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Tuning the Outward to Inward Swelling in Lithiated Silicon Nanotubes via Surface Oxide Coating

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Development of electrode materials with high energy density and long cycle stability is critically important for advanced lithium-ion batteries (LIBs). As anode with the highest theoretical capacity, silicon (Si) suffers from huge volume changes upon cycling, which causes the fracture of both Si and solid electrolyte interphases [1,2], resulting in electrically disconnected components and capacity fade. Considerable efforts have been made to mitigate the mechanical degradation of Si anodes through nanostructuring and surface coatings [3]. However, it is still unclear how the surface coatings influence the reaction dynamics and degradation of Si nanostructures and to what degree the volumetric swelling of Si nanostructures can be confined by surface coatings. *In situ* transmission electron microscopy (TEM) electrochemistry technique allows for not only direct observation of the real-time lithiation process, but also precise measurement of the geometrical changes of electrodes during cycling. Amorphous-Si (*a*-Si) nanotubes with surface silicon oxide (SiO_x) coating provides a model system to study the complicated lithiation-delithiation dynamics in which concurrent reactions occurs in two dynamic systems that can interact on each other.

In this presentation, the electrochemically induced swelling of *a*-Si nanotubes with different thicknesses of surface SiO_x layers was systematically studied by the integrated method of *in situ* TEM experiment and chemomechanical modeling [4]. Surprisingly, no inward expansion occurs at the inner surface during lithiation of *a*-Si nanotubes with native oxides with the introducing of open space; while the swelling behavior can be effectively tuned by introducing the surface oxide, from the outward to inward. while increasing the thickness of SiO_x at the *outer* surface can facilitate the mechanical confinement on the lithiated *a*-Si nanotubes, causing an inward expansion. In contrast, SiO_x coating on the *inner* surface can serve as a mechanical barrier to hinder the inward expansion. We further note that the reaction mechanism of *a*-Si nanotubes, including sandwich lithiation and two-stage lithiation process, remains unchanged with the increasing thickness of surface coatings [4,5]. The chemomechanical modeling reveals the mechanical confinement effects originated from SiO_x coatings on *a*-Si nanotubes, underscoring the important role of anisotropy of lithiation-induced chemical strains. Our work not only provides insights into the degradation of nanotube anodes with surface coatings, but also sheds light onto the optimal design of hollow anodes for high-performance lithium-ion batteries [6].

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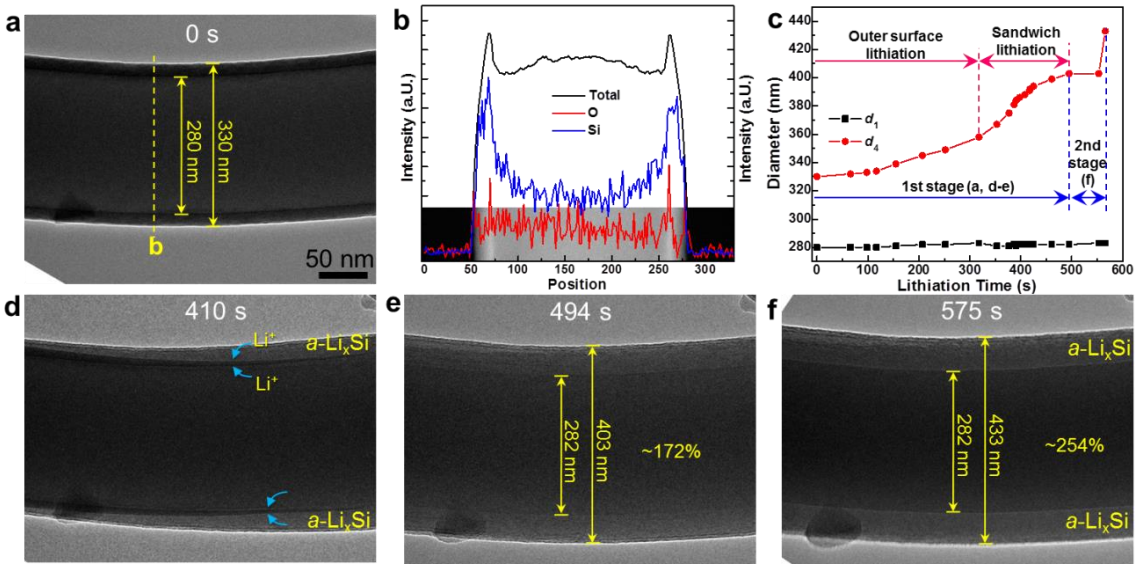

Figure 1. Lithiation dynamics of an *a*-Si nanotube with native oxide. (a-b) Structure of pristine a-Si nanotube with native oxide. (c) Change of the inner (d_1) and outer (d_4) as a function of lithiation time, showing a two-stage process. (d-f) Lithiation of the *a*-Si nanotube with native oxide.

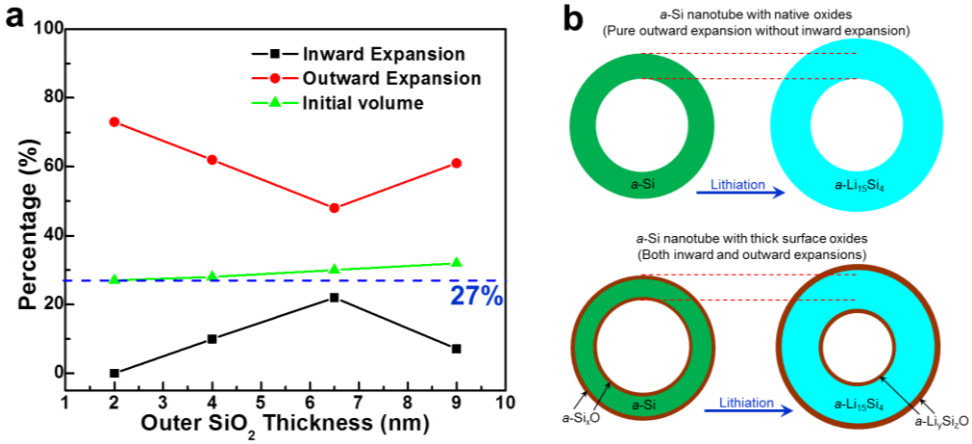

Figure 2. Mechanical confinement effects of the outer SiO_x layers on lithiated *a*-Si nanotubes. (a) Experimental measurements and (b) schematic illustration.

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