

# Nanoporous silicon flakes as anode active material for lithium-ion batteries



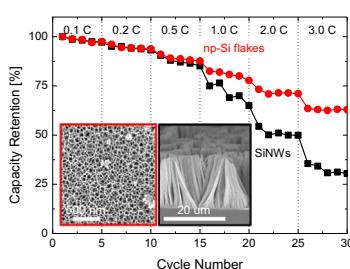
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## HIGHLIGHTS

- Nanoporous-silicon flakes were prepared by an electrochemical etching process.
- This method is a simple, reproducible, and cost-effective way to make high-capacity LIBs anode.
- The np-Si flake anode demonstrates a high performances compared with that of SiNWs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nanoporous-silicon (np-Si) flakes were prepared using a combination of an electrochemical etching process and an ultra-sonication treatment and the electrochemical properties were studied as an anode active material for rechargeable lithium-ion batteries (LIBs). This fabrication method is a simple, reproducible, and cost effective way to make high-performance Si-based anode active materials in LIBs. The anode based on np-Si flakes exhibited a higher performances (lower capacity fade rate, stability and excellent rate capability at high C-rate) than the anode based on Si nanowires. The excellent performance of the np-Si flake anode was attributed to the hollowness (nanoporous structure) of the anode active material, which allowed it to accommodate a large volume change during cycling.

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## 1. Introduction

Today, the development of rechargeable, long-lasting lithium-ion batteries (LIBs) continues to be of great technological importance because of their increasing use in portable electronics such as smart phones, laptops and digital cameras [1–5]. LIBs are also used in plug-in hybrid electric vehicles, handheld power tools, wireless communications and smart wearable devices [6–8].

Therefore, developing new electrodes (cathode and anode) with a higher capacity or higher energy density remains one of the most important and urgent issues in LIB research [9–13]. Currently, the most widely used anode active material for rechargeable LIBs is graphite. However, the theoretical specific capacity of graphite is 372 mA h/g, and due to the capacity limit of graphite, the energy density of a LIB cannot satisfy the requirements of portable electronics devices [3–5]. To meet the increasing demand for LIBs with high-energy density, much effort has been made to explore new anode active materials such as Si, Graphene (G), Germanium (Ge) and Tin (Sn) [9–11,14–17].

In the past decade, Si-based anodes have been widely studied because of their high theoretical specific capacity of ~4200 mA h/g, which is far larger than that of graphite (372 mA h/g) [9–11]. However, the volume of Si changes by about 400% during repeated

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insertion and extraction of lithium (Li) ions. This structural stress leads to cracking and pulverization of the Si anode, resulting in a loss of electrical contact with the current collector and rapid fading of capacity [4,9–12].

Recently, hollow-structured Si nanomaterials, such as porous Si nanowires (*p*-SiNWs), Si nanotubes (SiNTs), and porous Si nanoparticles (*p*-SiNPs) have been studied as anode active materials that can accommodate large volume changes and avoid rapid capacity fading during cycling because of their one-dimensional (1D) properties, including small size, large surface area, and stress alleviation induced by the distance between neighboring nanostructures [4,9–12]. Yi Cui et al. first reported the highly stable cycling of SiNT-based LIB anodes. The LIB anode, consisting of active SiNTs surrounded by an ion-permeable silicon oxide shell, can cycle over 6000 times in half-type cells while retaining more than 85% of its initial capacity [18]. Some research groups have proposed the porous Si-based anodes for high-performance LIBs. However, most of the fabrication (or synthesis) methods for porous Si-based anode active nanomaterials necessitate complex and expensive technologies [19–23]. Cho et al. reported a fabrication method to form porous bulk Si particles by the thermal annealing and etching of physical composites obtained from butyl-capped Si gels and Si dioxide (SiO<sub>2</sub>) nanoparticles at high temperature (900 °C) under an Argon (Ar) atmosphere [19]. Kang et al. reported a synthesis method for SiNTs using a surface sol-gel reaction on electro-spun organic nanowires [23]. Therefore, facile and cost effective approaches are essential for fabricating the Si-based nanoporous materials for high-performance LIB anodes.

