Silicon Nanopillar Anodes for Lithium-Ion Batteries Using Nanoimprint Lithography with Flexible Molds

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A major challenge in Li-ion batteries is to have both high overall energy capacity and high capacity retention after repeated cycling. Si nanowires (NWs) are a compelling solution, due to Si's theoretical gravimetric energy capacity (3,579 mAh/g) being ~10x that of graphite (372mAh/g), and the free space between wires to accommodate Si's 400% volume expansion during battery charging[1]. However, most NW syntheses are time and cost-intensive, and difficult to control. Nanoimprint Lithography (NIL) fabrication offers an ideal alternative, yielding uniformly patterned, well-oriented nanopillars across large areas at low cost, suitable for mass-production.

Here we report (a) fabrication of a Li-ion battery anode with 200nm-pitch Si nanopillars on stainless steel using NIL and deep Si etching, and (b) demonstration of the largest reported sustainable anode capacities for NIL-patterned Si NW structures[2].

In fabrication, amorphous Si film was first evaporated onto cleaned 1.5" diameter stainless steel substrates. Then a trilayer structure consisting of a thermally cross-linked polymer, SiO2, and NIL resist was deposited. Thermal NIL was then performed using a flexible mold with a 200 nm pitch pillar pattern, which was later transferred to the underlying Si via RIE of the trilayer structure, Cr deposition, liftoff, and subsequent deep Si etching.

The fabricated nanopillar structures had a 200nm pitch, up to 500nm heights, and 80 nm diameters, and had a good uniformity and quality as shown in SEM (Fig. 1). The good nanofabrication uniformity on a nonuniform stainless steel surfaces is due to the conformable nature of our flexible, high-fidelity mold technology.

The battery capacity experiments show a 2,300mAh/g initial capacity, with 1,500 mAh/g capacity remaining after 30 cycles at a charge rate of 2C (complete charging in 30 minutes) (Fig. 2). By comparison, comparably thick Si thin-film samples run even at much slower charging rates has much smaller capacities (<1,000 mAh/g). This indicates that the use of nanopillars allows the battery to retain high performance in repeated cycling at high charge/discharge rates, an impossible task with bulk Si or thin films.

Nanopillar Li-ion battery structures and the related nanoimprint fabrication offer new avenues in the design and manufacture of high-performance, low-cost, Si nanopillar battery anode technology.

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1 Chan, C. et al. High-performance lithium battery anodes using silicon nanowires. Nature Nanotech, 2008, 3, 31-35.
2 Nishio, K. et al. Highly ordered nanoporous Si for negative electrode of rechargeable lithium-ion battery. Electrochem. Solid-State Lett. 2012, 15 (4) A41-A44

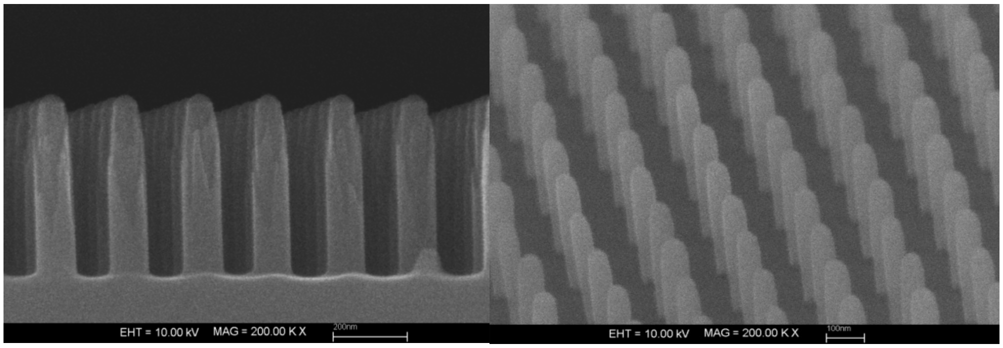

Fig. 1. (a) Cross-section SEM Micrograph of NIL-patterned, etched Si pillars; b) 60° SEM Micrograph of NIL-patterned, etched Si pillars. These images indicate the high degree of uniformity achievable by our flexible-mold imprint process. Etched pillars were up to 500nm high, with easily-tunable diameters.

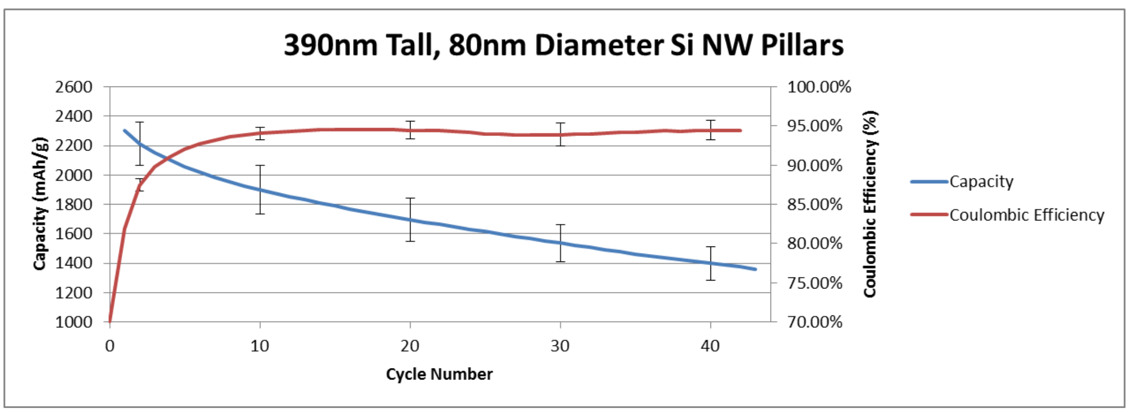

Fig. 2. Battery Capacity Curve, showing maximum battery capacity in mAh/g (blue) and Coulombic efficiency (red) as a function of cycle number. Our data indicates a final Coulombic Efficiency of about 95%, with 59% capacity retention after 40 cycles. These samples were cycled at a rate of 2C, or full discharge in 30 minutes, indicating that our Si features are quite stable at fast charging speeds.