

Lithium-Assisted Electrochemical Welding in Silicon Nanowire Battery Electrodes

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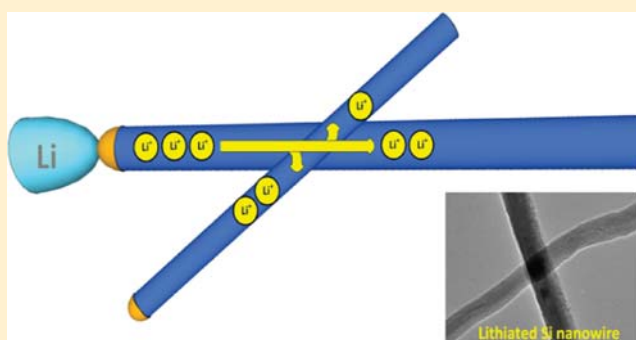
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S Supporting Information

ABSTRACT: From in situ transmission electron microscopy (TEM) observations, we present direct evidence of lithium-assisted welding between physically contacted silicon nanowires (SiNWs) induced by electrochemical lithiation and delithiation. This electrochemical weld between two SiNWs demonstrates facile transport of lithium ions and electrons across the interface. From our in situ observations, we estimate the shear strength of the welded region after delithiation to be approximately 200 MPa, indicating that a strong bond is formed at the junction of two SiNWs. This welding phenomenon could help address the issue of capacity fade in nanostructured silicon battery electrodes, which is typically caused by fracture and detachment of active materials from the current collector. The process could provide for more robust battery performance either through self-healing of fractured components that remain in contact or through the formation of a multiconnected network architecture.

KEYWORDS: Silicon nanowires, welding, self-healing, interfacial lithium diffusivity, in situ TEM, lithium-ion battery



Silicon is an auspicious candidate to replace today's widely utilized graphitic anodes in lithium ion batteries because its specific energy capacity (3579 mAh/g) is nearly 10 times that of carbon (372 mAh/g) and because it is an inexpensive and abundant resource.^{1–7} However, during lithiation and delithiation, Si undergoes a massive volume change (~300%), which has been reported to cause fracture and pulverization of the electrode, thereby leading to capacity degradation and failure of the battery cell.^{8–12} To circumvent the problem, researchers have developed nanostructured Si electrodes using thin films,¹³ nanoparticles,¹⁴ nanowires,⁶ and nanotubes.^{15,16} Compared to bulk forms, nanostructured Si exhibits higher yield strength and fracture strength and is better capable of accommodating massive volume strains.^{17,18} Despite these benefits, capacity fade during cycling remains a critical issue even for nanostructured Si electrodes, presenting challenges for their commercial development.

Cracking and pulverization are known to be mitigated in part by nanostructured forms of silicon, but several recent studies indicate that cracking can still occur in nanostructures subject to a variety of conditions.^{19–22} In contrast to this detrimental effect, we report an opposite effect, which may enable self-healing nanostructured Si-electrodes. While performing in situ transmission electron microscopy (TEM), we observe that

contacted surfaces of otherwise physically distinct silicon nanowires are fused together after lithiation and delithiation. To date, there have only been a few post-mortem studies suggesting the occurrence of bonding and coalescence of nanomaterials in lithium battery electrodes.^{23–27} For example, Li et al.²⁴ report the coalescence of Si nanoparticles from TEM images of cycled and dismantled composite electrodes. However, direct evidence and a detailed understanding of the process are both still lacking. We here report in situ TEM observations of the welding of physically contacted silicon nanowires (SiNWs) during electrochemical lithiation and delithiation. Our data indicates that this welding phenomenon is predominantly an electrochemically induced process, occurring at room temperature. Moreover, we demonstrate that the weld formed between SiNW surfaces is mechanically robust and exhibits evidence of facile transport of lithium ions, which are both desirable properties for enhanced battery performance.

