



Research paper

Interconnected silicon nanoparticles originated from halloysite nanotubes through the magnesiothermic reduction: A high-performance anode material for lithium-ion batteries

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ABSTRACT

Silicon (Si) is a promising high-capacity anode material for the next-generation of rechargeable lithium ion batteries (LIBs). Though there are formidable challenges from the large volumetric change during lithiation, well-designed nanostructure and reduced size of Si can remarkably alleviate the negative effects. Herein we apply a magnesiothermic reduction process to synthesize interconnected Si nanoparticles in large quantities. Earth abundant clay of halloysite with tubular structure has been used as silica precursor after acid washing. A high Si yield can be achieved upon pressing the precursor powder into a pallet before reduction. The obtained interconnected Si nanoparticles exhibit a high specific capacity of 3752.4 mA h g⁻¹ for the first cycle at 1 A g⁻¹ and 1469.0 mA h g⁻¹ after 400th cycles at current density of 3.5 A g⁻¹. Even tested at 5 A g⁻¹ for 1000 cycles, a high capacity of 735.1 mA h g⁻¹ is obtained. The rate capability is also evaluated and a high capacity of 1050 mA h g⁻¹ is achieved at 10 A g⁻¹.

1. Introduction

Silicon (Si) based materials have attracted enormous attention due to their important applications in many fields, such as solar energy conversion, electronic devices, photovoltaics, optoelectronics, sensing, and anodes for the rechargeable lithium-ion batteries (LIBs) (Lin et al., 2015). There are many merits for Si as anode materials in LIBs. Compared to commercial graphite anode (372 mA h g⁻¹), Si possesses high gravimetric capacity upon lithiation to Li_{3.5}Si (3579 mA h g⁻¹) (Chevrier et al., 2010). In addition, Si exhibits low lithiation/delithiation voltage (< 0.5 V vs. Li/Li⁺), (Liu et al., 2012a, 2012b; Xue et al., 2013; Zhou et al., 2013) which can retain high open circuit voltage for the full cell and avoid adverse lithium plating process. Low cost, non-toxicity, and elemental abundance in the earth also make it practical and commercially available (Wu and Cui, 2012; Zuo et al., 2017). Although Si has attracted great attention as promising negative electrode for LIBs, there are formidable challenges to replace the current commercial graphite anode due to serious capacity decay originating from their poor electronic conductivity, (Pan et al., 2018) huge volume

change over 300% and gradually enhanced pulverization during the charge-discharge processes, (Zhang, 2011) and continuous consumption of lithium ions during the formation-breaking-reformation process of solid electrolyte interface (SEI) layer (Besenhard et al., 1997; Cho, 2010; Huggins, 1999; Scrosati and Garche, 2010; Szczech and Jin, 2011; Zhang et al., 2004; Zuo et al., 2017). Several strategies are exploited to tackle the aforementioned critical issues, including combining Si with carbon or other materials, (Qu et al., 2012; Simon et al., 2011; Wu et al., 2003) and utilizing nanostructured Si (nanowires, nanotubes, nanoparticles, hollow materials), (Chan et al., 2009; Huang et al., 2014; Lee et al., 2004; Li and Zhi, 2013; Liu et al., 2012a, 2012b; Park et al., 2006; Ryu et al., 2016) to accommodate volume expansion or relieve their inner stress (Choi and Kang, 2015; Jiang et al., 2017).

Recently, considerable effort has been devoted to the preparation of Si based nanomaterials (Liang et al., 2014). In particular, silicon oxides such as silica and silicates were also widely utilized to fabricate nanoscale Si via reduction processes. Lin and coworkers designed a molten salt process to prepare Si nanoparticles through the reduction of silicon zeolite by metallic Al (or Mg) in molten AlCl₃ (Lin et al., 2015).

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However, once the reaction was triggered, the temperature of reactant would rise sharply, and the severe heat accumulation was considered as the main reason for collapsing and poor electrochemical performance. To reduce heat accumulation, sodium chloride (NaCl) is usually introduced in chemical reduction process (Wang et al., 2015). The melting point of NaCl is 801 °C, with a heat capacity of 517.1 J g⁻¹, which can effectively scavenge the heat released in reduction reaction and prevent the reactants from overheating.

Halloysite is a naturally abundant clay mineral with tubular morphology. The external diameter and length is about 20–30 nm and 600 nm, respectively. The chemical composition of halloysite is Al₂Si₂O₅(OH)₄·2H₂O, (Abdullayev et al., 2012; Yah et al., 2012) which is similar to kaolinite except for the presence of an additional water monolayer between the adjacent clay layers. Halloysite nanotubes consist of gibbsite octahedral sheet (Al-OH) groups on the internal surface and siloxane groups (Si-O-Si) on the external surface. In particular, Zhang et al. has reported that gibbsite octahedral layer could be etched, leaving silica nanotubes with porous structure (Zhang et al., 2012). In addition, using halloysite nanotubes as Si source is not only cost-efficient, but also favorable in structure and size. Very recently, Zhou et al. demonstrated the halloysite clay could be converted into Si nanoparticles through a magnesiothermic reduction process at a high temperature of 700 °C for 6 h (Zhou et al., 2016). Thus, it is of great significance to prepare nanoscale Si at a relatively mild condition.

