

# Deformations in Si-Li Anodes Upon Electrochemical Alloying in Nano-Confined Space

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## SUPPLEMENTARY INFORMATION

**Computational Modeling.** To model the expansion and contraction of Li-alloy we developed a simple lattice-based spring model (LSM) for a viscoplastic material<sup>1</sup>. In this model, the solid material is represented by a network of springs with Hooke's constant  $k$  and rest length  $l_0$ , connecting point masses. Elastic deformation of the Li-alloy shell corresponds to compression and stretching of the springs. Plastic yielding of the network at a yield strain  $\varepsilon_y$  is modeled by changes in the spring rest length  $l_0$  to satisfy the following constitutive law:

$$\sigma = \begin{cases} E\varepsilon, & |\varepsilon| < \varepsilon_y \\ E\varepsilon_y \text{sign}(\varepsilon), & |\varepsilon| > \varepsilon_y \end{cases}$$

Here,  $\sigma$  is the material stress and  $E$  the Young's modulus of the solid. In our simulations, we set  $\varepsilon_y = 0.005$ . The process of Li insertion/extraction is modeling by gradually changing the rest length  $l_0$ .

The Li-alloy two-dimensional shell is constructed from concentric layers of uniformly distributed nodes. Each layer contains 157 LSM nodes. The radial layers are separated by a distance that is equal to the average distance between nodes within layers. The springs in the LSM network connect the nearest and next-nearest neighbor nodes. With this spring arrangement, the Poisons ratio of the solid is  $\nu = 0.25$ , and the Young's modulus is  $E = 5k/2l_0$ . The elastic energy associated with a node at the position  $\mathbf{r}_i$  is  $E = 0.5 \sum_j k(r_{ij} - l_0)^2$ , where  $r_{ij}$  is the length of the spring between two neighbor nodes. This elastic energy results in a force  $\mathbf{F} = \partial E / \partial \mathbf{r}$ .

Since the Li insertion and extraction are relatively slow processes, the shell evolution proceeds through a series of equilibrium states. To capture the overdamped dynamics of shell deformation, we introduce a dissipative force into the model and iterate the spatial positions of the nodes using the velocity Verlet algorithm until forces on each node are balanced.

**Synthesis.** Si deposition was performed at  $\sim 1$  Torr in a horizontal tube furnace (inner tube diameter  $\sim 28$  mm) heated to 500 °C. High purity 5% SiH<sub>4</sub> in He precursor gas mixture (Airgas, USA) was

introduced at a flow rate of 50 sccm for the desired time<sup>2</sup>. Carbon deposition was performed at atmospheric pressure in a horizontal tube furnace (inner tube diameter ~ 20 mm) heated to 700 °C. High purity C<sub>3</sub>H<sub>6</sub> precursor gas (99.5 %, Airgas, USA) was introduced at a flow rate of 50 sccm<sup>2</sup>. A bubbler filled with mineral oil was placed at the exhaust to minimize the backflow of air into the system. Before and after the Si and C deposition experiments, the system was purged with high purity Ar (99.99 %, Airgas, USA) at a flow rate of 50 sccm. The samples were taken out of the furnace at temperatures below 50 °C. After the completion of the deposition processes, the coated alumina template was etched in a 10 % HF solution, with a subsequent DI water rinse. Due to the much smaller pore size at the very surface of one of the alumina membrane sides, the synthesized vertically aligned and ordered 60 µm long Si-C tubes had partially closed/sealed tips. Since these tips of the tubes later faced the separator membrane in a coin cell, we expect Li ions to mostly enter the tubes from the side, rather than from the tip. This should be particularly true after several cycles, when the partially closed tips become completely sealed by the products of the initial electrolyte decomposition during the first few SEI formation cycles.

**Characterization.** The wt. % of the deposited Si was estimated using a high precision analytical balance (AND GH-120, A&D Company, Japan) as well as by measuring the mass change during C and Si oxidation in air using a thermo-gravimetric analysis system (Q50, TA Instruments, USA). TEM samples were prepared by sonicating the anode and dispersing the isolated tubular particles on a lacey carbon grid. Samples after electrochemical cycling were extensively cleaned with carbonates and dried in vacuum prior to TEM studies. TEM observations were carried out using a JEOL 100CX microscope (JEOL, Japan) operating at 100 kV. SEM studies were performed using a LEO 1530 SEM microscope (LEO, Japan, now Nano Technology Systems Division of Carl Zeiss SMT, USA). An in-lens secondary electron detector was used for the studies, most of which were performed using an accelerating voltage of 10 kV and a working distance of 5-8 mm.

**Electrochemistry.** Working electrodes were prepared by attaching a solid C-Si nanotube membrane to a Cu foil using a pre-cast PVDF binder (pure 9305 (Kureha, Japan)). To ensure good electrical contact, a mechanical pressure of ~200 g/cm<sup>2</sup> was applied to the membrane during drying. The electrodes were degassed in vacuum at 100 °C for at least 2 hours inside an Ar-filled glove box (< 1 ppm. of oxygen and water, Innovative Technology, Inc., USA) and were not exposed to air prior to assembly into cells. The commercial electrolyte was composed of 1M LiPF<sub>6</sub> salt in the mixture of carbonates (Novolyte Technologies, USA). Lithium metal foil (1 mm thick) was used as a counter electrode. 2016 stainless steel coin cells (without any springs) were used for electrochemical measurements. The working electrode Cu current collector was spot-welded to the coin cell for improved electrical contact. Charge and discharge rates were calculated assuming the theoretical capacities for C and Si, given the composition of

the active material (either C or C-Si mixture). Coulombic efficiency was calculated as  $100\% \cdot (\frac{C^{dealloy}}{C^{alloy}})$ , where  $C^{alloy}$  and  $C^{dealloy}$  are the capacity of the anodes for Li insertion and extraction. Charge-discharge tests were performed between 0.01 and 2 V vs. Li/Li<sup>+</sup>.

## References

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