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In-situ TEM Study of Internal and External Stress on Lithiation behavior of High Capacity Anode Materials with a Large Volume Change

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Lithium ion batteries are widely used for powering our daily electronic devices, such as pocket gadgets and portable electronics. However, application of lithium ion batteries to a more broad basis such as all-electric vehicles and grid storage is still limited by the capacity and cycling stability[1-4]. Si and Ge possess high theoretical capacity of almost 10 times of graphite. However, Si and Ge are often invariably associated with a large volume change upon lithium ion insertion and extraction. Consequently, the volume change causes electrochemical instability and chemomechanical effect. Lithiation of Si and Ge are featured by the formation of a core-shell structure, characterizing the unreacted core and lithiated shell. Lithiation of crystalline Si will generate a concentrated hoop tension, which may cause fracture of the material. Large compressive stress is also generated at the reaction front, which is often characterized by a retardation of the reaction rate. However, lithiation of amorphous Si and crystalline Ge is less self-regulated than crystalline Si. Therefore, lithation induced internal stress can cause lithitaion retardation, fracture, and ultimately pulverization of the active materials, contributing to the limited extraction of the theoretical capacity, fast capacity fading, and poor rate capability of the battery. Understanding of lithiation induced internal stress effect has stimulated microstructural designing strategies for mitigating these problems.

Here we use in-situ TEM to directly visualize the effect of both internal and external stress on the lithiation behavior of Si and Ge. The in-situ TEM was carried using an open-cell nanobattery configuration based on a single nanowire electrode and Li/Li_2O counter electrode. The nanobattery device was carried out using a Nanofactory STM holder as reported in prior publication[5]. The surface Li_2O layer on the Li metal electrode serves as the solid electrolyte. In order to drive lithium ion through Li_2O, an overpotential of -0.5V to -2V is applied.

We found that both internal and external stress can affect the lithiation behavior of both Si and Ge. The internal stress induced lithation retardation is termed as self-retardation. Although crystalline Ge and amorphous Si show less degree of self-regulation, we have found that an external stress can dramatically modify the lithiation behavior and structural evolution of crystalline Ge nanowire. The lithiation behavior of a free-standing Ge nanowire is characterized by the formation of core-shell structure, with the boundary between the un-reacted core and the reacted shell moving inwards. For a free standing Ge nanowire, the lithiation induced core-shell structure possesses an axially symmetry.

The effect of an external stress on the lithiation behavior of Ge nanowire was carried out by the following experiment as illustrated in Figure 1. In the nanobattery configuration during the in-situ TEM testing, the Li metal electrode was pushed against the Ge nanowire, leading to the bending of the Ge nanowire. Upon bending, one side of the nanowire is under compression, while the other is under tension. We noticed that the lithiation rate is shows significant difference at the two sides of the Ge nanowire when the Ge nanowire is bent. The lithation speed at the tensile side is much faster than at the compressed side. Difference of the propagation speed of the reaction front at the tensile and compressive side gives to a non-symmetrical core-shell structure, which is characterized by more unreacted Ge at the compressive side as illustrated by the 2400s image in Figure 1. The experimental observation is consistently supported by chemomechanical calculations. Present observation has important implications for microstructural designing of anode materials based on Si and Ge for which the active materials should be free from impingement during lithiation. Otherwise, the impingement induced stress would limit the lithiation rate and capacity of the active material.

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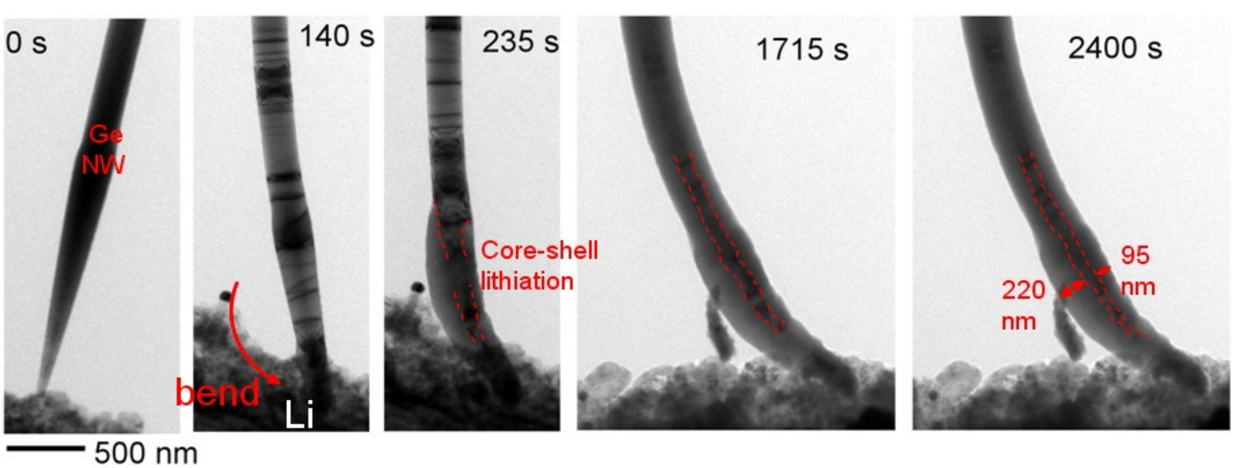

Figure 2 Time series of the TEM image showing the lithiation of the Ge nanowire at different stages of lithiation (Note that the GeNW is bent towards the right side when it is pushed against the Li metal electrode).

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