Mapping Structure Evolution During Lithiation of 2D Materials

CNF Project Number: 303522
Principal Investigator(s): Judy Cha
Users(s): Natalie Williams, Sihun Lee

Affiliations(s): Department of Materials Science and Engineering, Cornell University; Department of Chemistry and Chemical Biology, Cornell University

Primary Source(s) of Research Funding: The Gordon and Betty Moore Foundation's EpiQS Initiative (GBMF9062.01); Department of Energy, Basic Energy Sciences program Grant No. DE-SC0023905

Contact: jc476@cornell.edu, nlw49@cornell.edu, sl2859@cornell.edu

Research Group Website: cha.mse.cornell.edu

Primary CNF Tools Used: Heidelberg DWL66FS, Heidelberg MLA 150 Maskless Aligner, SC4500 Odd-Hour & Even-Hour Evaporator

Abstract:

To study promising materials for lithium-ion batteries, it is essential to track complete phase evolutions throughout lithiation. Lithium intercalation, the process by which lithium ions are reversibly inserted into a host material, typically induces structural and electronic phase transitions in electrode materials [1], directly influencing battery capacity and cycling stability. Techniques such as in situ Raman spectroscopy, electrical transport, and x-ray diffraction provide valuable insights into structural transformations but lack the spatial resolution to visualize these changes at the nanoscale in real space. Among available experimental methods, scanning transmission electron microscopy (STEM) uniquely offers simultaneous imaging, diffraction, and spectroscopy at atomic- scale resolution. Here, we employ multimodal in situ 4D STEM, along with in situ Raman spectroscopy and electrochemical data using coin-type cells, to map nanoscale phase evolutions during lithium intercalation in the layered material $LaTe_3$.

Summary of Research:

Figure 1a illustrates the structure of $LaTe_3$, and Figure 1b depicts the geometry of our electrochemical cell, which varies slightly based on experimental requirements. In situ Raman spectroscopy identifies four distinct lithiation phases in LaTe3 (Figure 2b). The initial phase corresponds to the pristine state of $LaTe_3$ at open-circuit voltage (OCV). At the first phase transition, phonon modes associated with the charge density wave (CDW) of LaTe3 disappear and are replaced by new modes that evolve continuously throughout lithiation. Optical imaging reveals dark lines forming on the flakes during lithiation, which are wrinkles caused by strain relaxation from structure transformations (Figure 2a).

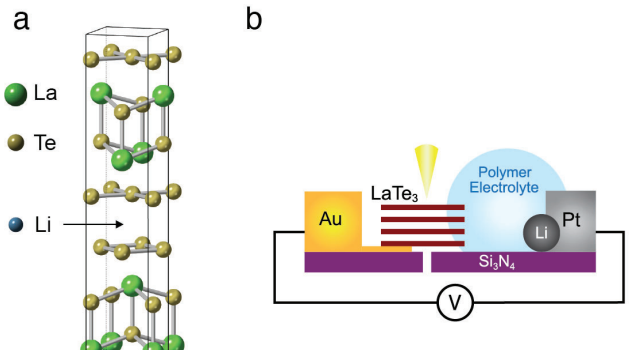

Figure 1: (a) Crystal structure of LaTe3. Li ions are intercalated electrochemically between the Te sheets. (b) Schematic of an electrochemical cell on a S/TEM e-chip for multimodal in situ STEM experiments.

A galvanostatic discharge curve from a LaTe3 coin-cell similarly portrays four distinct lithiation phases (Figure 2b).

To gain deeper insight into the lithiated phases, we performed an in situ lithiation experiment to acquire complementary datasets using STEM, including atomic-resolution and low-magnification STEM imaging, electron energy loss spectroscopy (EELS), and spatially resolved four-dimensional diffraction (4D STEM) using an Electron Microscopy Pixel Array Detector (EMPAD) [2]. Figure 3a shows electron diffraction acquired during in situ 4D STEM lithiation of $LaTe_3$. The original CDW is suppressed, as indicated by the disappearance of superlattice peaks at q = 2/7c* at the first phase transition, corroborating Raman results. A new lithium-induced superlattice emerges at q = 1/3c*, accompanied by changes in $LaTe_3$ layer stacking, seen in the varying intensities of lithium ordering peaks. We also observe initial in-plane lattice expansion followed by relaxation, along with evolving lithium occupancy in the host lattice. Ultimately, as lithium becomes fully incorporated, all ordering peaks vanish. Concurrent in

