

Supporting Online Materials For

High Performance Lithium Battery Anodes Using Silicon Nanowires

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Materials and Methods

Fig. S1 to S5

Materials and Methods

Single-crystalline Si nanowires (SiNWs) were grown inside a tube furnace using the vapor-liquid-solid growth method. Stainless steel 304 (0.002" thick, McMaster-Carr) substrates were decorated with Au catalysts, either by functionalizing with 0.1% w/v aqueous poly-L-lysine solution (Ted Pella) and dipping into 50 nm diameter Au colloid solution (Ted Pella), or by evaporating 75 nm Au using e-beam evaporation and annealing for 30 min at 530 °C just prior to growth. The substrates were heated to 530 °C and silane (SiH₄, 2% in Ar) was flowed in at 80 sccm with a total chamber pressure of 30 Torr. The mass of the SiNWs in a given experiment (~500 µg) was accurately determined by measuring the mass of the substrate using a microbalance (Sartorius SE2, 0.1 µg resolution) before and after growth. The α -FeSi₂ also formed during growth (as

confirmed by XRD) was found to make up about 25% of the mass measured after the growth and this was subtracted from the total mass to obtain the mass of the Si part of the NW structure only.

The electrochemical properties were evaluated by both cyclic voltammetry and galvanostatic cycling. They were performed in a glass cell with a three-electrode configuration, with the SiNWs on the stainless steel substrate as the working electrode and Li foil as both reference and counter electrodes. The electrolyte was 1.0 M LiPF₆ in 1:1 w/w ethylene carbonate: diethyl carbonate (Ferro Corporation). No binders or conducting carbon were used. All measurements were made in an Argon-filled glove box using an EcoChemie PGSTAT100 potentiostat. Scans were typically performed from 2.0 to 0.01 V vs. Li/Li⁺.

Characterization was done using scanning electron microscopy (FEI XL30 Sirion), transmission electron microscopy (Philips CM20-FEG, acceleration voltage 200 kV), and x-ray diffraction (PANalytical X'Pert, Cu K α -radiation). For transmission electron microscopy (TEM) characterization, the NWs were deposited via a dry transfer stamping technique onto lacey carbon film on copper grids. A 200 kV Hitachi HD-2300A scanning transmission electron microscope (STEM) was used to do chemical analysis with a high sensitivity energy dispersive X-ray spectrometer (EDS, NORAN System). In all cases where electrochemically cycled SiNWs were analyzed, great care was taken to limit exposure to air in order to preserve the compositional state of the NWs and avoid oxidation. NW samples were transported in Teflon-sealed glass vials filled with Ar to the characterization instrument and exposed to air for < 1 min during sample loading. For X-

ray diffraction (XRD), samples were placed inside an Ar filled sample chamber (Anton-Paar) that was transparent to X-rays.

The electrical transport properties of the pristine NWs were measured by using electron beam lithography to pattern electrodes onto individual NWs. The NWs were transferred from the growth substrate onto 175 nm thick silicon nitride on Si <100> substrates using a dry stamping technique. After lithography and just prior to metal deposition, the native oxide on the pristine SiNWs was etched away with hydrofluoric acid (HF). The electrodes were composed of 40 nm stainless steel 304/ 50 nm Ti/ 50 nm Au. Because e-beam lithography requires many steps, the focused-ion beam (FIB) was used to deposit metal contacts on the electrochemically cycled SiNWs (Fig. 3G) in order to minimize air-exposure (no HF etching was done to preserve the as-cycled NW composition). Pt contacts 500 nm thick were deposited on the cycled NWs using the electron beam in the FIB. The current-voltage characteristics were evaluated immediately after device fabrication under vacuum (10^{-6} bar).

Figure Captions

Figure S1. Cyclic voltammogram (CV) of a 75 nm Au film deposited onto stainless steel, scanned from 2.0 to 0.01 V vs. Li/Li⁺ at 1 mV/s. The oxidation peak indicated by the arrow is the only peak with large enough current to be observed in the SiNW CV (Fig. 2A).

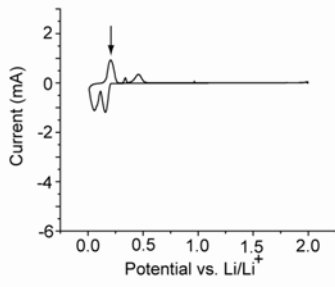
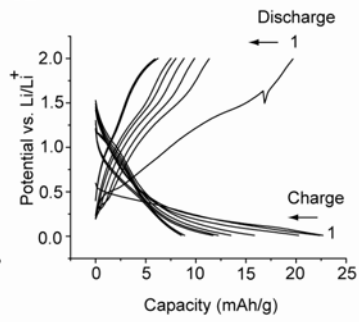
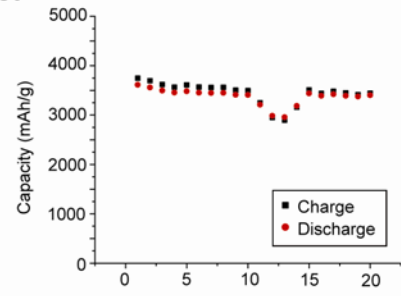
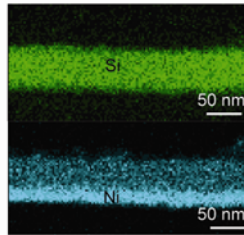
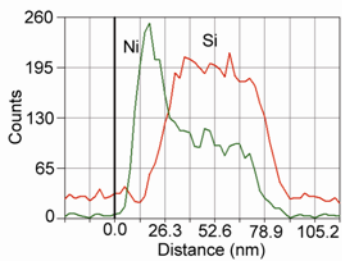
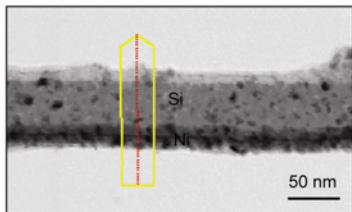
Figure S2. Galvanostatic charge and discharge curves for a 75 nm Au film on stainless steel at a C/20 rate based on the theoretical capacity of Li₁₅Au₄. The small observed

capacities indicate that the capacity contribution from Au (10 to 20 mAh/g) is negligible in the SiNW electrodes.

Figure S3. Capacity vs. cycle number for the SiNWs at the C/5 rate showing the charge (squares) and discharge capacity (circles). There is no irreversible capacity drop after the first C/5 cycle because this sample had already been cycled at C/20 beforehand (data not shown here). The small drop during 11 to 14 cycles is not due to SiNW anode itself but due to instrumental error from the battery tester.

Figure S4. EDS mapping data of a pristine SiNW with partial Ni coating. The linescan across the diameter of the NW shows that Ni is coated predominately on one side and not entirely around the NW. The EDS mapping confirms the compositional distribution of Ni and Si in the NW.

Figure S5. XRD pattern of the Au film that had been galvanostatically cycled. Peaks for $\text{Li}_{15}\text{Au}_4$ are indicated with arrows. The presence and high intensity of the crystalline Au peaks indicate that Au lithiation is minimal, in concurrence with the galvanostatic measurements. Stainless steel (SS) peaks are from the substrate.

S1**S2****S3****S4****S5**