Supplementary Information for

Improving the Cycling Stability of Silicon Nanowire Anodes with Conducting Polymer Coatings

Yan Yao[†], Nian Liu[‡], Matthew T. McDowell[†], Mauro Pasta[†], and Yi Cui[†1*]

[†] Department of Materials Science and Engineering, [‡] Department of Chemistry, Stanford University, Stanford, California, 94305, United States, [1] Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States

[*]Correspondence should be addressed to Y.C. (e-mail: yicui@stanford.edu)

Methods

Synthesis of Si NWs SiNWs were grown inside a tube furnace using the vapor-liquid-solid growth method. Stainless steel 304 (0.002" thick, McMaster-Carr) substrates were covered with a 50 nm-thick Au film by thermal evaporation. The substrates were heated to 485 °C in a tube furnace and silane (SiH_4, 2% in Ar) was flowed in at 50 sccm with a total chamber pressure of 30 Torr for 20 minutes. The mass of the SiNWs in a given experiment (~ 0.3 mg/cm^2) was accurately determined by measuring the mass of the substrate using a microbalance (Sartarious SE2, 0.1 μg resolution) before and after growth. After removing from the tube furnace, the as-formed Si NWs were immediately used as the working electrode for the polymer coating step.

Electrochemical polymerization of PEDOT on Si NWs The electrochemical polymerization was performed in a glass cell with a three-electrode configuration using Pt as the counter

electrode and Ag/AgCl as the reference electrode. 3,4-ethylenedioxythiophene (EDOT, 0.01 M) was dissolved in acetonitrile with 0.1 M lithium perchlorate. All chemicals were purchased from Sigma-Aldrich. The back side of the stainless steel substrate was coated with an insulating wax (Apiezon Wax W, SPI Supplies) to prevent polymer deposition on the back side of the substrate. The wax was removed by washing in toluene when polymerization was complete. Chronopotentiometry was used for electropolymerization at a constant current density of 1 mA/cm^2 for 2 minutes. The PEDOT-coated Si NWs were immediately transferred to an argon-filled glove box where they were rinsed with acetonitrile to remove excess monomer solution and then dried on a hot plate at 90 °C for 1 hour to completely remove the residual solvent. The mass of the coated PEDOT layer was weighed with the microbalance, and it accounts for ~10% of the total composite mass.

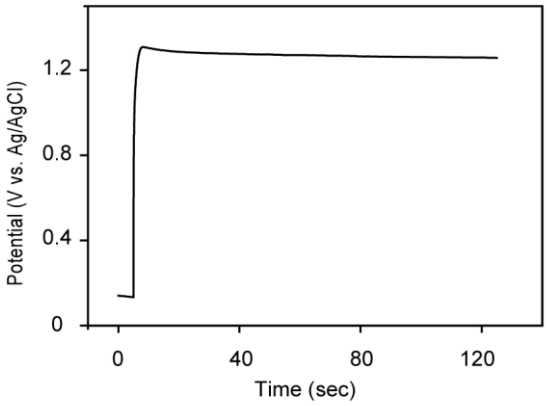

Figure S1 Potential profile of Si NWs electrode during electrochemical polymerization with 0.1 M $LiClO_4$ in acetonitrile electrolyte. An Ag/AgCl electrode was used as the reference, and Pt was used as the counter electrode. A current of 1 mA/cm^2 was passed for 2 minutes, which causes the EDOT monomers to become electro-oxidized and to polymerize at a potential of ~1.3 V *vs.* Ag/AgCl.

Electrochemical and morphological characterization of PEDOT-coated Si NWs For electrochemical characterization, standard coin cells (2032) were made using lithium foil as the counter electrode and Celgard 2250 as the separator. The electrolyte was 1.0 M $LiPF_6$ in 1:1 w/w ethylene carbonate: diethyl carbonate (Novolyte Technologies). Cyclic voltammetery (CV) and electrochemical impedance spectroscopy (EIS) were performed using a Bio-logic VMP3 battery tester. Galvanostatic cycling was performed with voltage cutoffs of 1.0 and 0.01 V vs. Li/Li^+. Scanning electron microscopy (SEM, FEI XL30 Sirion) and transmission electron microscopy (TEM, 200 kV FEI Tecnai F20) were used to characterize the material. XPS analysis of the surface was conducted with a PHI 5000 VersaProbe (Physical Electronics, Chanhassen, MN) equipped with an Al Kα X-ray radiation source. The X-ray takeoff angle was 45° and the spot size was about 200 μm. No charge neutralization was used. The survey scans were taken with an energy resolution of 1.0 eV using a source with power and current of 125 kW and 10 μA. The spectra were calibrated to the hydrocarbon peak at 284.5 eV.

Electrochemical Performance of PEDOT Film

A pure PEDOT film deposited on a Pt electrode with the same mass as that deposited on Si NWs was used as the working electrode for these control experiments. PEDOT contributed about 100 mAh/g in the voltage range of 0.01- 2V vs. Li/Li^+. The capacity is significantly smaller than that of Si NWs.

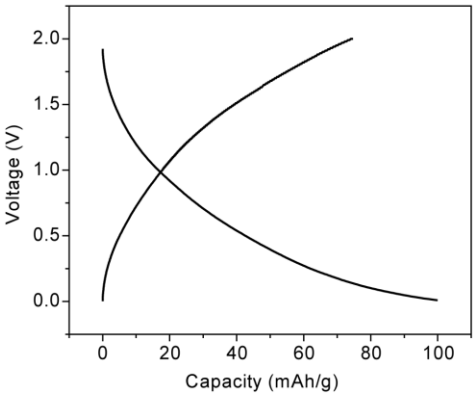

Figure S2 Voltage profile of PEDOT film.

Electrochemical Performance of Pristine Si NWs.

Pristine Si NWs anodes were fabricated and tested using the same conditions as PEDOT-coated Si NWs, as shown in Fig. 3. The pristine Si NW electrode demonstrates 3738 mAh/g discharge capacity and 89.5% CE for the first cycle. At the 100th cycle, the capacity decreases to 1077 mAh/g.

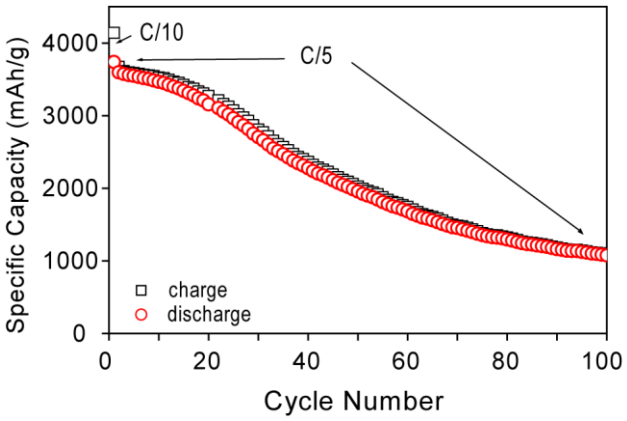

Figure S3 Capacity vs. cycle number for pristine Si NWs.