

Carbon Coated Tin-Seeded Silicon Nanowires for Lithium-Ion Battery Anodes

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Introduction:

Lithium-ion batteries (LIBs) are widely used in many applications, such as mobile phones, laptops, and electric vehicles due to their high power density compared to other battery types. However, improvements are needed to meet the upcoming demands of new technology. Silicon (Si) has the potential to increase the power density of LIBs by replacing commercial carbon-based anodes because it has a high lithium-ion insertion capacity (Si: 3579 mA h g⁻¹ vs. C: 372 mA h g⁻¹ [1]). To accommodate the lithium (Li), the Si lattice must expand by up to 280%. While bulk Si pulverizes under these conditions, Si nanowires (SiNWs) can tolerate this volume expansion (and contraction upon delithiation [2]). However, there are challenges that must be overcome before Si can be used commercially.

Si is a poor electrical conductor, and anodes require the addition of some conductive carbon to improve anode conductivity. Additionally, gold, the typical seed metal to grow SiNWs, is known to have a negative impact on conductivity of SiNWs as gold impurities create deep electron traps in Si. Also, gold catalyzes electrolyte decomposition resulting in continuous growth of a solid electrolyte interphase (SEI) layer, reducing anode stability [3]. Tin-seeding [4] and coating with conductive graphitic carbon [5] are promising ways to overcome these difficulties. In this report we demonstrate the synthesis of carbon coated tin-seeded SiNWs via the supercritical-fluid-liquid-solid (SFLS) growth and their performances as LIB anodes.

Growth of SiNWs:

A reactant solution of 0.5 mL of monophenylsilane and 24 μ L of bis(bis(trimethylsilyl)amino)tin (Sn(HMDS)₂) in 25 mL of toluene was injected to supercritical-fluid of toluene in a titanium reactor that was heated to 490°C and pressurized to 10.8 MPa at a rate of 0.5 mL/min for 40 minutes. The amount of Sn(HMDS)₂ was changed from 24 μ L to 48, 72, or 96 μ L, corresponding to Si:Sn ratios of 65:1, 32:1, 22:1, and 16:1, respectively, in order to optimize the morphology of the SiNWs. The obtained SiNWs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

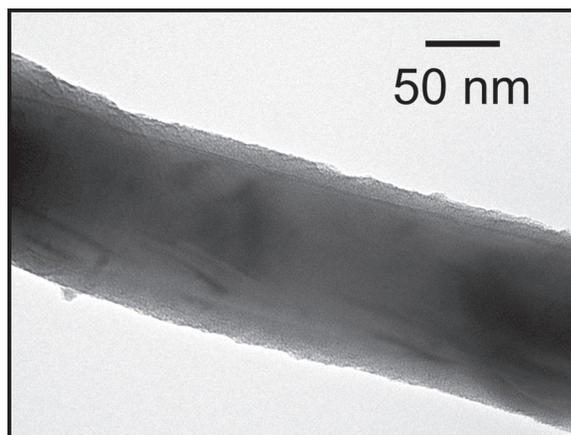
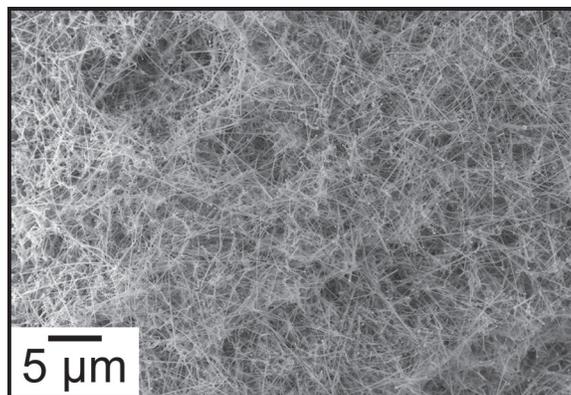


Figure 1, top: SEM of polyphenylsilane-coated tin-seeded SiNWs.

Figure 2, bottom: TEM of polyphenylsilane-coated tin-seeded SiNWs.

