

Supporting Information

The Effect of Lithium Surface Chemistry and Topography on Solid Electrolyte Interphase Composition and Dendrite Nucleation

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Optical three-electrode cell

A diagram of the optical three-electrode cell, used to observe *in-situ* Li electrodeposition on treated and untreated Li surfaces, is shown in **Fig. S1**. It consists of a t-shaped glass cell 36 mm in length and 9 mm in diameter with openings at either side for the working and counter electrodes and an opening at the top for the reference electrode. The working electrode was sealed to the cell with a series of gaskets. First, a Viton o-ring was placed in a groove in the glass, then a 3.2 mm thick piece of polypropylene with a 0.95 cm diameter hole drilled in it. Next a 0.79 mm thick fluorosilicone gasket with a 0.71 cm diameter hole was placed between the polypropylene and the Li working electrode to define the active area. A stainless steel backing was placed on top of the Li metal working electrode to provide support and maintain electrical contact. All of these components were then clamped into place. The counter electrode was a 0.75 mm thick piece of Li wrapped around the inside of the glass cell. The same series of gaskets was used as on the working electrode side, with the exception that the stainless steel backing was replaced with a quartz window that was then clamped in place. A piece of stainless steel shim was sandwiched underneath part of the Li counter electrode during assembly and allowed to dangle out the side of the cell between the Viton o-ring and glass in order to provide electrical contact to the counter electrode. The cell was filled with electrolyte and a Li strip was placed in the top opening as the reference electrode.

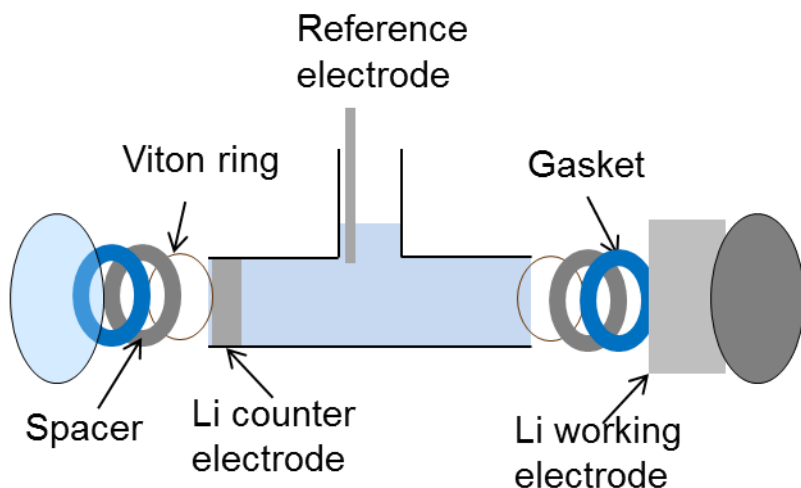


Figure S1. Diagram of optical three electrode cell.

SEM transfer apparatus

After electrodeposition, Li samples were transferred from the Ar filled glovebox to an FEI Quanta 650 SEM using a Quorum Technologies Cryo-SEM Preparation System (model PP2000TR/FEI) to avoid exposure to air during sample transfer and loading. The transfer device was interfaced with our MBRAUN glovebox by modifying a mini antechamber exterior door, as shown in **Fig. S2**, allowing the antechamber to act as a load lock with robust o-ring sealing. The in-house designed modifications involve removing the center, threaded knob and replacing it with three screws around the perimeter of the door, drilling out the center of the door to fit the circumference of the vacuum transfer device, and adding a second metal plate that fits on top of the transfer device and is clamped into place to seal the transfer device to the door. The usual glovebox antechamber door can then be replaced with the modified door/transfer device and the samples can be mounted onto the Quorum sample shuttle and sealed into the transfer device under Ar. Once the sample is secured, the transfer device can be removed from the glovebox and interfaced with the Cryo-SEM preparation system (used without the cooling function) to load the sample into the SEM without the need to expose it to ambient conditions.

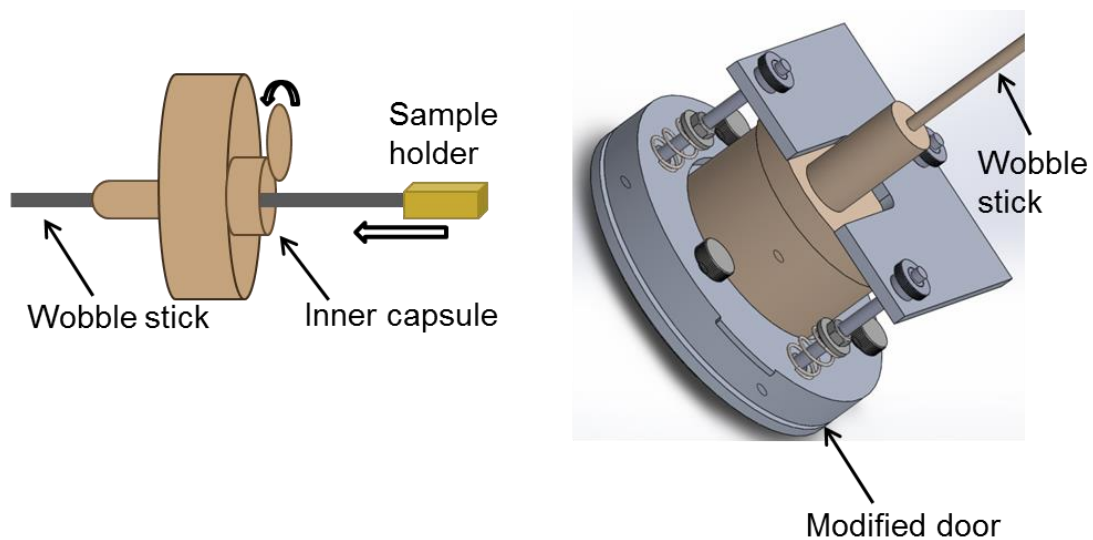


Figure S2. Diagram of Quorum specimen transfer device for vacuum or inert gas transfer and modified MBRAUN antechamber door.

