

Integrating Novel Microscopy into Battery Research: From Atomic Resolution to *In Situ* and Functional Imaging

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Despite their different configurations and chemistries, current energy-storage systems, e.g. Li-ion, Li-S, Li-air, and all-solid-state Li batteries, rely on the use of solid-state ion conducting materials as electrodes and/or electrolytes. Continuous ion hopping from one mobile ion site to adjacent vacancy sites in a crystalline lattice forms the basis for ion conduction in solids. Atomic-scale factors, such as lattice structure and the concentration and distribution of mobile carriers and vacancies, determine the ion conductivity in solids, and thus dictate the rate capability and capacity in batteries.

During the past few years, atomic-scale scanning transmission electron microscopy (STEM) imaging and electron energy loss spectroscopy (EELS) have revealed critical structural and chemical features in battery materials that are responsible for the degradation or enhancement in battery performance. As the structure and chemistry evolve during materials synthesis and battery operation, various *in situ* configurations, including open- and closed-cell platforms, have been used to study lithiation or the formation of interphase layers in batteries. These atomic-scale and *in situ* microscopy studies have provided significant insight and continue to highlight the importance of microscopy for battery research. Recent developments in faster cameras and highly stable electronics have enabled the emergence (re-emergence) of functional imaging methods such as ptychography, differential phase contrast imaging, and vibrational spectroscopy. These techniques, once developed and tailored for battery research, will not only allow us to probe the atomic structure and chemical species, but will also facilitate the ability to map, directly or indirectly, functionality associated with local nanofeatures in battery materials and devices. The evolving integration of new and emerging microscopy techniques into battery research, from atomic-resolution to *in situ* and functional imaging, will be demonstrated by several recent studies on solid electrolyte materials.

Solid electrolyte materials represent a major component in novel battery configurations to enable the use of lithium metal, which has the highest capacity as an anode material. An ideal solid electrolyte material must be highly ionically conductive and exhibit stability with metallic lithium. However, current solid electrolyte materials exhibit inherent, high grain-boundary (GB) resistance, which typically lowers the total ionic conductivity of the material by several orders of magnitude. Z-contrast imaging and EELS were used to reveal the structural and chemical origins of this high GB resistivity in a $(\text{Li}_{3x}\text{La}_{2/3-x})\text{TiO}_3$ (LLTO) prototype material. The LLTO GBs exhibit a severe structural and chemical modification, resulting in a Ti-O binary compound, intergranular thin film with a 2-3 unit cell thickness (Figure 1a). Such a GB structure is not energetically favorable for either Li accommodation or transport, giving rise to the poor GB conductivity. The structural and chemical basis for the large GB resistance in Li

superionic conductors was elucidated through direct visualization of the atomic structure and nature of the chemical bonding within the LLTO GBs [1].

Forming a conductive and stable interface between Li metal and a solid electrolyte is crucial towards the use of Li metal anodes. While most solid electrolyte materials are not stable with Li-metal, cubic-Li_{7-3x}Al_xLa₃Zr₂O₁₂ (c-LLZO) was shown to form a benign interface with lithium based on electrochemical characterization. However, theoretical calculations showed that LLZO is not thermodynamically stable and tends to decompose upon contact with lithium. Through the *in situ* formation of Li/c-LLZO interfaces inside a STEM, we discovered the formation of an ultra-thin, self-limiting tetragonal LLZO layer (Figure 1b). This interfacial layer effectively prevented further interfacial reactions without compromising the ionic conductivity. This work provides a new perspective for designing stable and conductive Li/solid electrolyte interfaces [2].

Lithium dendrite growth, which is a major issue in organic liquid electrolyte based lithium ion batteries, was recently observed in solid electrolyte materials. These dendrites grow along particular GBs and heterogeneous interfaces. As dendrites induce direct short-out in batteries, their formation mechanism in solids must be clearly understood. In this presentation, we will discuss the fundamental formation mechanism of lithium dendrites in LLZO by integrating emerging ptychography-based differential phase contrast imaging and valence EELS with conventional atomic-resolution STEM imaging [3].

References:

[1] C Ma *et al*, Energy & Environmental Science **7** (2014), p. 1638.

[2] C Ma *et al*, Nano Letters **16** (2016), p. 7030.

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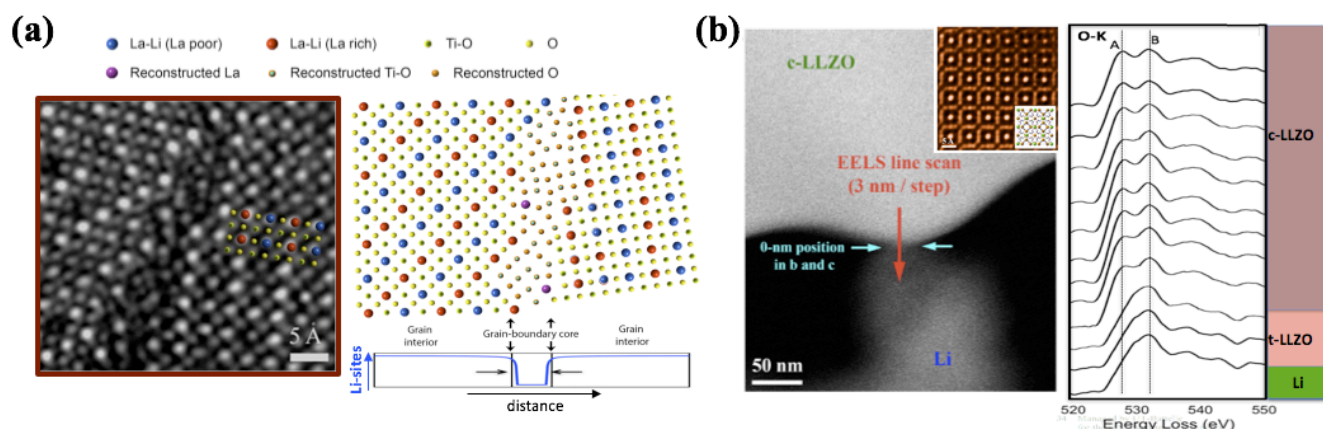


Figure 1. (a) Z-contrast STEM image of a typical LLTO GB (left) and corresponding GB atomic structural model based on Z-contrast image and atomic-scale EELS (right) [1]; (b) LLZO-Li interface formed during *in situ* experiment in a TEM (left); series of O-K edges acquired across the interface reveals fine-structure deviation at interface, indicating the formation of an interfacial layer [2].