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Hydrothermal Synthesis of Nano-silicon from Silica Sol and its Lithium Ion Batteries Property

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A large-scale hydrothermal synthetic strategy for synthesis of porous silicon nanospheres from industrial silica sol at 180 °C. The hydrothermal synthetic route reported here is relatively simple and low-cost, and the as-prepared porous silicon nanospheres anode delivers a high reversible specific capacity and significantly cycling stability.
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ABSTRACT

There are rare reports concerning hydrothermal synthesis of silicon anode materials. In this manuscript, starting from the very cheap silica sol, we hydrothermally prepared porous silicon nanospheres in autoclave at 180 °C. As anode materials for lithium-ion batteries (LIBs), the as-prepared nano-silicon anode without carbon coating delivers a high reversible specific capacity of 2650 mA h g⁻¹ at 0.36 A g⁻¹ and significantly cycling stability about 950 mA h g⁻¹ at 3.6 A g⁻¹ during 500 cycles.

1 Introduction

Silicon has been considered as a promising anode candidate material for advanced lithium-ion batteries (LIBs) due to their high theoretical capacity (3579 mAh g⁻¹), relatively low discharge potential (<0.5 V versus Li/Li⁺) [1]. However, Si exhibits serious volume change (>270 %) during lithiation-delithiation, which leads to a rapid reduction in capacity [2,3]. Similar with other electrode materials, using Si materials with nanostructure is one of means to relieve this problem [4-9].

For this purpose, various methods have been developed to produce nano-silicon anode materials improving LIBs performance. One of these methods was chemical vapour deposition (CVD) of silanes, by which silicon nanotubes were prepared. Then after SiO₂ surface-coating, the Si/SiO₂ nanotubes shown the long cycle life (6,000 cycles with 88% capacity retention), high specific charge capacity (~2971/1780 mAh g⁻¹ at 0.4 A g⁻¹, ~940/600 mAh g⁻¹ at 24 A g⁻¹) [10].

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Nano-Silicon anode materials are also prepared by the typical magnesiothermic reduction reaction [11-16]. For example, magnesiothermic reduction of SiO$_2$ at 650°C was used to synthesize Si nanotubes, which obtain a capacity of about 1900 mA h g$^{-1}$ at 0.4 A g$^{-1}$ and retention as ~50% after 90 cycles after carbon coating [11].

With regard to wet chemical synthesis of nano-silicon anode materials, much attention has been paid to the preparation in organic solvent [17-19]. For example, nest-like silicon nanospheres were prepared via reaction of NaSi and NH$_4$Br in the mixed solvent of pyridine and dimethoxymethane in autoclave at 80 °C for 24h, which exhibiting reversible specific capacity of 1095 mA h g$^{-1}$ at 2 A g$^{-1}$ after 50 cycles. Si nanoparticles were produced by reduction of SiCl$_4$ with naphthalene sodium in anhydrous tetrahydrofuran at 380 °C in Hastelloy Parr reactor, which showing specific charge capacity of 3535 mA h g$^{-1}$ at 0.9 A g$^{-1}$ and retention as 96 % after 40 cycles after carbon coating [17]. Si nanoparticle were synthesized via reduction of anhydrous SiCl$_4$ with sodium potassium alloy (NaK) in toluene solution under reflux for 4 h, followed by oxidation, the resulting sample as Si/SiO$_2$/SiO$_2$ shows an initial charge capacity of 610 mA h g$^{-1}$ at 0.2 A g$^{-1}$, good cycling stability (maintained at ~600 mA h g$^{-1}$ after 350 cycles) [20]. Recently, it is reported aqueous synthesis of hydrophilic silicon nanoparticles (~2.2 nm) based on the reaction of (3-Aminopropyl) trimethoxysilane (CH$_3$SiO$_3$N$_2$) and trisodium citrate dihydrate under the microwave irradiation at 140 °C [21]. Silicon nanowires were also grown in an aqueous solution [22]. Previously, we have fabricated silicon micromaterials by reducing crystalline Na$_2$SiO$_3$:9H$_2$O with Mg in autoclave at 200 °C [23]. After combined with graphene, the as-prepared anode shows reversible capacity of ~600 mA h g$^{-1}$ at the current density of 3.6 A g$^{-1}$ after 360 cycles.

