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Challenges for ABF-STEM characterization of Li battery materials.

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Annular Bright Field (ABF) STEM has attracted considerable interest for its potential to directly image light atomic columns within a crystal structure [1]. One promising application for ABF is imaging lithium columns in the crystalline intercalation electrodes of lithium-ion batteries, such as $LiFePO_4$, at various states of charge. However, low energy barriers for vacancy diffusion (< 0.2 eV), which are required by design in order to transport and store Li ions reversibly [2], make intercalation electrodes vulnerable to vacancy-enhanced displacement (VED) [3], a form of knock-on damage that can lead to rapid redistribution of Li by the electron beam. High electron doses are needed for high resolution imaging of Li, but this also causes high VED. Here we assess the limits placed on the quantification of Li column occupancy in $LiFePO_4$ by the competition between obtaining a sufficient dose for imaging, and the displacement of imaged atoms. Our methodology applies to other Li-ion cathode materials, and other energy materials containing light atoms.

From Poisson statistics, the dose-limited resolution [4] scales as the square root of the maximum allowable dose, and inversely with Li column contrast. The contrast depends on, inter alia, beam voltage, spot size, column occupancy, and sample thickness. For most imaging modes such as EELS or HAADF, higher beam voltages lead to lower contrast as scattering cross-sections are reduced. However, multi-slice simulations of $LiFePO_4$ (Fig. 1) show that for a fixed probe size, higher beam voltage leads to better Li contrast in ABF. This is a channeling effect for samples thicker than about 10 nm. The increased contrast and reduced damage cross section (Fig 2a) with beam voltage favor a higher beam voltage for imaging Li in ABF.

Fig 2a shows that the knock-on damage cross section [5] for VED, which redistributes Li in the sample, is ~10x larger than the cross section for surface sputtering, which removes Li from the sample. Fig 2b shows the intersection of the family of curves for dose needed to resolve a given contrast change vs the dose required to displace a given fraction of Li atoms. Multi-slice simulations indicate that a resolution of better than ~0.95 Å is needed to resolve Li columns in $LiFePO_4$ along the [001] axis. Reading off intersections from the 0.95 Å line, we find that the smallest change in Li concentration that can be determined without a comparable amount of Li being displaced to neighboring columns by VED is 38%. If one ignored column to column variations, and only sought to measure the average Li concentration, ABF-STEM could be used to determine average Li content in a partially charged $LiFePO_4$ sample to ~6% accuracy, but local ordering patterns in column occupancy are limited to 38% uncertainty before damage artifacts dominate.

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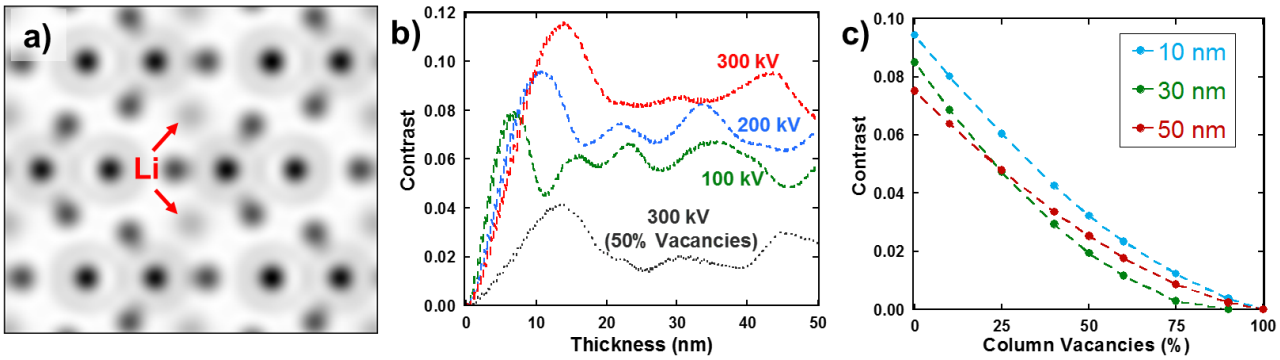

Figure 1. a) Multislice simulation of ABF image of $LiFePO_4$, 10 nm thickness viewed down c-axis. Field of view ~ 1 nm x 1 nm. 300kV beam voltage, probe size 0.7 Å. 0% column vacancies, defocus 0 nm. **b)** Contrast vs beam voltage over a Li column (along red line in a), no vacancies for 300 kV, 200 kV, and 100 kV, half occupancy for 300 kV. **c)** Contrast vs Occupancy as % of vacancies for Li columns at 300 kV, probe size 0.7 Å, defocus 0 nm.

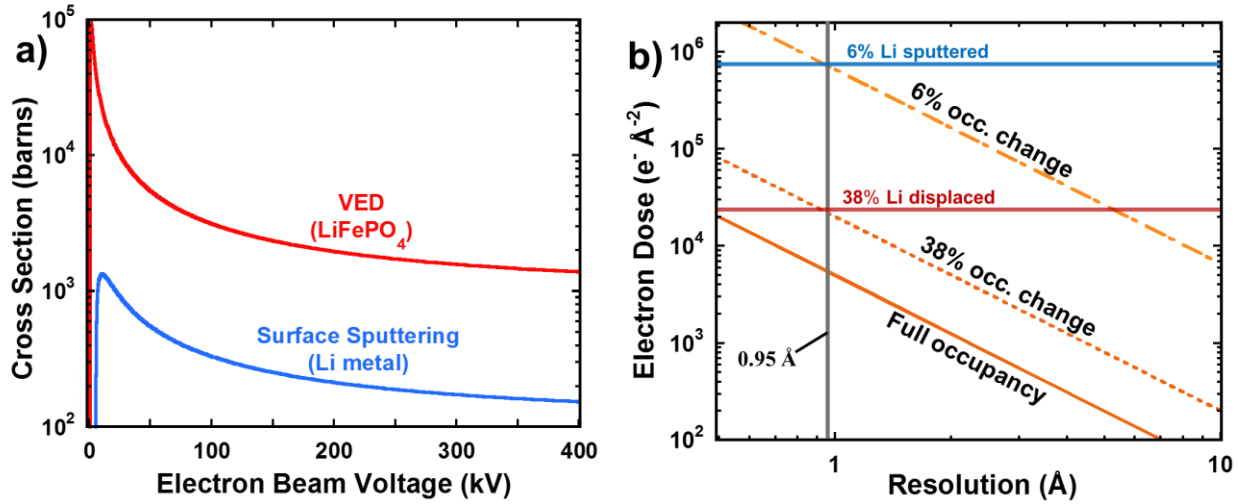

Figure 2. a) Surface sputtering cross section for Li metal [6] and the VED cross section for Li in $LiFePO_4$ vs beam voltage. **b)** Dose vs resolution for Li columns in 10 nm thick $LiFePO_4$, 300kV beam voltage, probe size 0.7 Å, defocus 0 nm imaged down c-axis. With Li columns resolvable at ≤ 0.95 Å resolution, 6% of Li atoms would be sputtered at the dose needed to detect ≥6% occupancy difference between columns. In $LiFePO_4$ sample with vacancies, 38% of Li would be displaced by VED for a dose needed to detect ≥ 38% occupancy differences between columns.