



Si micropyramid patterned anodes that can suppress fracture and solid electrolyte interface formation during electrochemical cycling



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HIGHLIGHTS

- Si micropyramid anodes have excellent cyclability at high cycling rates.
- Fracture is inhibited in micropyramids at high cycling rates.
- A thicker SEI layer forms for Si micropyramid anodes at lower cycling rates.

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ABSTRACT

Two new types of Si patterned surfaces are presented that have either a solid micropyramid structure or a double microstructure in which nanopores are induced on the pyramid surface. The pyramid diameter ranges between 1 and 6 μm , while the pores are 50–100 nm in diameter and \sim 100–400 nm deep. It is illustrated that when they are employed as anodes, in Li-ion batteries, these patterned anodes, at high current densities of 1C, can (i) retain their initial morphology intact, despite the \sim 400% expansion that Si experiences upon lithiation, and (ii) minimize the formation of the solid electrolyte interface (SEI) that forms upon decomposition of the electrolyte. Furthermore, for the nanoporous-micropyramids, scanning electron microscopy after twenty-five electrochemical cycles reveals that no fracture occurs in either high (1 C) or low (0.1 C) current densities. This is a unique and significant observation as similar experiments, at 0.1 C, on the solid micropyramid surfaces indicate severe fracture from the first Li-insertion. It is therefore concluded that introducing a nanostructure on micropyramids significantly enhances their structural stability. This suggests that microscale Si with induced nanopores is an alternative anode candidate to nanoscale Si.

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1. Introduction

Extensive research over the past decade has focused on developing high-capacity anodes that will replace the commercially used graphitic ones, which possess a theoretical capacity of 372 mAh g^{-1} [1,2]. Among all candidates, silicon has proven to be the most promising, considering its high theoretical capacity of 4200 mAh g^{-1} and low charging potential [3,4]. Despite their initial high capacity, however, Si-based anodes suffer from fast capacity decay

[5–8], which can drop to 200 mAh g^{-1} after the first few cycles [5]. This capacity fade is attributed to (i) mechanical degradation/fracture (pulverization) of the Si and (ii) the formation of the solid electrolyte interface (SEI) layer on the anode surface.

Fracture in Si is caused by the stresses induced during the significant volume changes (up to 400%) that take place during the lithiation/delithiation process [9–13]. The fragmented Si particles diffuse into the electrolyte, and the connectivity of the anode is disrupted, which as a result cannot be efficiently charged-discharged. In order to deal with the high volume expansions of Si, battery developers have resorted to employing nanoscale Si structures [14–16] as they possess a higher fracture toughness [17] and allow for a higher mechanical stability during lithiation.

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Next-generation porous Si electrodes (i.e. Si in combination with a binder and conductive additives) have therefore been fabricated that can allow for capacities that are >2.5 higher than that of graphite. For example Si nanowires allow for a capacity of 1000 mAh g⁻¹ for 100 cycles [14], while Si nanoparticles embedded in carbon allow an initial capacity of 1000 mAh g⁻¹, which can be retained for 30 cycles [15]. Despite these preferred electrochemical properties of nano Si when used in porous electrodes, a recent study [18] illustrated that when high aspect ratio Si nanowires, patterned on a wafer (planar electrodes), came in direct contact with the electrolyte, formation of excess SEI layer with a thickness of ~5 μm was observed, even though fracture was inhibited, and an areal capacity of 94.5 μA h/cm² was achieved. The thick SEI layer completely covered the nanopattern and resulted in low Li-insertion over extensive electrochemical cycles. A similar Si anode patterned with 500 nm Si columns resulted in a maximum areal capacity of 90 μAh/cm² [19]. Hence, although the nano-dimensions allowed for good mechanical stability, a high surface area of Si was in direct contact with the electrolyte, which resulted in significant formation of SEI on the patterned surface.

The study, herein, presents a new patterned planar Si anode with a double micro/nano structure that is efficient in inhibiting both fracture, as well as SEI formation, and allows for high coulombic efficiencies. The Si wafer is initially patterned with solid micropyramids (SMP anodes) and then nanopores are induced on their surface (NMP anodes). Such planar electrodes (as opposed to porous) are the most suitable for studying the effect that the active site morphology/microstructure has since the surface has a clear and characteristic outline, and hence the formation and growth of fracture and SEI can be well characterized with scanning electron microscopy (SEM). Similar studies examining directly the effect of the Si surface morphology on electrochemical performance have not been performed.

It should be noted that nanoporous micropyramid Si surfaces as the ones reported herein have not been presented before and their unique microstructure illustrates that it is not only nanoscale Si [14–16] that can withstand the volume expansions during lithiation but also microscale Si with appropriate surface modifications. In addition to the applicability of these patterned surfaces in examining the effects of lithiation, they can also be used in solar cells [20], hydrophobic coatings [20,21] and implants [21], as Si surfaces with double binary structures are promising in those areas since they can be used to increase the Si surface area and tune hydrophobicity.