In this study, we hydrothermally prepared porous silicon nanospheres by reducing silica sol with metallic magnesium in autoclave at 180 °C. Moreover, besides silica sol, this hydrothermal reduction reaction can be extended to the reduction of solid silica powders such as silica aerogel and silicic acid (hydrated silica). The as-prepared nano-silicon anode delivers a high reversible specific capacity of 2650 mA h g$^{-1}$ at 0.36 A g$^{-1}$ and cycling stability about 950 mA h g$^{-1}$ at 3.6 A g$^{-1}$ after 500 cycles.

2 Experimental

2.1 Materials

30% alkaline silica sol (industrial, pH = 13) was purchased from GuangZhou Sui Ze Environmental Protection Technology Co., Ltd (China, http://www.yuancailiao.net/company/shop1383670764546/index.aspx). Mg (99%, 100-200 mesh powder), HCl (37%) and Hydrofloric acid (≥ 40%) were purchased from Sinopharm Chemical Reagent Co., Ltd (China).

2.2 Hydrothermal synthesis of nano-silicon

The porous silicon nanospheres were prepared by reduction of industrial silica sol with magnesium according to hydrothermal reduction reaction under the stainless autoclave. 2.2g silica sol and 1.5g Mg powder were mixed and added into a 20 mL stainless autoclave before sealed. Subsequently, the autoclave was maintained at 180 °C for 10 h and cooled to room temperature. Here, the temperature as 180 °C is the lowest temperature in such reaction of silica sol and Mg. The samples were immersed in hydrochloric acid (1 mol L$^{-1}$) for several hours to remove MgO. The resultant solution was washed with distilled water and centrifuged (5000 rpm, 5 min) to collect silicon. The obtained silicon was dissolved in 10 wt% dilute HF solution for 10 min to remove unreacted silica and other impurities during reduction. The brown-black precipitate was collected by centrifuge, washed with deionized water and ethanol and dried for overnight at 60 °C in vacuum oven to evaporate rest solvent. We also tested the synthesis of silicon materials by using other kinds of silicon precursor such as silica aerogel and silicic acid (hydrated silica). Experimental detail is shown in supporting information.

2.3 Material Characterization

The morphology of the reaction product were
characterized by scanning electron microscopy (SEM, JEOL-JSM-6700F), Transmission electron microscopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). X-ray diffractometer (XRD) was performed on a Philips X’ Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å). The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore distribution plots were measured on a Micromeritics ASAP 2020 accelerated surface area and porosimetry system. Before analysis, the samples were allowed to dry under vacuum and degas at 300 °C for 0.5h under vacuum (10⁻³ bar).

2.4 Electrochemical Measurement

The electrochemical properties of nano-silicon electrodes were measured with coin-type half cells (2016 R-type) which assemble under an argon-filled glove box (H₂O, O₂ < 1 ppm). Working electrode was prepared by mixing the nano-silicon material, super P carbon black and sodium alginate (SA) binder in a weight ratio of 60:20:20 in water solvent. The slurry was pasted onto a Cu foil and then dried in a vacuum oven at 80 °C for 12 h. The active material density of each cell was determined to be 0.5-1.0 mg cm⁻². Metallic Li sheet was used as counter electrode, and 1 M LiPF₆ in a mixture of ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by Volume) and 10 wt% fluoroethylene carbonate (FEC) was used as the electrolyte (Zhuhai Smoothway Electronic Materials Co., Ltd (china)). Galvanostatic measurements were made using a LAND-CT2001A instrument at room temperature that was cycled between 0.005 V and 1.50 V versus Li/Li at a rate of 0.36-18 A g⁻¹.

3 Results and discussion

Silica sol was converted into H₂/Si as-prepared products by the hydrothermal reduction process with Mg under the stainless steel autoclave. X-ray powder diffraction (XRD) analysis (Figure S1) confirmed the main component of MgO and Si in the reacted specimens. A trace amount of Mg(OH)₂ and Mg₂SiO₄ was also detected from the XRD pattern. The composite reacted specimens were then immersed in a 1 M HCl solution for several hours to remove MgO and Mg(OH)₂ (Fig. S2) and further dissolved in HF solution to remove unreacted silica and other impurities during reduction. The XRD pattern of the resulting silicon-based product is shown in Figure 1a. All the peaks can be indexed to the cubic silicon (JPCDS 27-1402) with calculated lattice constants of a=5.408 Å, which is close to the reported value of 5.430 Å. The yield of this Si material is above 25%. Moreover, 2p Si XPS (X-ray photoelectron spectroscopy) spectrum of the as-prepared sample (Figure 1b) exhibits that besides the strong peak of silicon at 99 eV, a weak peak at 103.5 eV appears, indicating the existence of small amount of amorphous SiO₂.[24]

