

# Prelithiated Silicon Nanowires as an Anode for Lithium Ion Batteries

Nian Liu,<sup>†</sup> Liangbing Hu,<sup>‡</sup> Matthew T. McDowell,<sup>‡</sup> Ariel Jackson,<sup>‡</sup> and Yi Cui<sup>†,\*</sup>

<sup>†</sup>Department of Chemistry and <sup>‡</sup>Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States

Due to its high capacity and wide abundance, silicon is regarded one of the most promising anodes for the next-generation lithium ion battery (LIB). Various Si morphologies have been investigated, initially as thin film<sup>1</sup> and micrometer size particles,<sup>2</sup> and more recently, Si nanostructures have been reported to allow high battery performance.<sup>3–6</sup> These nanostructures not only effectively solve the pulverization problem of the Si anode but also allow high operation rate. The specific capacity of >3500 mAh/g has been achieved,<sup>3</sup> which is close to silicon's theoretical capacity.<sup>7</sup> Recently, a full cell composed of a carbon–silicon core–shell nanowire anode and a traditional LiCoO<sub>2</sub> cathode has been demonstrated,<sup>8</sup> which paves the way for practical applications of Si anodes.

By replacing traditional graphite anodes with Si anodes, the specific energy or energy density of LIBs increases a lot. To further increase the energy, it is desirable to pair Si anodes with high capacity cathodes. Recently, many cathode materials, such as V<sub>2</sub>O<sub>5</sub>,<sup>9</sup> MnO<sub>2</sub>,<sup>10,11</sup> FeSe<sub>2</sub>,<sup>12</sup> and sulfur,<sup>13–15</sup> have shown the potential to have high Li storage capacity. However, neither Si anode nor any of these cathodes contains lithium. Therefore, for this type of combination, either the cathode or the Si anode needs to be prelithiated. Several prelithiation methods have been reported on Li-free cathode materials, such as hydrothermal treatment with LiCl<sup>16</sup> and chemical reaction with *n*-butyllithium.<sup>17</sup> However, different applications (grid storage, electric vehicles, and portable electronic devices) may require different cathodes for pairing with Si anodes, for the balance of power, capacity, cost, and safety. Therefore, instead of developing an individual prelithiation method for every Li-free cathode material, it is strategically preferable to develop one single prelithiation method for the Si anode and pair it with all the Li-free cathodes.

**ABSTRACT** Silicon is one of the most promising anode materials for the next-generation high-energy lithium ion battery (LIB), while sulfur and some other lithium-free materials have recently shown high promise as cathode materials. To make a full battery out of them, either the cathode or the anode needs to be prelithiated. Here, we present a method for prelithiating a silicon nanowire (SiNW) anode by a facile self-discharge mechanism. Through a time dependence study, we found that 20 min of prelithiation loads ~50% of the full capacity into the SiNWs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies show that the nanostructure of SiNWs is maintained after prelithiation. We constructed a full battery using our prelithiated SiNW anode with a sulfur cathode. Our work provides a protocol for pairing lithium-free electrodes to make the next-generation high-energy LIB.

**KEYWORDS:** lithium ion battery · silicon nanowires · prelithiation · lithium–sulfur battery

Experimentally, anode materials are harder to prelithiate than cathode materials because a more reactive Li source is needed; the product is relatively unstable; and the reaction is hard to control. Carbon anodes can be prelithiated using stabilized lithium metal powder (SLMP).<sup>18</sup> In a full battery utilizing such a prelithiated carbon anode and a Li-free V<sub>6</sub>O<sub>13</sub> cathode, a decrease of irreversible capacity was observed in the carbon anode.<sup>19</sup> However, SLMP is expensive and not easily available. A cheaper and simpler prelithiation method is desirable. Moreover, an additional requirement for the prelithiation of a nanostructured Si anode is that the morphology of the nanostructure must survive; otherwise, the huge volume changes during battery cycling could pulverize the Si anode.

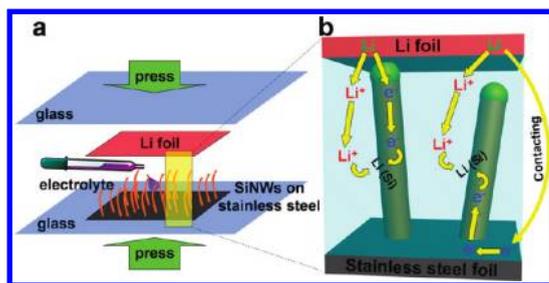
Here, we present a facile method for prelithiating a Si nanowire (SiNW) anode by a self-discharge mechanism. Cheap Li metal foil is used as the Li source. Both inner and outer structure changes of SiNWs are studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Electrochemical testing is carried out to study the prelithiated SiNW half-cell. The time dependence of the prelithiation degree is investigated. To prove the concept,

\* Address correspondence to yicui@stanford.edu.