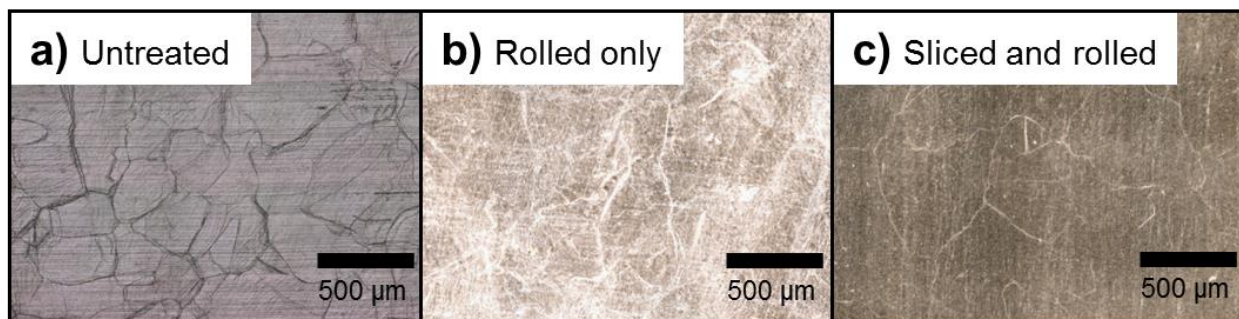


Figure S3. Optical micrographs of a) untreated, b) rolled only, and c) sliced and rolled Li before exposure to electrolyte taken with Keyence digital 3D microscope.

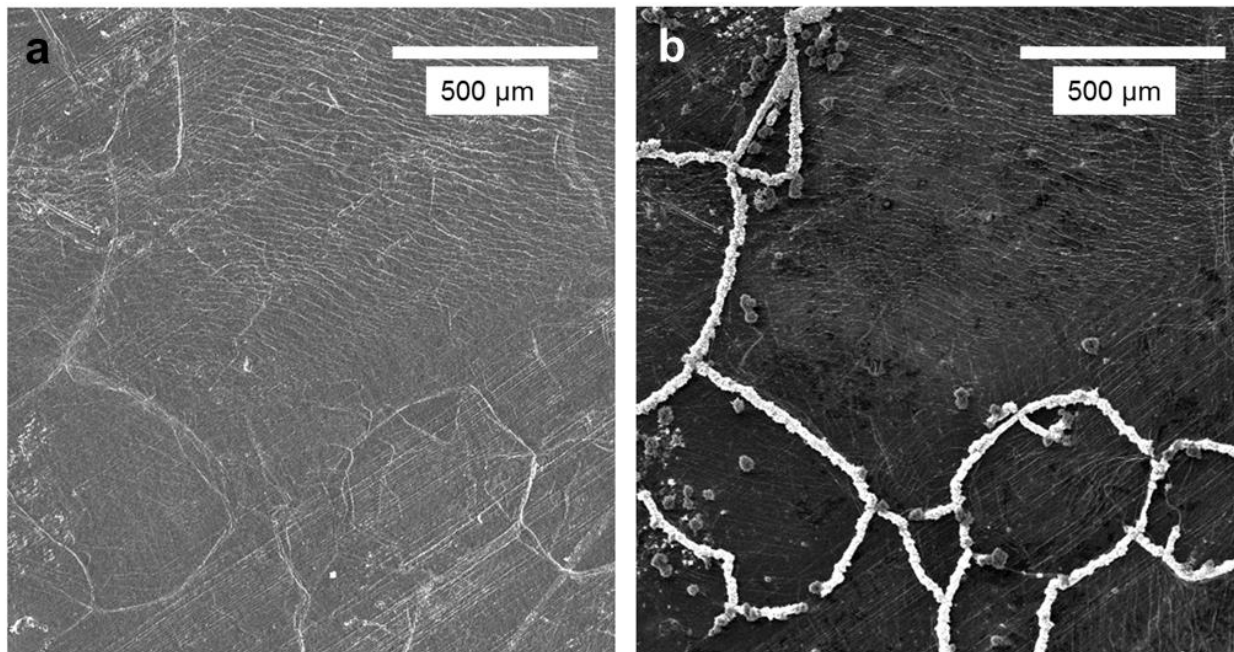


Figure S4. Scanning electron micrographs of untreated Li a) before, and b) after electrodeposition of Li at 12.5 mA cm^{-2} for 20 s in 1 M LiPF_6 in 1:1 (v/v) EC:DEC.

