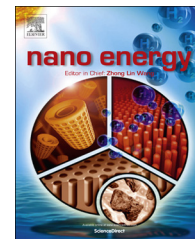


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COMMUNICATION

A stable nanoporous silicon anode prepared by modified magnesiothermic reactions



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Abstract

Porous silicon prepared by low-cost and scalable magnesiothermic reactions is a promising anode material for Li-ion batteries; yet, retaining good cycling stability for such materials in electrodes of practical loading remains a challenge. Here, we engineered the nanoporous silicon from a modified magnesiothermic reaction by controlled surface oxidation forming a <5 nm oxide layer on the 10–20 nm Si nanocrystallites. High loading electrodes of ~3 mAh/cm² demonstrates stable cycling with ~80% capacity retention over 150 cycles. The specific discharge capacity based on the total electrode weight is ~1000 mAh/g at the lithiation/delithiation current density of 0.5/0.75 mA/cm². This work reveals the importance of the surface treatment on nanostructured Si, which will lead to a well-controlled ratio of silicon and surface oxide layer and provide guidance on further improvement on silicon-based anode materials.

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Introduction

Silicon (Si) has ~10 times theoretical specific capacity of graphite and is one of the most promising anode for Li-ion batteries used in long range electrical vehicles [1]. However, practical use of Si is largely limited by both the unsatisfactory electrochemical performance and challenges associated with

the high manufacture cost and poor scalability. Si materials experienced large volume expansion and contraction under lithiation and delithiation, which leads to pulverization of large Si particles (>200 nm) and subsequent loss of electrical contact, repeated breaking/formation of solid electrolyte interphase (SEI) and continuous consumption of electrolyte [1–4]. As a result, Si electrodes, especially at high mass loading, exhibit rapid capacity fade upon electrochemical cycling. There has been tremendous effort on understanding and mitigation of the capacity fading using nanostructured Si materials including the synthesis of ultra-fine Si nanoparticles (<50 nm), surface coating, development of new binders, and design of novel

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nanostructured Si materials such as nanowires, nanotubes, hollow spheres, and core-shell structures [5-41]. Recently, pomegranate-like Si-C yolk-shell structures have demonstrated over 100 stable cycles at high loading Si electrodes [32]. Porous Si and Si-based composites with the pre-engineered void space to accommodate the volume change of Si and a surface coating layer to minimize the electrolyte decomposition and stabilize the SEI layer, can have limited apparent volume change of Si particles and greatly improved electrochemical performance of Si anode even at relatively high loading [13,23-29,32-34,36]. Recently, porous Si prepared by electrochemical etching also demonstrates good long-term cycling stability at high Si loading conditions [33]. Electrodes of high area-specific-capacity of $\sim 1.5 \text{ mAh/cm}^2$ and 3 /cm^2 demonstrated $\sim 92\%$ capacity over 300 cycles and $\sim 90\%$ capacity retention over 100 cycles, respectively. Micro-sized porous Si obtained from the disproportionation reaction of SiO was composited with engineered graphene wrap or nonfilling carbon coating and demonstrated stable performance over 100 cycles at an area-specific-capacity $\sim 3 \text{ /cm}^2$ [29,34,36]. However, scalable low cost production of porous Si materials with good long term cycling stability at high mass loading remains a significant challenge.

Magnesiothermic reaction (MR) is a well-known low-cost and scalable approach for the production of Si materials. Since 2007, various kinds of Si nanostructures including nanocrystals, nanotubes, nanowires, and porous films have been synthesized using MR with different silica precursors [25,27,35,37-47]. Yet, because of the exothermic nature of the MR, the local reaction temperature is much higher than the set temperature and hence results in great difficulty in controlling the nano structure of the produced Si. Recently, a modified MR with the use of heat scavenger has demonstrated good control on the local reaction temperature and subsequent nano-structure of Si product [48]. Porous silicon spheres or nanowires prepared by the method demonstrated good performance as Li-ion battery anodes [40,41]. In this study, we engineered the porous Si by modified MR with controlled surface oxidization and demonstrated its good performance as stable high loading Li-ion battery anodes. The engineered porous Si has a surface oxide coating layer of $\sim 2\text{-}5 \text{ nm}$ on the Si nanocrystallites of $\sim 10\text{-}20 \text{ nm}$. High loading electrodes of $\sim 3 \text{ /cm}^2$ area-specific-capacity demonstrates stable cycling with $\sim 80\%$ capacity retention over 150 cycles, similar to the porous Si from anodization. The specific discharge capacity based on the total electrode weight is $\sim 1000 \text{ mAh/g}$ at the lithiation/delithiation current density of $0.5/0.75 \text{ mA/cm}^2$. These results suggest that stable bulk Si anode materials from low cost scalable production are possible even at deep lithiation and high loading conditions required for practical applications.