When the Si:Sn ratio was as high as 65:1 or 32:1, SiNWs were tortuous and highly kinked with particulate reaction byproduct. TEM also showed that there was a thick carbonaceous shell surrounding the nanowires. At a Si:Sn ratio of 22:1, the SiNWs were predominantly straight and long, 10's to 100's of microns, with no significant particulate inclusions. Figure 1 shows an SEM image of a typical nanowire sample. Figure 2 shows a TEM image of a Si nanowire with a crystalline Si core and polyphenylsilane shell.

Although the Si:Sn ratio of 16:1 also provided with straight and long SiNWs, there was almost no phenylsilane shell on these nanowires. The Si nanowires made with Si:Sn ratio of 22:1 were studied for LIB applications by electrochemically cycling against Li metal in a coin cell.

Battery Assembly and Testing:

The polyphenylsilane shell was converted to conductive graphitic carbon by annealing the nanowires under forming gas (7% H₂ in N₂) at 900°C for one hour (pyrolysis). Nanowires were tested in LIB coin cells with and without this heat treatment.

For testing in LIB coin cells, SiNWs were combined with poly(acrylic acid) binder with a 4:1 weight ratio. No conductive carbon particles were added. The mixture was dispersed in 1-methyl 2-pyrrolidinone to obtain a viscous slurry. The slurry was doctor-bladed (150 μm gap) onto copper (Cu) foil and vacuum-dried. Individual 11 mm diameter circular electrodes are hole-punched from the coated Cu foil and combined in coin cells. The assembly and testing procedures are detailed in Ref. 4.

Charge and discharge capacities were measured at rates of one cycle per ten hours (C/10) and one cycle per one hour (1C) (Figures 3, 4). At both rates, the charge capacities of the unpyrolyzed SiNWs were very low (< 1000 mA h g⁻¹) in the first cycle and decayed to 0 mA h g⁻¹ after a few cycles. On the other hand, the pyrolyzed SiNWs showed high capacities over 2500 mA h g⁻¹. Even at the higher rate of 1C, the capacities of the pyrolyzed SiNWs were over 1000 mA h g⁻¹ and stable for more than 200 cycles.

These results revealed that the carbon-coated Si nanowires have sufficient electrical conductivity for good battery performance without the need for additional carbon in the formulation, thus increasing the total battery anode gravimetric charge storage capacity.

Conclusions:

Long and straight SiNWs with nanometers-thick polyphenylsilane coatings were synthesized by SFLS growth with tin seeds. Pyrolysis of the polyphenylsilane shell to carbon led

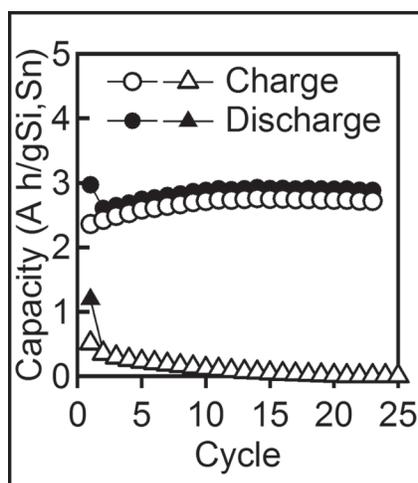


Figure 3: Charge and discharge capacities of the lithium-ion batteries with the pyrolyzed/unpyrolyzed carbon coated tin-seeded SiNWs anodes at the cycle rate of C/10.

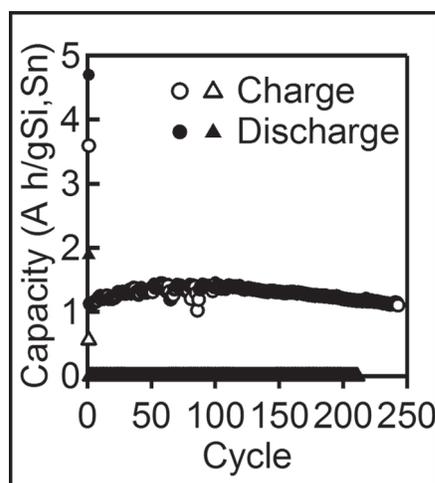


Figure 4: Charge and discharge capacities of the lithium-ion batteries with the pyrolyzed/unpyrolyzed carbon coated tin-seeded SiNWs anodes at the cycle rate of 1C.

to SiNWs with high and stable lithium insertion capacities, eliminating the need to use gold seeds for nanowire growth and the need for additional conductive carbon in the Si-based battery anode.

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