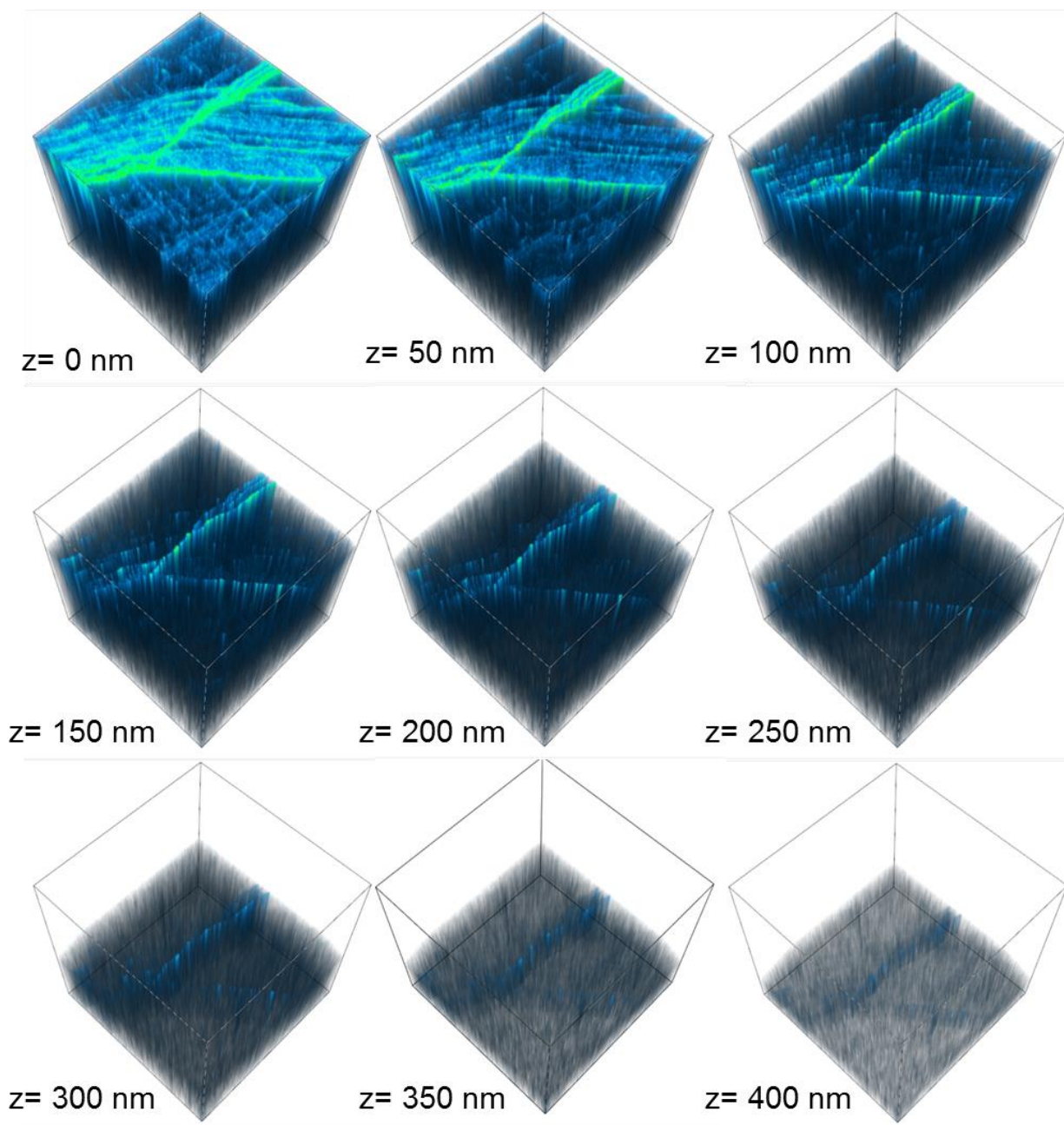


Figure S5. 3D ToF-SIMS ion maps of C_2H^- on untreated Li without exposure to electrolyte. $100 \times 100 \mu m$. Sputter depth is based on 1 nm of depth per second of sputtering. Brighter blue to green corresponds to higher ion counts. Sputtering into the surface reveals the lines of C_2H^- are segregated into points.

