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Physical Limitations on Transmission Electron Microscope Imaging of Lithium Battery Materials

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Lithium ion battery samples are vulnerable to both environmental and radiation damage in the transmission electron microscope. As a light element, Lithium is particularly vulnerable to knock- on displacement damage. Features such as the Solid Electrolyte Interphase (SEI) layer are disrupted by ionization damage. Optimizing the microscope for ultra-low voltage operation could lead to a factor of 4 increase in allowed signal, with additional benefits from cryo-immobilization in reduced environmental and beam-induced degradation.

In the metallic electrodes, the primary damage mechanism is Knock-on displacement damage from the collisions between electrons from the beam and the nuclei of atoms in the sample. This is normally computed from the McKinley-Fesbach or Mott cross sections [1]. However, this gives only a lower bound to the knock-on damage cross section because it neglects the possibility of displaced atoms causing atomic cascades. An upper bound is obtained using the Kinchin-Pease cross section, which assumes displaced atoms with sufficient energy cause a cascade [2]. When one also considers that a single electron may displace multiple atoms, one finds that the total knock-on damage cross section for Lithium decreases more slowly with electron beam energy than one might otherwise expect (Fig. 1a) [3]. Ionization damage occurs when an electron from the beam ionizes atoms in the sample. In conductors, an ionized electron is easily replaced; however, in an insulating material, this may break bonds. Fig. 1b shows the Lithium valence cross section (the primary ionization cross section), the knock-on damage cross section, and as a potential spectroscopic signal the Lithium K-edge cross section [4]. The best imaging conditions for a sample are achieved when the ratio of signal events per damage event is maximized. This ensures the maximum signal for the maximum allowed dose when imaging [5, 6]. Figure 1 c) shows that more signal Li K-edge events occur per knock-on damage event at lower electron beam energies. The effect is especially dramatic from 60 to 20 keV. A similar result can be found for elastic annular dark field imaging as the chosen signal as well. This implies that lower voltage electron microscopes are more suitable for studying Lithium ion batteries. Of course, the actual energy used will be balanced by the need for high resolution and penetration of the sample.

Typical battery elements are air sensitive making it difficult to prepare and transfer thin sections. Common electrolytes, as well as some electrode materials like Sulfur, are prone to sublimate when exposed to high vacuum. Both problems can be solved by cryotransfer and imaging. Fig. 2a shows the vapor pressure curve for solid Sulfur [7]. Figure 2 b) shows the mass loss rate of selected solids along their vapor pressure curves. Both indicate that mass loss by sublimation can be significantly reduced by handling battery samples at low temperatures. This could be readily achieved with Cryo-TEM. Freezing a battery sample to cryogenic temperatures in its electrolyte, would allow oxygen-free transfer to the TEM, preserving oxygen-sensitive features such as the SEI layer.

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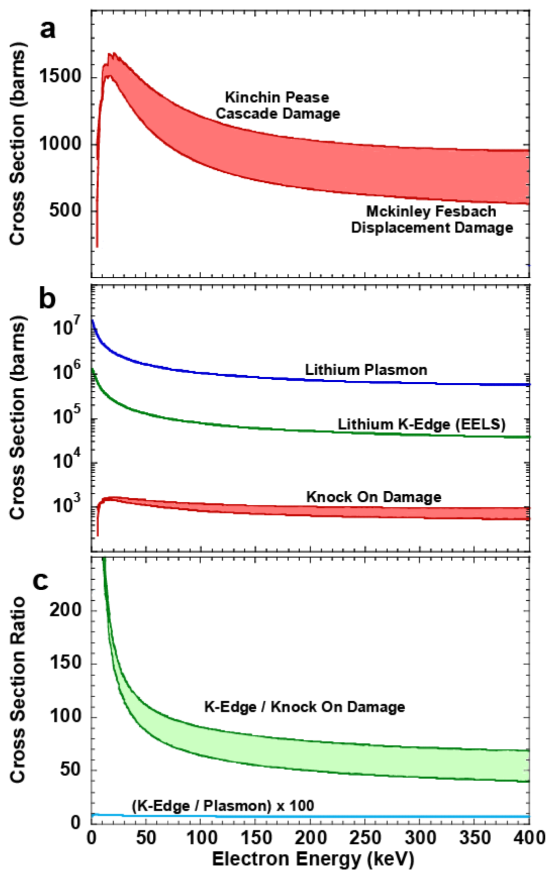

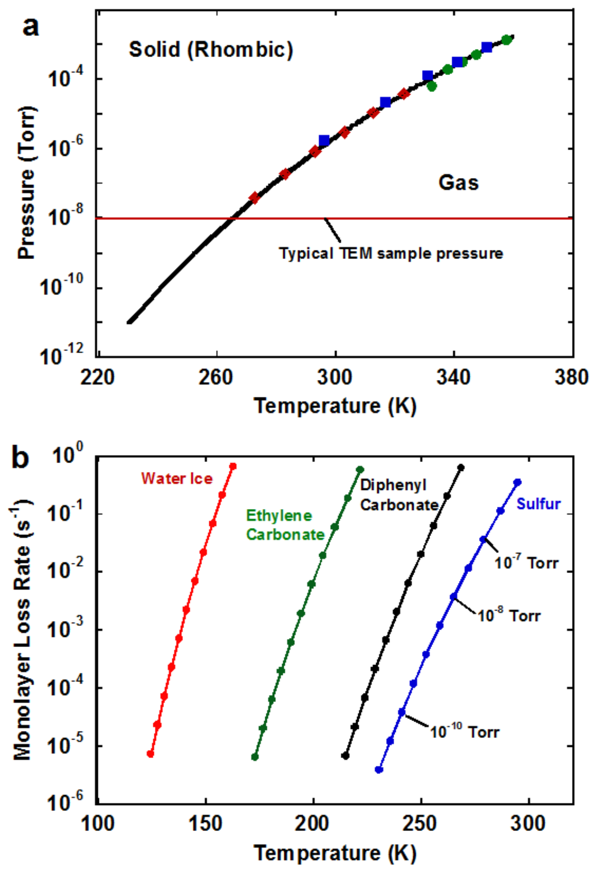

Figure 1. a Knock-on damage cross cross section for Lithium. The lower bound is given by the McKinley Fesbach approximation to the Mott scattering cross section, assuming no interactions between displaced atoms. The upper bound is given by Kinchin and Pease, assuming displaced atoms will cause an atomic cascade. **b** Cross section for Li plasmon edge - the major part of the ionization cross section, Li K-edge cross section, and Knock-on damage cross section. **c** Ratios of Li K-edge cross section to knock-on damage cross section and to plasmon cross section. A larger ratio implies that radiation damage will be lower when imaging. The ratio of K-edge signal to knock on damage cross section increases as electron beam energy decreases.

Figure 2. a Extrapolated vapor pressure curve of solid Sulfur. **b** Rate of sublimation of different materials along their vapor pressure curve, measured in molecular monolayers per second. Note the rapid decrease in loss rate as temperature is reduced, even as pressure is reduced.

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