The SiNWs used in this study (typically with $\langle 211 \rangle$ growth direction) are synthesized directly on TEM grids using bottom-

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up chemical vapor deposition (CVD) via the vapor–liquid–solid (VLS) process (see Supporting Information, Figure S1). The in situ operation and characterization is employed using a JEOL JEM-2100 LaB₆ TEM. We use a specialized piezo-actuated NanoFactory holder capable of three-dimensional coarse motion with subangstrom accuracy and simultaneous ability to image during manipulation (Figure 1a). The

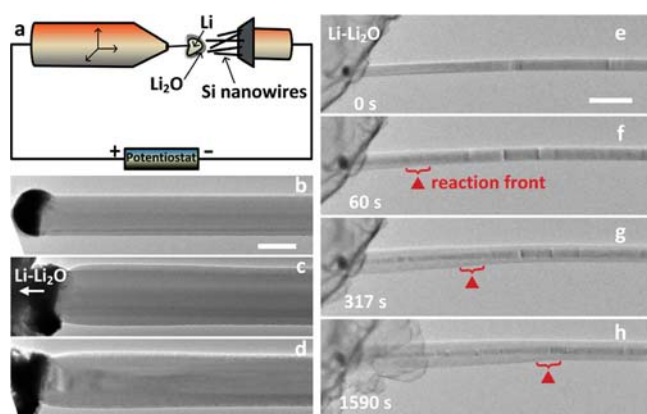


Figure 1. In situ lithiation and delithiation of silicon nanowires in TEM. (a) Schematic of experimental setup using lithium metal as a counter electrode. (b) A pristine nanowire approaching a lithium metal source. Scale bar of 200 nm. (c) Volume expansion as seen after lithiation for 30 min with a potential of -4 V applied to silicon nanowire versus the lithium electrode. (d) Volume contraction of nanowire after delithiation for 30 min with applied potential $+4$ V vs lithium. (e–h) Lithiation propagation front observed as a function of time in another SiNW. Scale bar of 500 nm.

manipulation tip carries a piece of lithium metal, which acts simultaneously as a Li source, a reference electrode, and a counter electrode, while a thin layer of native Li₂O due to the residual vacuum of the microscope serves as a solid electrolyte, allowing the diffusion of Li⁺ between the electrodes under potential bias.^{22,28,29} Figure 1b shows a pristine crystalline SiNW of diameter 212 nm adjacent to the approaching Li₂O-coated Li source. Figure 1c shows that partial lithiation occurs when a potential of -4 V is applied to the SiNW with respect to lithium metal. Upon lithiation, the increase in diameter of the nanowire is observed to be 50% (318 nm). Upon delithiation, with an applied bias of $+4$ V versus lithium metal, the nanowire shrinks to a diameter of 278 nm (Figure 1d). Because of large volume and structural changes during lithiation and delithiation, the reaction front can be readily identified from in situ TEM images as it traverses along the length of a NW (Figure 1e–h). Therefore, relative Li transport rates within various sections of a SiNW during lithiation and delithiation can be estimated from the speed of the reaction front, as determined by a series of TEM images captured during lithiation and delithiation.

To investigate Li transport across contacted SiNWs, two separate nanowires are brought into contact with each other by bending one of them with the manipulator probe at 0 V bias, as shown in Figure 2. One nanowire with a diameter of 143 nm is contacted by the lithium source while the other with diameter of 98 nm remains isolated (Figure 2a,d), contacted only indirectly, via the larger nanowire. Both nanowires are connected at the base to the silicon growth substrate. When a potential of -3 V with respect to lithium metal is applied to the silicon substrate, lithiation proceeds in the nanowire