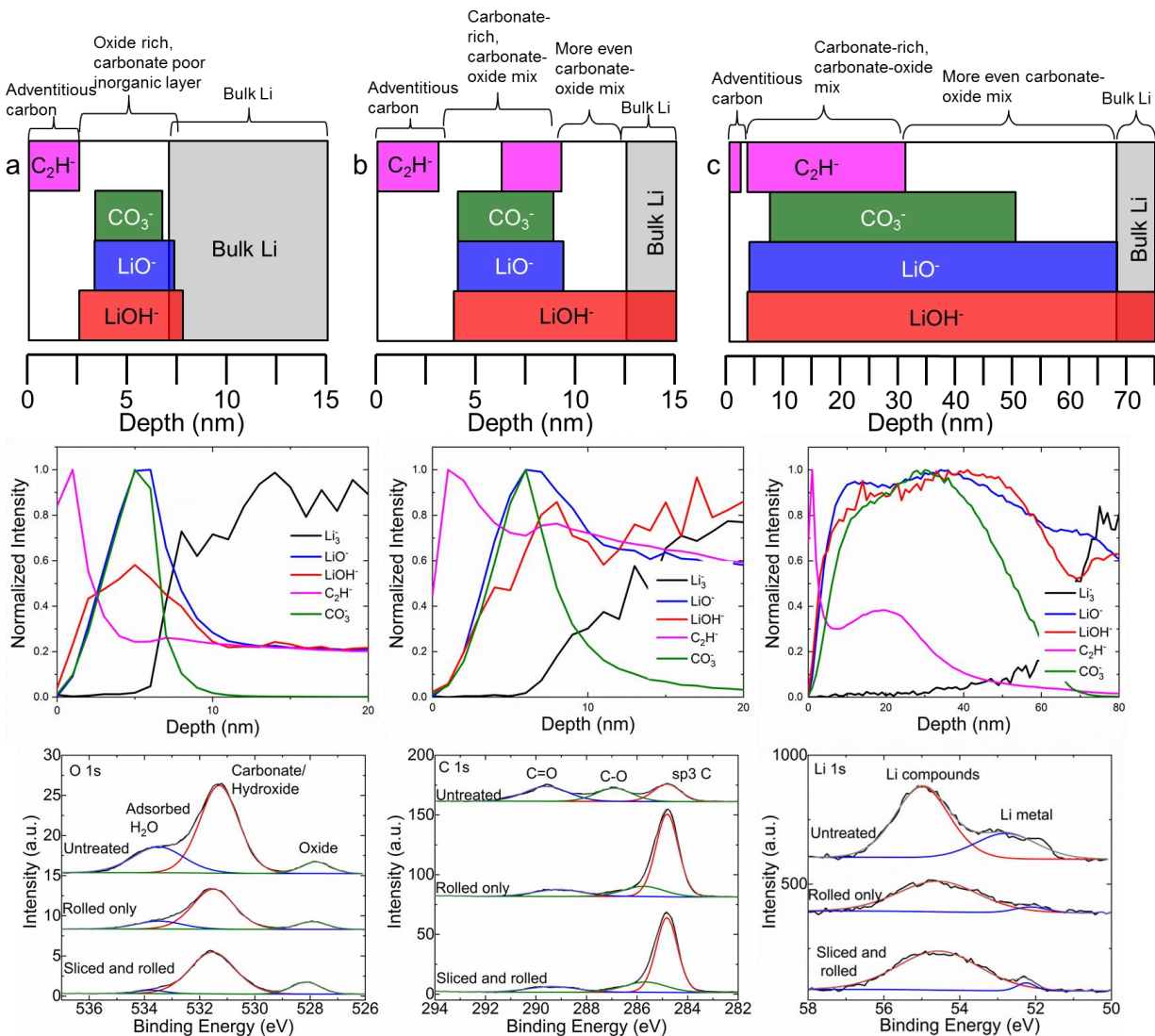


Figure S6. Diagrams of native Li surface chemistry before exposure to electrolyte constructed from ToF-SIMS depth profiles and XPS data. a) untreated Li, b) rolled only Li, and c) sliced and rolled Li. Middle row are ToF-SIMS depth profiles and bottom row are XPS spectra for corresponding diagrams in top row. Note that XPS spectra are shown for only O_s sputtering, but all sputtered spectra were fit similarly and the comparisons of peak areas used to determine surface composition are given in Fig. S9.

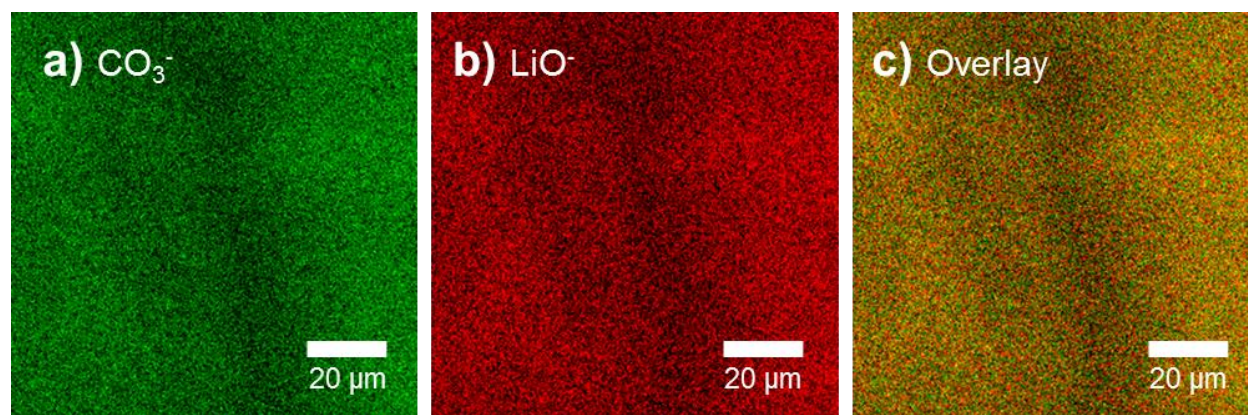


Figure S7. ToF SIMS secondary ion maps of a) CO_3^- , b) LiO^- , and c) overlay of CO_3^- (green) and LiO^- (red) on the surface of untreated Li without exposure to electrolyte.

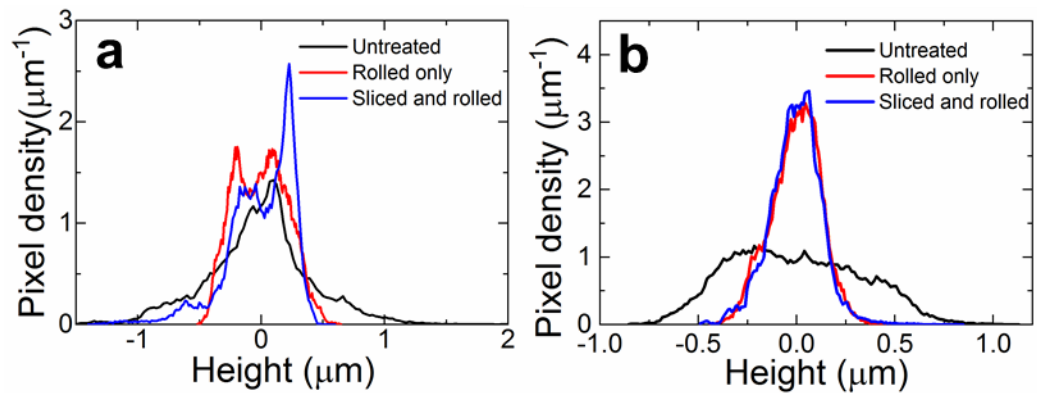


Figure S8. Histograms of height distribution from a) vein region and b) plateau region of Li surfaces.

