Determining Out-of-Plane Structure via Electron Diffraction

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Abstract:

In situ studies of phase transitions in materials are essential to understanding structure evolution, and thus engineering for novel or advanced applications [1]. This is especially true in battery materials where dramatic, intercalation-induced phase transitions impact safety, reliability, and performance [2]. Scanning transmission electron microscopy (S/TEM) provides simultaneous imaging, diffraction, and spectroscopy data from a single instrument. However, in situ intercalation experiments in the TEM are uncommon and often rely on highly specialized holders [3]. Here we characterize the complete lithiation-induced phase transition in the layered van der Waals (vdW) material, lanthanum tritelluride ($LaTe_3$), using a standard electrical biasing holder by fabricating electrochemical cells that are liquid-free.

Throughout lithiation of the $LaTe_3$ flake, we observed at least two distinct phase transformations, various $LaTe_3$ stackings, and an expansion and subsequent relaxation of the in-plane lattice. During this experiment, several types of data were acquired: atomic resolution and low-magnification STEM imaging, electron energy loss spectroscopy (EELS), and spatially resolved diffraction using four-dimensional STEM (4D STEM). The combined analysis of these datasets reveals the morphological, electronic, chemical and structural changes of the flake during intercalation. The experimental patterns observed were replicated by multislice simulations (abTEM [5]) from different 1x1x3 supercells with lithium ordering in vdW gap interstitials (Figure 2).

A later experiment includes 4D STEM data from convergent beam electron diffraction (CBED). This provides out-of-plane structure due to interactions with the higher order Laue zone (HOLZ) of the reciprocal lattice. Simulations confirm individual stackings are distinguishable from each other and from out-of-plane disorder. CBED analysis via Hough circle transforms [6] allows us to measure out-of-plane strain.

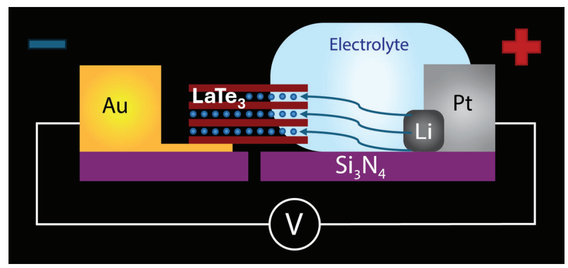

Figure 1: The all solid-state electrochemical cell, where the voltage bias controls lithium intercalation in the vdW gaps between $LaTe_3$ layers.

Summary of Research:

In each in situ experiment, we utilize an off-the-shelf electronic chip (e-chip) placed in a standard Protochips Fusion350 heating/biasing holder. The all solid-state electrochemical cell is displayed in Figure 1. At the start of the experiments, the $LaTe_3$ flake is in the pristine state, as shown in Figure 2a. EELS analysis tells us there is no detectable lithium in this phase. In the first experiment, after measuring an open circuit voltage of 2.3 V, we initiated intercalation by lowering the cathode potential to 0 V (vs Li anode). After 10 minutes, we observed an intercalation-induced new phase propagated across the flake, verified by low magnification STEM imaging. The EELS data taken 35 minutes after initiating intercalation showed an increase in intensity following the Li-K edge onset at 57 eV. Representative diffraction patterns in this phase revealed two lithiated structures with the same ordering: one maintaining the bulk stacking and one with a layer shifted by half the lattice (Figure 2b), as seen in the alignment of Te-nets across the vdW gap. 4D STEM analysis at this stage showed significant in-plane lattice expansion of approximately 1.5%.

After continuing intercalation at the 0 V cathode potential, the flake did not exhibit further significant changes. Approximately 4 hours into the experiment, we lowered the cell voltage to -9 V. By the 5.5-hour mark, we observed a second major phase transformation. The lithium-ordering superlattice disappeared (Figure 2c) and the previous in-plane lattice expansion had relaxed. Simulated diffraction of the proposed structures matches the experimental diffraction patterns from their respective lithiated phases (Figure 2). We attribute the in-plane strain relaxation to the addition of out-of-plane unit cell expansion. CBED simulations result in diffraction patterns containing HOLZ rings, whose radii we measure with Hough circle transforms. This analysis is robust to sample tilt, and the measured radius of HOLZ rings is inversely correlated with the out-of-plane strain of each stacking (Figure 3). The CBED patterns of different stackings are distinguishable from one another, which allows us to measure out-of-plane strain while preserving phase information.

We determined the optimal TEM parameters with more simulations, then ran the experiment again using scanning CBED. Preliminary analysis shows significant out-of-plane disorder in later stages of lithiation. This causes the HOLZ rings to blur, making them more challenging to measure with the Hough circle transform alone. We aim to increase the precision of our measurement method and subsequently pair it with a radial average integration technique. Currently, we are using simulations to investigate the resultant diffraction patterns caused by various types of disorder.

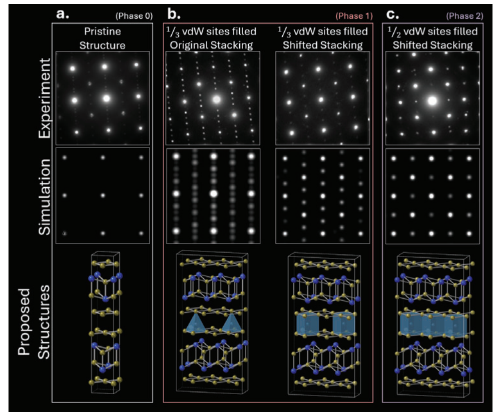

Figure 2: (a) The pristine structure, which contains no lithium, (b) the first phase transformation, where 1/3 of the vdW sites are filled and we observe the original as well as a shifted stacking, and (c) the second phase transformation, where 1/2 of the vdW sites are filled and we only observe shifted stacking.

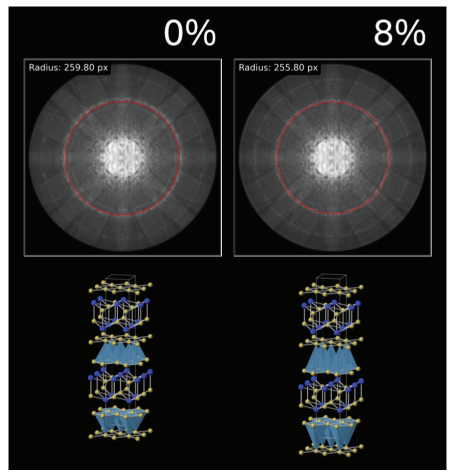

Figure 3: A demonstration of the inverse relationship between out-of-plane unit cell expansion and HOLZ ring radius.

Conclusions and Future Steps:

In situ experiments allowed us to identify two distinct phase transformations of $LaTe_3$ via multimodal STEM (imaging, EELS, and 4D STEM). To enable this complete characterization in a single experiment, we developed an all solid-state electrochemical cell on a standard Si_3N_4 membrane-style TEM e-chip. We developed techniques for mapping structural information during the intercalation process, including out-of-plane stacking and unit cell expansion. We perform these measurements over large fields of view using 4D STEM. With abTEM multislice simulations, we determined optimal CBED parameters and repeated the intercalation experiment. Looking forward, we aim to improve measurement precision, further investigate out-of-plane disorder, and complete the remaining analysis of our latest dataset. Our method should enable future investigations of other intercalation materials to directly and comprehensively observe their phase transformations.

References:

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