# Mosaic Mapping for Analysis of Heterogeneous Battery Degradation

Introduction:

Batteries are complex, multi-layered systems with many layers and interfaces that need to be understood. In a typical battery cell, there is a separator/electrolyte at the center, sandwiched between a cathode and anode, with current collectors on either end. During charge and discharge, ions will flow across these layers, interacting with many components including organic and inorganic species, solvents, and active materials. As a result, interfacial layers form at the electrode-electrolyte interface, with chemical and structural consequences on battery stability. At the cathode electrolyte interphase (CEI), changes can happen such as transition metal redox reactions and particle dissolution, while in the solid electrolyte interphase (SEI), lithiation and delithiation processes can lead to particle cracking, dendrite growth, and harmful side reactions with the binder (Figure 1). Battery materials must be analyzed in detail to understand how and where interfacial products are formed to improve material performance for long-term device operation. Specifically, understanding the chemical composition, distribution, and morphology of electrode-electrolyte interfaces is necessary to prepare well-dispersed, stable, high-capacity electrodes.
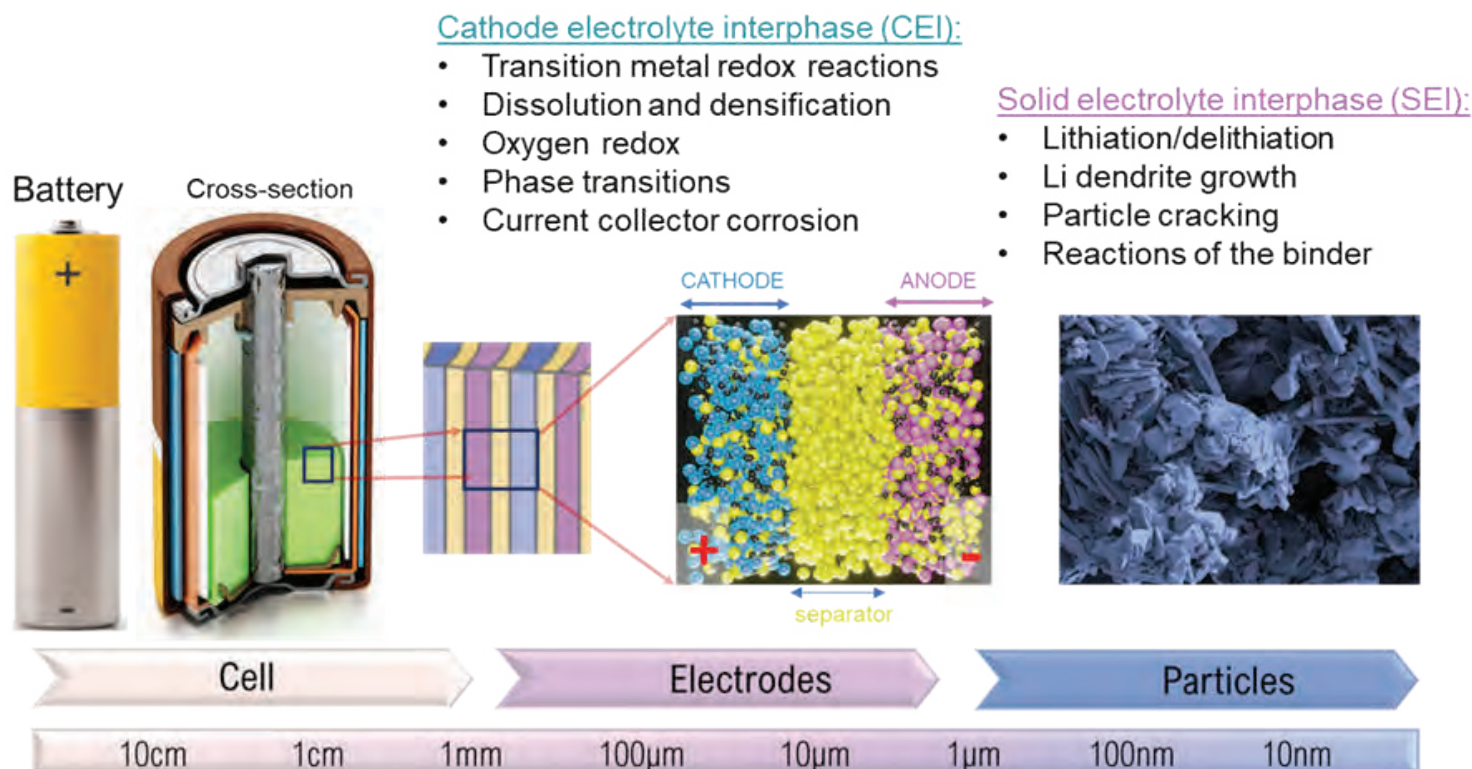
Figure 1: *Diagram of length-scales relevant to characterization of battery devices, and interfacial regions and processes of interest.*

