In-situ (S)TEM Study of Synthesis and Degradation Process of Titanium-Based MXene Lithium-ion Anodes

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The rising demand for extended driving ranges for electric vehicles has created the need for improved performance of Li-ion batteries; specifically, higher energy density and high-power capability. However, the current commonly used graphite anodes in Li-ion batteries do not allow for fast solid-state diffusion processes to occur and therefore high-power output is not possible for these novel electric vehicle applications. Additionally, while the lithiation potential of graphite is very low, which is good for producing a high cell voltage, it is not ideal as it enables the formation of lithium dendrites, which are both flammable and impose a limitation on the cycling stability of the cells. [1, 2, 3] In order to address above issues, we focus on new battery nanomaterials such as MXene anodes. This family of 2D nanomaterials have now emerged as potential alternatives to graphite and are the most promising new candidate for anode materials in Li-ion batteries due to both their unique and tailorable 2-D transition metal carbide (nitride) structures and their higher lithiation potential than graphite. Furthermore, the wider interlayer spacing (~1nm) of MXenes potentially allows for quicker intercalation of Li^+ with minimal lattice distortion and improved rate performance along with better cycling stability. One of the most significant challenges in the use of MXene anodes is a rapid degradation and energy storage capacity after first few cycles, which currently leads to rapid anode failure and a decreased cycle lifetime. [3] Understanding the degradation mechanisms in MXene anodes is therefore of critical importance in order to meet the requirements of the future anode materials.

In this work we utilize *in-situ* electrochemical liquid and gas (S)TEM cells that have previously found many applications in the energy storage materials and electrolytes, to study synthesis and degradation processes of MXene anodes.[4] Specifically, we study degradation of the $Ti_3C_2T_x$-type MXene anode material during cycling in a full-cell configuration and dynamic process of MXene formation from the Ti-based MAX phase. The direct observation of dynamic processes at high spatial and temporal resolution allows us to identify a wide range of complex phenomena such as chemomechanical degradation of the electrodes, electrolyte decomposition, SEI formation, and Li intercalation/deintercalation processes at the electrolyte/MXene interface. Consequently, these results increase our understanding of transition from MAX phase to MXene phase and will help to develop new strategies for enhancing their performance [5].
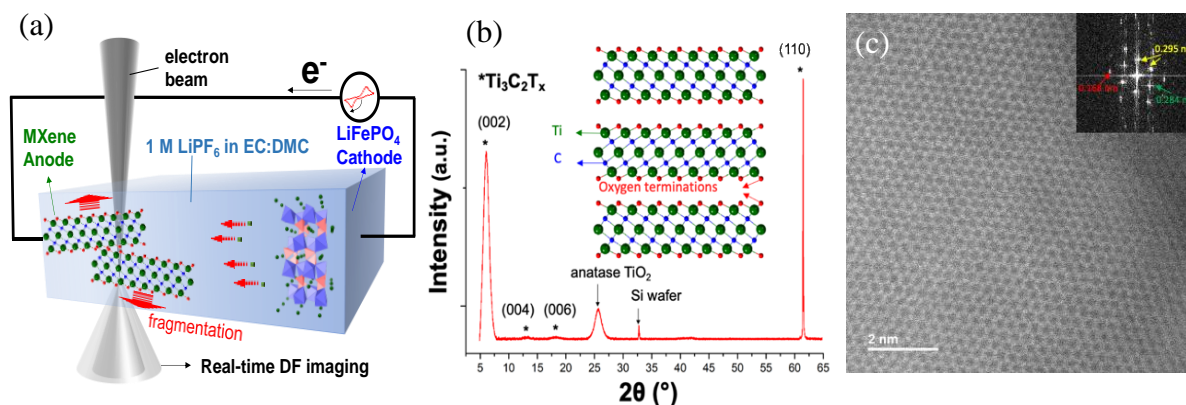
Figure 1. (a) Schematic of the *in situ* electrochemical STEM nanobattery cell with MXene anode and LiFePO$_4$ cathode in 1M LiPF6 in EC/DMC. (b) X-ray diffraction pattern of the MXene-coated Si substrate. The crystal structure of the Ti$_3$C$_2$T$_x$-type (T$_x$ for surface terminations) MXene is illustrated in the inset. (c) in-situ HAADF (S)TEM image of Ti-based MAX phase and its corresponding FFT.

References:

[1] JM Tarascon and M. Armand, Nature **414** (2001), p. 359.
[2] N Nitta et al., Mater. Today **18** (2015), p. 252
[3] M Greaves, S Barg and MA Bissett Batteries & Supercaps **3** (2020), p. 214.
[4] BL Mehdi et al., NanoLetters **15** (2015), p. 2168
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