Received for review May 10, 2011 and accepted June 28, 2011.

Published online 10.1021/nn2017167

© XXXX American Chemical Society



**Figure 1.** Schematic diagrams showing (a) the prelithiation of SiNWs on stainless steel (SS) foil, and (b) the internal electron and  $\text{Li}^+$  pathways during the prelithiation. Two possible electron pathways are shown in (b). Electron can directly flow into the SiNW if the nanowire tip contacts the Li foil, or the electron can flow across the contacting point of Li foil and SS and enter the SiNW through the bottom.

we demonstrate a full battery using our prelithiated SiNW anode and a sulfur/mesoporous carbon nano-composite cathode.

## RESULTS AND DISCUSSION

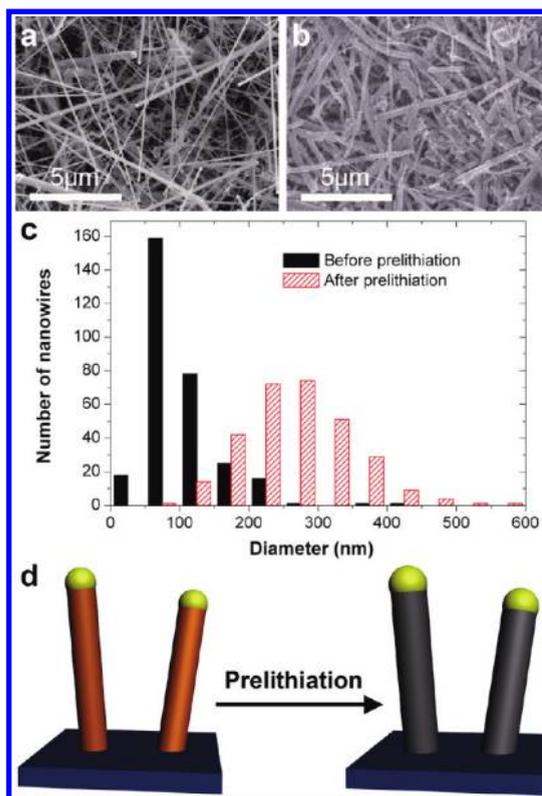
From a simple thermodynamic estimation, lithium metal will spontaneously react with crystalline silicon (c-Si) to form the Li–Si alloy, as shown below:



$$\begin{aligned} \Delta G &= -nEF \approx -4.4 \times 0.1 \times 96500 \\ &= -42 \text{ kJ/mol} \end{aligned}$$

where  $\Delta G$  is the Gibbs free energy of the total reaction,  $E$  the potential of the total reaction, and  $F$  the Faraday constant.  $E$  is assumed to be  $\sim 0.1$  V according to experimental data.<sup>3</sup> Since this reaction is spontaneous and Li metal is easily available, we choose Li metal as the Li source to prelithiate crystalline SiNWs.

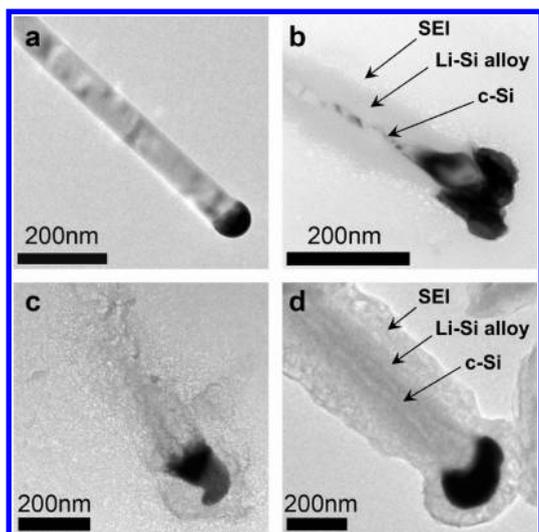
The schematic of our experiment is shown in Figure 1a. SiNWs were grown on stainless steel (SS) using our previously reported method.<sup>3</sup> In the prelithiation process, SiNWs were directly attached to a piece of Li metal foil in the presence of electrolyte between. Pressure was applied to induce electrical shorting between the SiNWs and the Li foil. As soon as the SiNWs and Li foil are shorted, the SiNWs begin to be electrochemically lithiated. The prelithiation mechanism is similar to a battery shorting mechanism. There are two pathways for a SiNW to be lithiated (Figure 1b). If the SiNW touches the Li foil (left of Figure 1b), electrons will pass through the tip of the wire. If the SiNW does not touch the Li foil (right of Figure 1b), electrons will pass through the contact point between the Li foil and the SS substrate, and then up through the bottom of the SiNW. These are the two pathways for SiNWs to be prelithiated. After prelithiation, the Li metal foil can be cleaned and



**Figure 2.** SEM images of SiNWs (a) before and (b) after 10 min prelithiation. After prelithiation, the SiNWs were washed with acetonitrile before taking SEM images. (c) Size distribution of SiNWs before and after prelithiation. (d) Schematic showing the increase of SiNW diameter after prelithiation.

repeatedly used; the nominal utilization of Li metal is  $\sim 100\%$ .

