Supplementary Information

Operando Transmission Electron Microscopy Study of All-Solid-State Battery Interface: Redistribution of Lithium among Interconnected Particles

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Operando experiments were performed using a FEI Titan G2 transmission electron microscope (TEM) operated at 300 kV. Half TEM grid with Si nanoparticles (NPs) and electro-polished tungsten needle with lithium were mounted onto a Nanofactory TEM holder in an Ar glovebox and transferred to the TEM in an Ar-filled glove bag. The glove bag with the TEM holder was kept inside another glove bag, which was wrapped around the entrance of the goniometer, with Ar flowing while inserting the holder into the TEM. In order to reduce the influence of the electron beam on the specimen, a low electron dose rate of below 10 $e^-/Å^2/s$ was used for recording image sequences using a Gatan K2 IS direct electron detection camera. A negative voltage with respect to Li was applied to Si nanoparticles (NPs) to lithiate NPs electrochemically, while positive voltage with respect to Li was applied to NPs electrochemically. No bias was applied between the Li and NPs during chemical lithiation.

For proper comparison between the chemical and electrochemical lithiation process, it is imperative that other than the removal of the LiOx layer from a small part of LiOx@Li, conditions such as connections between the silicon NPs in the cluster as well as cluster and copper grid connection must remain intact. To ensure this, we identify the exact position of the electrode-electrolyte contact and carefully retract the W needle, thanks to the precise control of the piezo device. The W needle was then moved away from the silicon cluster (> 200µm) and the LiOx layer was removed locally by carefully scratching the front edge of the LiOx@Li using precise up-down movements. The needle was then brought back and connected to the NP cluster at the same point.

Movie S1. Lithiation of a typical Si NP cluster.

Movie S2. Loss of contact between the electrode and electrolyte.

Movie S3. Lithiation and delithiation a Si NP cluster during direct contact between Li and Si.

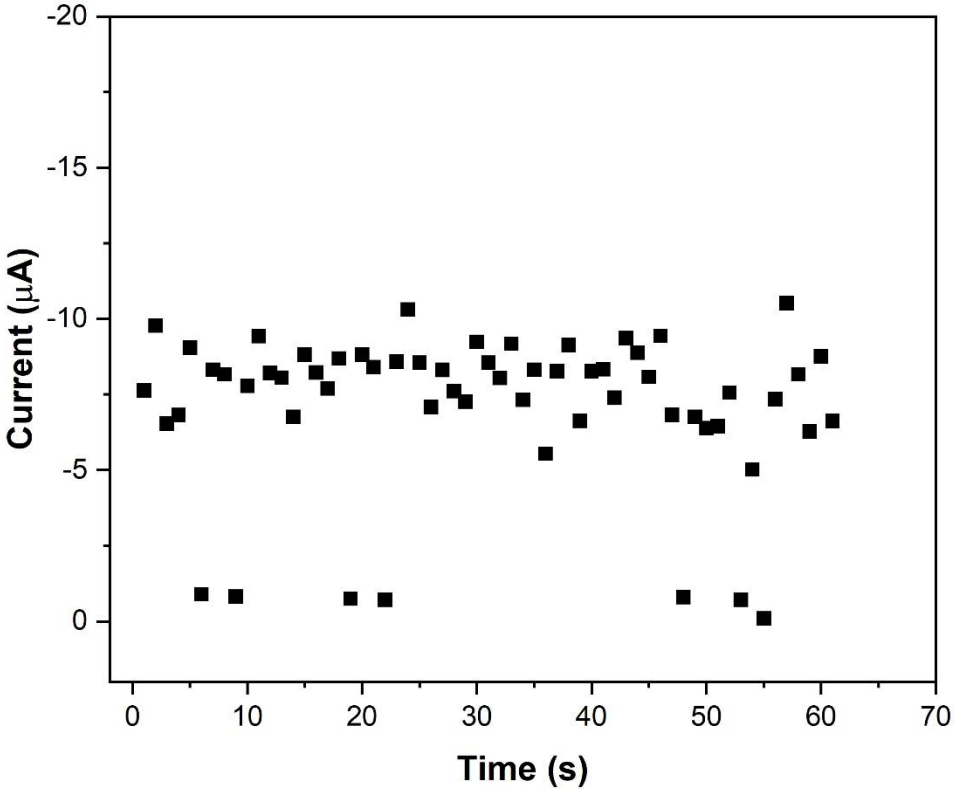

Figure S4. Current during the lithiation of the Si nanoparticle cluster shown in Figure 2 at -0.2V.