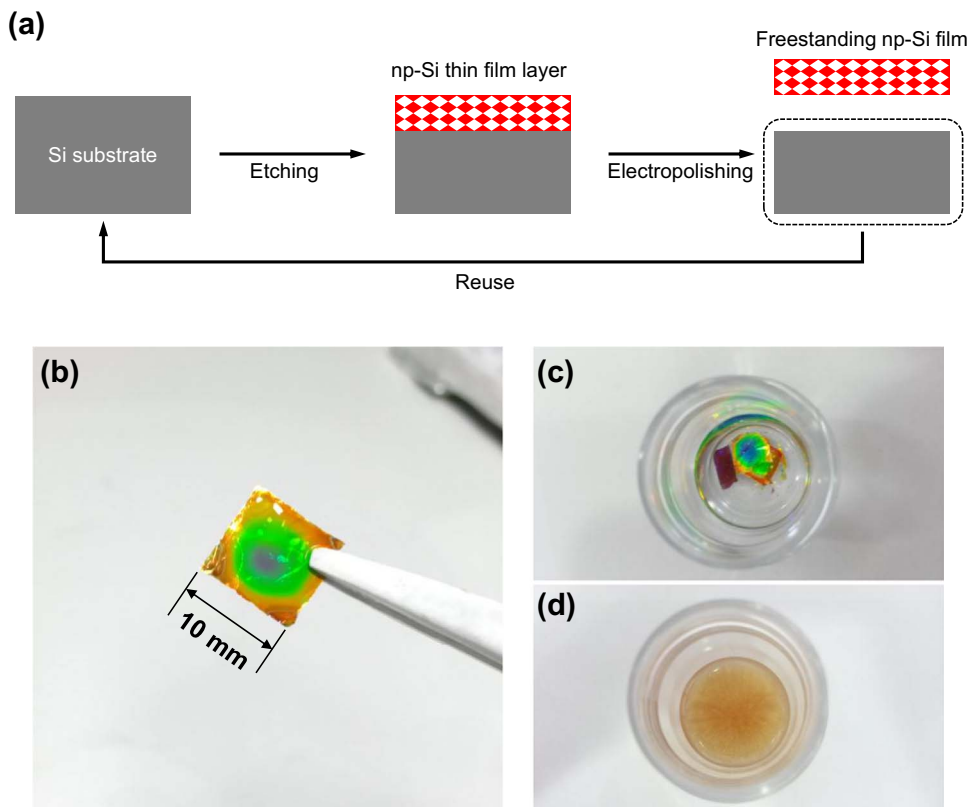
We devised a facile method for fabricating nanoporous Si (np-Si) flakes and investigated their capacity performance and stability as an anode active material for rechargeable LIBs. The np-Si flakes were obtained from a Si substrate using a combination of an

electrochemical etching method and an ultra-sonication treatment. The prepared np-Si flake anode demonstrated a high initial capacity of approximately 2073 mA h/g and the specific capacity remained more than 70% after 100 cycles. The np-Si flake anode also had an excellent current rate capability compared to that of the SiNW electrode, especially at high C-rates.

## 2. Experimental details

### 2.1. Preparation of the np-Si flakes

The freestanding np-Si film was prepared by electrochemically etching a Si substrate (*p*-type, polished on the  $\langle 100 \rangle$  face, 0.010–0.020 Ω cm), followed by an electro-polishing process to release the np-Si thin film from the Si substrate [24]. Fig. 1 (a) shows the fabrication process of the freestanding np-Si thin film. First, the back side of the Si substrate was connected to aluminum (Al) wires and fixed to an anode. A platinum (Pt) plate was used as a cathode. The Si substrate containing the Al back contact was then placed in a Teflon cell filled with an ethanolic HF etching solution (a mixture of 50% hydrofluoric acid and 99.9% ethanol). The etching solution consisted of a 3:7 by volume mixture of aqueous 50% HF and absolute ethanol. A sinusoidal current density waveform varying between 83.0 and 25.0 mA/cm<sup>2</sup> was applied for 200 cycles and a periodicity of 10.75 s. Here, the thickness of the np-Si thin film (etching rate for np-Si thin film layer) was controlled by the changing the electrochemical etching parameters (HF concentration in the etching solution, current density, etching time etc.). The electrochemical etching was carried out in a dark chemical hood using a potentiostat/galvanostat (HA 301, Hokuto Denko) and an arbitrary function generator (HB



**Fig. 1.** (a) Fabrication process of the freestanding np-Si thin film. (b) Photograph image of the freestanding np-Si film prepared using a combination of an electrochemical etching method and an ultra-sonication process. (c) Photograph image of the np-Si thin films in an ethanol solution. (d) Photograph image of the np-Si flakes well-dispersed in the ethanol solution.

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