After the prelithiation, the color of SiNWs turned from brown to black, which is the typical color of Li–Si alloys. This implied that Li was inserted into the SiNWs. As discussed in our previous work,<sup>3</sup> the NW morphology is a benefit to electrochemical performance in three primary aspects: efficient 1D electron transport, good contact with the current collector, and facile stress relaxation. Therefore, it is preferable to retain the morphology of the SiNWs after the prelithiation process. SEM images of SiNWs before and after prelithiation indicate that the 1D NW morphology was well-maintained after prelithiation process (Figure 2a,b): there is very little evident damage of cracking in the morphology. On the basis of multiple SEM images (see Supporting Information, Figure S1), a statistical comparison of the nanowire diameter before and after prelithiation was carried out (Figure 2c). The average diameter of SiNWs changed from  $\sim 100$  to  $\sim 250$  nm after prelithiation, which indicates that SiNWs were lithiated and expanded volumetrically.<sup>3</sup> The formation of solid-electrolyte interphase (SEI) may also count some of the increase of diameter.<sup>20</sup> The maintenance of the nanostructure of SiNWs is very helpful to their battery performance. Figure 2d shows the schematic of the change of SiNWs after prelithiation.



**Figure 3.** TEM images of (a) a pristine SiNW, (b) a 10 min prelithiated SiNW, (c) a 20 min prelithiated SiNW, and (d) a ~50% electrochemically lithiated SiNW using constant current ( $C/20$  for 10 h). The arrows in (b,d) indicate solid–electrolyte interphase (SEI), Li–Si alloy shell and crystalline Si core. In (d), pristine SiNWs were made into a coin cell with Li metal as the counter electrode. Then the cell was galvanostatically discharged for 10 h with  $C/20$  rate. The SiNWs were lithiated to ~50% of their full capacity.

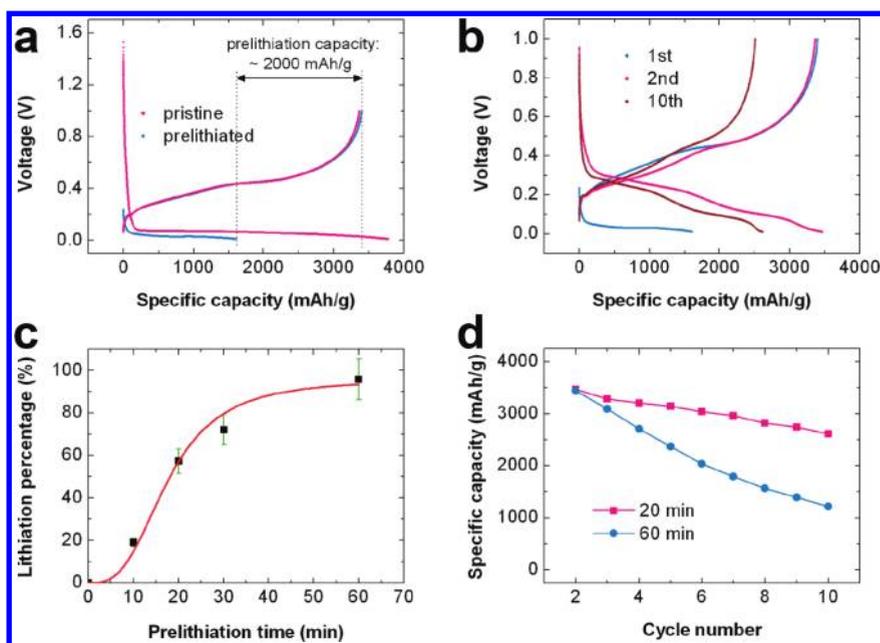
Transmission electron microscopy (TEM) was used to further study the inner structural changes in SiNWs after prelithiation. Pristine SiNWs were crystalline and had smooth surface (Figure 3a). Hemispherical Au catalyst nanoparticles located at the tip of the nanowires. After 10 min prelithiation, the SiNWs transformed into a core–shell structure, as shown in Figure 3b. The core was still crystalline Si, while the shell was lithiated amorphous Si. The Au catalyst nanoparticles adopt an irregular shape, which suggests that the Au is also lithiated during the prelithiation process. Longer prelithiation time (20 min) resulted in fully lithiated SiNWs (Figure 3c). From experimental observations<sup>21</sup> and *ab initio* studies,<sup>22</sup> lithium is inserted into SiNWs from the surface to the core. Thus, our prelithiation process is quite similar to the electrochemical lithiation process. It should be noted that a thin coating layer was observed on the surface of both the 10 and 20 min prelithiated SiNWs. The thin layer tended to decompose under a highly concentrated electron beam, which indicates that it has high organic content. The formation of this thin layer is probably due to the decomposition of the electrolyte on SiNWs surface during prelithiation, which is very similar to the formation of SEI during battery cycling (Figure 3d). A similar organic layer was also reported on a prelithiated carbon anode by SLMP method.<sup>19</sup> However, this layer formed during prelithiation is confirmed by TEM for the first time. Since the SEI formation will cause irreversible capacity, forming this decomposition layer on SiNWs before using them in full batteries might reduce the irreversible capacity of SiNW anodes and give higher energy efficiency.