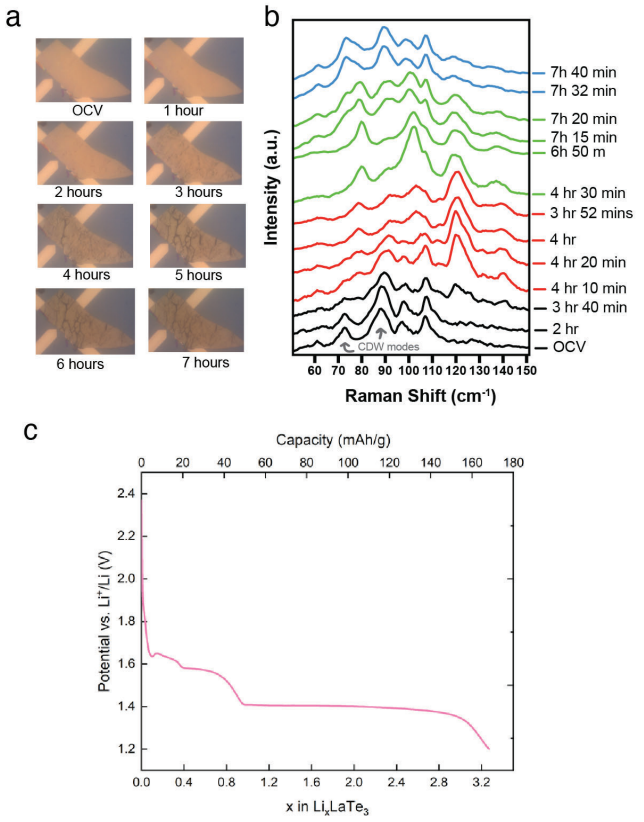

Figure 2: (a) Optical images and (b) in situ Raman spectra during lithiation of LaTe3. (c) Galvanostatic discharge curve of LaTe3 coin cell, suggesting three distinct lithated phases.

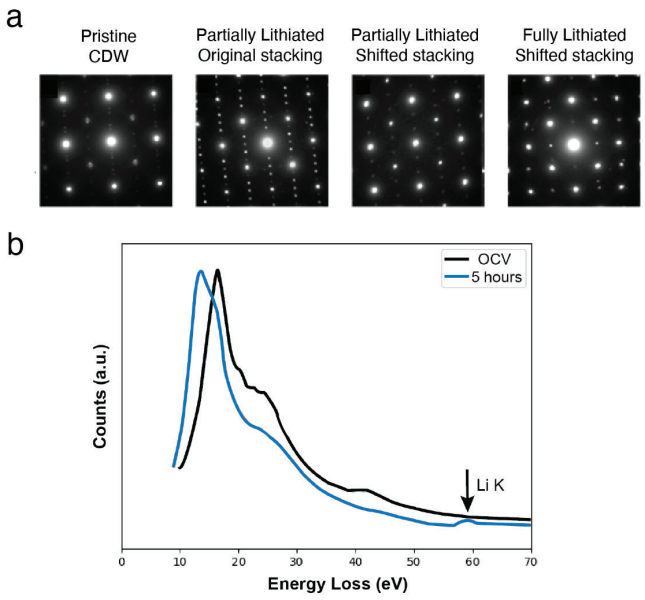

Figure 3: (a) Diffraction patterns of the four main structures acquired during in situ STEM of lithium intercalation into LaTe3. (b) Low loss EEL spectra from 2 points in the experiment, depicting the emerging Lithium K-edge edge in the host lattice.

situ EELS confirms the emergence and gradual increase of lithium content during intercalation (Figure 3b).

Conclusions and Future Steps:

We have successfully mapped structural, chemical, and electronic transitions in $LaTe_3$ induced by lithium intercalation through combined in situ Raman spectroscopy, electrochemical data of coin-cells, and multimodal in situ STEM techniques (imaging, EELS, and 4D STEM). The observed lithiated phases of LaTe3 are new and have not been observed previously. Our methodology provides a robust framework applicable to future investigations of phase transformations in other intercalation materials.

References:

[1] 1. M. Wang, S. Xu, and J. J. Cha, "Revisiting Intercalation-Induced Phase Transitions in 2D Group VI Transition Metal Dichalcogenides," Advanced Energy and Sustainability Research, vol. 2, no. 8, p. 2100027, 2021, doi: 10.1002/aesr.202100027.

[2] M. W. Tate et al., "High Dynamic Range Pixel Array Detector for Scanning Transmission Electron Microscopy," Microscopy and Microanalysis, vol. 22, no. 1, pp. 237–249, Feb. 2016, doi: 10.1017/S1431927615015664.