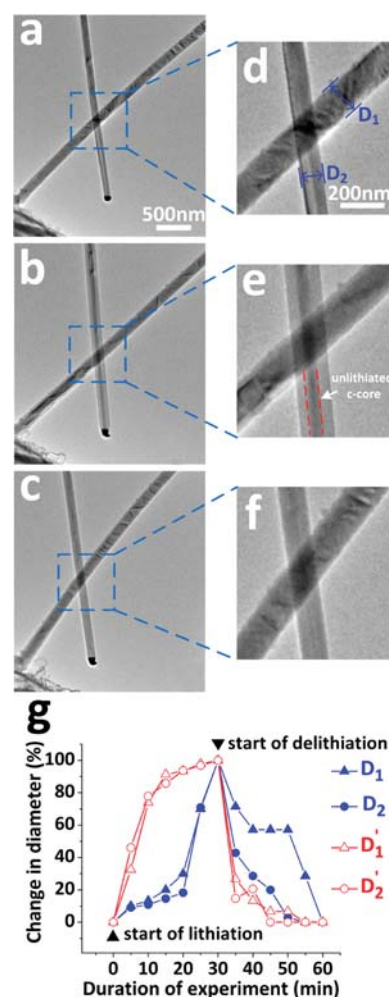


Figure 2. Lithiation and delithiation observed in crossed silicon nanowires. (a) Pristine nanowires. (b) Swelling of both nanowires after lithiation. (c) With delithiation, both nanowires contract, however, and fail to reach the original volume. (d–f) Blown up images focusing on crossed part of nanowire representing panels a–c, respectively. The measured D₁ and D₂ diameters for d–f are (143, 98) nm, (167, 148) nm, and (161, 125) nm respectively. (g) Changes in diameter in the D₁ and D₂ section of the crossed SiNWs (Figure 2d) plotted with respect to duration of experiment. Also observed results are plotted for another set of crossed SiNWs (Figure S2, Supporting Information) denoted as D₁' and D₂'.

directly contacting the Li₂O, propagating in both the radial and axial directions (Figure 2b,e). At the same time, we also observe lithiation advancing in the crossed nanowire, which is not itself contacting the lithium source. To test Li transport across the resulting interface of the two SiNWs, the diameter changes were subsequently monitored during delithiation by supplying the Si substrate with a bias of $+3$ V versus the lithium metal source (Figure 2c,f). As delithiation progresses, both nanowires are observed to decrease in diameter. We controlled the lithiation and delithiation times to make sure that the reaction front in the primary SiNW proceeded past the contact point of the two nanowires but did not reach to the Si substrate. Adjacent nanowires that are not in contact with the lithiated nanowires show no lithiation behavior, also confirming that the lithium transport is indeed through the SiNW–SiNW contact and not, for example, mediated via the Si substrate.

To test for any possible delay due to diffusion across the welded interface, we quantify the relative diameter changes of directly contacted and indirectly contacted nanowires during lithiation and delithiation, as shown in Figure 2g. These experiments were conducted by applying the bias voltages and observing the nanowire evolution at video rates for approximately 15 s, periodically every five minutes during lithiation. At times between observations, the illuminating electron beam is blanked in order to avoid possible beam effects on the sample. We define the variable diameters of the directly contacted and indirectly contacted nanowires in the vicinity of the junction as D_1 and D_2 , respectively, as shown in Figure 2d. We also define a corresponding pair of diameters, D_1' and D_2' , for a second pair of nanowires shown in Supporting Information Figure S2. Table 1 shows the diameters D_1 , D_2 ,

Table 1. Diameters of Two Sets of Crossed SiNWs in the Vicinity of the Crossing in Their Pristine, Lithiated, and Delithiated States

| SiNW diameter | pristine (D_p , nm) | lithiated (D_L , nm) | delithiated (D_D , nm) |
|---------------|------------------------|-------------------------|---------------------------|
| D_1 | 143 | 173 | 159 |
| D_2 | 98 | 153 | 118 |
| D_1' | 108 | 154 | 139 |
| D_2' | 142 | 205 | 171 |