Galvanostatic charging/discharging was used to study the electrochemical behavior of the prelithiated SiNWs. Pristine and prelithiated SiNWs were first lithiated to 10 mV, then delithiated to 1 V (Figure 4a). The open circuit voltages (OCV) of pristine and prelithiated SiNWs versus Li metal were 1.55 and 0.25 V, respectively. This is reasonable because the insertion of lithium reduces the electrochemical potential of Si (Figure 4a, pink line). The electrochemical lithiation capacity of the prelithiated SiNWs (~1600 mAh/g) is much less than that of the pristine SiNWs (~3800 mAh/g).<sup>23</sup> The OCV and the lithiation capacity indicate that, after the prelithiation, Si is already partially alloyed with Li. After reaching 10 mV, the pristine and prelithiated SiNWs were delithiated to 1 V. The delithiation capacity of the pristine and prelithiated SiNWs is almost the same (Figure 4a), which suggests that the prelithiated SiNWs still retain good contact with SS current collector. We attribute this contact retention to the use of electrolyte in the prelithiation process. If no electrolyte is added between the Li foil and the SiNWs, the SiNWs will detach from the SS substrate and stick to the Li foil after prelithiation. During delithiation, pristine and prelithiated SiNWs showed a similar electrochemical signature. Therefore, prelithiation does not alter the electrochemical behavior of SiNWs. Subtracting the first lithiation capacity from the first delithiation capacity, prelithiated SiNWs have a prelithiation capacity of ~2000 mAh/g. This means that, during a simple 20 min prelithiation, the SiNWs were lithiated to ~50% of their theoretical capacity. This is equivalent to electrochemically lithiating the SiNWs at close to a 2C rate.

In later cycles, the prelithiated SiNWs have similar voltage profile with pristine SiNWs (Figure 4b). There is no plateau below 100 mV, which indicates the SiNWs became amorphous after the first cycle. The SiNWs maintained ~75% of their capacity after 10 cycles. As shown in the SEM study (Figure 2a), the retention of capacity is due to the survival of the nanostructure of SiNWs in our prelithiation process. Therefore, the prelithiation treatment is not harmful to the cyclability of the SiNW anode.

The amount of lithium preloaded into SiNWs as a function of prelithiation time was also systematically studied (Figure 4c). With 20 min of prelithiation, the SiNWs are ~50% lithiated. With 60 min of prelithiation, the lithiation percentage saturates and the SiNWs are prelithiated to ~100% of their theoretical capacity. This prelithiation process is fast and complete because it resembles the shorting of a galvanic cell. The highly spontaneous chemical reaction ( $\Delta G = -42$  kJ/mol) drives the prelithiation process to take place quickly and completely.

While longer prelithiation time loads more Li into SiNWs, shorter prelithiation time results in better cyclability of the SiNWs. To study how the prelithiation time affects the cyclability, two SiNW samples were



**Figure 4.** Electrochemical characterization of prelithiated SiNW half-cells. The pristine and prelithiated SiNWs were galvanostatically cycled between 0.01 and 1.0 V starting with charging (Li insertion). The rate was C/10. (a) Comparison of first cycle voltage profiles of pristine and 20 min prelithiated SiNWs with Li metal as the counter electrode. Prelithiation capacity is calculated by (first cycle discharge capacity) – (first cycle charge capacity). (b) First, second, and 10th cycle voltage profiles of 20 min prelithiated SiNWs. (c) Time dependence study of prelithiation of SiNWs. The red curve is merely for eye guidance. Lithiation percentage is calculated by (prelithiation capacity)/(total capacity). (d) Cycling performance of SiNWs prelithiated for 20 and 60 min. The first cycle is omitted for clarity.

prelithiated for 20 and 60 min, and then they were made into half-cells and cycled between 10 mV and 1 V using Li metal foil as the counter electrodes. The specific capacity with cycling (Figure 4d) shows that the 20 min prelithiated SiNW sample retains capacity better than the 60 min sample. This difference can be attributed to the shallower lithiation of the 20 min sample than the 60 min sample. The slow and shallow lithiation/delithiation improves the cyclability.<sup>21</sup> So in terms of cyclability, the 20 min prelithiated SiNW sample is better than the sample prelithiated for 60 min. On the other hand, even though a 20 min prelithiated SiNW sample has a smaller lithiation percentage than the 60 min prelithiated sample (Figure 4c), with the huge specific capacity of Si, they still have sufficient amount of Li inside to match the capacity of many Li-free cathodes. Therefore, we choose the 20 min prelithiated SiNWs for the full cell study.