Herein we demonstrated interconnected Si nanoparticles could be synthesized in large quantities through the acid etching and subsequent magnesiothermic reduction of silica nanotubes at 650 °C for 3 h. In particular, after etching by hydrochloric acid, aluminum oxide can be removed from the halloysite, leaving amorphous and porous silica tubes. The mixed precursor could be pressed into a pallet to improve the yield. The morphology evolution of different stage was monitored, exhibiting tubular morphology is difficult to retain. However, the porous structure can be saved after chemical reduction with the addition of NaCl, which can alleviate the volume expansion during lithiation. The interconnected Si nanoparticles with large specific area exhibited a high specific capacity, outstanding cycling stability and excellent rate capability.

2. Materials and methods

2.1. Materials

The clay mineral used in this work was commercial yellowish-brown powder. Hydrochloric acid (HCl), NaCl, Mg powder and hydrofluoric acid (HF), all the chemicals of analytical grade were purchased from China National Pharmaceutical Group. They were used without further purification. Milli-Q water was used throughout the experiments.

2.2. Quantify SiO₂ content in raw halloysite

10 g halloysite was dispersed in a beaker which contains 300 mL 3 M HCl. Then the mixture was continuous agitating and heating to 80 °C for 4 h. To obtain further purified SiO₂, the white product was re-dispersed in 80 mL 3 mol/L HCl and then transferred to a 100 mL Teflon-lined stainless-steel autoclave and kept in an electric oven at 120 °C for 12 h. The amorphous pure SiO₂ was collected by centrifugation, washed several times with water, and dried at 120 °C.

2.3. Magnesiothermic reduction

Purified halloysite was mixed with Mg powder and NaCl at a weight ratio of 1: 0.8: 1. First, purified halloysite was mixed with NaCl dispersed in water and stir for 1 h. Then the mixture was dried in 100 °C oven and accumulated in a mortar. Then Mg powder was added in to mortar and grind together to form a high dispersed mixture. The

mixtures were compacted into a pallet by an oil press under a pressure of 20 MPa for 2 min. And then the wafer was transferred to a corundum crucible. Next, this crucible was placed in a tube furnace fill with argon atmosphere and heated up to 650 °C for 3 h. After the completion of Mg reduction, the resulting powders were dissolved in 100 mL water under mild stirring, 1 M HCl was dropping to this solution to remove residual NaCl as well as Mg, and MgO byproducts and other possible impurities. Finally, the Si was obtained by etching with diluted 2% HF.

2.4. Materials characterization

The crystallographic structures of the materials were determined by a RIGAKU Rint-2000 X-ray diffractometer equipped with Cu – K α radiation ($\lambda = 1.54184 \text{ \AA}$). Scanning electron microscopy (SEM) was tested with a FEI Helios Nanolab 600i field emission scanning electron microscope. Transmission electron microscopy (TEM), and high-resolution images (HRTEM) were obtained with an FEI Tecnai G2 F20 field emission transmission electron microscope operated at 200 kV.

2.5. Electrochemical characterization

The electrochemical properties of as-prepared Si were evaluated through coin type cells (2025 R-type) which were assembled under an argon-filled glove box (H₂O, O₂ < 1 ppm). Metallic Li sheet was used as counter and reference electrode. 1 M LiPF₆ in a mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/EDC; 1: 1: 1 by volume) was served as the electrolyte. For preparing working electrode, the slurry mixed with as-prepared active Si material, carbon black and sodium alginate (SA) binder in a weight ratio of 6: 2: 2 in water solvent were pasted onto a Cu foil. The foil at first dried in air at 60 °C and then dried in a vacuum oven at 100 °C overnight. The typical loading mass of Si was approximately 0.8 mg cm⁻². Galvanostatic charge/discharge (GCD) measurements were conducted using a LAND-CT2001A instrument at room temperature with a fixed voltage range of 0.005–1.5 V (vs. Li/Li⁺). Cyclic voltammetry (CV) was performed on electrochemistry workstation (CHI660D), with a scanning rate of 0.1 mV s⁻¹ at room temperature.

3. Results and discussion

Fig. 1a exhibits the detailed schematic illustration of the different stage, from raw clay powder to pure Si. Fig. 1b displays the corresponding digital photographs of products at different stage. First, pre-purified clay minerals were prepared by HCl washing treatment. Halloysite comprises naturally occurring aluminosilicate nanotubes with a 1: 1 ratio of Al to Si and usually containing a small amount of other metal element, such as Fe, Ti, K, which makes their color yellowish-brown as shown in Fig. 1b. All the metal elements can be removed through inorganic acid etching. After the purified processing with treatment by 3 M HCl at 120 °C, the light orange clay turns white, which remains about 45% in weight. The acid treated halloysite could be totally dissolved in 1% HF, which implies the white powder is silica.

The detail of magnesiothermic reduction are illustrate in Fig. 1c. First we mixed NaCl and pre-treated halloysite in water, and then dried in oven. Next, we added Mg powder and ground in an agate mortar to form a homogeneous mixture. The mixed powder was pressing into a wafer at a pressure over 20 MPa for at least 2 min. The magnesiothermic reduction is actually a solid-phase reaction, thus compacting the reagents can promote the reaction and boost the productivity. A previous report has depict that by tableting treatment, the temperature of the reaction could be reduced to under 500 °C, (Zhuang et al., 2017) which is much lower than traditional condition of magnesiothermic reduction.

The XRD pattern in Fig. 2a i) and ii) shows the transformation process from typical halloysite to amorphous broad peak. Therefore, the white power is mainly amorphous SiO₂. Then SiO₂, mixed with

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