**Supporting Information**

**From ion to atom to dendrite: Formation and nanomechanical behavior of electrodeposited lithium**

Michael A. Citrin\*1, Heng Yang1, Simon K. Nieh2, Joel Berry3,4, Wenpei Gao5, Xiaoqing Pan5, David J. Srolovitz6, and Julia R. Greer1

1 Division of Engineering and Applied Science, California Institute of Science and Technology

2 Front Edge Technology, Baldwin Park, CA

3 Department of Materials Science and Engineering, University of Pennsylvania

4 Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA

5 Department of Materials Science and Engineering, University of California, Irvine

6 Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR

**Transmission electron microscopy**

To transfer the Li, in an argon-filled glovebox (**Figure S1**), the cell is taped to a stainless steel disc (**Figure S2**a,i). A 3 mm Cu TEM grid with a carbon support film is placed on the surface of the cell, carbon side down (Figure S2a,ii), and a 15.9 mm diameter PDMS disc is placed on top of the grid (Figure S2a,iii). Binder clips are clamped around the whole assembly to apply stress to improve the contact between the grid and cell (Figure S2b). The PDMS is used to distribute the stress and also to help improve contact between the grid and cell.

The cell was then charged at 4.1 V to plate Li out of the surface of the cell and onto the grid. After charging, the grid was placed in a polytetrafluoroethylene (PTFE)-sealed microcentrifuge tube. The tube was placed in two polycarbonate containers, one sealed with paraffin film, and an Al heat seal bag, all to protect the sample from atmosphere during transfer from the glovebox to LN2. All containers were baked under vacuum at 80°C for 5 hours before introduction into the glovebox. At the TEM facility, the tube was quickly placed into LN2, and once cool, the tube was opened with tweezers under LN2, and the grid was removed. The grid was moved under LN2 into the TEM holder and was transferred into the LN2-cooled TEM in ~1 second.

**Strain rate**

The compression experiments with a prescribed constant loading rate of 0.5 μN/s were in effect performed under a relatively constant displacement (strain) rate (**Figure S3**). The constant strain rate is due to the applied force being linear with time, but when corrected for the spring stiffness, load deviates from linearity because the sample dynamic stiffness is on the same order as the spring stiffness. This allows the displacement rate to be relatively constant, although small deviations in linearity correspond to the deviations in linearity in load and stress-strain behavior.

To calculate the effective strain rate for a prescribed loading rate, the depth vs. time curves needs to be analyzed (Figure S3). The depth is approximately linear with time until unloading near the end of the experiment. The curves can also be nonlinear at the very beginning of the experiment as the indenter tip contacts the sample. Figure S3b removes these nonlinearities by cutting off the very beginning and end of the data. The displacement rates, and thus strain rates, are relatively constant throughout the experiment. The R2 values for linear fits in this region of the experiment range from 0.997 to 0.999. The maximum effective strain rate, taken at 3 second intervals (Figure S3c), is 3.4x10–3s–1, with an average of 1.2x10–3s–1 between the three pillars, demonstrating the quasistatic nature of the prescribed load-rate compression experiments.

**Observed Li growth**

Upon charging, Li is formed at the LiPON/Cu interface, and then fractures through the thin Cu layer once the Li particle is large enough. More evidence of this is shown in the SEM images in **Figure S4**. Figure S4a shows the bumps in the Cu that form at the beginning of charge as the Li has grown but hasn’t yet fully fractured the Cu surface. Figure S4b reveals Li growing at areas with fractured Cu. The dark areas in the red circles likely arise from the underlying LiPON layer, as the 10 kV electron beam could partially penetrate through the Li, illustrating the lack of Cu directly under the Li. Finally, Figure S4c shows Li particles with Cu “caps” attached from puncturing through the Cu current collector at the beginning of growth. The contrast is due to the low Z of Li, which appears darker under secondary electron imaging.