D_1' , and D_2' of each respective SiNW in their pristine, lithiated, and delithiated states. We calculate fractional diameter changes during the lithiation phase according to the ratio $(D - D_p)/(D_L - D_p)$, and during the delithiation phase according to $(D - D_D)/(D_L - D_D)$, where in both expressions, D_p , D_L , and D_D correspond to the diameter of each SiNW in its pristine, lithiated, and delithiated state, respectively, and D represents the measured diameter as it varies with time. Using these expressions, we report the relative change in diameter of contacted nanowires as a function of time during lithiation and delithiation in Figure 2g. These measurements were obtained from experiments, during which we lithiated each crossed-SiNW system for 30 min, and subsequently delithiated for 30 min. Using the incremental diameter changes of each nanowire, we qualitatively compare the lithium propagation rates among SiNWs. With the exception of a delayed contraction briefly exhibited by D_2 upon delithiation, we observe that the rates of Li propagation in the indirectly contacted SiNWs are identical to those in the directly contacted SiNWs. Here, we note that SiNW system D_1' – D_2' lithiates faster and with less time-delay than SiNW system D_1 – D_2 . This difference in electrochemical behavior may be attributed to variable response of the Li_2O electrolyte to the applied potential between separate experiments.³⁰ We may also attribute the delayed contraction of D_2 to variant behavior of Li_2O or, alternatively, to different mechanical behavior of the larger nanowire (D_1 , e.g., increased stress and cracking) as compared to the smaller nanowire (D_2). Despite these experimental variations, the curves of Figure 2g provide evidence for identical rates of Li propagation in indirectly contacted SiNWs to those in SiNWs directly contacting the Li source. Therefore, we conclude that there is no additional barrier to Li diffusion between physically contacted SiNW surfaces at the charging rates used for these studies (approximately 2C, a rate which corresponds to charging or discharging in 0.5 hours).

We investigate the strength of the weld formed between two SiNWs using an experimental procedure shown in Figure 3.

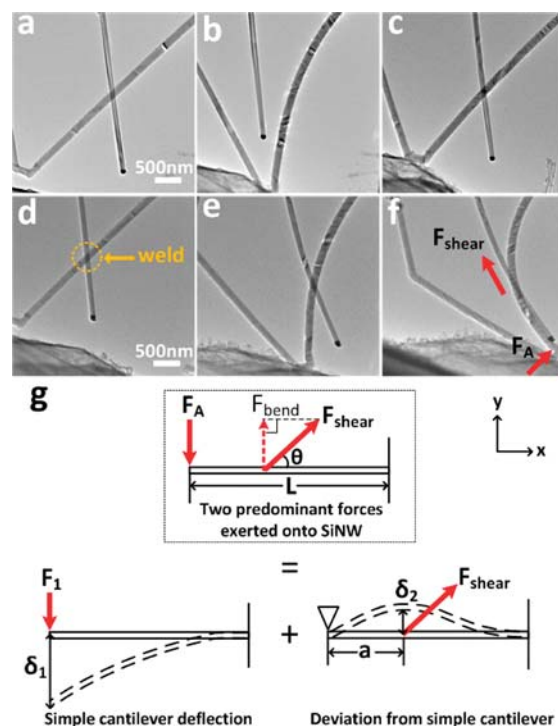


Figure 3. Determination of welding strength at the interface of crossed SiNWs after lithiation/delithiation. (a) As seen crossed nanowires. Same scale bar of 500 nm from (a–c). (b) Nanowires that are pulled apart to demonstrate they are grown independently. (c) Bend contours seen in both nanowires suggest they are in contact with each other. (d) Crossed nanowires after lithiation and delithiation. Same scale bar of 500 nm from (d–f). (e,f) Stress applied on nanowires in order to separate them. (g) The free-body-diagram (top), which depicts the total deflection of the SiNW in (f), illustrates the two predominant forces that generate the total deflection of the nanowire; F_A is the transverse force applied by nanomanipulator, and F_{shear} is the shear force exerted by the weld. The total deflection is a linear superposition of two distinct deflections: δ_1 , generated by F_1 (a component of the unknown, total applied force F_A) and δ_2 , generated by F_{shear} . To calculate F_1 , we model the system as a simple cantilever. To calculate F_{shear} , we model the system as a beam fixed at one end and pinned at the tip. F_{bend} is the transverse component of F_{shear} , a is the distance from the free end of the NW to F_{shear} , and L is the total length of the NW.

