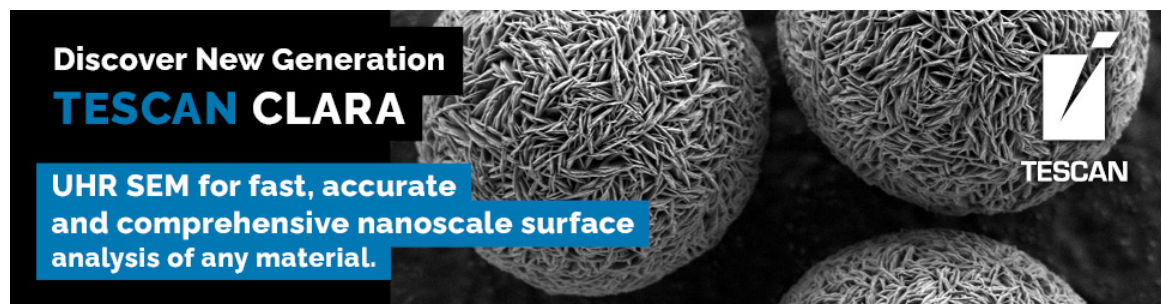


Imaging Li Vacancies in a Li-Ion Battery Cathode Material by Depth Sectioning Multi-slice Electron Ptychographic Reconstructions

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Imaging Li Vacancies in a Li-Ion Battery Cathode Material by Depth Sectioning Multi-slice Electron Ptychographic Reconstructions

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Probing Li atoms concurrently with heavy elements at the atomic scale to better understand Li diffusion mechanism has been a challenge in the Li-ion battery community. Although there have been studies implementing annular bright-field (ABF) scanning transmission electron microscopy (STEM) and single-slice electron ptychography, the resulting projected images have provided limited information of the sample along the beam direction [1]. Furthermore, contrast in ABF imaging can be dominated by artifacts due to defocus, sample mistilt, and thickness variations [2]. Differential phase contrast and single-slice ptychography are more dose efficient than ABF, but still are unreliable at retrieving the phase from a sample with thickness of tens of nanometers due to multiple scattering and beam channeling/mistilt within the sample [3].

In this work, we provide the depth information of the sample while retaining high lateral resolution by using multi-slice electron ptychography. Multi-slice electron ptychography solves the multiple scattering problem by iteratively solving for both the probe and the object in three dimensions (3D), sliced layer by layer [3]. These advances take advantage of a fast high-dynamic-range electron microscope pixel array detector which records the full distribution of momentum transfer at each probe position, resulting in four-dimensional (4D) datasets [4]. For multi-slice electron ptychography, the recorded 4D-STEM dataset does not require a tilt or through-focal series. Instead, single pass 4D-STEM dataset is recorded with a defocused probe as shown in Fig. 1a. Then the dataset is used to reconstruct the 3D slices of electrostatic potential of the sample along the beam direction as depicted in Fig. 1b. Next, line profiles from each slice of the potential are stacked to form the depth profile as in Fig. 1c.

We use a pristine lithium nickel manganese cobalt oxide (NMC-111) cathode material to study variations in local structures and Li distribution. Fig. 2a shows a ptychographic reconstruction of NMC along [211], capturing lighter elements (Li and O) and heavier transition metal (TM) elements (Ni, Mn, and Co) at the same time. In contrast, the lighter elements are invisible in the high-angle annular dark-field (HAADF) image (top right inset of Fig. 2a). One of the Li columns with partial occupation (i.e., vacancies) is pointed with a red arrow. Depth sectioning of the multi-slice ptychographic reconstruction of the NMC (Fig. 1c) shows where in depth the Li vacancies are located along the column. The pink slice in Fig. 1c from the surface of the film shows TM have replaced the Li atoms at the surface, consistent with a TM-oxide rock-salt phase (Fig. 2b). These multi-slice electron ptychography experiments demonstrate that we are able to disentangle the multiple scattering in the sample to both identify the location of Li vacancies inside the sample and simultaneously resolve the surface phases and reconstructions in a single scan, details that would be hidden in conventional STEM imaging modes [5].