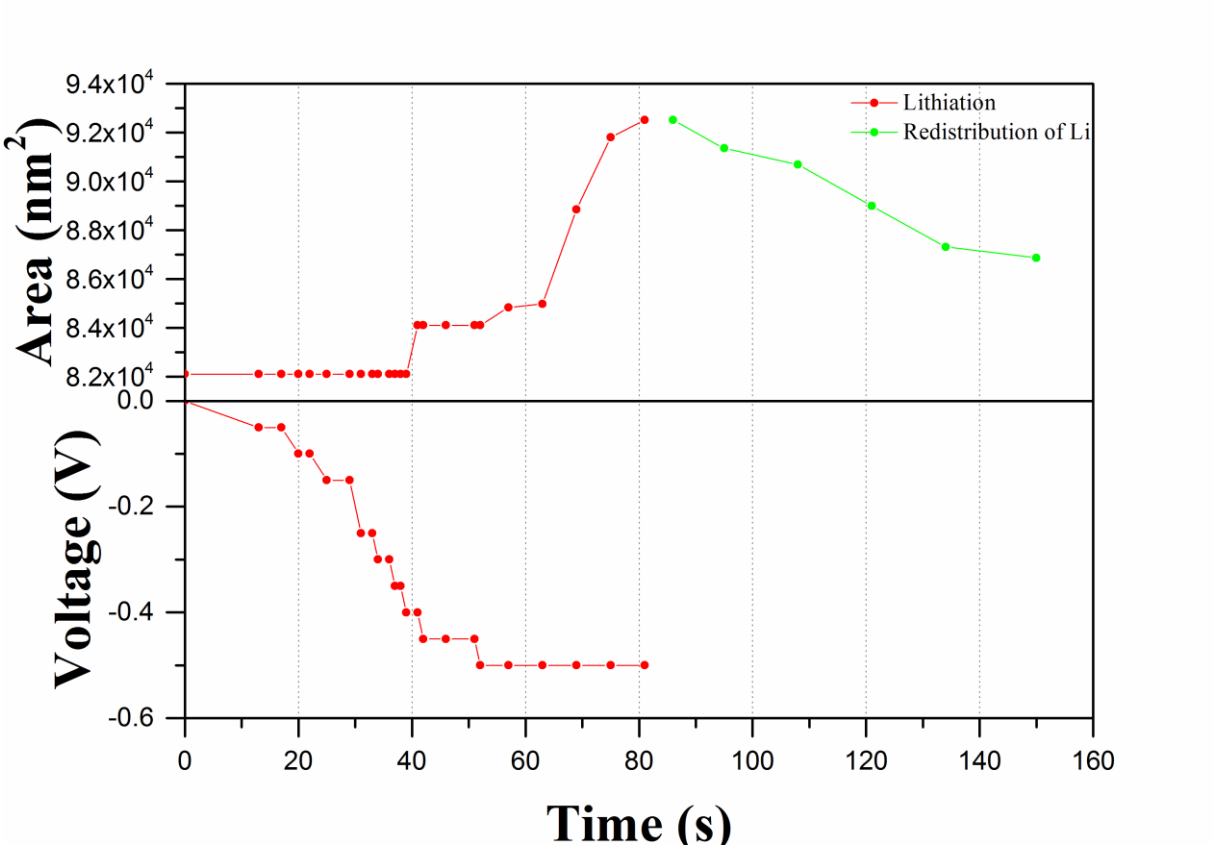

Figure S5. Expansion and contraction of a Si nanoparticle cluster during lithiation and subsequent redistribution of lithium. The plots show the area of the cluster measured from TEM micrographs and the corresponding applied bias voltage as a function of time.