X-ray photoelectron spectroscopy (XPS) is well-suited to analyze chemical speciation at a sample surface, such as the surface of an electrode where an interphase has formed. The unique scanning microprobe technology on PHI XPS instruments enables scanning X-ray induced secondary electron imaging (SXI), to quickly identify regions of interest (ROIs) for further spectral investigation, particularly useful for materials with heterogeneous surfaces when specific areas must be targeted or avoided. As seen in Figure 2, an SXI collected on an electrode surface after cycling demonstrates clearly that the electrode-electrolyte interphase does not form homogeneously. Small-area spectra collected from ROIs on the SXI confirm differences in CEI formation in the three areas analyzed. Measuring composition of such heterogeneous materials to accurately compare samples requires two main capabilities: high small-area sensitivity, to determine where the degradation products are forming across the interface, and the ability to collect data efficiently and automatically at many points on the sample.
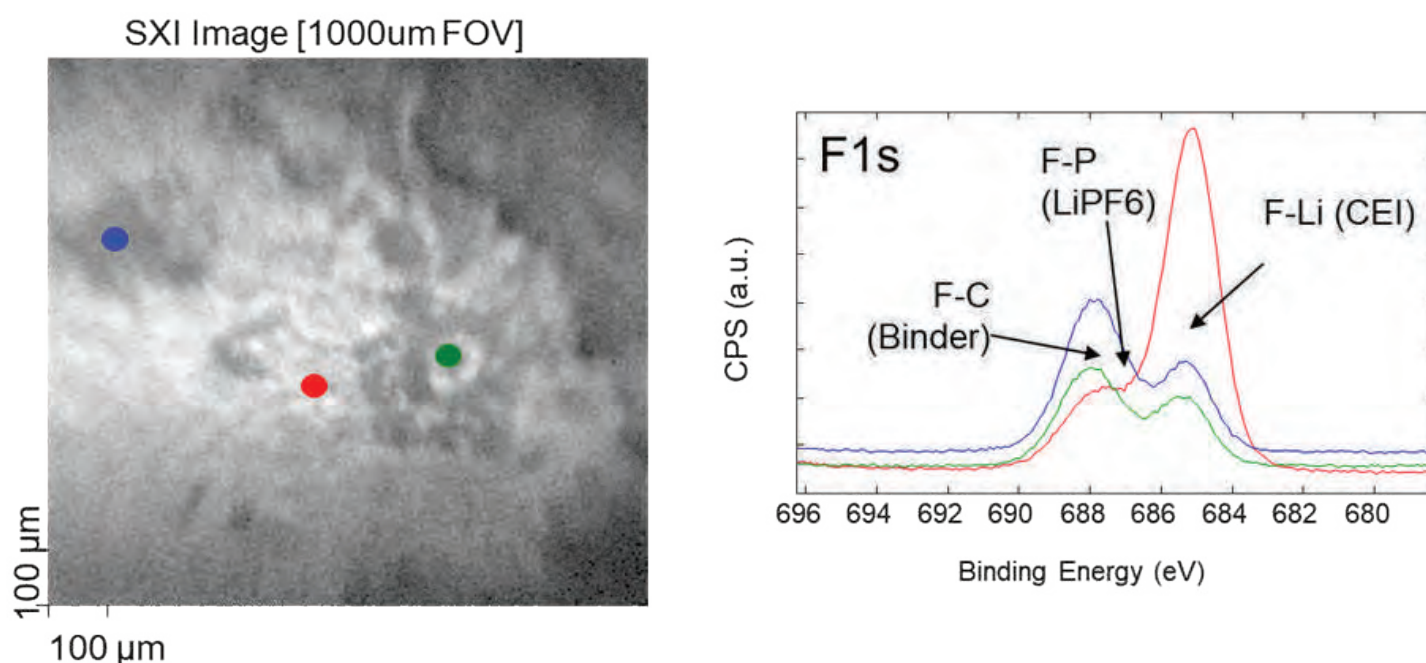
Figure 2: X-ray induced secondary electron image (SXI) and multi-point spectra collected at the electrode-electrolyte interphase of a cycled battery.