2. Experimental section

2.1. Materials fabrication

P-type Si wafers were purchased from University Wafer Co. Ltd. They had a (100) orientation, a resistivity of 1–10 Ohm cm, and a thickness of 500 μm. 40 wt% NaOH solution was purchased from BDH chemicals, and isopropyl alcohol (IPA) was purchased from Pharmco-AAPER. 30 wt% H₂O₂ aqueous solution, 40% ammonia and 49 wt% hydrofluoric acid were purchased from Sigma Aldrich.

The Si wafer was cleaned with acetone and sonicated with DI water to remove surface contaminants before texturing. Then a mixture of 4 ml 40 wt% NaOH solution, 6 ml IPA, and DI water, with a total volume of 200 ml was prepared. The mixture was heated to 85 °C, and a silicon wafer sample with a 2 cm² surface area was etched in it for 40 min to create SMP. The Si sample was then removed from the etchants, washed with DI water and dried with Ar. To create NMP surface the as-prepared SMP samples were first coated with a Ag thin film with a thickness of 15 nm via electron beam evaporation. The coated samples were etched in the etching

solution containing HF and H₂O₂ for 2 min to create the nanoporous structure; the concentrations of HF and H₂O₂ were 4.0 M and 0.5 M respectively. Then the samples were removed from the etchants and were dipped in a solution containing ammonia and H₂O₂ for 1 min to completely remove the Ag coating. This fabrication method is similar to that used in [22], but in there sputtering was used to coat with Ag. The difference in Ag deposition resulted in the formation of nanopores rather than nanowires [22], allowing for the unique nanoporous-micropyramid patterns to be obtained herein.

2.2. Electrochemical testing

Swagelok-type two-electrode batteries were assembled in an Ar atmosphere in a glove box (MBraun, H₂O and O₂ < 0.1 ppm). The as-prepared SMP and NMP samples were sectioned accordingly and were used as the working electrode. The thickness of the SMP and NMP electrodes was approximately the same as the Si wafer. Lithium foil was used as the counter electrode. The electrolyte was 1 M LiPF₆ dissolved in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1, v/v). Electrochemical cycling of the half-cells was performed using a Land BA2100A battery tester (Wuhan, China). All batteries were galvanostatically discharged to a limited capacity (100 μA h/cm²) and charged to 2.0 V vs. Li⁺/Li at room temperature. The reason for choosing 100 μA h/cm² is that by doing this the electrochemical reaction of NMP could be primarily confined to the surface porous layer, which is of special interest in this study. Both the SMP and NMP samples were cycled at various rates, namely, 0.1C, 0.5C, 1C, with 100 μA/cm² corresponding to 1C. For the 1st, 5th, 10th and 25th cycles a separate cell was disassembled and analyzed. The depth of discharge achieved by stopping discharge at 100 μA h/cm² is not high. However, the purpose of this study was not to achieve a high reversible capacity, but to examine the effect that surface micro-morphology had on electrochemical cycling and SEI formation. It was estimated that 100 μA h/cm² would allow the 100 nm porous layer on the surface to fully discharge.

2.3. Characterization

After electrochemical testing, the batteries after various cycles

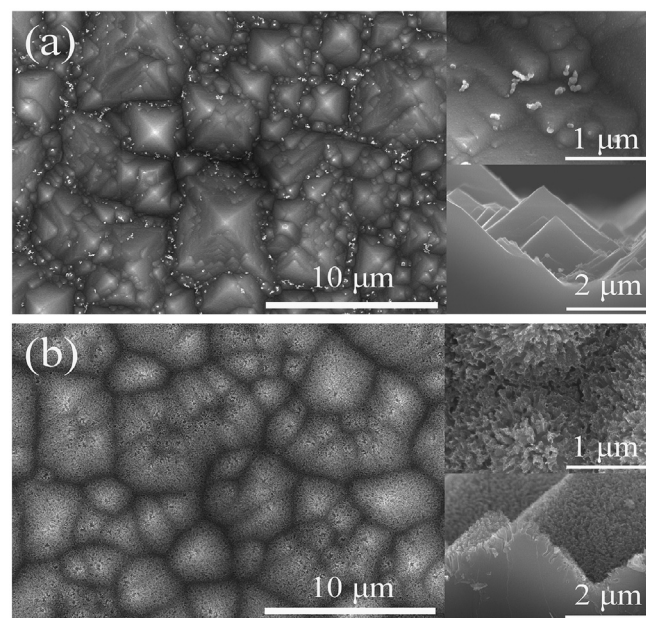


Fig. 1. Micro-morphology of (a) SMP and (b) NMP before cycling.

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