

Relevance of In-Situ Electrochemical STEM Observations to Li-Metal Batteries for Evaluating Performance

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Electrochemical liquid-cell scanning transmission electron microscopy (STEM) allows for the investigation of air-sensitive battery materials *in situ* [1-3], though there has been debate about the relevance of the mechanistic processes under these conditions to qualify the experiments as *operando*. This debate can only be solved through gaining a comprehensive understanding of a battery (comprised of electrodes, current collectors, electrolyte, and separator). These materials and interfaces change during cycling in a coin cell or pouch cell, where the electrode configuration and environment is very different from that of an electrochemical liquid-cell. Our work has determined that the electrochemical liquid-cell STEM experiments provide insights that may easily be overlooked in mesoscale characterization [4,5], though these microscale mechanisms are likely the majority in the interactions that take place on Li-metal anode's surface during initial electrodeposition.

A lithium metal battery is composed of lithium metal deposited on a current collector, which is placed into contact with an electrolyte-saturated polymer separator, and then enclosed against a cathode on a current collector within a coin or pouch cell for research testing. Pressure applied by the coin cell casing or steric limitations on the pouch cell, retains contact of all battery interfaces during cycling [6,7]. Alternatively, the electrochemical liquid-cell is composed of electrodes in a planar configuration that do not contact a polymer separator, but instead perform electrochemical reactions with an electrolyte that coats the electrode surfaces in a nanoconfined cell [1-3]. The major difference therefore is that electrode in the electrochemical liquid-cell do not experience any contact pressure, which we have shown will impact the electrochemical reactions, solid-electrolyte product formation, and electrodeposited Li morphology [5]. These impacts were found through the lens of mesoscale studies of the batteries with characterization provided by cryogenic scanning electron microscopy (SEM) and focused ion beam milling (FIB) [6-9].

This work covers the major results on electrodeposition of lithium metal on current collectors using electrochemical liquid-cell STEM and uses cryogenic SEM/FIB cross-sections from coin and pouch cell Li-metal anodes to demonstrate the relevance of these in-situ observations to the overall performance of the battery. Details will be covered on how the electrochemical liquid-cell experiments were optimized, electron-beam artifacts were mitigated, and the use of novel approach with a cryogenic stage on a femtosecond-laser plasma FIB for cross-sectioning were explored [8]. The electrochemical liquid-cell STEM datasets are useful in the initial stages of understanding electrodeposition and dissolution, but

since batteries have been found to be extremely inhomogeneous across the battery components, the need for meso-to-micro-to-nanoscale imaging is critical to define the predominant charge transfer and failure mechanisms within evolving Li-metal electrodes.

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