To prove our concept, we pair our prelithiated SiNWs with a sulfur-based cathode because sulfur, to the best of our knowledge, has the highest specific capacity of ~1670 mAh/g among all solid LIB cathodes. However, sulfur cathode is a Li-free cathode, which is essentially different from most of the commercialized LIB cathodes (LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, etc.). In order to utilize the sulfur cathode, an anode that contains Li is needed. Unfortunately, Li is not present in most anode materials either. Several approaches have been addressed to solve this problem. First, a sulfur cathode has been directly paired with a lithium metal anode.<sup>13</sup> Second, sulfur has been

replaced by its Li<sub>2</sub>S counterpart (or Li<sub>2</sub>S/metal composites) as electrode materials.<sup>24–26</sup> Third, a sulfur cathode has been converted to Li<sub>2</sub>S electrode by reacting with *n*-butyllithium.<sup>17</sup> The first approach has safety issues because lithium metal anode will generate Li dendrites, which may cause shorting of the cell and cause safety issues. The second and third approaches have limited application prospective because they involve highly flammable chemicals Li<sub>2</sub>S and *n*-butyllithium, respectively. Also, the insulating nature of Li<sub>2</sub>S might cause big overpotential, which limits the power of the battery.

Here, we tackle the problem of the lack of lithium in both anode and sulfur cathode by pairing our prelithiated SiNW anode with a sulfur/mesoporous carbon nanocomposite cathode, in which the active material is sulfur. In this full cell configuration, the only lithium source is the prelithiated SiNW anode. The electrolyte is 1 M lithium bis(trifluoromethane)sulfonamide (LiTFSI) in 1:1 v/v dioxolane (DOL)/dimethoxyethane (DME). SiNWs have been proven to work in this type of electrolyte.<sup>17</sup> Since lithium is prelithiated on the anode side, the full cell is originally in the charged state with an OCV of ~2.1 V. The voltage profiles of the first, second, and 10th charge and discharge cycles of the sulfur/prelithiated SiNW full battery are shown in Figure 5a. The cell was galvanostatically discharged to 1.7 V in the first cycle, charged to 2.8 V and discharged to 1.7 V in the second cycle, and charged to 2.6 V and discharged to 1.7 V in the following cycles. The C rate

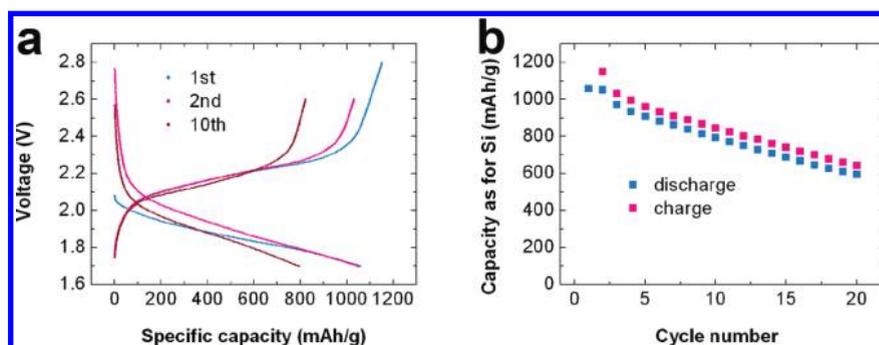


Figure 5. Electrochemical characterization of a full cell made of prelithiated SiNW anode and sulfur/mesoporous carbon cathode. (a) Voltage profiles of the first, second, and 10th cycles of the full cell, which was cycled between 1.7 and 2.8 V for the first cycle and 1.7 and 2.6 V for following cycles. (b) Cycling performance of the full cell.

was  $C/5$  with respect to the SiNWs. Since the main purpose of fabricating the sulfur/prelithiated SiNWs battery is to prove the concept of the prelithiated SiNW anode, an excess amount of cathode material is used. Therefore, upon full discharge, the SiNWs were completely delithiated while the sulfur cathode was only partially lithiated. Generally, there are two plateaus during electrochemical lithiation of sulfur. In the first plateau, sulfur is reduced to high-order polysulfides ( $\text{Li}_2\text{S}_x$ ,  $4 \leq x \leq 8$ ), while in the second plateau, it is further reduced to lower-order polysulfides ( $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$ ).<sup>27</sup> In our sulfur/prelithiated SiNW full cell, the sulfur cathode never reaches the second plateau because it is in excess amount. Also, silicon has only one plateau during delithiation. Therefore, only one plateau appeared in the discharge profile of the full cell.