PHI XPS spectrometers offer the highest sensitivity for the smallest area of analysis on the market, allowing sample heterogeneities to be investigated, while the SmartMosaic® software allows data points to be collected across an entire sample and automatically merged into a map to visualize differences in composition and chemistry. Additionally, the scanning X-ray technology on PHI systems is effective at quickly collecting data from specific sample regions while minimizing damage for sensitive materials compared to a flood source. The ability to focus on small features and scan across an area is a unique method for analyzing Li-containing batteries with less risk of inducing chemical changes during the analysis.

In this work, CEI interphases were compared for a traditional cathode and a cathode coated with a protective layer used to inhibit chemical decomposition. The ability to visually assess the distribution of degradation products at the mm-scale with µm-scale resolution is essential to design stable, long-lifetime battery materials using next-generation materials.

Experimental:

Battery electrodes were prepared with cathode active material, binder, and solvents. Battery cells were prepared in pouch-cell configuration and cycled until performance deteriorated. The pouch cells were disassembled in a glovebox and the cathode was mounted on double-sided non-conductive tape on the XPS sample holder. The Vacuum Transfer Vessel (VTV) was used to transport the battery samples to the XPS instrument without exposure to air.

The Mosaic data acquisition process is illustrated in Figure 3. Tiles were drawn across the entire sample such that datapoints were only collected on the curved sample piece itself and not on the current collector. An SXI image or spectra were collected at every single tile, and SmartMosaic automatically stitched the Mosaic from the individual tiles.
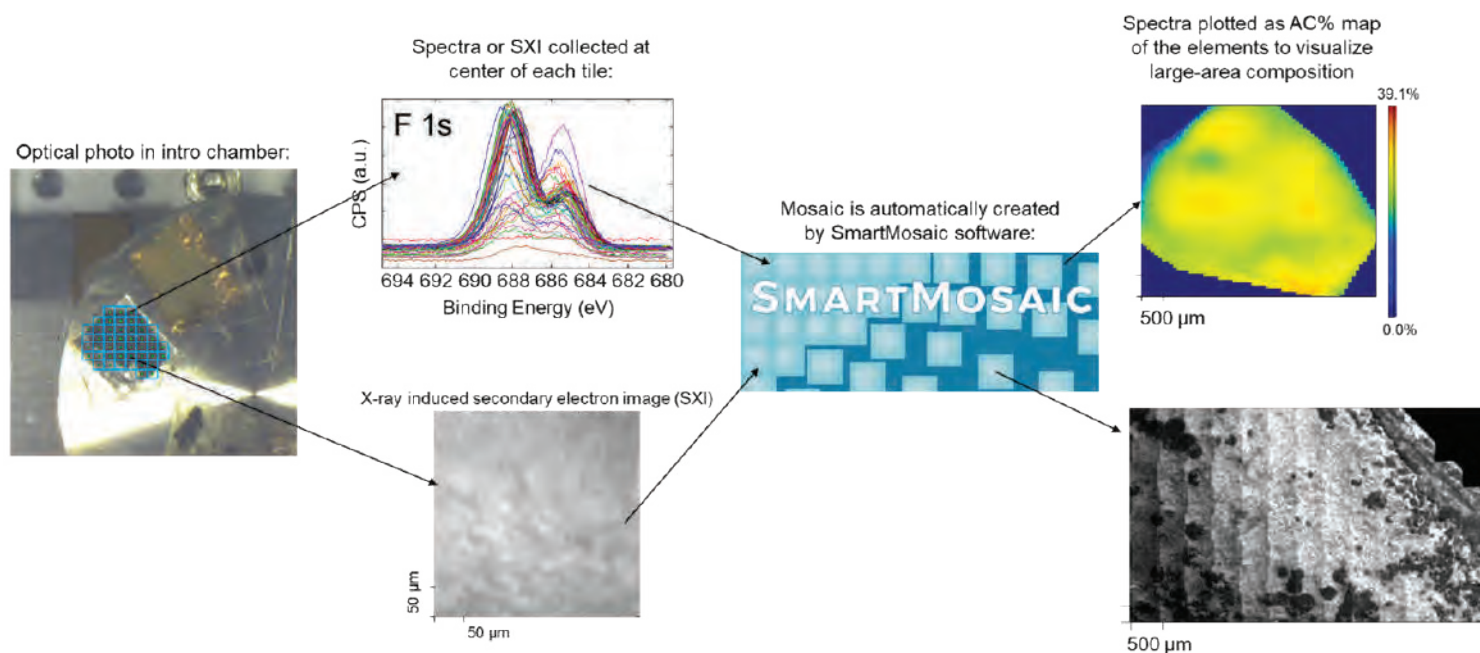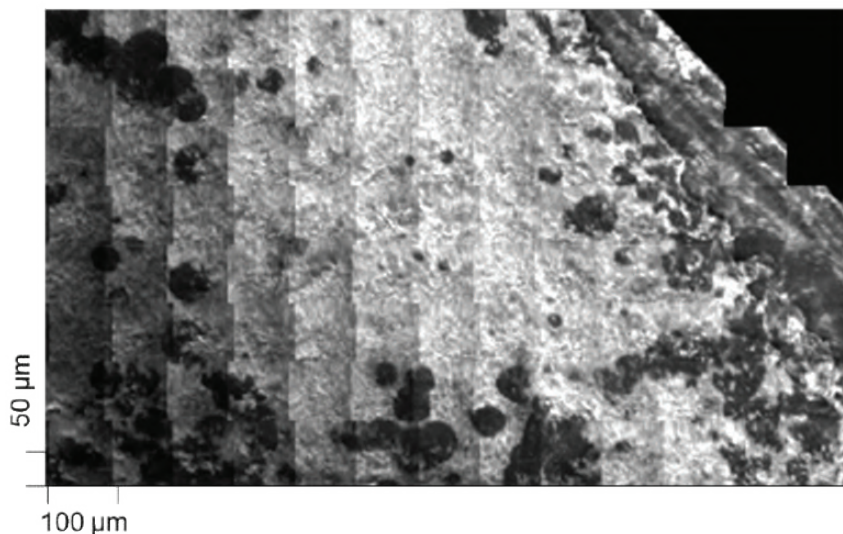