Figure 2 is the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-prepared nano-silicon. From the SEM image (Figure 2a), one can see that the as-prepared silicon is composed of uniform sphere-like nanoparticles with average diameter of 80 nm. TEM image in Figure 2b shows the presence of pores in the spherical nanostructures, which is further confirmed by the enlarged TEM image of Figure 2c. It is obvious that the primary pores with the size of several nanometers are homogeneously distributed. A HRTEM image in Figure 2d taken on the edge of an individual nanosphere presents that the porous nanosphere is composed of many nanocrystallites and porous size is 2-5 nm. The interplanar spacing is about 3.1 Å, corresponding to the (111) planes of the crystalline Si. Nitrogen adsorption measurements (Figure S3) indicated that the specific surface areas of nano-silicon were about 11 m² g⁻¹. BJH analyses (Figure S4) of the nitrogen desorption curves indicated that the porous Si nanosphere possessed a large amount of nanoporous (~4nm and ~10nm) and a small amount of macroporous.

Moreover, we also synthesized silicon materials by using other kinds of silicon precursor such as silica aerogel and silicic acid (hydrated silica). Experimental detail is shown in supporting information (Extension experiment 1, 2). XRD, SEM and TEM analysis (Figure S5-8) clearly reveals that the crystalline phase of nano-silicon can be analogously hydrothermal synthesized by using
other kinds of silicon precursor under the low temperature (~200 °C).

Different with the previous reports, silica sol hydrothermal reduction proceeds through the formation of active H intermediates. First, the reaction of H₂O and Mg by the reaction equation as H₂O + Mg = MgO + H₂ (ΔH° = -316 KJ mol⁻¹) could produce highly reaction heat in instant to stimulate the following reaction for the production of silicon. On the other hand, based on the chemical potential evaluation E(H/H₂O) = -0.93, E(Mg/Mg²⁺) = -2.36 and E(Si/SiO₂) = -0.86 (where E° is the standard potential), reaction as (1) Mg + H₂O = MgO + 2H, (2) H +SiO₂ = Si +H₂O and (3) Mg +SiO₂ = MgO + Si are thermodynamically spontaneous. It is proposed that the generating of the active H intermediates will promote the reaction, which is similar to the Clemmensen reaction in traditional organic synthesis [25]. In Clemmensen reaction, active H intermediates generated from Zn and HCl to transform methylene from carbonyl. Moreover, such silica sol hydrothermal reduction reaction can be carried out even lower than 180 °C through activated the reaction of active H intermediates formation by adding acid, which provide the direct proof that the formation of active H intermediates should facilitate the reaction to silicon. An Extension experiment by adjusting the pH of reaction system has been provided in Supporting Information (Extension experiment 3 and Figure S9).

The electrochemical performance of spherical porous Si nanostructures as anode was investigated in CR2016 coin cells with lithium foil as a counter electrode. Figure 3a shows typical voltage curves during the first 5 cycles in the voltage window of 0.005–1.50 V versus Li/Li⁺ at a current density of 0.36 A g⁻¹. In the first discharge curve, a discharge plateau at around 0.8 V was assigned to the formation of a solid electrolyte interface (SEI) layer, which disappear in the following cycle and relate to an initial irreversible capacity loss. [12, 26, 27] The discharge plateau located at around 0.2 V is related to the alloy formation process between Li and crystal Si. [28, 29] Subsequent discharge and charge cycles curves had the voltage profiles characteristic of amorphous Si. [30, 31] The porous silicon nanospheres anode delivers initial discharge and charge capacities of 4055 and 3015 mAh g⁻¹ at 0.36 A g⁻¹, respectively, corresponding to a first cycle coulombic efficiency (CE) of 74%. The irreversible capacity loss can be mainly attributed to the formation of SEI layer on the electrode surface and presumably arises partly from electrolyte decomposition, partly from electrically disconnected particles due to the large volume changes, [10] and perhaps also from Li atoms “trapped” in the electrically connected particles. [32, 33] Meanwhile, after cycling up to 40 cycles at 0.36 A g⁻¹, the porous silicon nanospheres anode retained 2650 mAh g⁻¹ (Figure 3b), corresponding to about 89 % of its initial charge capacity (3015 mAh g⁻¹). Furthermore, the coulombic efficiency retains near 100 % after the first cycle, which means that the porous silicon nanospheres structure can enhance the coulombic efficiency of the electrode due to the increasing of the active sites for reversible electrochemical Li storage [14]. A capacity of 950 mAh g⁻¹ after 500 cycles at a higher current density of 3.6 A g⁻¹ and good capacity retention were also attained, with the first three cycles activated at 0.72 A g⁻¹ (Figure 3e). Some oscillations in the specific capacity values over several cycle periods could sometimes be observed (Figure 3e), while neither the average value of the specific capacities, nor the ability for long cycles were affected. Such oscillations have sometime been observed in the previous reports for not only Si anodes [34-36] but other kind of electrode materials [37, 38]. The slight capacity oscillations might result from the temperature variation (the inside of the cell and the measurement environment, Figure S10-11 for temperature variation measure), the surface condition and the active site of the sample and the SEI layer thickness [39].

