Atomic-Resolution Imaging of Li Vacancies in a Battery Cathode through Depth Sectioning with Multi-slice Electron Ptychography

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Meeting-report

Atomic-Resolution Imaging of Li Vacancies in a Battery Cathode through Depth Sectioning with Multi-slice Electron Ptychography

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Examining Li atoms at the atomic scale in 3D and monitoring structural alterations in batteries could enhance our comprehension of Li diffusion mechanisms. Nevertheless, achieving atomic-scale visualization of Li atoms alongside heavier elements poses challenges for scanning transmission electron microscopy (STEM) techniques such as annular bright field, differential phase contrast, and single-slice ptychography. With these methods, there are artifacts from mis-tilt, defocus, and thickness variations in the sample, and also there are limitations to sample thickness of a few nanometers due to multiple scattering and probe channeling [1, 2].

Multi-slice electron ptychography addresses these issues by iteratively solving both the probe and object through the sample's depth, achieving high lateral resolution while providing depth information of the sample as well [2]. The use of a fast high-dynamic-range electron microscope pixel array detector plays a crucial role by capturing the full distribution of momentum transfer at each probe position [3]. With a defocused probe (as shown in Figure 1(a)), a single-pass, four-dimensional (4D)-STEM dataset is sufficient for multi-slice electron ptychography, eliminating the need of tilt or through-focal series. Instead, solving the multiple scattering problem with a multi-slice approach reveals layers of the electrostatic potential of the sample along the beam direction. Stacking the line profiles from these potential slices yields the depth profile of the sample.

In this study, we investigate the 3D structural variations and Li distribution within a pristine lithium nickel manganese cobalt (NMC) battery cathode. Depth slices from a multi-slice ptychographic reconstruction of the NMC sample along [211] axis at depths of 9 nm and 16 nm are illustrated in Figure 1(b, c). The middle slice (Fig. 1(b)) displays the expected trigonal phase of the bulk sample. Conversely, the depth slice at the sample's exit surface (Fig. 1(c)) reveals a rock-salt-like phase, suggesting surface reconstruction. Beyond discerning the structural variations, depth sectioning facilitates the analysis of the Li distribution along the beam direction. Figure 2(a) illustrates the sum of all depth slices from a different region than that shown in Figure 1. Unlike the high angle annular dark field (HAADF) image in the inset of Fig. 2(a), Li and O are visualized simultaneously with the transition metal columns. Depth profile along a row of atoms, indicated by the blue box, is shown in Figure 2(b). The green arrows indicate the depth locations of Li vacancies along atom columns. These experimental findings demonstrate that multi-slice electron ptychography can unravel multiple scattering in the sample, enabling the identification of structural changes throughout the depth direction and the detection of Li vacancies inside the sample in a single scan. Such information remains concealed when conventional projection-based imaging methods are employed [4].