Figure 3: Schematic of the Mosaic data setup and acquisition process.

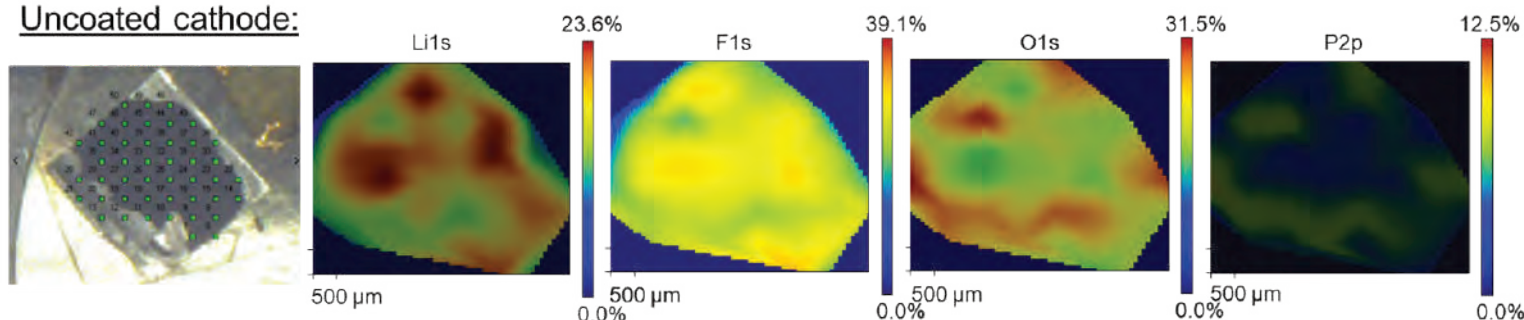# Results and Discussion:

Cycled battery cathodes with and without a protective surface coating were analyzed. First, SXI Mosaics were collected to visualize heterogeneity across the sample surface (Figure 4). Since SXI images are collected from secondary electrons, related to photoelectron yield, contrast differences can indicate chemical differences in addition to topography. The impact of the coating is seen clearly in the SXI Mosaics. The cathode without the coating is extremely heterogeneous, with clear contrast differences all over the analyzed area, and there are cracks and pockmarks visible in many areas. By comparison, the coated sample is much more homogeneously dispersed after cycling; ripples are present as an artifact of cycling, but the contrast is much less pronounced than the coated sample and there are less structural defects visible.