The full cell maintains  $\sim 80\%$  of its initial capacity after 10 cycles (Figure 5b), but it decays with a constant slope throughout cycling. The decay of the full cell capacity could be due to the following: (1) The full cell has a limited supply of Li. Side reactions at both electrodes consume Li and therefore cause capacity loss. (2) High-order polysulfides are soluble in the electrolyte and carry the Li with them into the electrolyte, which causes the loss of the total Li in electrodes. (3) The voltage of the cathode and the anode are not separately controlled. One of the two electrodes might be overcharged or deeply discharged, which may harm the cyclability of the full cell. This sulfur/prelithiated SiNW full cell has similar capacity decay behavior over the first 20 cycles to a full cell in previous work utilizing  $\text{Li}_2\text{S}$  as the cathode and SiNWs as the anode.<sup>17</sup> However, the fabrication method here utilizes a cheaper and safer Li source (Li metal foil instead of *n*-butyllithium).

SEM images were taken of the prelithiated SiNW anode after the full cell was cycled for 200 times (Figure 6). Compared with freshly prelithiated SiNWs, they become porous after 200 cycles. Similar results have been observed during the cycling of SiNWs.<sup>3,28</sup> This is probably due to the repeated expansion/contraction of SiNWs during cycling. It should be noted

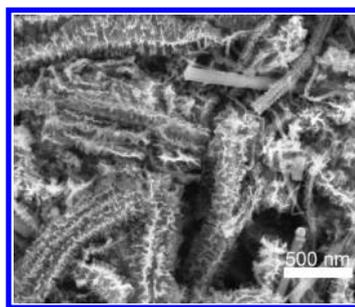


Figure 6. SEM images of prelithiated SiNWs after 200 cycles with sulfur/mesoporous carbon cathode. The SiNWs were washed with acetonitrile and 0.5 M  $\text{HNO}_3$  to remove the SEI before taking SEM images.

that some of the SiNWs remain intact after 200 cycles. These could be the NWs that were not prelithiated initially, as seen in the SEM image in Figure 2b. These NWs might have had poor electrical contact to the current collector and the Li metal foil during prelithiation.

## CONCLUSION

In summary, we have demonstrated a facile and rapid prelithiation method for SiNWs. Cheap and easily available Li foil is used as the lithium source. The thermodynamically spontaneous reaction between lithium and silicon is experimentally realized. A self-discharge mechanism is proposed. With a simple 20 min prelithiation, the amount of lithium preloaded into the SiNWs is measured to be  $\sim 2000$  mAh/g of Si. The degree of prelithiation can be easily controlled by changing the prelithiation time. More importantly, the nanostructure of SiNWs is successfully maintained after prelithiation. The optimal time of prelithiation for balancing cycling performance and capacity was found to be 20 min. By directly pairing this prelithiated SiNW anode with a Li-free sulfur cathode, we demonstrated a proof-of-concept sulfur/Li–Si full battery. With further optimization on the prelithiation condition, cathode/anode capacity matching, and the electrolyte, a sulfur/prelithiated SiNW full battery with improved performance is anticipated. This prelithiation

method removes the requirement that the cathode must contain lithium in its original state and opens up

new avenues of pairing Li-free electrodes for the next-generation high-energy lithium ion batteries.

## METHODS

**Prelithiated SiNW Fabrication and Characterization.** The SiNWs were grown directly onto stainless steel (SS) 304 substrates by using gold-catalyzed vapor–liquid–solid (VLS) growth, as described previously.<sup>3</sup> Prelithiation and cell assembly were both carried out inside an Ar-filled glovebox. SiNWs on SS were directly attached to a piece of Li metal foil (0.38 mm thick, Sigma-Aldrich Co.) with electrolyte between. The electrolyte was made by adding 1 vol % vinylene carbonate (Novolyte Technologies) into 1.0 M LiPF<sub>6</sub> in 1:1 w/w ethylene carbonate/diethyl carbonate (EMD Chemicals). Glass slides were used to sandwich the structure, and pressure was applied onto the two sides by using two binder clips. After a certain time of prelithiation, SiNWs were peeled off from the Li foil carefully and washed with acetonitrile to remove the residual electrolyte and lithium salts. The Li foil was cleaned by abrasion and reused. Characterization was carried out after drying the prelithiated SiNWs inside the glovebox at room temperature.

The prelithiated SiNWs were characterized by a FEI Sirion scanning electron microscope (SEM) and a Tecnai F20 transmission electron microscope (TEM).

**Prelithiated SiNW Half-Cells.** Prelithiated SiNW half-cells were fabricated using SiNWs/SS electrode, Li metal foil, and Celgard 2250 separator soaked in the self-made electrolyte as used in prelithiation. The masses of SiNWs were measured using Sartorius SE2 microbalance (0.1 μg resolution). All calculated capacities are based on the weight of the active Si material only. The electrochemical performance of the prelithiated SiNWs was evaluated using galvanostatic cycling on a MTI 8 channels battery analyzer (0.002–1 mA). The voltage cutoffs are 1.0 and 0.01 V vs Li/Li<sup>+</sup>, and the rate was C/10 in terms of the theoretical capacity of SiNWs (4200 mAh/g).