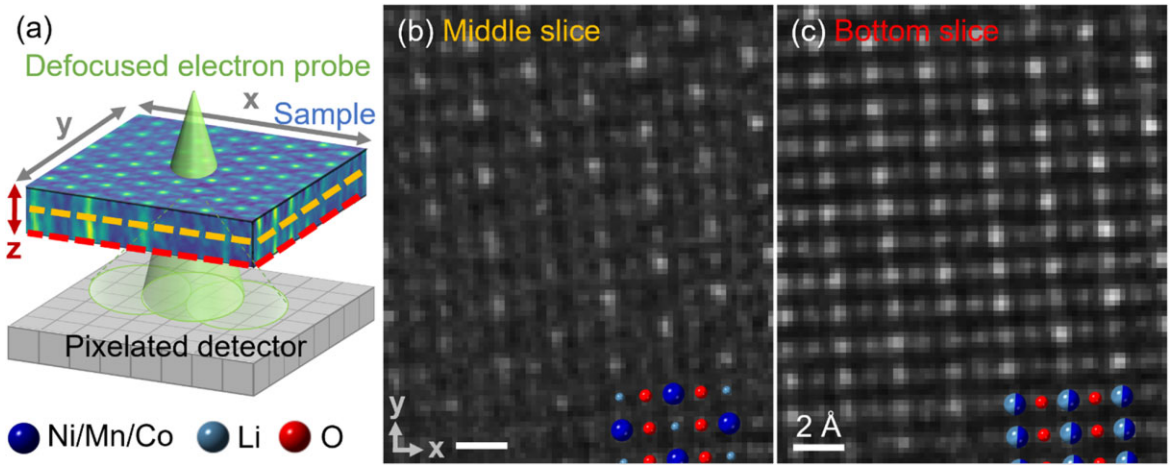

Fig. 1. (a) Illustration of the experimental configuration. Depth slices from the multi-slice ptychographic reconstruction of the potential at the depths (b) 9 nm and (c) 16 nm. The slice from the middle of the sample (b) displays trigonal phase of the bulk, while the slice at the lower part (c) exhibits a rock-salt-like phase, capturing the newly exposed surface from the focused ion beam sectioning of the sample. Corresponding structural models are presented in the bottom right corners.

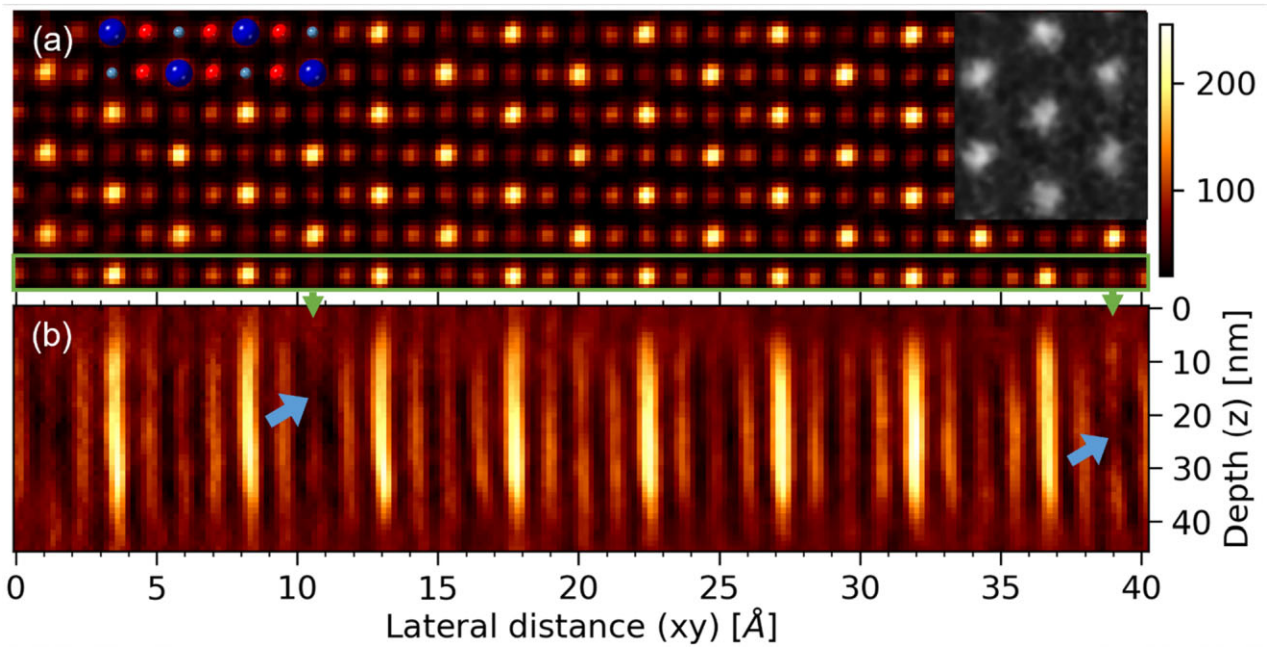

Fig. 2. (a) Sum of all slices from the multi-slice ptychographic reconstruction of the NMC-111 observed along the [211] axis. The top right inset displays a corresponding HAADF image of the same sample, where the Li and O are not observable. The structural model is shown on the top left. Note that this dataset is taken from a region different from the one shown in Figure 1. (b) Depth profile of the reconstructions along the atom columns enclosed by the green box in (a). Li vacancies are indicated with blue arrows.

References

1. SD Findlay *et al.*, *Ultramicroscopy* **110** (2010), p. 903. https://doi.org/10.1016/j.ultramic.2010.04.004
2. Z Chen *et al.*, *Science* **372** (2021), p. 826. https://doi.org/10.1126/science.abg2533
3. H Philipp *et al.*, *Microscopy and Microanalysis* **28** (2022), p. 425. doi:10.1017/S1431927622000174
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