Uncoated Cycled Battery Cathode: Coated Cycled Battery Cathode:
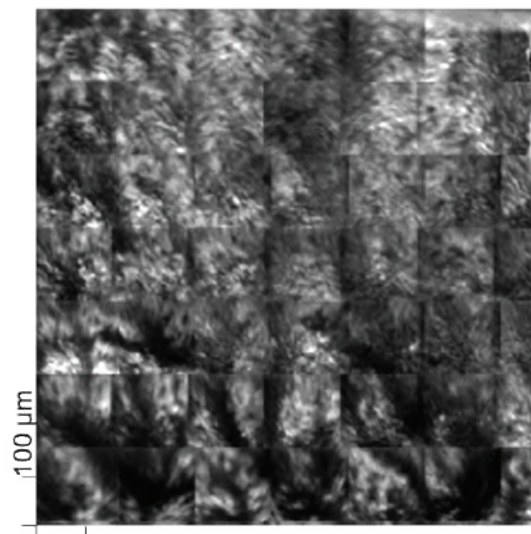
Figure 4: SXI Mosaics of cycled cathodes without (left) and with (right) a protective surface coating.

Based on the imaging analysis, it is clear that many spectral data points must be collected to track sample chemistry that is reflective of the sample as a whole. Therefore, Spectral Mosaics were collected on the entire cathode pieces (Figure 5) to assess wide-scale composition. The uncoated sample has a very heterogeneous distribution of all elements, with Li concentrations scattered along the sample piece. The P2p and O1s distribution is correlated in many areas, and the Li1s and F1s are co-located in certain areas, but the Li has different areas of high concentration compared to F1s. The coated sample has a much more homogeneous dispersion of all elements, with the Li slightly more unevenly distributed than the other elements, but still more uniform than in the uncoated sample.
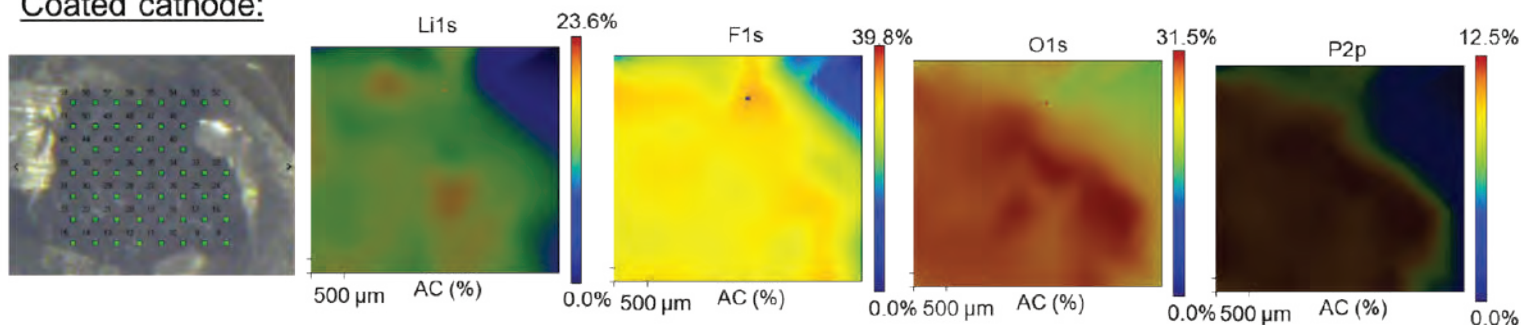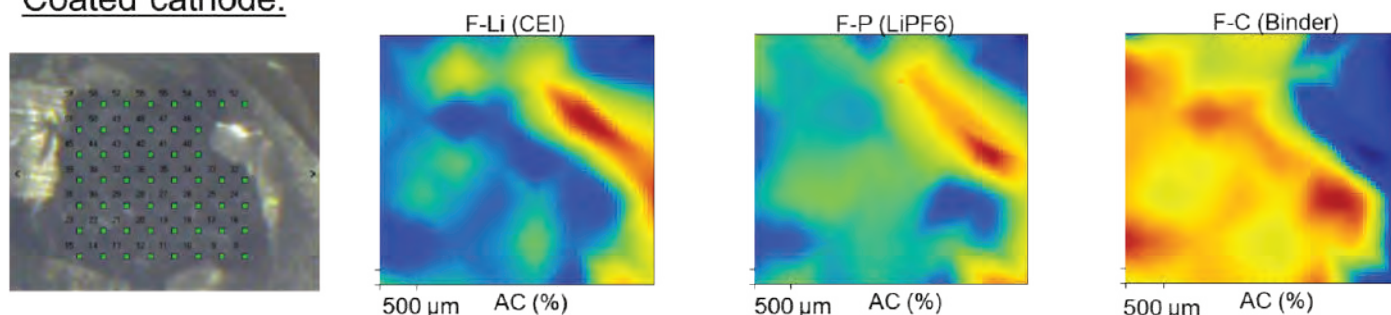