The rate capability for the spherical porous Si anode is evaluated using galvanostatic charge-discharge measurements with increasing the current density from a low current density of 0.36 A g⁻¹ to a high current density of 18 A g⁻¹ and then back to 1.8 A g⁻¹ and 0.72 A g⁻¹ (showing in Figure 3 c-d). The discharge specific capacity is ~2900, 2600, 2000, 1500, 800 and 350 mAh g⁻¹ and the coulombic efficiency is almost 100% at the current density of
0.36, 0.72, 1.8, 3.6, 7.2, and 18 A g\(^{-1}\), respectively. It is worthwhile to indicate that the specific capacity reversibly recovers to approximately 1800 mAh g\(^{-1}\) once the current density goes back to 1.8 A g\(^{-1}\) and then go back to about 2450 mAh g\(^{-1}\) when the current density back to 0.72 A g\(^{-1}\). The specific capacity is almost recovered, indicating a fine rate performance of such silicon anode. The high electrochemical performance of the silicon may be attributed to the porous nanostructure \[12, 40, 41\] as well as the presence of amorphous SiO\(_2\)\[10, 42, 43\]. The porous nanostructure offers a path way for the efficient access of electrons and electrolytes, increased number of active sites and enhanced the contact surface between the electrode material and electrolyte. Besides, the existence of pore and amorphous SiO\(_2\) may effectively accommodate the volume changes of silicon and allow for facile strain relaxation without strong mechanical stress during cycling. It would provide a new avenue for large-scale production of high electrochemical performance anode materials.

4 Conclusions

In conclusion, porous Si nanospheres were hydrothermally synthesized based on the reduction of silica sol by magnesium metal in autoclave at 180 °C. Moreover, besides silica sol, this hydrothermal reduction reaction can be extended to the reduction of solid silica powders such as silica aerogel and silicic acid (hydrated silica). The porous Si nanospheres without carbon coating exhibit excellent lithium-storage capacity, high-rate capability and long cycling performance, which may be attributed to the porous nanostructure as well as the presence of amorphous SiO\(_2\). Since the reactant is cheap and the reaction condition is relatively mild, this study would provide a new avenue for large-scale production of silicon anode materials.

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Figure 1  a) XRD pattern and b) XPS spectrum of the porous Si nanospheres after hydrothermal reduction silica sol process.

Figure 2  The morphology, size, and structure of the resulting porous Si nanospheres. a) SEM and b-c) TEM image of the spherical porous silicon. d) HRTEM image taken on the edge of an individual nanosphere.
Figure 3 Electrochemical performances of spherical porous silicon anode. a) Typical galvanastatic discharge-charge curves of the cell with spherical porous silicon in the potential region of 0.005–1.5 V versus Li⁺/Li at a current density of 0.36 A g⁻¹. b) Cycling property and coulombic efficiency of the cell with spherical porous silicon at the constant current density of 0.36 A g⁻¹. ■ as discharge capacity (Q_d), ● as charge capacity (Q_c) and ◆ as coulombic efficiency (Q_c/Q_d). c) The typical galvanastatic discharge–charge curves of spherical porous silicon at different current densities, and d) the rate performance of spherical porous silicon anode. e) Cycling property at 3.6 A g⁻¹ for 500 cycles.