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Curiously Absent Knock-On Damage of Lithium Metal at Cryogenic Temperatures

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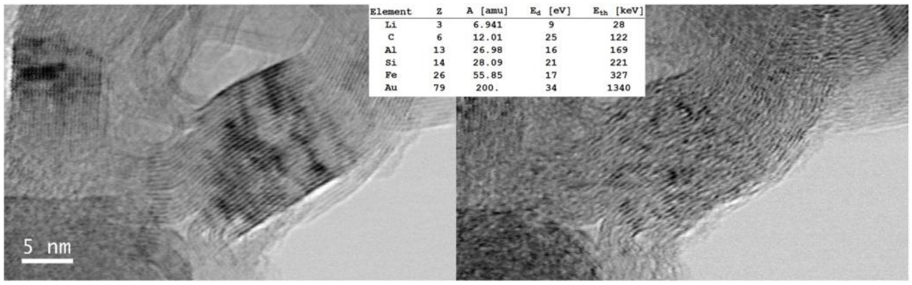
Damage from the electron beam in a transmission electron microscope can be grouped into two categories: knock-on damage and sputtering (electron-nuclear scattering) and radiolysis (electron-electron scattering). The nuclear scattering is nearly elastic at small angles (the electron being so much lighter than the nucleus) and radiolysis is inelastic. There exists an easily calculable knock-on damage threshold below which crystals such as graphite and silicon are effectively stable under the electron beam, regardless of temperature. (The beam current determines the rate at which atoms are sputtered off the surface, a small effect when the number of volume atoms to surface atoms is large.) Carbon allotropes vary considerably in this threshold, but in the case of graphite we see stability below a high tension of roughly 120 kV [1, 2], and silicon below 200 kV [2]. With a 300 kV accelerating voltage, graphite suffers from knock-on damage; before and after such damage is shown in Figure 1. Cryogenic temperatures offer no protection here (the energy transfer to the nucleus is much larger than any thermal energy) and the walls are visibly deformed after a few minutes of exposure to a differential fluence of 200 e/Å^2/µs. A summary of calculated knock-on damage thresholds is shown in the Figure 1 inset.

The knock-on damage mechanism seems curiously absent in lithium metal, which has a damage threshold of approximately 30 kV (assuming a conservative activation/displacement energy of 9 eV [3]). Lithium metal dendrites electrodeposited in a battery coin cell [4] can be readily imaged after cryo-transfer techniques that prevent oxidation of the air-sensitive metal. Our expectations, given known physics and damage mechanisms, that lithium dendrites ***cannot*** withstand hours of differential fluence of 50 e/Å^2/µs at a high tension set to 300 kV, is shown to be incorrect. Unlike the heavier and more tightly bound atoms in graphite and silicon, lithium survives. An example STEM image that deposited roughly 200 e/Å^2 is shown in Figure 2 at lattice resolution. This image was acquired after nearly an hour of combined TEM and STEM imaging on the same region.

Are the dendrites really metallic lithium or is there some other compound that provides radiation protection to this light element? We test this question by analyzing the dendrites using cryo-STEM EELS. We find that the dendrites are clearly composed of lithium metal, both through a signature plasmon excitation (calculated to be 7.9 eV with an electron density of 46 e/nm^3, measured at 7.4 eV), and from the position of the core-loss signal of the K-edge, along with the signature metallic density of states, all captured simultaneously.

We will discuss possible explanations for this unexpected effect, such as self-diffusion of lithium atoms, encapsulation by the dendrite's SEI layer, and whether other materials can be similarly protected at lower temperatures than liquid nitrogen's boiling point (clearly graphite cannot). The possibility of protecting such a light element as lithium opens up the exciting possibility of protecting structures from radiation damage. Such protection could lead to both higher stability and resolution of biological structures [5], which has many important implications [6].



Element	Z	A [amu]	E_d [eV]	E_{th} [keV]
Li	3	6.941	9	28
C	6	12.01	25	122
Al	13	26.98	16	169
Si	14	28.09	21	221
Fe	26	55.85	17	327
Au	79	200.	34	1340

Figure 1. Graphite after one STEM image acquisition (left) and after several minutes (right). The fluence after the initial image in the sample was approximately 700 e/Å^2. The sample was imaged at an accelerating voltage of 300 kV and liquid nitrogen temperatures. The left most image shows a clear example of the effects of knock-on damage. Inset shows calculated knock-on damage thresholds.

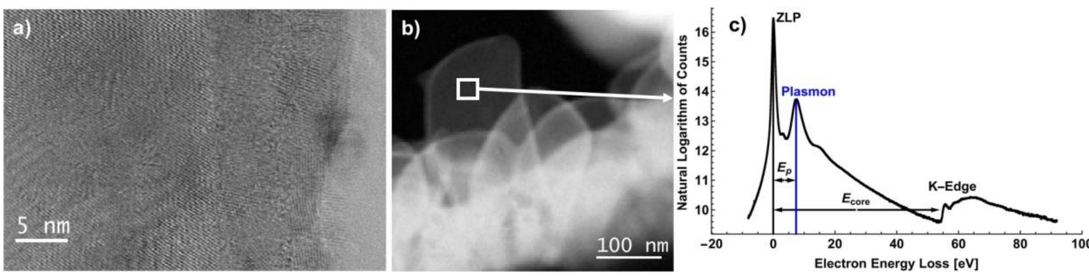


Figure 2. a) A cryo-STEM image of lithium dendrites at lattice resolution. b) A cryo-STEM EELS spectrum image (SI) of lithium dendrites. c) A 9x8 summed spectrum image (contrast in the SI using a window around the lithium k-edge) from the ROI in b). The lattice resolution cryo-STEM image was one of several acquired over an hour and a half session of differential fluence of 50 e/Å^2/μs, during which no damage was visible in the metal. The signature EELS metallic plasmon and lithium K-edge are clearly visible, indicating lithium metal.

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[5] RF Egerton, Micron **119** (2019), p. 72.
[6] Data was acquired at the Electron Imaging Center for Nanomachines (EICN) at the University of California, Los Angeles's California for NanoSystems Institute (CNSI) and at UCI's IMRI. This work was supported by the BioPACIFIC Materials Innovation Platform of the National Science Foundation under Award No. DMR-1933487. We would also like to acknowledge Toshihiro Aoki and Li Xing for their assistance at UCI's Materials Research Institute.

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