



Graphene wrapped silicon nanocomposites for enhanced electrochemical performance in lithium ion batteries



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ARTICLE INFO

Article history:

Received 5 December 2013
Received in revised form 24 January 2014
Accepted 24 February 2014
Available online 11 March 2014

Keywords:

Silicon Electrodes
Graphene Wrapping
Lithium ion battery
Electrochemical Performance
Freeze Drying

ABSTRACT

The electrical isolation of fractured silicon and unstable solid electrolyte interphase formed on silicon's surface are two major issues preventing commercialization of silicon anodes in next-generation lithium ion batteries. In this work, we wrap silicon nanoparticles with graphene to maintain the electrical connection, meanwhile, isolating Si from the electrolyte to suppress SEI formation on the Si surface. A facile freeze-drying method followed by thermal reduction was used to synthesize the silicon-graphene (Si-G) composites. We found that the Si-NP's can be tightly wrapped by graphene when the composites utilized an optimal starting ratio of 1:2 (Si-NP:GO), attributing to significantly improved cyclic stability and cycle efficiency. Taking the facile fabrication method and the use of commercial Si-NP's into account, Si-G composites could be a promising candidate for the anode material in lithium ion batteries (LIBs).

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1. Introduction

Silicon has been considered the anode material for next generation lithium ion batteries with high energy density because of its high theoretical specific capacity, reaching 4200 mA h g⁻¹ at full lithiation (Si-Li alloy, Li₂₂Si₅). [1,2] This is highly favourable compared to the Graphite anode materials used in current Li-ion batteries, which exhibit theoretical capacity of only 372 mA h g⁻¹ and low density. Unfortunately, the high specific capacity of Si is accompanied by substantial volume expansion and contraction during the lithiation/delithiation of silicon (>300%), which results in poor cycling stability due to the rapid pulverization of silicon electrodes, disconnection of electrical contacts, and instability of the solid electrolyte interphase (SEI). [3–7] To achieve next-generation lithium-ion batteries containing Si anode materials and offering long cycle life, it is critical to develop a strategy to either accommodate or restrict this volume change and form a stable SEI layer. One approach has been to engineer silicon nanostructure, including

the development of silicon nanowire, silicon nanotube, hollow silicon nanoparticle, and nano-porous silicon. [8–11] Another effective strategy is to apply carbon coatings on silicon, which can not only accommodate the volume change of silicon, but also enhance the electric conductivity of the electrode and contribute to a stable SEI layer. [12–17]

Graphene, a two-dimensional structure composed of carbon atoms, has garnered remarkable attention due to its unique structure and properties, such as: excellent electrical conductivity, high surface area, good flexibility and high mechanical strength. [18–21] As an anode material for LIBs, graphene has demonstrated promising performance compared to graphite [22,23] and more recently Si-G materials have been shown to alleviate the issues associated with bare Si. [24–26] However, it remains a challenge to evenly disperse Si within the graphene sheets. As a result, it is difficult to form stable composites [27] and lithium diffusion could be hindered by sluggish ion diffusion within the poorly distributed composite materials. [28,29]

In this work, we synthesized Si-G composites with a freeze-drying method in order to combine the merits of Si, graphene and freeze drying. We believe that an effective strategy for the production of uniformly dispersed Si-G composites is to reduce GO to graphene after mixing with silicon. This is attributed to graphene being very hydrophobic and thus difficult to disperse in aqueous solution, while GO is highly hydrophilic and Si-NPs are slightly

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hydrophilic due to the native oxygen functionality on the surface of Si. However, the agglomeration of nano-sized silicon caused by the surface tension when drying in aqueous solution [30] can also lead to inadequate composite performance. Freeze-drying has been reported as an effective way to fabricate three-dimensional (3D) architectures and aligned structures, avoiding the agglomeration that commonly occurs during drying. [31,32] After the Si and GO are well dispersed in water, the mixture is frozen immediately with liquid nitrogen so that GO and silicon nanoparticles can maintain their original morphology. Then the water is sublimated to vapour phase directly in a freeze-dryer, and a 3-D network of graphene wrapping silicon is formed by the following heat treatment. The 3-D structure will benefit LIBs in terms of easier lithium ion transportation, faster electrolyte diffusion, as well as better retention of its structure during cycling. In a previous communication published by Zhou *et al.*, one ratio of Si-G composite was synthesized by the freeze drying method and tested in LIBs. [33] However, advanced study for an optimal composition of Si-G is suggested to improve cycle stability and investigate the trade-off between capacity and stability. We systematically investigate the impact of varying the graphene content on the performance of Si-G composites in LIBs, in order to obtain an optimal Si to graphene ratio with enhanced cyclic stability and high specific capacity. All composites had improved stability compared to bare Si-NPs, but most notable was the superior cyclic stability and rate capability of the composite employing a starting ratio of 1:2 (Si-NP:GO). The 3D architecture of the Si-G 1:2 composite materials reveal capacity retention after 200 cycles was 96% @ 0.2 C and around 100% @ 1 C, corresponding to 786.3 mA h g⁻¹ and 594.6 mA h g⁻¹ respectively. We believe that the graphene wrapped silicon will maintain the electrical connection even if the fracture and pulverization occur in silicon due to diffusion-induced stress exceeding the fracture strength. At the same time, the silicon particles are most likely isolated from the electrolyte, so that the majority of SEI will form just on graphene surface which would not go through the huge volume expansion and contraction along with Si. As a result, the cycle efficiency can be improved. In addition, hydrofluoric acid (HF) has been widely used to remove the SiO_x layer on pristine silicon, [34,35] but recent studies have shown that an amorphous SiO_x layer can help prevent the electroactive silicon from agglomerating during cycling. More importantly, the SiO_x also form lithium silicate during cycling (Li₂Si₂O₅), which can function as a buffer layer to reduce the damage to and restrict the volume expansion of Si and stabilize SEI layer. [26,36] For these reasons and to increase cost effectiveness of the material, HF treatment was avoided. In addition, no expensive electrolyte additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC) were used in the electrolyte.

