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In Situ Transmission Electron Microscopy of Oxide Shell-Induced Pore Formation in De)lithiated Silicon Nanowires

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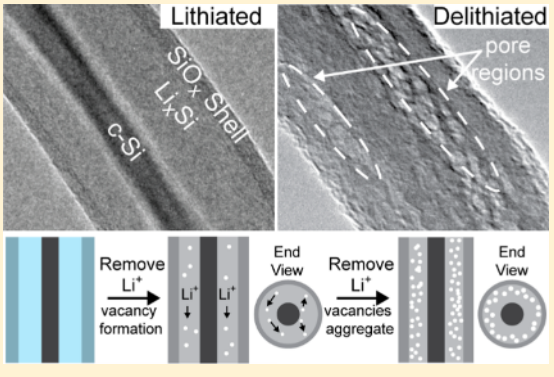
Supporting nformation

ABSTRACT: Silicon (Si) nanowires with a silicon oxide (SiO) shell undergoing lithiation and delithiation were examined by in situ transmission electron microscopy (TEM). Large pores formed in the nanowires during the delithiation cycle. We found that the oxide shell constrains the expansion of the Si nanowires during lithitation and then induces pore formation in the nanowires. We propose that the SiO shell prevents the vacancies that result from the loss of lithium from escaping the Si core, leading to pore nucleation and growth. It is also possible that the di erence in mechanical properties of the expanding and contracting Si nanowire and SiO shell contribute to the observed pore formation. This in situ study reaffirms the need to directly observe structural changes that occur during cycling in battery materials, especially when modified by coatings.



Many emerging technologies require lithium ion batteries (LIBs) with improved energy density, rate capability, cost, and safety.[1 3] Silicon (Si) is an attractive next-generation anode material because it is inexpensive and abundant and has a high theoretical gravimetric storage capacity of 3579 mAh/g, nearly 10 times that of present graphite electrodes.[4 6] Si, however, expands signi cantly during lithiation, increasing in volume by about 300 to reach its fully lithiated state.[7,8] Although nanostructured Si can withstand these lithium-induced volume changes without pulverization,[9] the repeated expansion and contraction can lead to loss of electrical connection between the nanowire and conductive additives, destabilize the solid-electrolyte-interphase (SEI) layer, and lower Coulumbic efficiency over time.[10 12]

One strategy to improve the performance of nanostructured Si is to add a surface coating layer. A wide variety of coating materials have been explored, including silicon oxide (SiO_x), carbon, Al_2O_3, and TiO_2.[10 26] The surface coating can increase electrical conductivity, improve mechanical stability, provide stronger adhesion to added binder, and protect the active material from reaction with the electrolyte. Silicon oxide is an especially interesting coating because it can be grown conformally on the Si surface by straightforward oxidation processes. Ex situ transmission electron microscopy (TEM) studies have found that such shells can limit the volume expansion during lithiation, which has been correlated to improved cycling stability in coin cell experiments, although with reduced capacity.[14,19] Here we show that SiO_x shells on Si nanowires can also lead to the rapid evolution of pores in the material during delithiation.

We discovered this unusual evolution of pores in Si nanowires coated with SiO_x while observing nanowires undergoing lithiation and delithiation by in situ TEM. In situ TEM allows real-time, direct investigation of morphology changes that occur during cycling, such as inhomogeneous lithiation of the material, self-limiting lithiation, and as in this study, pore formation, which may not be noticed by ex situ characterization.[16,18,20,27 34] In the materials studied here, a thin SiO_x surface layer that is about 10 nm thick, constrains the expansion of the Si nanowire and prevents complete lithiation. This SiO_x shell also induces pore formation in the nanowire during delithiation. The resulting pore volume in the nanowires is signi cant, increasing the total volume of the Si nanowires by more than 40 after just one lithiation and delithiation cycle. We propose that the oxide shell restricts the migration of vacancies to the nanowire surface, leading to the

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nucleation and accumulation of pores. Differences in the mechanical properties of the lithiating and delithiating shell and core materials could also be playing a role. If the shell burst during the lithiation cycle, the nanowires did not form pores upon delithiation.

Si nanowires were made by supercritical fluid liquid solid (SFLS) growth in toluene with Au nanocrystal seeds and trisilane as a reactant and then heated in air at 800 °C for 3 h to generate a surface oxide layer that was about 10 nm thick. Most of the nanowires used in the study had 211⟩ growth direction with (111) twins extending down their length (see the Supporting Information for scanning transmission electron microscopy (STEM) high-angle annular dark- eld (HAADF) images and elemental mapping by energy-dispersive X-ray spectroscopy (EDS) of a Si nanowire with a SiO_x shell). In situ TEM studies were carried out using a Nanofactory TEM-STM holder inside a Titan 80-300 scanning/transmission electron microscope (S/TEM).