**Modulus calculations using dynamic stiffness**

The Young’s modulus, E, is calculated from the CSM data of the pillar with an initial length of and cylindrical cross-sectional area using the instantaneous plastic area, and length, . can be calculated using:

|  |  |  |
| --- | --- | --- |
|  |  | , (1) |

where is the total displacement measured by the indenter, is the applied load, and is the stiffness measured by the CSM mode. The modulus is then calculated as:

|  |  |  |
| --- | --- | --- |
|  | , | (2) |

where is the contact compliance of a cylindrical punch into an elastic half-space. Further details can be found in Reference 1.

To calculate the theoretical dynamic stiffness of the pillar, a similar approach is taken in the reverse direction, with the modulus as an input and the dynamic stiffness as an output. The instantaneous length of the pillar can be calculated as:

|  |  |  |
| --- | --- | --- |
|  | . | (3) |

The theoretical stiffness is then simply calculated as:

|  |  |  |
| --- | --- | --- |
|  | . | (4) |

Further details can be found in Reference 2. Due to the large noise in the CSM data, a suitable part of the dynamic stiffness needs to be chosen for the Young’s modulus calculation. This happens after the pillar is in full contact with the indenter tip, and the dynamic stiffness is relatively flat. The theoretical stiffness is used to check where the pillar deviates from the expected stiffness. The theoretical and measured stiffnesses will match in the region chosen for the modulus calculations because the theoretical stiffness’s inputs include the modulus calculated from the measured dynamic stiffness. A region between 50 and 150 nm is chosen and an average value is used with a low-pass filter to remove a few extraneously large stiffness data points.

**Deformation behavior**

The 520 nm diameter pillar supported a maximum load of 11.76 ± 5.05 μN, which corresponds to a maximum stress of 69.4 MPa (point 4 in **Figure S8**b), followed by a pillar bending-induced gradual decrease in stress as a result of a slight misorientation between the indenter tip and the pillar axis, then unloading at a final strain of ~25-30%. The bending is corroborated by a lower measured dynamic contact stiffness post-max flow stress (Figure S8d), which starts deviating from theoretical compression stiffness at a strain of ~13% (**Figure S7**).

**Resolved strength**

The resolved strength is calculated as:

|  |  |  |
| --- | --- | --- |
|  | , | (5) |

where is the strength resolved onto the {110}<111> slip system, is the yield stress, is the angle between and the normal to the slip plane, and is the angle between and the slip direction. The out-of-plane orientation was determined by the measured elastic moduli and is used to calculate the Schmid factor and resolved strength. The results for all samples are illustrated in **Table S1**.

**Local current density**

The charge passed , for a Li particle at a time step is defined as

|  |  |  |
| --- | --- | --- |
|  |  | , (6) |

where is volume at time step , is the density of Li, is the molar mass of Li, and is the Faraday constant, assuming a Li+ transference number of 1 through LiPON. was plotted against time to obtain a linear relationship where the slope of the versus plot is defined as the local current. The area to determine current density was calculated using a circular cross section using the diameter (for a fiber or pillar) (**Figure S5**) and the square of the measured length of the contact between the particle and surface for a sphere (the sphere-like Li contacts the surface as a spherical cap). The volume of the sphere was calculated by estimating the depth as the average between two orthogonal axes across the surface and multiplying it by the area seen in the SEM. The local current density required to grow a Li pillar was estimated to be ~5 mA/cm2 at a global current density of 0.3 mA/cm2, while the local current density where the rounded Li metal forms is ~90 mA/cm2 when the macroscopic current density was 0.1 mA/cm2.

**Considerations of mechanical data analysis**

The compression experiment videos (**SV1**) show stochastic lateral motion of the indenter tip during compression on the timescale of seconds for all samples. This is likely due to an electrostatic effect caused by the connection of the cell to the potentiostat during mechanical compression and has a negligible effect on the mechanical data (**Figure S9**). The motion does not correlate with any mechanical response and was not visible on any other sample in our instrument, none of which had an electrical connection outside the chamber. Besides these general common characteristics, some samples underwent minor strain excursions, an example of which can be seen at 4% strain in **Figure S10** for the 622 nm diameter sample.