**Sulfur Cathode Fabrication.** Sulfur/mesoporous carbon nanocomposite cathodes were fabricated using previously reported method.<sup>17</sup> First, CMK-3 mesoporous carbon was synthesized from the SBA-15 mesoporous silica template. The CMK-3 mesoporous carbon was ball milled and heated with sulfur to form the sulfur/mesoporous carbon nanocomposite. A 4:3 mass ratio of sulfur to carbon was used. Sulfur/CMK-3 nanocomposite particles were further mixed with Super P conductive carbon and poly(vinylidene fluoride) binder (PVDF) with a weight ratio of 80:10:10 in cyclopentanone to form a slurry. This slurry was coated onto carbon-coated aluminum foil (Showa Denko America, Inc.) and dried under vacuum at room temperature.

**Prelithiated SiNW Anode/Sulfur Cathode Full Cell.** Full cells were fabricated using SiNW anodes prelithiated for 20 min, sulfur/CMK-3 cathodes, and Celgard 2250 separators soaked in self-made electrolyte. To prepare the electrolyte, dioxolane and dimethoxyethane (DOL/DME) were mixed in a 1:1 ratio by volume. A proper amount of lithium salt, lithium bis(trifluoromethane) sulfonamide (LiTFSI), was added to achieve a concentration of 1 M. In the full cell, cathode materials are in excess amount compared to the anode materials. Galvanostatic cycling of the full cell was carried out between 1.7 and 2.8 V for the first cycle and 1.7 and 2.6 V for the following cycles. The rate was set to C/5 in terms of the total capacity of the SiNWs.

**Acknowledgment.** This work was partially supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, Subcontract No. 6951379, under the Batteries for Advanced Transportation Technologies (BATT) Program. Y.C. acknowledges support from the ONR Young Investigator Award and the King Abdullah University of Science and Technology (KAUST) Investigator Award (No. KUS-I1-001-12). M.T.M. acknowledges support from the Chevron Stanford Graduate Fellowship, the National Defense

Science and Engineering Graduate Fellowship, and the National Science Foundation Graduate Fellowship. A.J. acknowledges support from the National Defense Science and Engineering Graduate Fellowship.

*Supporting Information Available:* Supporting figure of the SEM images used for nanowire diameter statistics before and after prelithiation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Lee, K. L.; Jung, J. Y.; Lee, S. W.; Moon, H. S.; Park, J. W. Electrochemical Characteristics of a-Si Thin Film Anode for Li-Ion Rechargeable Batteries. *J. Power Sources* **2004**, *129*, 270–274.
- Obrovac, M. N.; Krause, L. J. Reversible Cycling of Crystalline Silicon Powder. *J. Electrochem. Soc.* **2007**, *154*, A103–A108.
- Chan, C. K.; Peng, H. L.; Liu, G.; McIlwrath, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y. High-Performance Lithium Battery Anodes Using Silicon Nanowires. *Nat. Nanotechnol.* **2008**, *3*, 31–35.
- Park, M. H.; Kim, M. G.; Joo, J.; Kim, K.; Kim, J.; Ahn, S.; Cui, Y.; Cho, J. Silicon Nanotube Battery Anodes. *Nano Lett.* **2009**, *9*, 3844–3847.
- Kim, H.; Seo, M.; Park, M. H.; Cho, J. A Critical Size of Silicon Nano-anodes for Lithium Rechargeable Batteries. *Angew. Chem., Int. Ed.* **2010**, *49*, 2146–2149.
- Magasinski, A.; Dixon, P.; Hertzberg, B.; Kvit, A.; Ayala, J.; Yushin, G. High-Performance Lithium-Ion Anodes Using a Hierarchical Bottom-Up Approach. *Nat. Mater.* **2010**, *9*, 353–358.
- Boukamp, B. A.; Lesh, G. C.; Huggins, R. A. All-Solid Lithium Electrodes with Mixed-Conductor Matrix. *J. Electrochem. Soc.* **1981**, *128*, 725–729.
- Cui, L. F.; Yang, Y.; Hsu, C. M.; Cui, Y. Carbon–Silicon Core–Shell Nanowires as High Capacity Electrode for Lithium Ion Batteries. *Nano Lett.* **2009**, *9*, 3370–3374.
- Chan, C. K.; Peng, H. L.; Twisten, R. D.; Jarausch, K.; Zhang, X. F.; Cui, Y. Fast, Completely Reversible Li Insertion in Vanadium Pentoxide Nanoribbons. *Nano Lett.* **2007**, *7*, 490–495.
- Chernova, N. A.; Roppolo, M.; Dillon, A. C.; Whittingham, M. S. Layered Vanadium and Molybdenum Oxides: Batteries and Electrochromics. *J. Mater. Chem.* **2009**, *19*, 2526–2552.
- Reddy, A. L. M.; Shaijumon, M. M.; Gowda, S. R.; Ajayan, P. M. Coaxial MnO<sub>2</sub>/Carbon Nanotube Array Electrodes for High-Performance Lithium Batteries. *Nano Lett.* **2009**, *9*, 1002–1006.
- Mai, L. Q.; Gao, Y.; Guan, J. G.; Hu, B.; Xu, L.; Jin, W. Formation and Lithiation of Ferroselite Nanoflowers as High-Energy Li-Ion Battery Electrodes. *Int. J. Electrochem. Sci.* **2009**, *4*, 755–761.
- Ji, X. L.; Lee, K. T.; Nazar, L. F. A Highly Ordered Nanostructured Carbon–Sulphur Cathode for Lithium–Sulphur Batteries. *Nat. Mater.* **2009**, *8*, 500–506.
- Ji, X. L.; Nazar, L. F. Advances in Li–S Batteries. *J. Mater. Chem.* **2010**, *20*, 9821–9826.
- Yuan, L. X.; Qiu, X. P.; Chen, L. Q.; Zhu, W. T. New Insight into the Discharge Process of Sulfur Cathode by Electrochemical Impedance Spectroscopy. *J. Power Sources* **2009**, *189*, 127–132.
- Mai, L. Q.; Hu, B.; Chen, W.; Qi, Y. Y.; Lao, C. S.; Yang, R. S.; Dai, Y.; Wang, Z. L. Lithiated MoO<sub>3</sub> Nanobelts with Greatly Improved Performance for Lithium Batteries. *Adv. Mater.* **2007**, *19*, 3712–3716.
- Yang, Y.; McDowell, M. T.; Jackson, A.; Cha, J. J.; Hong, S. S.; Cui, Y. New Nanostructured Li<sub>2</sub>S/Silicon Rechargeable

