

## Observing the Lithiation of MoS<sub>2</sub>

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The design/discovery of layered materials for applicability in next-generation battery technologies requires a fundamental understanding of the links between the atomic scale structure, chemistry and the mechanisms and energetics of intercalation and de-intercalation reactions. Two-dimensional (2D) materials (e.g., transition metal dichalcogenides, TMDCs) show significant promise offering fast ion transport for the intercalating species, a high density of electrochemically active sites and hence find applicability in various elements (anode, cathode, electrolytes, separators, etc.) in lithium-ion-batteries (LIBs) [1]. The interest in the intercalation of layer materials with graphite and MoS<sub>2</sub> being prototypical materials. They are both layer materials but with important differences. Although intercalation of layer materials has been known for many years and intercalated materials were first studied in the TEM more than 45 years ago [2], the mechanism of the intercalation process is still not understood. Plan-view imaging was used in this initial study and has been extensively used since then (e.g. Figure 1). However, it is essential also to view to the process with the electron beam parallel to the basal planes of the layer material in order to characterize the reaction process directly and unambiguously. Lattice-fringe images have been discussed for several systems but the orientation of the specimen tended to be less than ideally uncontrolled, relying on microtoming or simply curving of the thin layers.

Recently a new approach has been developed that uses the FIB to prepare TEM specimens that are ideally oriented for detailed study of the intercalation process using TEM [3]. A new direct electron detection camera has two advantages: the electron dose can be minimized and changes that occur in the specimen very quickly can be recorded. This study of the lithiation and delithiation behavior of TMDCs uses in-situ TEMs, namely a Tecnai F30 and a Cs/image-corrected Titan equipped with a direct electron detector camera. Specific attention is being focused on the behavior of the transition metal atoms as the materials are cycled, the formation of intermetallics which would lead to failure of the LIB. While the mechanisms of intercalation and de-intercalation of lithium-ions and sodium-ions are similar, the larger size of sodium-ions requires larger channels in the electrode materials. As a result, the same electrode (for example, graphite) may not render the same capacities with sodium ions as the intercalating species as compared to lithium ions as the intercalating species.

We are using density functional theory (DFT) simulations to investigate the links between the bonding environments and structural accommodation of the layered material during insertion and exertion of the intercalating species (energy barriers, volumetric expansion, and phase transformations and the role of defects, doping, and interfaces) to understand the cycling stability for various microstructures. In addition, *ab initio* molecular dynamics simulations are being used to investigate the dynamics of the structural response during these reactions. In-situ characterization using high-resolution transmission electron microscopy (HRTEM) then becomes the essential tool to characterize the dynamic evolution of microstructure that actually occurs during these solid-state reactions and thus to test the modeling-based results [4].

References:

