Observing the Lithiation of MoS_2

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Two-dimensional (2D) materials (especially transition metal dichalcogenides, TMDCs) show fast ion transport for an intercalating species, and have a high density of electrochemically active sites. They are candidates for several applications as the anode, the cathode, or the electrolytes, in lithium-ion-batteries (LIBs) [1]. However, the incorporation of these layered materials in the next generation of batteries requires an improved understanding of the dependence of the mechanisms and energetics of intercalation and de-intercalation reactions, and how chemistry impacts processes on the atomic scale. Graphite and MoS_2 are both layer materials but with important differences. Intercalated materials were first studied in the TEM more than 45 years ago [2], but as recent results have demonstrated [3], the mechanism of the intercalation process is still not understood. Plan-view imaging was used in the initial study with the starting specimen being prepared using the 'adhesive-tape method', the process now avoids contamination with the polymer but is otherwise essentially unchanged. (See Figure 1.) Viewing the process with the electron beam parallel to the basal planes allows the reaction process to be observed directly and unambiguously. Previously lattice-fringe images have been obtained for several systems, but the orientation of the specimen was not well controlled, relying on microtoming or simply curving of the thin layers to produce edge-on specimens

Using a focused ion beam (FIB) instrument, TEM specimens can be prepared that are oriented in a controlled manner allowing a detailed study of the intercalation process. In this presentation, new results will be presented that make use of a new direct electron detection camera. This camera offers critical improvements: i) the electron dose can be minimized and ii) rapid changes in the specimen can be recorded. Two different TEMs have been used for in-situ studies; the FEI Tecnai F30 is used for technique development, while a Cs/image-corrected FEI Titan equipped with a Gatan K2 camera is used for high speed and low-dose imaging. Particular attention is being paid to exploring the behavior of the transition metal atoms as the materials are cycled. Although LIBs are currently inexpensive, Li is a strategic metal. There are large potential cost savings in the long term if Li can be replaced by Na. The reaction mechanisms for Li and Na are quite similar, but, of course, the larger size of Na requires larger channels in the electrode materials. Hence a particular layer material may not exhibit the same capacities with Na as it does with Li. Exploring all the possible variations experimentally is not possible; computer modeling (using density functional theory, DFT, and *ab initio* molecular dynamics, MD) can access combinations of material, an assess the importance of energy barriers, volumetric expansion, phase transformations and the role of defects, doping, and interfaces, thus predicting the cycling stability for different materials combinations. High-resolution transmission electron microscopy (HRTEM) of the reactions as they occur then becomes the essential tool for characterizing the microstructural and chemical changes that occurs during these solid-state reactions and provide a validation of the modeling results.

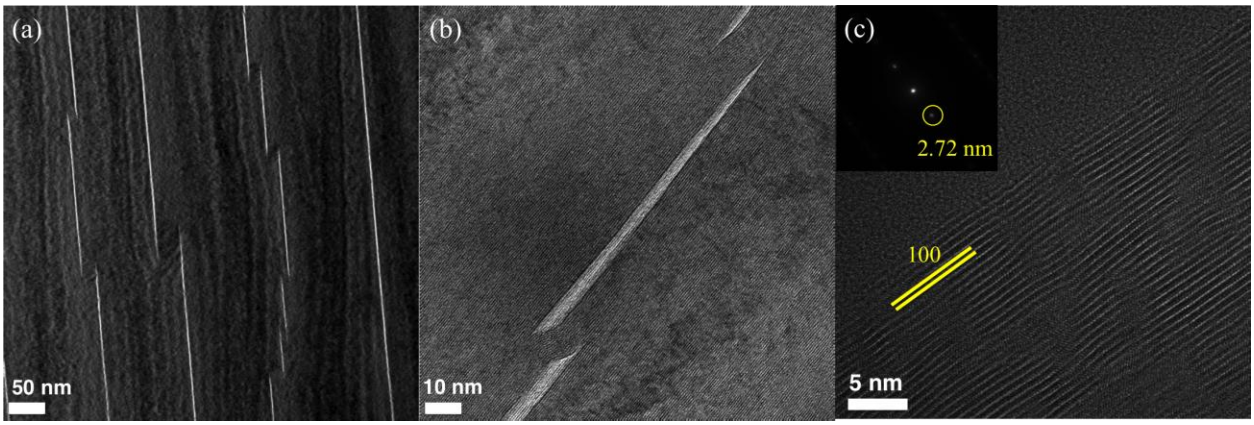

Figure 1: (a-b) These two images show the formation of the white-line defects as the reaction proceeds between MoS_2 and Li. The low-magnification bright-field image shows that the defects are not equally spaced, while the high-magnification image shows that the defects can actually increase in width. Both images 1a and 1b shows that the defects can step across several basal planes in the MoS_2 (either forwards or backwards) still maintaining essentially the same width after each step. In the planar-view of specimen, variations which are normal to the basal plane are lost in the projection; **(c)** high resolution TEM image of the layered MoS_2 sample with a d-spacing corresponding to 0.27 nm corresponding to 100 plane (inset showing the SAED pattern)

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Acknowledgment: This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science (Contract DE-NA-0003525) and Los Alamos National Laboratory (Contract DE-AC52-06NA25396)