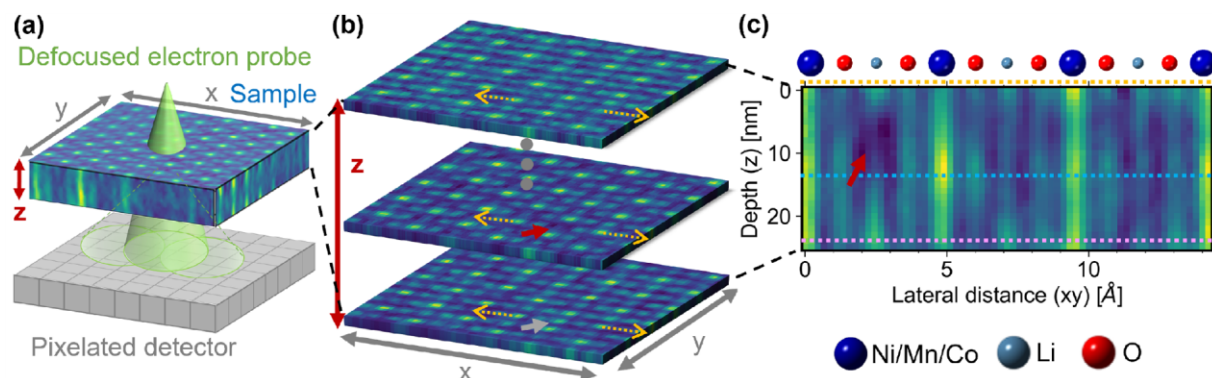


Fig. 1. (a) A schematic of the 4D-STEM experimental setup. (b) Recovered slices of the electrostatic potential along the z-direction of the sample (beam direction), reconstructed using multi-slice electron ptychography. The top slice shows a surface reconstruction layer; the middle, a Li vacancy site in the bulk (red arrow); the bottom, the same lattice site with TM atoms (gray arrow). (c) The depth profile of the reconstructed sample along the yellow dotted lines of slices in (b) (boxes in 2(a,b)), showing Li vacancies (red arrow). Chemical identities of the atom columns are indicated by the spheres at the top.

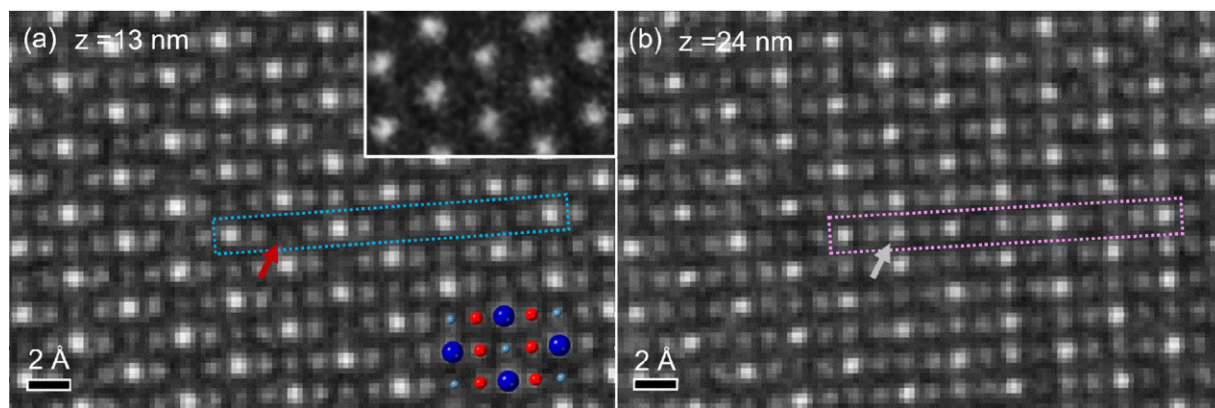


Fig. 2 Multi-slice ptychographic reconstructions of NMC-111 [211] at different depths showing (a) one of the Li vacancies (red arrow) within the bulk phase at the depth of the blue slice in Figure 1c. Top right inset in (a) shows a HAADF image of the same sample, which does not capture the lighter elements—Li and O. The structural model is shown on the bottom right. (b) Slice from the pink layer in figure 1c, showing the lower surface of the sample has a different atomic arrangement from the bulk. Some Li sites in (a) are replaced with NMC in (b) (gray arrow).

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