

Ultra-high Resolution *In-operando* X-ray Microscopy of Fuel cells and Batteries

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Here we report on the development of *in-operando* electrochemical cells that we employ in the study of fuel cells and batteries using ultra-high resolution X-ray microscopy, including three-dimensional and four-dimensional computed tomography techniques with a resolution down to 50 nm. Batteries and fuel cells are key technologies in realizing broad vehicle electrification of across all ranges of vehicles size and driving range. However, significant challenges in performance, durability, and cost limit the rate of production and consumer adoption. *In-operando* imaging that is an inherently temporally-resolved imaging approach is an extremely valuable tool in understanding the performance and durability bottlenecks that prevent the use of lower cost materials and processes.

In regards to batteries, there are two key areas of our research in using X-ray microscopy: safety and high energy density anodes. Firstly, we are concerned with the safety of existing Li-ion battery materials and designs. State of the art graphite anodes that lithiate by intercalation will approach potentials close to that of electroplating under normal operation. Under cold temperatures and high currents, the intercalation process can transition to electroplating of Li metal and potentially yield the growth of Li metal dendrites that can pierce the separator, short the cell, and cause a fire. Our second area of study on Li-ion batteries is the development of high energy density anodes. These include silicon (Si) and tin (Sn) based materials that can offer significantly higher energy density versus graphite. However, the large >100% volume expansion with Li alloying leads to particle fracturing and pulverization of the electrode that yields rapid capacity loss. We are also investigating Li metal electrodes that could play a significant role in Beyond Li battery chemistries like Li-sulfur and Li-oxygen cells. However, Li metal anodes continue to be plagued by instabilities during electroplating and dendrite growth [1].

With respect to fuel cells, our focus for *in-operando* studies relate to performance degradation. One aspect is the dissolution of alloying elements that are used to increase electrocatalytic activity versus pure platinum catalysts. Alloying elements, such as cobalt and nickel, dissolve into the electrolyte once exposed and replace the electrochemically active protons, degrading the performance during high power operation. Another degradation mechanism of study is the carbon corrosion that can occur at the cathode during start-up and at the anode during fuel starvation. Carbon corrosion leads to electrical isolation of the Pt electrocatalyst and the commensurate performance loss. Finally, the evolution and accumulation of liquid water in low temperature polymer electrolyte fuel cells can severely restrict oxygen reactant transport and power density, but little is known about the water transport in the cathode microstructure.

Our imaging employs a commercial, laboratory-scale X-ray CT system (Xradia UltraXRM-L200, Xradia, Inc., Pleasanton, CA) with nano-scale resolution (nano-CT). This particular instrument has an 8 keV rotating copper anode source, monocapillary condenser, Fresnel zone plate objective, and a phase contrast ring for Zernike phase contrast imaging. The combination of optics provides resolutions down to 50 nm (16 nm pixels) and fields of view as large as 65 μm . The Zernike phase contrast capability is an important for the imaging of fuel cells and batteries, as it allows us to image low atomic number (Z) materials such as carbon, lithium metal, and polymers.

The combination of sub-100 nm resolution and a field of view on the order 100 μm makes this instrument well-suited for studying fuel cell and battery electrodes where the particles are on the order of 100 nm or larger and the full electrode thickness are typically less than 100 μm , meaning the imaging covers the spatial spectrum of electrode-scale processes. It is also easily recognized that X-ray imaging does not require a vacuum environment and thus allows us to image cells that use a wide variety of liquid and polymer electrolyte. Although, laboratory scale nano-CT systems can require significantly longer exposure times, this becomes less problematic when imaging slow processes, particularly during the charging and discharging of batteries which in comparison requires significant amounts of synchrotron access.

In our group, we have adopted two distinct approaches to assembling batteries for *in-operando* imaging; one approach uses capillaries to house the wire-coated electrodes and liquid electrolyte whereas the other approach is a planar cell that can use commercial electrodes and separators. Each approach has its relative advantages and disadvantages in terms of image quality, ease of assembly, and similarity to commercial cell structure and design. The cell design for the *in-operando* imaging requires special consideration to ensure the transient phenomena is visible in the nano-CT while also ensuring the cell is otherwise stable in the nano-CT environment. The key constraints of any *in-operando* Li-ion cell are the following:

1. The entire cell diameter must be less than 1 cm to avoid hitting the optics.
2. The thickness and density along the beam should not be so large they overly attenuate the X-ray.
3. There needs to be access for current collectors.
4. The electrolyte needs to be sealed to prevent electrolyte evaporation during the imaging.
5. There needs to be good contrast between the electrode sample and its surroundings.
6. The cell must be able to be rotated for tomography.
7. The cell should be relatively easy to assemble within a glovebox.
8. Epoxy should be avoided due to impurities that may leach.