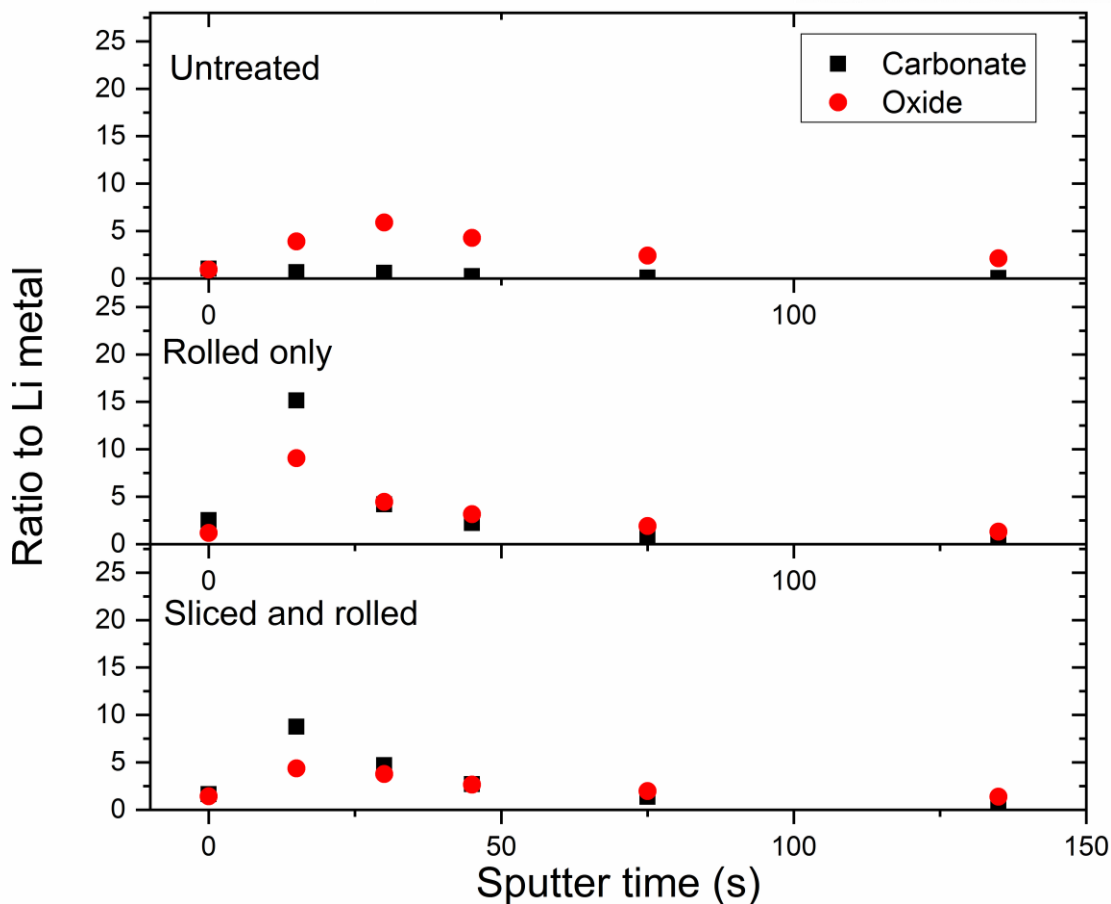
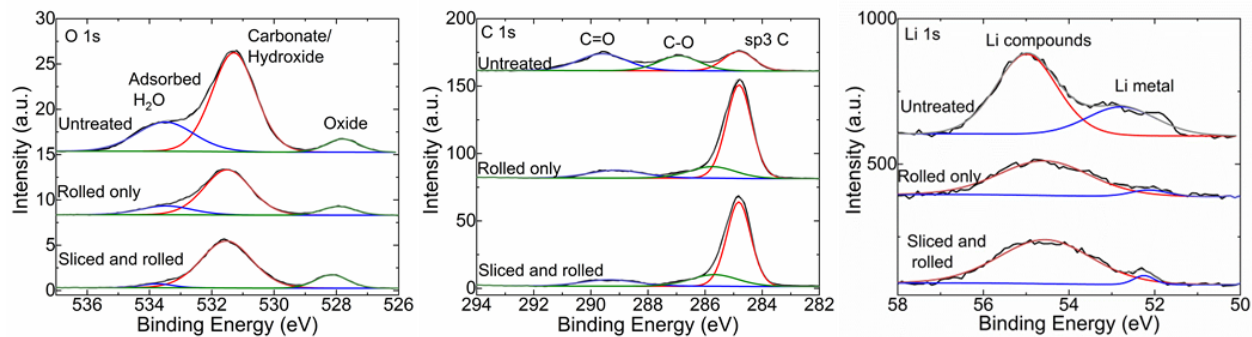


Figure S9. Top: O 1s, C 1s, and Li 1s regions of XPS spectra taken before sputtering. Sputtered spectra were fit similarly. Bottom: ratio of carbonate peak area from C 1s XPS region to Li metal peak from Li 1s XPS region (black squares) and ratio of oxide peak area from O 1s XPS region to Li metal peak from Li 1s XPS region (red circles).