Figure 1 shows a time-series of TEM images of a Si nanowire with a SiO_x surface oxide shell undergoing lithiation and

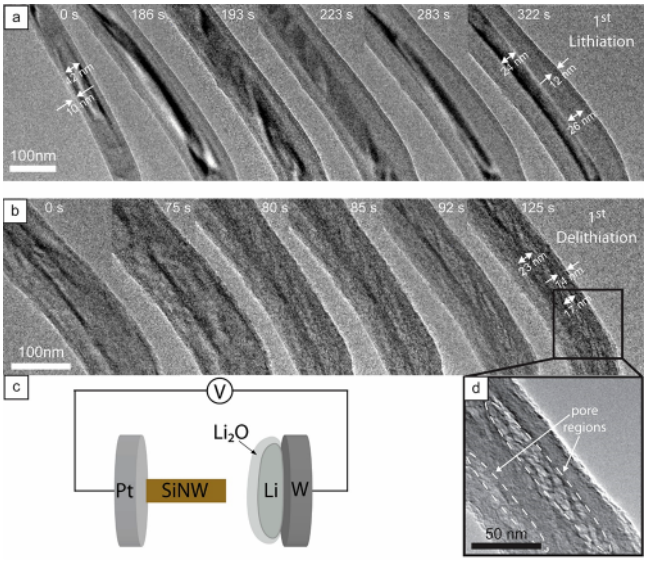

Figure 1. TEM images of a Si nanowire (42 nm diameter) with a SiO shell (11 nm thick) during the first (a) lithiation and (b) delithiation cycle. The nanowire increased in volume by 130 . A 24 nm diameter crystalline core of Si is still present after lithiation (see the Supporting Information for the accompanying video file, LithiationVideo_1.mp4.) (c) Illustration of the in situ TEM nanobattery setup. (d) A higher-magnification TEM image of pores that form in the amorphous Si region of the nanowire after delithiation.

delithiation. Lithiation initially proceeds down the length of the Si surface of the nanowire and then extends radially into the core. This mechanism of *surface-into-core* lithiation is well-established for Si nanowires.[31,32] Lithiation expands the nanowire in both the radial and axial directions and stops when the nanowire has increased in volume by about 130 . This amount of expansion is signi cantly less than the 300 volume expansion[16] that is typical for complete lithiation of a Si nanowire. In this case, the oxide shell has constrained the volume expansion and as a result prevented complete lithiation. This is consistent with published coin cell data showing that Si anodes with SiO_x surface coatings tend to have reduced speci c capacity during cycling.[14,19] Because the nanowire in Figure 1 has not fully lithiated, there is still crystalline Si within the core of the nanowire surrounded by the amorphized, lithiated region of the nanowire. This thin Si core region remains crystalline after the rst delithiation cycle, but eventually becomes amorphous with further cycling.

During the rst delithiation cycle, the nanowire with the SiO_x shell evolves a large number of pores, as shown in Figure 1d. Similar densely packed pores have been observed in a Si nanoparticle with an oxide shell after delithiation.[18] After delithiation, the nanowire remains expanded by 40 compared to its initial state because of the additional pore volume in the nanowire. The pores disappear when the nanowire is again lithiated and then reappear when delithiated. The total volume occupied by the pores further increases after the second cycle, expanding by an additional 25 compared to its size after the rst delithiation cycle. This is signi cantly larger than the typical amount of plastic deformation that can occur as a result of the lithiation delithiation cycling of Si.[35] Figure 2 shows

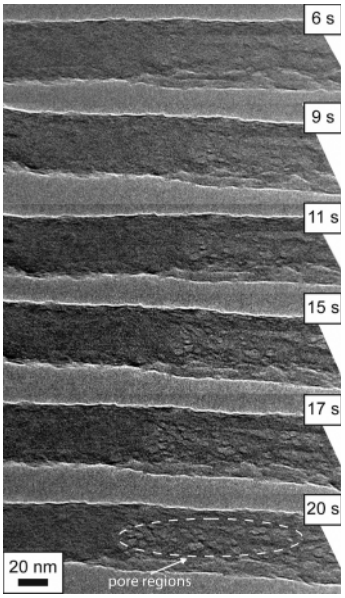

Figure 2. Time series of in situ TEM images showing the evolution of pores in a Si nanowire coated with SiO undergoing its first delithiation cycle (see the Supporting Information for the accompanying video file, PoreVideo_2.mp4).

another time series of TEM images of a Si nanowire with a SiO_x shell exhibiting pore formation during the delithiation step (see the Supporting Information for additional TEM images).

In some instances, the SiO_x shell ruptured during lithiation and the nanowire expanded to its fully lithiated state. Figure 3 shows an example of a time series of TEM images where the SiO_x shell bursts and the nanowire expands by 270 and becomes fully amorphous by the end of this rst lithiation cycle. In this case, pores do not form in the nanowire upon delithiation. Without an intact oxide shell, there is no pore formation. For example, the TEM images in Figure 4 show a nanowire undergoing lithiation and delithiation with an oxide shell that has burst at a speci c point along the nanowire. Pores did not form near the point of rupture of the oxide shell; the rest of the wire still coated by intact oxide lled with pores during delithiation (see the Supporting Information for more

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