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Periodic porous silicon thin films with interconnected channels as durable anode materials for lithium ion batteries

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HIGHLIGHTS

- Free-standing porous Si films with interconnected channels have been fabricated.
- These PSi films as anode deliver a high reversible specific capacity over 2500 mAh g^{-1}.
- The special porous structure plays an important role in stabilizing the anodes.

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ABSTRACT

A novel porous Si (PSi) films with interconnected channels and periodic nanostructures are fabricated by a facile electrochemical etching method. The films thus obtained feature highly porous structures with nano-branches connecting pores, possessing periodically varying porosity profiles along the film thickness direction. These periodic porous Si films are found to be promising anode materials for rechargeable lithium ion batteries with a high reversible specific capacity over 2500 mAh g^{-1} and capacity retention over 83% after 60 cycles, which compares favorably with the conventional Si-based electrodes, including the commercially available Si nanoparticles, sputtered Si thin films, and the normal porous Si films with homogenous porosities. The improved cycling stability achieved on the periodic porous Si film is ascribed to its special nanoporous morphology featuring high surface area, interconnecting nano-branches, and structural periodicity, which helps efficiently accommodate the volume expansion and contraction along both the vertical and the planner directions during lithiation and delithiation.

1. Introduction

Li-ion batteries (LIBs) are powering most of today's portable electronics, such as laptop computers, cell phones and cameras, etc. LIBs are also generally considered as the most promising power sources for defense applications, hybrid electric vehicles, and electric vehicles [1]. To realize these demanding applications, high specific energy and power density is essential. However, in the present commercial Li-ion batteries, graphite-based materials with a very low theoretical capacity of 370 mAh g^{-1} are commonly used as the anode materials. To improve the energy density of LIBs, a major challenge is to develop alternatives having higher theoretical capacity than the conventional graphite anode materials. In this regard, Si has attracted great attention due to its extremely high theoretical lithium storage capacity (4200 mAh g^{-1}) and being the second most abundant element on earth [2,3]. However, the potential of Si-based anodes has not been fully realized due to the huge volume change (>400%) during the lithiation and delithiation processes of Si which result in pulverization and cracking of the Si anodes [4,5]. Recent studies on Si nanostructures such as nanowires [6–10], macro- [11–13], meso- [14,15] and nano-porous materials [16–18], nanocomposites [2,19–21], thin films [22,23], and nanotubes [24–26] show great promise in overcoming this issue by utilizing specific geometries to accommodate the volume changes and strain relaxation during lithiation and delithiation [27,28].

Among the various nanostructured Si anode materials for LIBs, porous nanomaterials are particularly attractive for its capability to

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accommodate volume changes [29]. For instance, Cho et al. produced Si-based porous particles by chemically etching SiO_2/Si composites which show much improved capacity retentions than Si/carbon composites or Si nanoparticles [12]. Recently, Maier et al. synthesized macroporous Ag-decorated Si anodes with homogeneous macropores (~200 nm wide) using a magnesiothermal method. A remarkable reversible capacity of 2122 mAh g^{-1} at a rate of 1C after 100 cycles was obtained [11]. The observed performance enhancement is attributed to the presence of macropores, which act as interconnected buffer cushions to alleviate the volume change during lithiation/delithiation. These studies clearly demonstrate the merits of porous structures on improving the electrochemical performance of Si LIB anodes.

However, most of the reported studies on Si-based porous LIB anode materials are based on porous particles that are fabricated by thermal methods or templating methods, which often entails harsh fabrication conditions or complex multi-step procedures. By contrast, little attention has been paid to the electrochemically etched porous silicon (PSi) films. On the other hand, electrochemical etching has proven to be a powerful bottom-up fabrication method to enable Si-based porous nanomaterials in a one-pot one-step manner. By simply controlling the etching current waveform, etching time, and etchant composition, PSi with different structure features (e.g., pore size, porosity, and film thickness) and advanced architectures (e.g., multi-layered structures) can be conveniently fabricated.

To our knowledge, reports on electrochemically etched PSi LIB anode materials are few. Liu et al. [13] first reported a microporous Si anodes which feature micron-sized cylindrical pores that are isolated from each other, delivering a reversible specific capacity of 43 μAh cm^{-2}. It should be pointed out that in this pioneering work the PSi anodes were tested with the Si substrates attached, which made it difficult to accurately evaluate the PSi anodes, considering that the Si substrates may also work as active materials for lithium storage. Following this pioneering work, macroporous Si with [30] and without added conductive binders [31] was reported by Biswal et al. and Yan et al. More recently, Foll et al. showed a type of free-standing Si microwire whose geometry can be fine-tuned for anode applications [32,33]. However, to our best knowledge, there is the first study of applying periodic mesoporous Si in lithium ion battery anodes.