- Battery with High Specific Energy. *Nano Lett.* **2010**, *10*, 1486–1491.
18. Jarvis, C. R.; Lain, M. J.; Yakovleva, M. V.; Gao, Y. A Prelithiated Carbon Anode for Lithium-Ion Battery Applications. *J. Power Sources* **2006**, *162*, 800–802.
  19. Jarvis, C. R.; Lain, M. J.; Gao, Y.; Yakovleva, M. A Lithium Ion Cell Containing a Non-lithiated Cathode. *J. Power Sources* **2005**, *146*, 331–334.
  20. Chan, C. K.; Ruffo, R.; Hong, S. S.; Cui, Y. Surface Chemistry and Morphology of the Solid Electrolyte Interphase on Silicon Nanowire Lithium-Ion Battery Anodes. *J. Power Sources* **2009**, *189*, 1132–1140.
  21. Cui, L. F.; Ruffo, R.; Chan, C. K.; Peng, H. L.; Cui, Y. Crystalline-Amorphous Core–Shell Silicon Nanowires for High Capacity and High Current Battery Electrodes. *Nano Lett.* **2009**, *9*, 491–495.
  22. Zhang, Q. F.; Zhang, W. X.; Wan, W. H.; Cui, Y.; Wang, E. G. Lithium Insertion in Silicon Nanowires: An *Ab Initio* Study. *Nano Lett.* **2010**, *10*, 3243–3249.
  23. The specific capacity is calculated based only on the mass of silicon.
  24. Obrovac, M. N.; Dahn, J. R. Electrochemically Active Lithia/Metal and Lithium Sulfide/Metal Composites. *Electrochem. Solid State Lett.* **2002**, *5*, A70–A73.
  25. Zhou, Y. N.; Wu, C. L.; Zhang, H.; Wu, X. J.; Fu, Z. W. Electrochemical Reactivity of Co-Li<sub>2</sub>S Nanocomposite for Lithium-Ion Batteries. *Electrochim. Acta* **2007**, *52*, 3130–3136.
  26. Hayashi, A.; Ohtsubo, R.; Ohtomo, T.; Mizuno, F.; Tatsumisago, M. All-Solid-State Rechargeable Lithium Batteries with Li<sub>2</sub>S as a Positive Electrode Material. *J. Power Sources* **2008**, *183*, 422–426.
  27. Shim, J.; Striebel, K. A.; Cairns, E. J. The Lithium/Sulfur Rechargeable Cell: Effects of Electrode Composition and Solvent on Cell Performance. *J. Electrochem. Soc.* **2002**, *149*, A1321–A1325.
  28. Choi, J. W.; McDonough, J.; Jeong, S.; Yoo, J. S.; Chan, C. K.; Cui, Y. Stepwise Nanopore Evolution in One-Dimensional Nanostructures. *Nano Lett.* **2010**, *10*, 1409–1413.