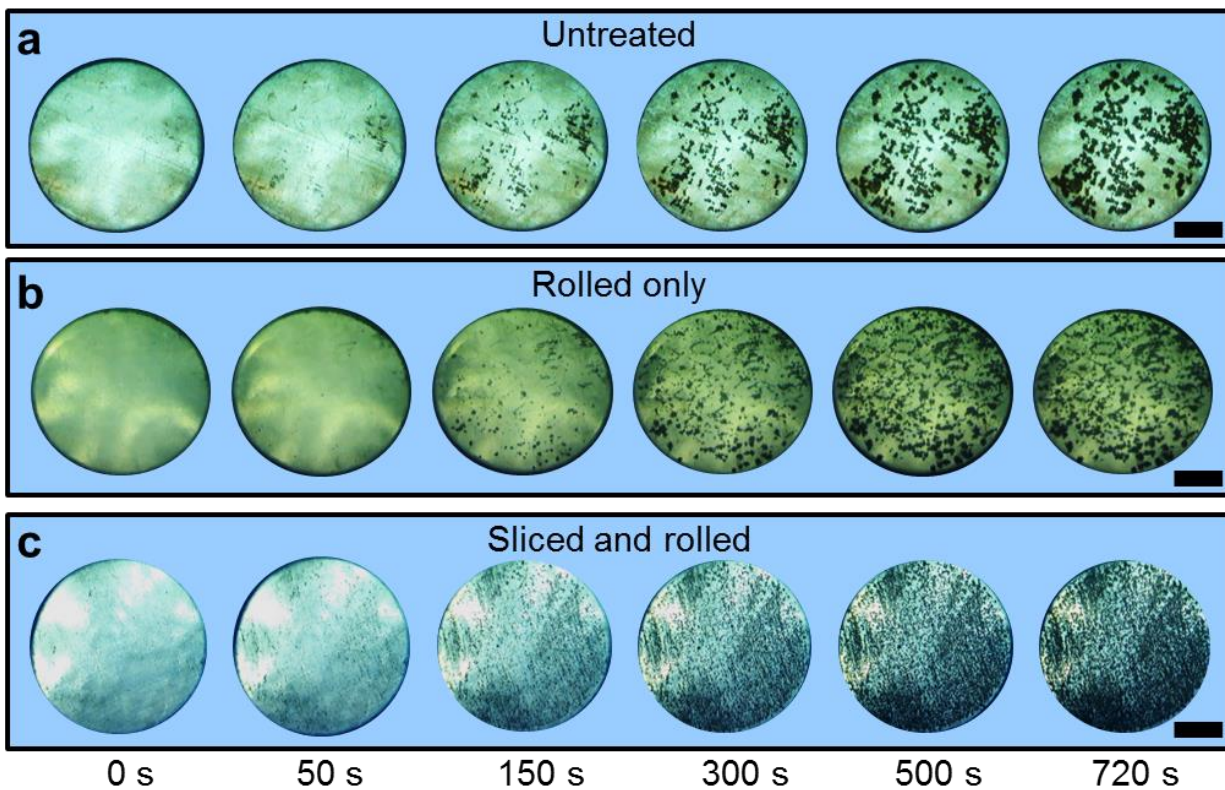


Figure S10. Time lapse of depositions at 2.5 mA cm^{-2} of Li deposited on a) untreated, b) rolled only, and c) sliced and rolled Li in an optical three-electrode cell with 1 M LiPF_6 in 1:1 (v/v) EC:DEC electrolyte. All electrodes are $9/32''$ in diameter. Scale bar is 2 mm.

