life. Graphite, with low theoretical capacity (372 mA h g^{-1}) were used as anode materials in commercial LIBs, which limits its applications in high energy density electric vehicles. Si, Ge, Sn with high theoretical capacity (4200 mA h g^{-1} , 1624 mA h g^{-1} and 994 mA h g^{-1} , respectively)

and about 2.6–11.2 times higher than graphite are regarded as candidates for next generation anode materials for LIBs [7–11]. In the old days, the higher cost nature of Ge than Si and Sn restricts its applications in energy storage. But reports show that Ge has a smaller band gap (0.6 eV) than Si and provides wonderful electrical conductivity (about 10^4 times than Si), the diffusion of Li in Ge 400 times higher than that in Si at room temperature, and the higher capacity than Sn makes it has a huge potential in high performance energy storage [12–14].

Poor-use-ratio of active materials on account of insufficient reaction and structural damage by the reason of inevitable large volume change of electrode materials during charge-discharge process lead to fast fade of the capacity and poor cycle performance (Ge included), giving a big challenge to researchers. Plentiful strategies for nanostructures of different dimensionalities, for instance, nanoparticles (NPs) [15–17], nanofibers (NFs) [18–20], nanotubes (NTs) [21–24], have been reported to overcome such big volume change. Numerous efforts demonstrate that the enhanced electronic conductivity of the active materials can achieve a better electrochemical performance [5]. As a direct and relatively easy method for preparing small diameter nanofiber, electrospinning is most hopeful for realizing the commercial production of nanofibers [19]. SnO_2 @carbon nanofibers (SnO_2 @CNFs) and SnO_2 @graphene nanofibers (SnO_2 @G NFs) were synthesized by

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electrospinning showing an excellent rate capability. In order to protect active material from pulverization during charging and discharging and increase the electronic conductivity, Jian Zhu etc. fabricated SnO₂@carbon, and SnO₂@G as electrode obtaining wonderful cycle performance [18,19].

Graphene, a two-dimensional material, as a promising substrate to host active nanomaterials, with many superior characters, such as excellent electrical conductivity, good flexibility and chemical stability, has been vastly studied in developing high performance energy conversion and storage devices [25–28]. In the last few years, graphene, carbon nanotubes and reduced graphene oxide (RGO) received more attentions due to their better electrical conductivity than ordinary carbon, which was previously reported [10,29–34].

Recently, various RGO and graphene mixed with Ge nanoparticles had been reported, for example, Zhong etc. synthesized Ge-RGO nanocomposites by a one-pot, aqueous-based method, exhibiting a reversible specific capacity of 814 mA h g⁻¹ after 50 cycles at a current density of 0.1 A g⁻¹; Ren's group obtained Ge-graphene composite using a low-pressure thermal evaporation approach, showing a capacity retention of 84.9% after 400 full cycles [12,35]. In this study, we firstly, for all I know, fabricate germanium nanofibers with reduced graphene oxide nanofibers (Ge@RGO NFs) by electrospinning. The novel nanofibers have a large number of electrochemical active sites for storing Li⁺. Besides, the elastic RGO can provide adequate room for the huge volume change during charge and discharge process [36,37]. Additionally, RGO can also promote rate capability of Ge@RGO NFs electrodes when used as anodes, which was attributed to the excellent electroconductibility. The results show that the as-obtained Ge@RGO NFs electrodes delivered a high specific capacity of 1727.0 mA h g⁻¹ in the initial discharge process, and still have a specific capacity of 1205.1 mA h g⁻¹ after 100 cycles at a constant current density of 200 mA g⁻¹. Such high capacity and excellent cycle performance were attributed to the combination of Ge nanofibers and the enhanced-conductivity RGO.

2. Experimental Section

2.1. Materials synthesis

2.1.1. Preparation of precursor solutions

In a typical procedure, 0.01 g graphene oxide (GO) were dissolved in a mixture of 2.2 g ethanol and 2.2 g N, N-dimethyl formamide (DMF). The solution was sonicated for 30 min to disperse the GO and then 0.12 g Germanium tetrachloride (GeCl₄, 99.9999%, Alfa Aesar) were added by magnetic stirring for 1 h at room temperature [38,39]. Furthermore, 0.4 g polyvinyl pyrrolidone (PVP, Sigma Aldrich, Mw ≈ 1300 000) were pour into the resulting solution and vigorously stirred for 3 h at room temperature.