Figure 3a shows two pristine crystalline SiNWs, which appear to cross each other as viewed through the TEM. We note that the nanowire closest to the lithium source exhibits kinking, which is believed to be due to twinning along the growth direction. This is commonly observed among bottom-up grown SiNWs (approximately 40% of the total SiNWs),^{31,32} but has no contribution or observed effect on the lithiation processes in this study. In order to confirm that the crossed nanowires are not the branches of the same parent nanowire, but instead, physically distinct nanostructures, we separated one of the nanowires from the other using the nanomanipulator (Figure 3b). Because they are easily separated from one another, both nanowires are observed to be separate entities rather than a single, branched, or defective nanostructure. Next, the nanowires are brought back into physical contact with each other using the piezo-controlled STM probe. Single-crystal nanowires

that are bent exhibit a strong diffraction contrast in the form of Bragg-condition bend contours. These bend contours appear to move along the length of the nanowire as it is being strained.³³ The observed motion of the bend contours in both SiNWs unambiguously confirms that they contact one another (Figure 3c). Next, the SiNWs are lithiated and delithiated (Figure 3d) using similar parameters to those used for the experiment shown in Figure 2.

We perform two tests to determine if strong bonds are formed between two SiNWs after a single lithiation/delithiation cycle. First, we attempt to bring two SiNWs into and out of contact by applying positive and negative forces, normal to the plane of the SiNW junction (see Figure S4 in Supporting Information). Prior to lithiation, the negative normal force overcomes any van der Waals bonding that occurs when the two nanowires touch. After lithiation and delithiation, application of a negative normal force no longer separates the nanowires, suggesting the presence of a strong bond. Our second test, as demonstrated in Figure 3d–f and described in detail as follows, allows us to assign a value to the mechanical strength of the weld. Although the strength of the weld cannot be precisely determined using our experimental data, we can estimate a lower limit to its mechanical strength by the observation that it was able to withstand the loading depicted in Figure 3f, just prior to failure of the weld. To estimate this lower bound, we modeled the primary SiNW as a suspended cantilever, as shown in the free-body diagram of Figure 3g. This SiNW is fixed at one end at the silicon growth substrate and is fully suspended in vacuum at all other points along its axis. The deformed shape of this SiNW, as shown in Figure 3f, results from two concentrated forces, a transverse force at its free end exerted by the moving Li source (F_A in Figure 3f,g), and a shear force from the weld with the secondary SiNW (F_{shear} in Figure 3f,g). The combined effect of these two forces on the deformation of the suspended SiNW is equivalent to the superposition of two decoupled configurations as illustrated in Figure 3g. In one configuration, the suspended SiNW is subject to a transverse force (labeled as F_1) at its free end. In another configuration, the displacement of the free end of the SiNW is fixed by a pin and the SiNW is subject to the concentrated force F_{shear} . The resulting deflection of the SiNW in these two configurations can be solved analytically (as detailed in Section III of Supporting Information) from which F_{shear} and the shear strength can be estimated. From this analysis, we estimate the shear strength to be at least 200 MPa. Thus, our analytical model suggests that the strength of the fused Si region is comparable to that of stainless steel (205 MPa)³⁴ and ceramic silicon carbide (~ 200 MPa),³⁵ thus demonstrating that a strong bond has been formed by the electrochemical cycling. To further verify the calculated strength, we also perform three-dimensional nonlinear finite-element analysis (FEA) (as detailed in Section IV of Supporting Information). This analysis addresses any nonlinear effects arising from large deformations as depicted in Figure 3e,f, and it leads to an estimated shear stress at the welded region of about 308 MPa, confirming the robust strength of the weld. Similar mechanical studies were carried out on a total of five separate nanowire junctions with qualitatively similar results, confirming that the strong bonding is a reproducible feature.