This combination of constraints has led us to use electrodes inserted into the ends of low attenuating capillaries filled with electrolyte. The benefit being that the capillary has a narrow imaging cross-section and only has to be sealed at the ends. A downside of our prior studies and others [2] using capillaries is the epoxying of the wires into the capillary, which makes consistent assembly difficult and electrolyte sealing often unsatisfactory (causes electrolyte loss by evaporation). In addition, there is potential for epoxy to introduce unwanted impurities. To address the issues of the epoxied capillaries, we have developed our cell designs based on high performance liquid chromatography (HPLC) fittings, which are reusable and also inexpensive. One possible implementation is where HPLC fittings (IDEX) are combined with adapters for 360 μm outer diameter (OD) capillaries. A wide variety of capillaries with different inner diameters and materials are easily obtainable. Materials include Kapton (polyimide) and PEEK, which have good chemical stability. Using diameters this much larger than the field of view is acceptable since most Li electrolyte solutions and these capillary polymers have attenuation lengths on the order of 1 mm at 8 keV and neither feature structure that will impact the signal to noise ratio. The current collector wires are also sealed using the HPLC fittings.

Figure 1 shows a demonstration of *in-operando* imaging with the capillary cell. In this case, the working electrode in the imaging field of view was a bare copper wire and the counter electrode was a Li metal coated copper wire. The cell was mounted in the nano-CT and galvanostatic deposition of Li on the copper wire was performed. The two images show the copper and electrolyte interface at the beginning

and end of the electrodeposition. Zernike phase contrast was used so that the low Z Li electrodeposits would be visible.

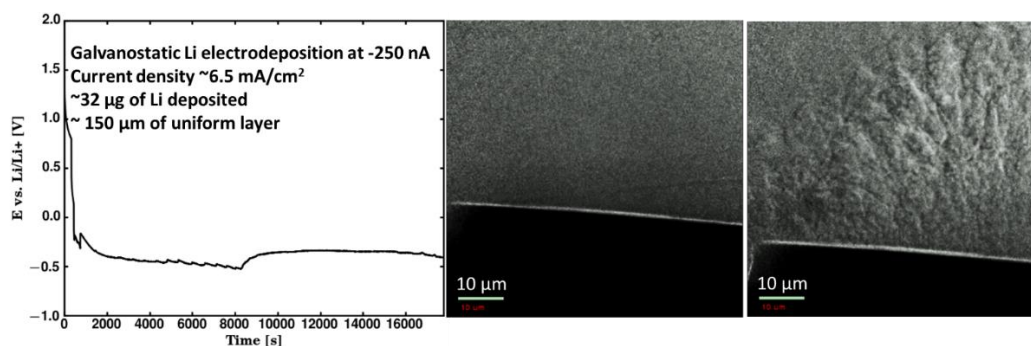


Figure 1. Capillary cell imaging of galvanostatic Li electrodeposition on copper wire. Potential time series over the duration of the electrodeposition and Zernike phase contrast images of before and after the electrodeposition.

Our other approach to *in-operando* imaging is using a planar cell arrangement. The design is similar to a traditional pouch cell, but scaled down for nano-CT. The cell is encapsulated in Kapton for X-ray transparency and acceptable electrolyte solvent retention. The cells are assembled with commercial electrodes coated on current collectors along with commercial separators. Small circles of the commercial materials are extracted and then carefully stacked to form the cells. The materials are then soaked with conventional Li-ion battery electrolyte and sealed.

A key benefit of the planar approach is that we can use dense, calendared electrodes produced by standard means and we can image the electrode/separator interface, which is a key capability for investigating dendrite and safety aspects. Figure 2 shows orthoslices (left to right) from inside the separator, within the graphite anode, and across the separator and graphite interface.

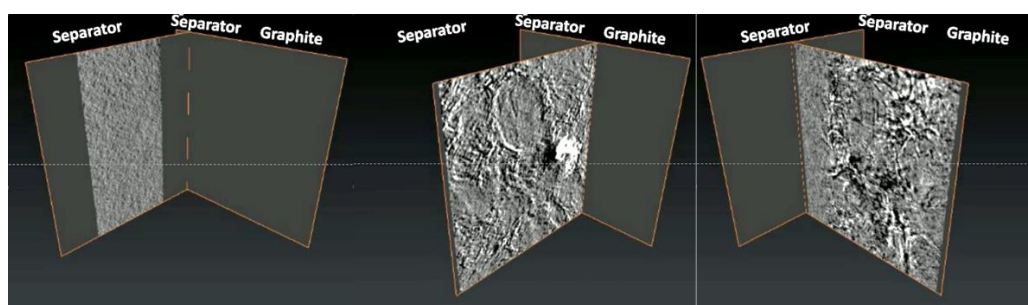


Figure 2. CT imaging of a commercial graphite anode coated on copper foil adjacent to a Celgard separator. The planar cell allows the imaging of the electrode separator interface as shown.

References:

- [1] Frisco *et al.*, ACS Applied Materials and Interfaces, **9** (2017), p. 18748-18757.
- [2] Eastwood *et al.*, Chemical Communications, **51** (2015), p. 266-268.
- [3] The authors acknowledge funding from the US National Science Foundation for the study of high energy density anodes under grant 1705321, the US Office of Naval Research for the battery safety studies under grant N00173-17-1-G009, and the US Dept. of Energy for the fuel cell studies under grant DE-EE0007271.