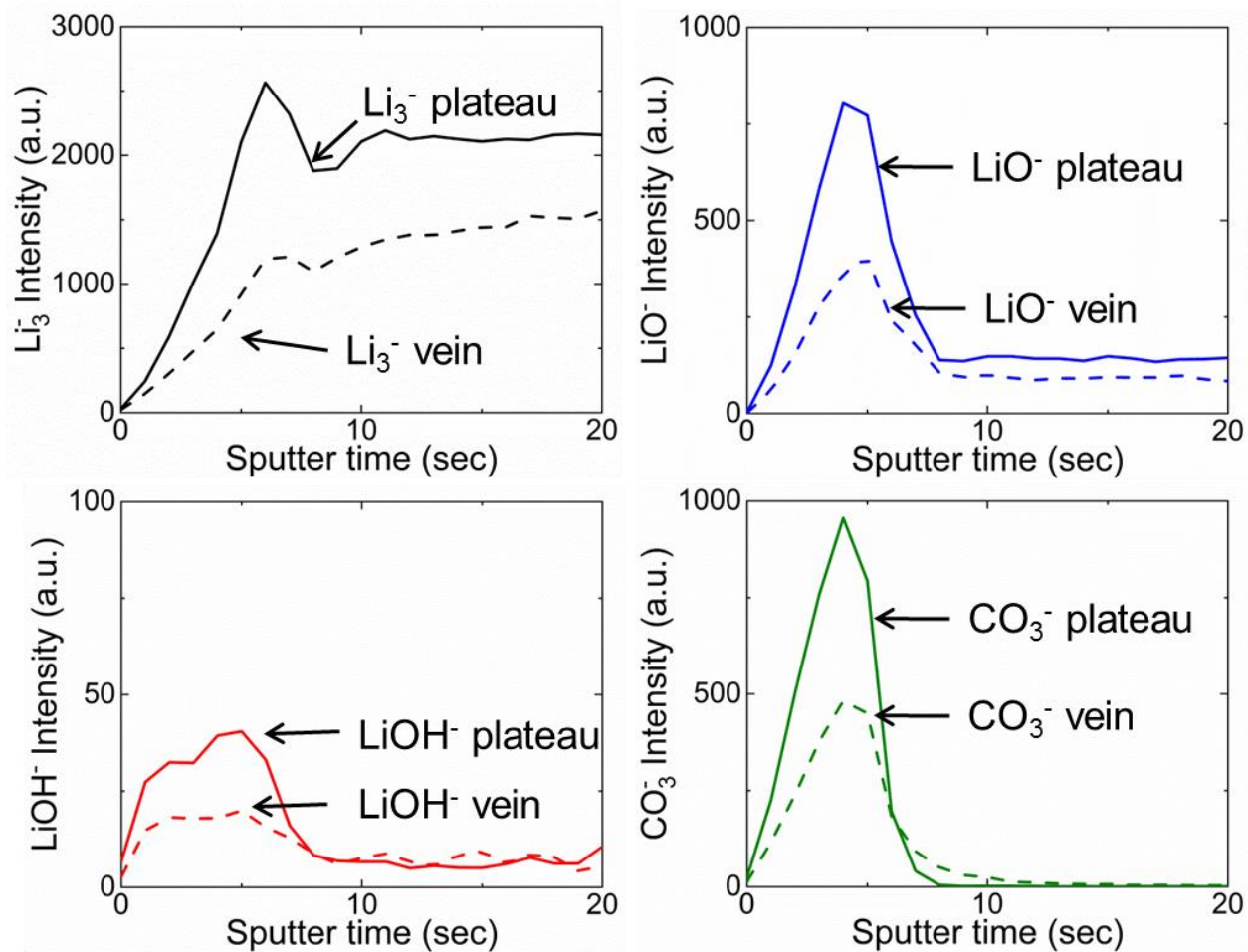


Figure S11. ToF-SIMS depth profiles of Li_3^- and inorganic compounds in the SEI on and off the vein of untreated Li after soaking in 1M LiPF_6 in 1:1 EC:DEC for 7 hours. 1 s of sputter time corresponds to ~ 1 nm in depth.

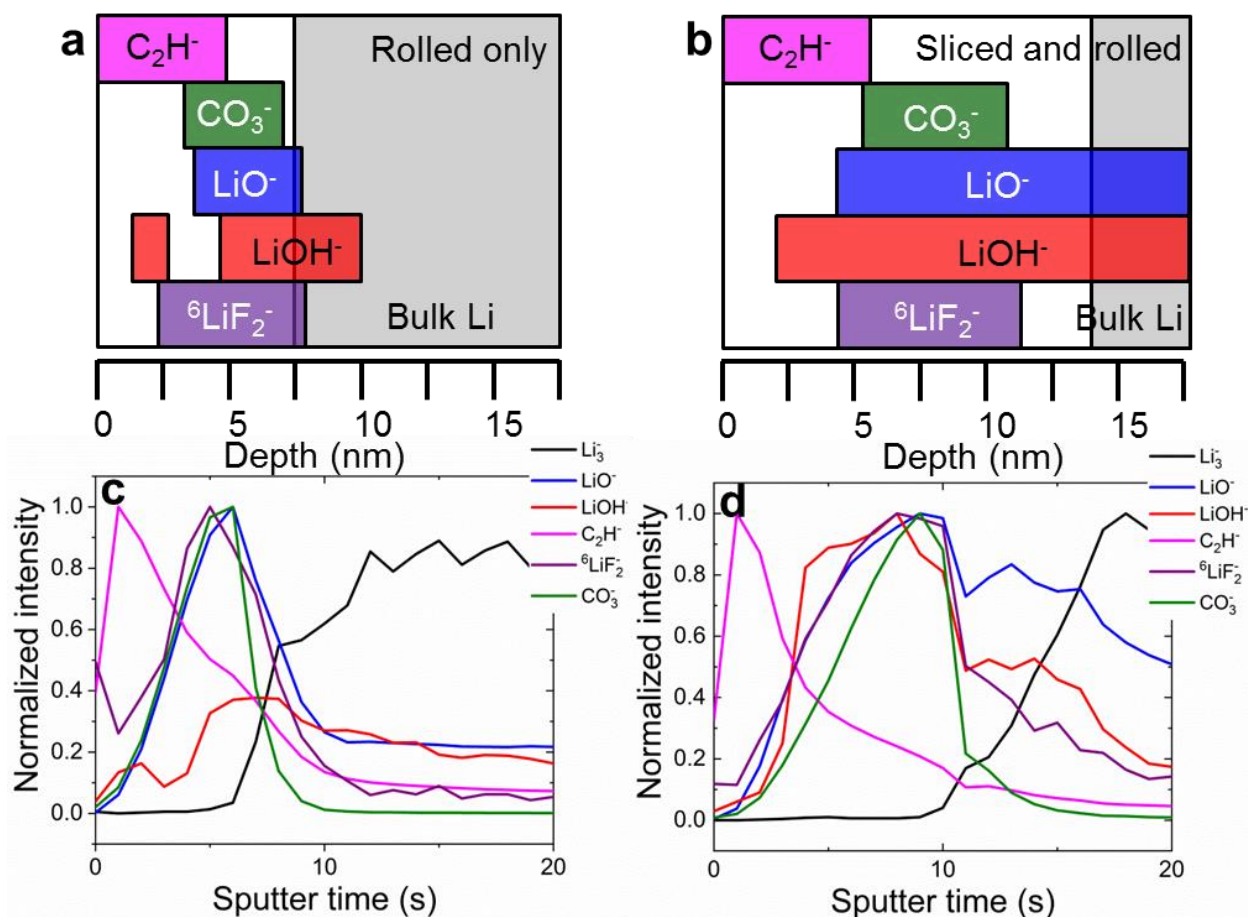


Figure S12. Diagrams of SEI composition on a) rolled only and b) sliced and rolled Li surfaces after soaking in 1 M LiPF_6 in 1:1 (v/v) EC:DEC for 7 hours constructed from data in depth profiles (c, d) taken with ToF-SIMS.