While all experiments were performed under a nominal strain rate of ~1x10–3 (see Figure S3), our experiments revealed that the load-displacement data for tests conducted under a prescribed fixed loading rate consistently showed less noise than those at a prescribed fixed displacement (strain) rate. The latter contained large fluctuations in load, usually between 1 and 5 μN, that did not correlate with the corresponding mechanical response (**SV2**) and that were likely caused by an extra feedback loop in the indenter system, which is inherently load controlled (**Figure S6**). Beyond these load fluctuations in the post-yield, the general signature of the mechanical behavior, as well as the elastic modulus and the yield strength, under these two different loading conditions is very similar.

We have observed the tip touching a thin Li fiber bent at roughly 60**°**. During the compression, the tip still exhibits lateral motion, while the indenter bends the Li fiber farther down, but negligible load is measured until the tip contacts a vertically oriented Li pillar, as expected (**Figure S11**). The tip does not move in this manner when it is not in contact with the sample; the lateral movement of the tip does not correspond to any feature of the mechanical data. We therefore believe this movement has an insignificant effect on the mechanical response.

**Sneddon correction**

Sneddon3 first described the contact compliance,, of a flat punch indenting into an elastic half-space as:

|  |  |  |
| --- | --- | --- |
|  | , | (6) |

where is the Poisson’s ratio of Li (0.3624), and is the instantaneous plastic area of the pillar, which can be approximated as the initial area of the pillar . Since LiPON is an amorphous ceramic, it can be taken as elastically isotropic, so is the measured elastic modulus of LiPON, 77 GPa.5 The Sneddon compliance is multiplied by the load and subtracted from the displacement. The Sneddon correction will slightly increase the measured stiffness and modulus of the material. This correction is small (<2%) because the Young’s modulus of LiPON is significantly higher than that of Li in all crystallographic orientations.5,6

**Uncertainty in cross-sectional area**

When calculating the area to convert force to stress, we measure the diameter of the pillars in the SEM and convert to area assuming a circular cross-section. However, it is possible that the pillars do not have circular cross-sections due to any faceting on the pillars. The faceted Li fibers seen in cryo-SEM by Li et al. are triangular, hexagonal, and rectangular, with a 2:1 aspect ratio.7 Using these geometries, the difference in cross-sectional area can be calculated by assuming a constant diameter, defined as the largest distance perpendicular to the electron beam. **Figure S12** demonstrates the largest and smallest area for each cross-sectional geometry. Only the large aspect ratio rectangular cross-section shows a large (>30%) difference in area, but in our images, we did not observe these geometries, and only saw close to circular or triangular cross-sections.

**References**

1. S.-W. Lee, S.M. Han, W.D. Nix, Uniaxial compression of fcc Au nanopillars on an MgO substrate: The effects of prestraining and annealing. *Acta Mater.* **57**, 4404 (2009).

2. J.R. Greer, W.C. Oliver, W.D. Nix, Size dependence of mechanical properties of gold at the micron scale in the absence of strain gradients. *Acta Mater.* **53**, 1821 (2005).

3. I.N. Sneddon, The relation between load and penetration in the axisymmetric Boussinesq problem for a punch of arbitrary profile. *Int. J. Eng. Sci.* **3**, 47 (1965).

4. E.G. Herbert, S.A. Hackney, N.J. Dudney, P.S. Phani, Nanoindentation of high-purity vapor deposited lithium films: The elastic modulus. *J. Mater. Res.* **33**, 1335 (2018).

5. E.G. Herbert, W.E. Tenhaeff, N.J. Dudney, G.M. Pharr, Mechanical characterization of LiPON films using nanoindentation. *Thin Solid Films* **520**, 413 (2011).

6. C. Xu, Z. Ahmad, A. Aryanfar, V. Viswanathan, J.R. Greer, Enhanced strength and temperature dependence of mechanical properties of Li at small scales and its implications for Li metal anodes. *Proc. Natl. Acad. Sci.* **114**, 57 (2017).

7. Y. Li, Y. Li, A. Pei, Y. Sun, C.-L. Wu, L.-M. Joubert, R. Chin, A.L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui, Atomic structure of sensitive battery materials and interfaces revealed by cryo–electron microscopy. *Science* **358**, 506 (2017).