2.1.2. Preparation of Ge@RGO NFs, Ge@CNFs, pure Ge NFs

The precursor solutions were pumped into a 5 mL syringe with a stainless steel nozzle (inner diameter is 0.5 mm) and ejected to the collector by high-voltage DC electrostatic field with 20 kV between the collector and the nozzle tip. The obtained NFs were dried at 70 °C in vacuum for 24 h to remove DMF, and calcined in air at 450 °C for 2 h with a heating rate of 3 °C min⁻¹. Then the target product Ge@RGO NFs were obtained by annealing at 600 °C for 3 h in a horizontal tube furnace under Ar/H₂ (10%) atmosphere [32,33].

Ge@carbon nanofibers (Ge@CNFs) were obtained by the same way of Ge@RGO NFs, but without GO in precursor solution and needn't calcined in air at 450 °C before annealing in Ar/H₂. Pure Ge NFs were prepared using the same precursor solution of Ge@CNFs, and the same process of Ge@RGO NFs later.

2.2. Material characterization

The obtained material Ge@RGO were characterized by X-ray diffraction (XRD, Philips, X'pert pro, Cu Ka, 0.154056 nm) to acquire the crystal structures and morphologies. In order to present low and high magnification morphologies of the material, scanning electron microscope (SEM, Hitachi S-4800, 5 KV), transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM, JEOLJEM-2100F) were conducted. Raman spectra were taken on a Raman spectroscopy (LabRAM HR800) to confirm the existence of RGO. A WQF-410 Fourier transform infrared spectrophotometer (FT-IR, potassium bromide-disk technique) were used to express the change of sample's oxygen-containing groups before and after annealing in Ar/H₂. Thermogravimetric analysis (TGA) was obtained on a Thermo-Gravimetric Analyzer (TGA, PerkinElmer, Diamond TG/DTA) from 30 °C to 900 °C at a heating rate of 3.5 °C min⁻¹ in air. Electrochemical impedance spectroscopy (EIS) was undertaken on a electrochemical workstation (CHI 660E).

2.3. Electrochemical measurements

Ge@RGO, conductive carbon black and sodium carboxymethyl-cellulose (CMC) in the weight ratio 8:1:1 were dissolved in 1.0 g deionized water and 0.25 g ethanol. The mixture was slurry-cast on a 10 μm thick Cu foil, dried under vacuum at 80 °C for overnight, and the obtained film were punched into disk electrodes. The coin type of lithium half-cells (CR2032) with 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 v/v) as the electrolyte were assembled in the glove box filled with pure argon with microporous polypropylene as the separator and metallic lithium sheet as the reference and counter electrode. The loading mass of active material is about 0.4–0.7 mg. The galvanostatical charge-discharge was carried out within the voltage range of 0.01 and 3.0 V (vs. Li⁺/Li) at the current densities of 100, 200, 500, 1000, 2000, 5000 mA g⁻¹ using a Battery Testing System (Neware CT-3008). All cyclic voltammetry measurements were performed on an electrochemistry working station at a scanning rate of 0.2 mV s⁻¹ within the potential range of 0.01–3.0 V (vs. Li⁺/Li).

3. Result and discussion

3.1. Morphology and Structure

Scheme 1a presents the electrospinning equipment, which consists of four important components: high voltage DC power supply, collector, syringe and precursor solutions. The solutions were spilled via a stainless needle about 20 cm away from collector at a flow rate of 0.5 mL h⁻¹. A high voltage of 20 kV was used between the needle and collector so as to solutions can be stretched to uniform nanofibers and gathered by collector. As show in Scheme 1b, the as-spun nanofibers were heated at 450 °C for 2 h with a heating rate of 3 °C min⁻¹ in air and then annealed at 600 °C for 3 h in Ar/H₂. After double annealed, PVP was removed leading to a drop in diameter, and GO was reduced to RGO [32,33].

In order to explore the morphology of the obtained Ge@RGO NFs, field emission scanning electron spectrometry (FE-SEM) and transmission electron microscopy (TEM) were used to analyze the materials. The typical low-magnification TEM images of Ge@RGO NFs (Fig. 1a–c) show that the nanofibers with an average diameter of 50 nm, the small diameter increasing the specific surface area, offering a large number of active site for sufficient electrochemical reaction. As shown in the red tag area of Fig. 1a, it can be easily found the fold sheets are RGO nanosheets (TEM of pure GO was shown in the lower left of Fig. 1a). In order to further study Ge@RGO NFs. Fig. 1c and d display the remarkably uniform NFs.

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