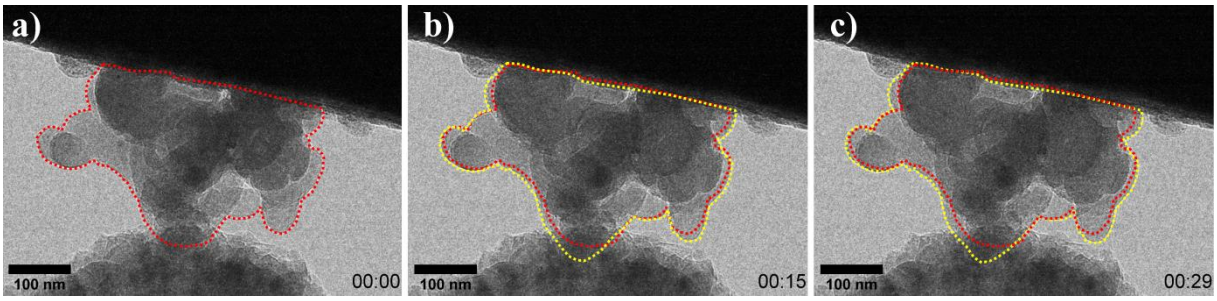

Figure S6. Chemical lithiation of a Si nanoparticle cluster. The red dotted line marks the shape of the cluster before chemical lithiation. The yellow dotted line shows the shape of the cluster at the indicated point in time during chemical lithiation.

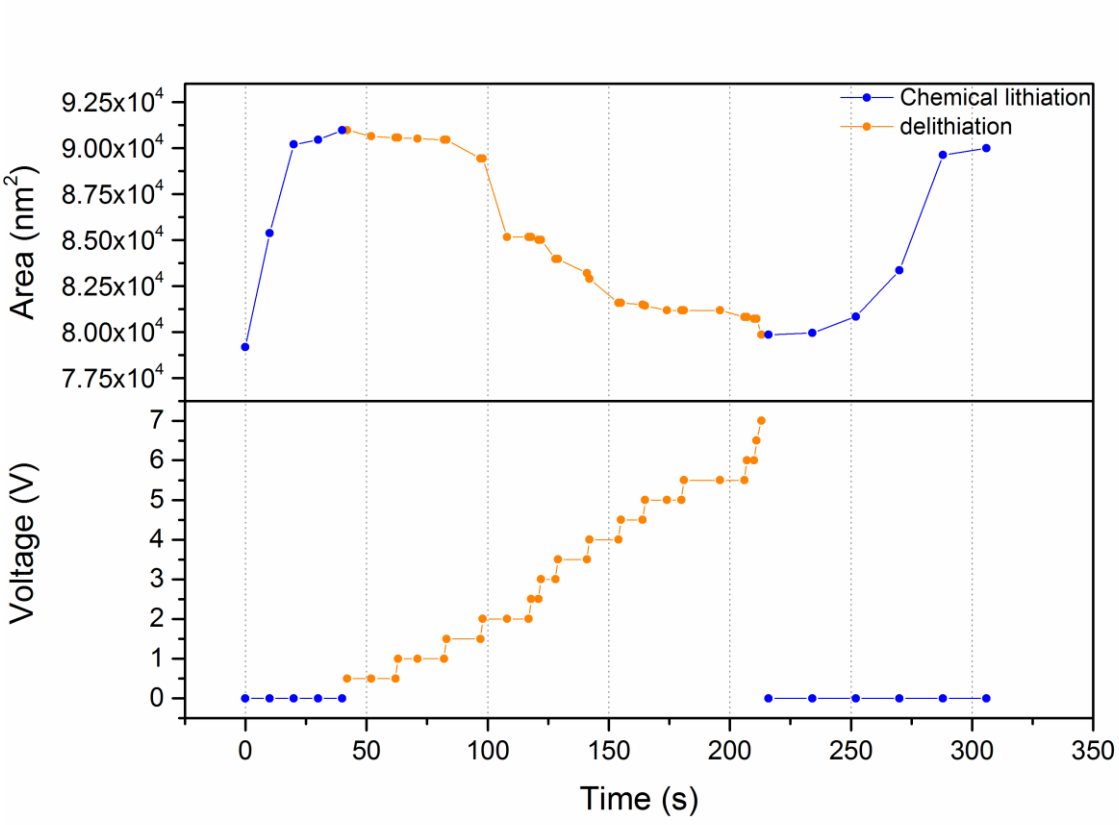

Figure S7: Expansion and contraction of a Si nanoparticle cluster during repeated (chemical) lithiation and delithiation. The plots show the area of the cluster measured from TEM micrographs and the corresponding bias voltage as a function of time.