In this paper, we report a facile electrochemical etching method to fabricate free-standing porous Si LIB anode materials which feature inter-connected channels and periodic nanostructures and exhibit much enhanced performance particularly in terms of specific capacity and cycling stability comparing to the previous Si structures. The free-standing nature of the fabricated PSi film eliminates the disturbance from the silicon substrates on the evaluation accuracy of the PSi film as LIB anode materials. The interconnected nanoporous and periodic nanostructures of the fabricated PSi films are desirable for electrolyte penetration and accommodating volume changes and strain relaxation during the lithiation and delithiation.

2. Experimental

2.1. Materials preparation

PSi films were prepared by electrochemical etching of silicon wafers (p-type, B-doped, <1 mΩ cm resistivity, polished on the (100) face, from Siltronix, Inc.). The etching solution consisted of a 1:3 (v/v) mixture of absolute ethanol and aqueous 48% HF. Electrochemical etching was carried out in a Teflon cell using a two-electrode configuration. The current density was modulated with a sine wave, which oscillated between 125 and 208 mA cm^{-2} for 90 repeats with a typical periodicity of 1.7 s, to generate a periodically varying porosity profile along the film thickness direction. Removal of the PSi film from the Si wafer was performed with a short DC current pulse of 618 mA cm^{-2} at the end of the etching, resulting in a free-standing PSi film floating in the electrolyte. The PSi film was carefully collected and transferred onto a Cu foil, rinsed with ethanol and acetone for several times, and then dried in a vacuum oven. After drying, the PSi films were found adhering closely onto the Cu foils, which as a whole were directly employed as the LIB electrode for electrochemical characterizations. The fabricated free-standing PSi film was circular with a diameter ~1.0 cm. Some edge area of the PSi film might be broken when the film was transferred onto the Cu foil for the anode application. The final size of the PSi film on the Cu foil was usually measured to be ~0.6–0.8 cm.

For comparison, free-standing normal porous Si films with homogenous porosity along the film thickness were fabricated with a DC etching step at 166.5 mA cm^{-2} for 120 s followed by an electropolishing step as described above. Traditional Si thin-film electrodes were fabricated by depositing Si on Cu foils using the DC magnetron sputtering method as described in a previous report [22]. For the electrode based on the Si nanoparticle, a paste was made by shock-milling 70 wt% of the commercial Si nanoparticles (mean particle size of ~100 nm, Aldrich), 20 wt% carbon black, and 10 wt% PVDF dissolved in *N*-methylpyrrolidinone, and then blade-coated on Cu foils. We performed the cycling test under constant temperature at a fixed current rate of 0.1C. The cut-off charging and discharging voltages were set at 2.0 V and 0.05 V, respectively.

2.2. Morphology characterizations

Sample morphologies were examined with a scanning electron microscope (SEM) (JEOL-820) and a transmission electron microscope (Philip CM-20) and a high resolution transmission electron microscope (JEOL-2100F). Material porosities were measured using the BET method (Quantachrome Nova 1200e). X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2550 XRD instrument using Cu Kα radiation ($\lambda = 1.5405$ Å).

2.3. Cell assembly and electrochemical characterizations

Electrochemical characterizations were performed using Swagelok-type cells. The as-prepared Si-based films on Cu foils were directly used as positive electrodes for electrochemical characterizations. The Swagelok-type cells were assembled in an argon-filled glove-box with a Li metal foil as the counter electrode, the Si materials as working electrode, one sheet of glass fiber disk and one layer of Celgard 2025 as the separators, and an ethylene carbonate/dimethyl carbonate (1/1:w/w) solution of $LiPF_6$ (1 M) as the electrolyte. Electrochemical experiments were carried out with an Arbin BT 200 Battery Testing System at room temperature.

3. Results and discussion

The synthesis scheme followed to prepare the free-standing PSi films is outlined in Fig. 1.The porosity, pore size, layer thickness, and layer number of the PSi films can be easily tuned by adjusting the etching current waveform used for fabricating the free-standing PSi films. For the free-standing periodic PSi film studied in this report, the porosity was measured to be 51% by the BET and the pore size around 10–50 nm by the SEM. The XRD results indicate that the prepared PSi films are highly (100)-oriented (Fig. S2 in the Supporting information).

Figs. 2 and 3 show the cross-sectional SEM and TEM images of the fabricated periodic porous Si films. The film thickness is about