Quantification of nucleation distribution at 12.5 mA cm^{-2}

Dendrite size and distribution were measured after Li electrodeposition at 12.5 mA cm^{-2} for 2.5 s, so that we could distinguish individual nucleation sites before the dendritic clusters had grown together. Scanning electron micrographs, **Fig. S13**, of the untreated surface show the largest dendrites with an average area of $5 \pm 7 \mu\text{m}^2$ and nucleation density of $0.016 \text{ dendrites}/\mu\text{m}^2$. Dendrites on rolled only Li are smaller, $2.3 \pm 1.5 \mu\text{m}^2$, and have a higher nucleation density, $0.026 \text{ dendrites}/\mu\text{m}^2$. Dendrites on the sliced and rolled Li are the smallest and have fewer needles in each cluster than the untreated and rolled only surfaces. In this case, we can only estimate an average dendrite size less than $0.5 \mu\text{m}^2$, as high resolution SEM imaging was unable to detect but few dendrites with areas in the order of $0.5 \mu\text{m}^2$.

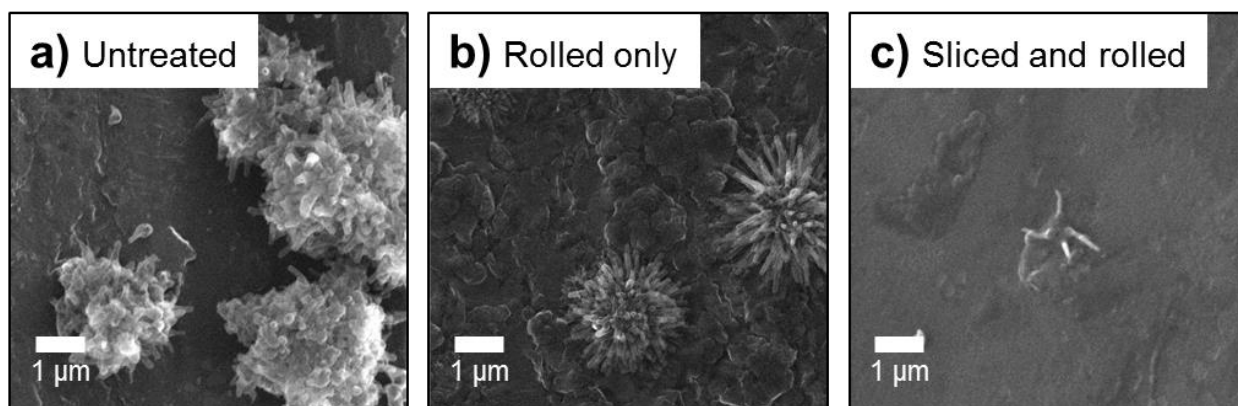


Figure S13. Scanning electron micrographs of Li deposited on a) untreated, b) rolled only, and c) sliced and rolled Li in 1 M LiPF₆ in 1:1 (v/v) EC:DEC at 12.5 mA cm⁻² for 2.5 s.

Electrochemical impedance spectroscopy

Electrochemical impedance spectra of Li|Li symmetric cells were taken between 10 mHz and 100 kHz with an amplitude of 5 mV. The semicircle in the resulting Nyquist plots were fit to the equivalent circuit model in **Fig. S14** using ZView software. The resulting R_{SEI} was divided in half to get the reported figure which is representative of the SEI on a single electrode. R_S is the solution resistance, R_{SEI} is the SEI resistance and CPE1 is a constant phase element. Reported resistance is average of at least three cells for each treatment.

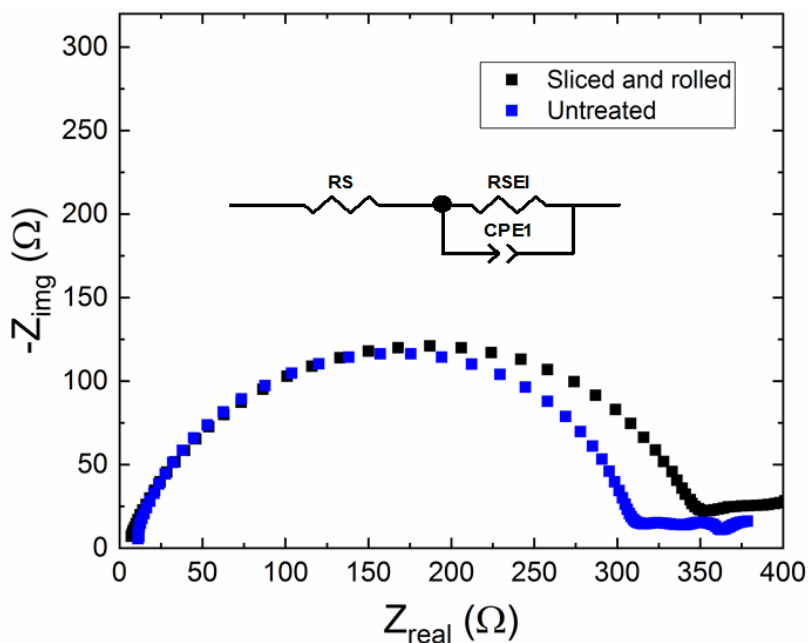


Figure S14. Representative Nyquist plots of sliced and rolled and untreated Li|Li symmetric cells after 7 hr exposure to electrolyte and equivalent circuit model describing the solution resistance (R_S) and the SEI resistance (R_{SEI}) in these cells.