The observation of strong bonding in the welded region and facile lithium transport through the SiNW interface during lithiation and delithiation can be explained as follows. Generally, as Li intercalates into the SiNW, the energy barrier

for breaking the strongly covalent Si–Si bonds is significantly reduced. Initially, the Si–Si bonding energy is very high (2.72 eV) but, according to a model put forth by Zhao et al.,³⁶ when a single Si–Si bond is surrounded by four Li atoms the energy barrier for breaking the bond is reduced to a mere 0.08 eV. Consequently, Si–Si bonds readily break, as they also tend to stretch, during Li intercalation. As Si–Si bonds are broken, the dangling bonds are saturated by neighboring Li atoms in order to lower the system's free energy. This model may be extended to our specific study of Li-assisted welding at the interface of two SiNWs. We observe that Li–Si bond formation occurs first at the high-energy nanowire surface before the lithiation reaction propagates inward toward the nanowire core. When the surfaces of two nanowires are directly in contact, Li atoms can bond simultaneously with the surface atoms on both the primary and secondary nanowires. Our results indicate that there is no additional energy barrier to diffusing to the surface of the second nanowire along this interfacial contact and reacting with this secondary surface as well. As a result, during intercalation, the surface energy of the crossed-SiNW system is reduced by forming metastable Li–Si bonds, which bridge the two nanowires at the interface. However, during Li extraction this Si–Li–Si bridge is broken and there is a kinetic driving force for neighboring Si atoms at the interface to bond to one another. Thus, the decrease of surface energy is the kinetic driving force for welding SiNWs. Moreover, the reconstructing of surface Si–Si bonds by Li transport across connected SiNWs makes the welding phenomenon possible at room temperature. Finally, we note that the SiNWs used in our experiments were all encompassed by a ~ 2 nm layer of native SiO_x , but, this SiO_x layer apparently does not complicate the Si–Si bonding process. One possible explanation for this is that the SiO_x may be reduced into Si, Li_2O and Li-containing silicates upon Li^+ insertion, of which the latter two may also be serving to enhance the strength of the welded junction.^{37–39} A second possibility is that the volume expansion of the SiNW during lithium insertion may also break the SiO_x layer, thereby enabling direct contact between the interfacial host atoms.^{24,26,40} This explains the Li–Si bonding and corresponding phase changes at the interface of the crossed SiNW system.

To summarize, we have directly observed electrochemical welding of cross-contacted SiNWs at ambient temperatures during lithiation and delithiation by in situ TEM studies. By comparing the incremental expansion and contraction of the SiNWs that are in direct contact with the Li source to those that are not, we have demonstrated that there is facile Li transport between two SiNW interfaces. We also estimate the minimum mechanical shear strength of the interfacial weld between two SiNWs to be ~ 200 MPa, indicating that this welding process generates strong interfacial bonds. The inherently high capacity of silicon, combined with facile Li diffusion between surface-contacted Si nanostructures, may enable the self-assembly of an interconnected network for Si nanowires in anodes, leading to high energy density lithium ion batteries with improved cycling stability. We suggest that this welding phenomenon may also serve as a self-healing mechanism in Li-ion battery electrodes. It is well-known that during cycling SiNWs may lose electrical contact with the electrode support, but our experimental results indicate that such detached nanowires may still actively participate in Li storage if they remain part of a robust contacted network, formed during the first lithiation cycle.⁴¹ Furthermore, the welding and self-healing processes that we have observed in

SiNWs may equally apply to other alloy-based anode materials, such as germanium and tin.

■ ASSOCIATED CONTENT

Supporting Information

Sample preparation technique (Figure S1), lithiation and delithiation behavior in another set of physically contacted crossed SiNWs (Figure S2), and detailed description of the simplified analytical model and nonlinear finite element analysis for shear strength at its welded interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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