

In Situ TEM Investigation of Lithium Intercalation in $Ti_3C_2T_x$ MXenes for Energy Storage Applications

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MXenes are a new class of two-dimensional (2D) transition metal carbides (nitrides and carbonitrides) that have unique electronic, optical, electrochemical, and mechanical properties [1]. MXenes have high volumetric capacitance, which is attributed to their unique atomic structure and surface functional group chemistry that allows for high electronic and ionic conductivity, important properties for energy storage materials [2]. In addition to fast surface redox reaction pathways, ion intercalation within MXenes layers provides an additional charge storage mechanism [2,3]; thus, it is crucial to fundamentally understand the mechanisms of ion intercalation. Among the family of synthesized MXenes, the most widely studied phase is $Ti_3C_2T_x$, where T_x represents the surface functional groups (-F, -OH, and =O). Bulk measurements of $Ti_3C_2T_x$ MXenes show that cation intercalation can lead to changes in the surface chemistry and enhance volumetric capacitance [4]. Additionally, recent density functional theory-based calculations show that lithium uptake in $Ti_3C_2T_x$ is reduced by four times due to -F and -OH surface terminations [5]. Measurements on bulk MXene electrodes in electrochemical cells have demonstrated the redox reactions and charge storage due to ion intercalation; however, the mechanism of ion intercalation at the nanoscale is still unclear [2].

In this study, *in situ* transmission electron microscopy (TEM) was used to study Li^+ intercalation in $Ti_3C_2T_x$ MXene. $Ti_3C_2T_x$ flakes were dispersed on a carbon-coated, copper TEM half grid and mounted on a specialized *in situ* TEM electrical biasing holder equipped with a piezo-controlled biasing probe, which was sourced with lithium metal (Figure 1a) [6]. This platform simulates a nanoscale electrochemical cell when the lithium-sourced probe comes in contact with the MXene flake and a negative 2V potential is applied to drive Li^+ ions into MXene (Figure 1b). This approach allows for real-time monitoring of phase changes and lattice expansion occurring due to ion intercalation. Figure 1c shows a series of bright-field (BF) TEM images of the MXene flakes acquired at different times during the Li^+ intercalation. A 12% increase in the average interlayer spacing is observed post-lithiation (Figure 2a and 2b), which is indicative of Li^+ intercalation. Additionally, lithium oxide (Li_2O) and lithium hydroxide ($LiOH$) phases are observed after intercalation (Figure 2c and d), indicating that lithium interacted with the $Ti_3C_2T_x$ surface functional groups (=O and -OH) to form inorganic compounds. This study shows that investigating Li^+ intercalation *in situ* can provide a mechanistic understanding of the reaction pathway for ion intercalation in real-time at nanoscale resolution [7].

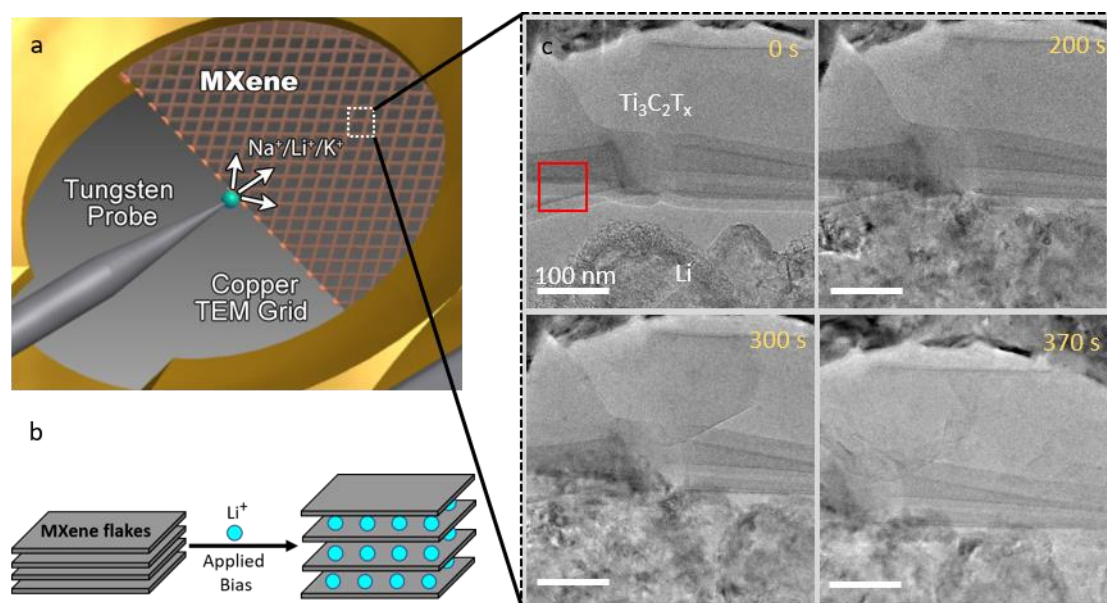


Figure 1. Figure 1. (a) Schematic representation of in situ lithiation experiments with a piezo-controlled probing electrical biasing in situ TEM holder. (b) Schematic showing Li^+ ions intercalating between MXene layers. (c) Sequence of BF-TEM images during Li^+ intercalation in multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. The highlighted red box is the region of tracked interlayer distance during intercalation.

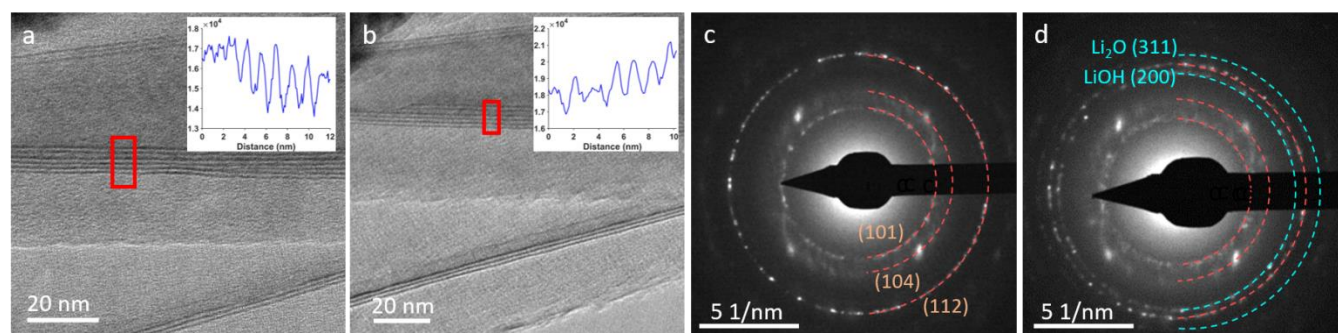


Figure 2. Figure 2. BF-TEM image of the same $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flake (a) pre-intercalation and (b) post-intercalation. Insets show the integrated line profiles of the regions highlighted by red box for interlayer spacing measurements. Average interlayer spacing increased from 6.3 Å to 7.1 Å after intercalation. Selected area diffraction patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ (c) pre-intercalation and (d) post-intercalation showing formation of Li_2O and LiOH phases after lithium intercalation.

References

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