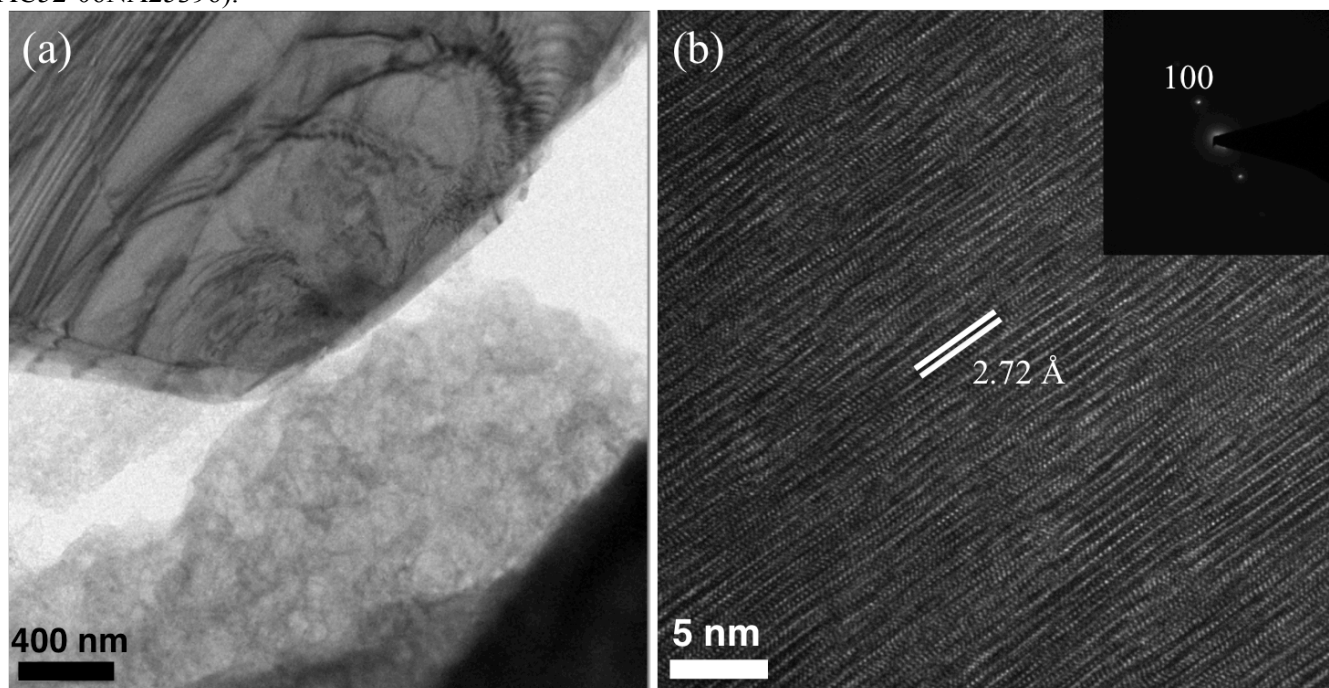
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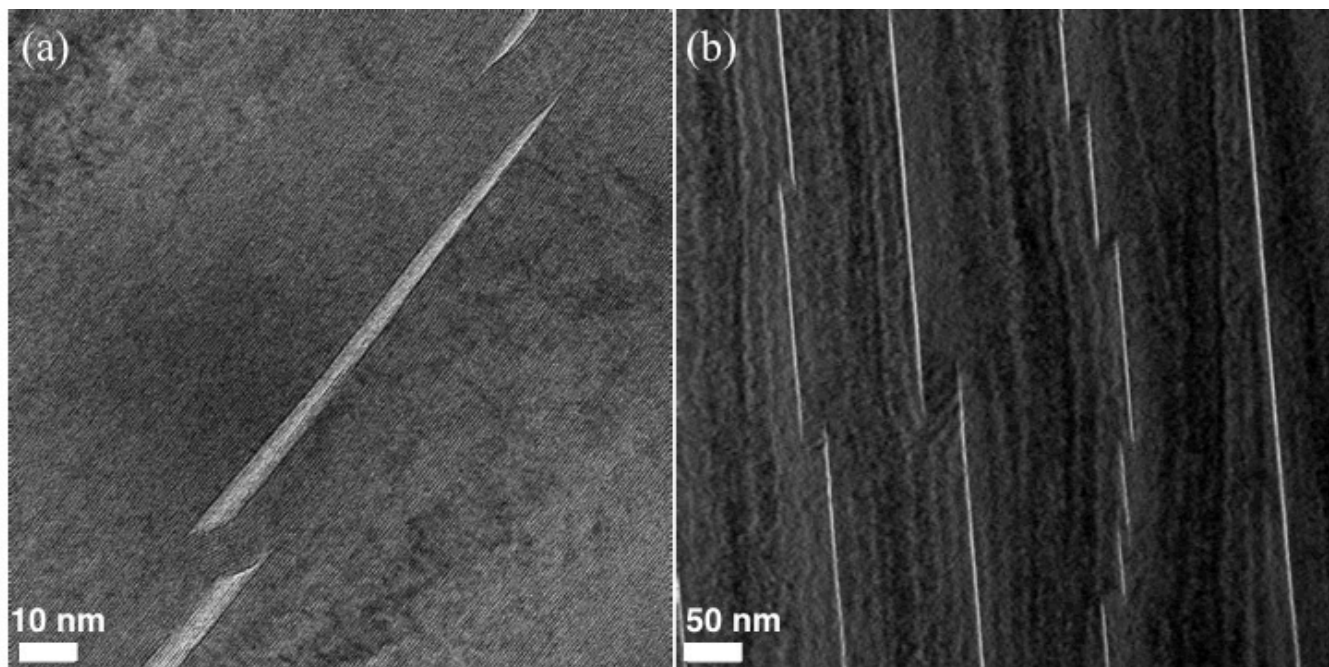
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**Figure 1.** (a) In the plan-view specimen, variations normal to the basal plane are lost in the projection. Defects associated with the reactions, such as the dissociated dislocations in the image on the left, can be seen gliding away from the edge of the specimen. (A frame from the video.); (b) HR-TEM image of the layered MoS<sub>2</sub> sample showing a d-spacing of 0.27 nm corresponding to 100 plane (inset showing the SAED pattern)



**Figure 2.** These two images show the formation of the white-line defects as the reaction between MoS<sub>2</sub> and Li proceeds. The lower-magnification image shows that the defects are not equally spaced, while the higher-magnification image shows that these defects can actually increase in width. In both images it can be seen that the defects can step across several basal planes in the MoS<sub>2</sub> (either forwards or backwards) but maintain essentially the same width after the step.