2. Experimental

Fig. 1 schematically shows the process to synthesize the Si-G nanocomposite. Silicon nanoparticles (Si-NPs) (Nanostructured & Amorphous Materials Inc, USA, 50–70 nm) were sonicated in water for five hours. Meanwhile, graphene oxide (GO) synthesized by a modified Hummers' method was sonicated separately for five hours as well. Detailed procedures for the fabrication of GO were described in a paper previously published by our group. [37] The two suspensions were then mixed and sonicated for another five hours to achieve a thorough dispersion. Next, the mixture was frozen rapidly with liquid nitrogen and a freeze-dryer (Labconco Freezone 1, USA) was subsequently used to freeze dry the sample for 48 hours, retaining its as-frozen shape. Then the Si-G composite was pyrolysed under an argon atmosphere with 10% hydrogen at a flow rate of 70 cm³ min⁻¹, purging for 30 min before the furnace was turned on. Finally, the sample was heated up to

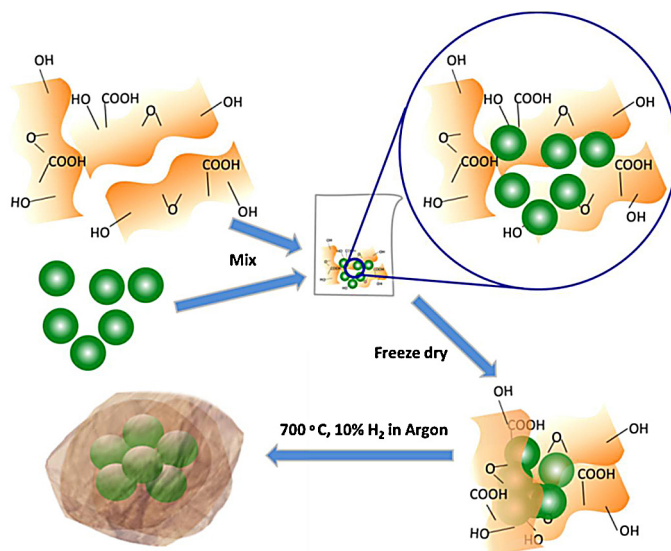


Fig. 1. Schematic view for synthesis of the Si-G composites.

700 °C @ 0.5 °C min⁻¹ and held for 3 hours to generate the final graphene-wrapped silicon composites. Characterization of the graphene formation and Si stability in the as-prepared Si-graphene composites was studied by X-ray diffraction. Field Emission Scanning Electron Microscopy (FESEM) (Zeiss Ultra Plus, UK) and Transmission Electron Microscopy (TEM) (FEI Philips CM300, USA) were utilized to obtain the morphology and further reveal the structure of the composites. Thermal Gravimetric Analysis (TGA) (TA instrument Q500, USA) was used to determine Si/G mass ratio in the composites. TGA testing was performed in air with a temperature range of 25 °C to 900 °C and a ramp rate of 10 °C min⁻¹.

To study the balance between the high capacity of Si and the cycle stability of graphene, as well as optimize battery performance, graphene-wrapped silicon composites were prepared by varying the ratios of the starting materials. The initial Si:GO ratios tested include 1:3, 1:2, 1:1 and 1:0.5, in addition to pure GO and bare Si-NP. The graphene-wrapped composites produced will be further referred to as Si-G 1:3, Si-G 1:2, Si-G 1:1, and Si-G 1:0.5, respectively. Coin cells (CR 2032) were fabricated to study the electrochemical properties of the nanocomposites using a slurry containing: 60 wt% of the active composite material, 20 wt% Super P carbon black as a conductive material, and 20% polyvinylidene fluoride (PVDF). Lithium metal (Aldrich, USA) was used as a counter/reference electrode. The electrolyte was a 1 M LiPF₆ solution with a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (3:7) as a solvent, with no additives. The two electrodes were separated by a polypropylene membrane (high porosity, 20 μm micro porous, Celgard PP2075, USA) and assembled in an argon-filled glove box (MBRAUN 10, USA). Charging and discharging of cells was conducted on battery testing equipment (Neware, China), employing a cut-off voltage range from 0.05 V to 1.5 V. Cyclic voltammetry (CV) was conducted on an electrochemical station (Versa Stat MC, Princeton Applied Research, USA) with a scanning rate of 0.1 mV s⁻¹. All tests above were conducted at room temperature.

3. Results and Discussion

The SEM analysis in Fig. 2 demonstrates the 3D morphology of the synthesized Si-G composites, depicting the well-distributed Si-NP encapsulated by the graphene after freeze-drying and reduction. For Si-G 1:3, shown in the Fig. 2 (a) image, the Si-NPs (homogenous 50–70 nm size distribution, Fig. S1 (a) in Supporting Information)

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