

## TEM Studies of Nanoscale Phase Transformation during in-situ reaction of Li with 2D Materials (MoS<sub>2</sub>, WS<sub>2</sub>, Graphite)

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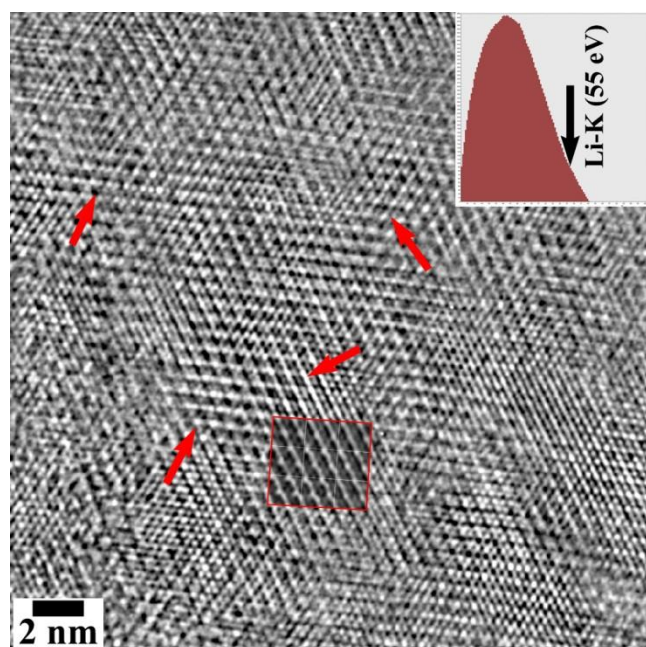
Intercalation reactions are the central to lithium-ion and sodium-ion batteries where the intercalating ions (e.g., Li, Na) are driven along the van der Waals gaps of the layered materials with the application of externally applied electrical bias (Whittingham, 2004). Subsequently, these ions move out of the materials with the generation of electrical currents. Movement of the alkaline ions within the 2D-materials also promotes solid-state reactions in the host materials and followed by subsequent phase and structural transformations (Carter & Williams, 1972; Chen, et al., 2018; Li, et al., 2017). Understanding of these nanoscale phase transformations are quite important to develop safer cathode materials with higher capacities. Direct observation of the in-situ reactions inside the TEM takes a major role in understanding the mechanism of these localized structural transformations (Carter & Williams, 2016; Williams & Carter, 2009).

In the present study, in-situ solid-state reactions between Li and the 2D materials MoS<sub>2</sub>, WS<sub>2</sub> and Graphite have been carried out inside a Tecnai F30 (S)TEM using a Nanofactory TEM-STM holder with the application of external bias (Ghosh, et al., 2020). Post-lithiation analysis of the intercalated materials have been performed in an image-aberration-corrected Titan ETEM using a camera sensitive to a low electron dose and having a large field of view (Gatan/Ametek K3-IS). Image analysis of the partially lithiated phases have been carried out using DFT modeling and multislice image simulation using java-based EMS (j-EMS) software (Stadelmann, 1987).

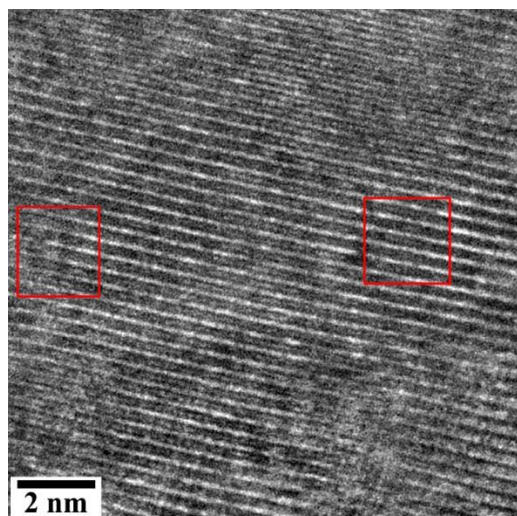
Earlier reports confirm the structural transformation in the host layered materials (MoS<sub>2</sub>, WS<sub>2</sub> and graphite) during the intercalation reaction with Li inside TEM (Janish & Carter, 2015; Singh, et al., 2020). Chemical analysis of the intercalated domains has been analyzed using the X-ray energy dispersive spectroscopy (XEDS) and electron-energy loss spectroscopy (EELS), confirming the presence of Li in the intercalated structures. However, the challenge is to analyze the nanoscale structures of the partially lithiated domains as they involve only a minimal amount of atomic reshuffling from their corresponding pristine structures. Figure 1 shows the HRTEM micrograph from a partially lithiated MoS<sub>2</sub> where the concentration of the intercalated Li measured as 0.6 atom-fraction as quantified from the EELS profile (shown as inset). The EELS profile has been acquired from a relatively large field of view and provides an average chemical measurement; in practical the intercalated Li concentration in the nanostructured domains can vary significantly. In order to determine the localized structure and the intercalated Li concentration, DFT modeling has been employed considering a 10-layered MoS<sub>2</sub> structure of 2H, 1T and hybrid 2H-1T structure with varying Li concentration. These calculated structures are further simulated and compared with the experimental results to quantify the intercalated Li concentration in addition to identify localized hetero structures.

A similar approach has been followed for the partially lithiated graphite. One-to-one comparison between the experimental results and the DFT calculated structures confirms the formation of nanoscale partially lithiated domains in the graphite matrix as shown in Figure 2. Even though the entire specimen at the field of view of the HRTEM micrograph is lithiated, the propensity of intercalation is not same throughout. Detailed analysis of the micrograph confirms the presence of different pockets of partially lithiated domains. The presence of the fully lithiated  $\text{LiC}_6$  structures in the vicinity of Li-lean zones is an indicative that the transformation propagates in similar approach as of ‘‘Oswald ripening’’ where the stable phases nucleates and in the cost of unstable phases to generate overall minimization of the system potential. Moreover, the present results shows that the intercalation mechanism is fundamentally different from the currently available models and governed mainly by the distribution of the Li in the matrix. This essentially establish the intercalation mechanism as a ‘distribution-dependent phenomenon’ rather ‘concentration-dependent phenomena’.

**Acknowledgements:** This research is funded by NSF under award DMR- 1820565. TEM investigation was carried out at CINT, an Office of Science User Facility operated for the U.S. DOE, and in the Materials Characterization Department. Sandia National Labs is managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE’s NNSA contract DE-NA-0003525. The views expressed here do not necessarily represent the views of the U.S. DOE or the U.S. Government. Matt Janish is now a member of staff at Los Alamos Laboratories.



**Figure 1.** Figure 1: HRTEM micrograph depicting the nanoscale phase transformed domains in partially lithiated MoS2. The phase transformed regions are marked with red arrows. EELS profile corresponding to Li-K edge at 55 eV is shown at top-right corner of the image. (inset) shows the phase contrast simulated image using the DFT calculated partially lithiated MoS2 supercell with hybrid 2H-1T structure.



**Figure 2.** Figure 2: Aberration-corrected HRTEM micrograph from a partially lithiated graphite specimen at the edge-on condition recorded with a low-electron dose and large field of view camera. Regions with the interplanar spacing matching with LiC<sub>6</sub> phase are marked in the micrograph.

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