Material and methods

Synthesis

Magnesiothermic porous Si was prepared via a modified reaction with NaCl as the thermal scavenger [48]. Diatom with the size of $\sim 10 \mu\text{m}$ was dispersed to an aqueous NaCl solution under stirring at room temperature (Silica/NaCl: 1/10 in weight). The mixture was heated to $60 \text{ }^\circ\text{C}$ under vigorous stirring followed by drying under vacuum at $150 \text{ }^\circ\text{C}$ to remove water. Dried diatom/NaCl powder (11 g)

and 0.9 g Mg powder was ground together under an Ar atmosphere and then sealed in a Swagelok[®] reactor. Then, the diatom/NaCl/Mg mixture was heated in a tube furnace at $650 \text{ }^\circ\text{C}$ for 2.5 h under an Ar atmosphere. After cooling to room temperature, the obtained products were first immersed in a $\text{H}_2\text{O}/\text{EtOH}$ solution, where NaCl can be recycled by drying the filtrate. Then, 1 M HCl and 5% aqueous HF were used to remove MgO and excess diatom precursor, respectively. Finally, the products were collected, washed with EtOH, and vacuum-dried at $60 \text{ }^\circ\text{C}$ overnight. Surface oxidization of the magnesiothermic porous Si was carried out by calcining the sample in a box furnace in air at $500 \text{ }^\circ\text{C}$ for 1 h.

Electrochemical etched porous Si was prepared according to the procedure reported before [33] by electrochemical etching of heavily boron-doped, $\langle 100 \rangle$ oriented single crystal Si wafers ($< 1 \text{ m}\Omega \text{ cm}$ resistivity, Siltronix Inc.) by application of a constant current density of $\sim 225 \text{ mA/cm}^2$ for 358 s in an aqueous 48% hydrofluoric acid (HF)/ethanol electrolyte (HF: EtOH=3:1, v-v). A freestanding film of the MSS was then removed from the crystalline Si substrate by application of a constant current density of $\sim 10 \text{ mA/cm}^2$ for 750 s in an aqueous HF/ethanol electrolyte (HF: EtOH=1:30, v-v). The film was washed several times with ethanol, then fractured by ultrasonication in ethanol to form $\sim 40\text{-}\mu\text{m}$ particles, and dried for further use.

Carbon coating was conducted using a vacuum CVD system. The porous Si sample was loaded in a tube furnace, which then was evacuated at room temperature to a vacuum level of $\leq 1 \text{ mTorr}$. The furnace was heated to $600 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}$, and when at $600 \text{ }^\circ\text{C}$, the precursor gas (argon: acetylene=9:1) was introduced. The furnace temperature was increased to $690 \text{ }^\circ\text{C}$ and maintained at that temperature for 30 min. After carbon deposition, the furnace was cooled to room temperature in pure argon.

Characterization

XRD spectra were obtained on a Philips X'Pert X-ray diffractometer using a Cu K_α sealed tube ($\lambda=1.54178 \text{ \AA}$) at $0.5^\circ \text{ min}^{-1}$. SEM measurement were conducted on an FEI Helios Nanolab dual-beam focused ion beam scanning electron microscope (FIB/SEM). After cycling, the samples were obtained from disassembled cells, washed three times with anhydrous diethyl carbonate, and dried in the antechamber of the glove box under vacuum. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) measurements were performed using an FEI Titan 80-300 microscope operating at an accelerating voltage of 300 kV .

Electrochemical measurement

The electrode was prepared by mixing an appropriate amount of the carbon-coated porous Si sample with Super P (Timcal), and carboxymethyl cellulose sodium salt (Na-CMC, Sigma Aldrich) in distilled water to form a slurry, which was then pasted on a copper foil (Pred. Materials International, Inc.). The Si loading in the mixture was kept at $\sim 50 \text{ wt}\%$. The binder of Na-CMC was kept at $20 \text{ wt}\%$ in all electrodes. After drying in vacuum at $70 \text{ }^\circ\text{C}$, the electrodes were tested in coin cells with Li metal as the counter and the reference electrode. The

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