Figure 5: Spectral Mosaics across the entire cathode sample piece. Color contrast was adjusted to reflect total concentration (such that F1s appears the brightest and P2p appears the least bright due to their relative at%).

Because a full spectrum was collected at every analysis tile, chemical state information can also be analyzed (Figure 6). The F1s spectra were curve-fitted into three main components: F-Li, a degradation product formed in the CEI due to chemical interactions; F-P, from the LiPF6 salt in the cathode; and F-C, from the binder in the cathode. Similar to elemental composition trends, the dispersion of F chemical species is very heterogeneous in the uncoated cathode, including the F-P and F-C species that come from materials within the cathode, while each F1s species is more well-dispersed in the coated cathode. Additionally, there is a lower concentration of F-Li species in the coated cathode, which is a degradation product from side reactions during cycling. This indicates that the coating was effective at limiting some of the degradation reactions occurring during cycling.
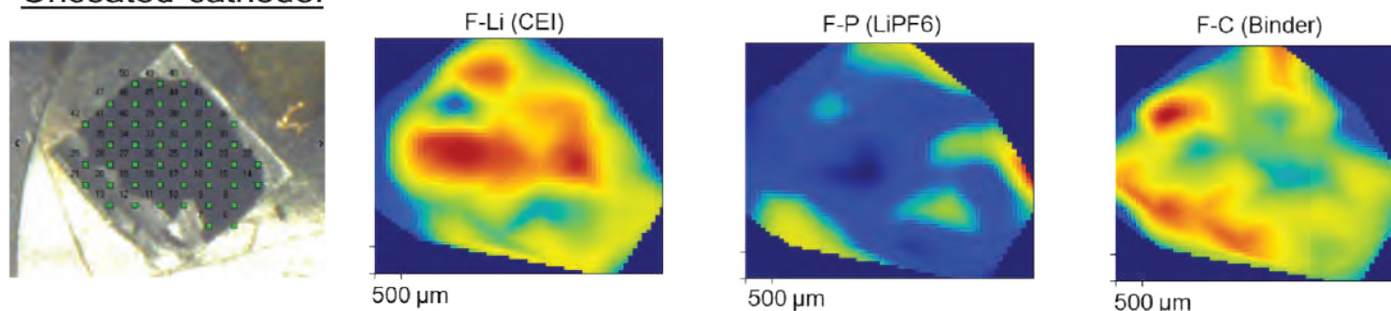
Figure 6: Spectral Mosaics for F1s chemical speciation across the entire cathode sample piece.
Note: The sharp feature in the top right corner of the bottom row is due to the interpolation of data across the current collector.

Conclusion:

Understanding the chemistry of the interfacial (degradation-induced) layers is critical to understand how to design next-generation battery materials for improved stability and long-term performance. Since the interphase layers do not form homogeneously either laterally or with depth, in order to determine representative composition and compare samples accurately, it is necessary to have small-area capabilities along with the ability to analyze large sample areas. PHI's unique scanning XPS microprobe technology enables small-area and area-scanned imaging and spectral Mosaic acquisitions, which are critical capabilities for analyzing heterogeneous materials. In this work, SXI Mosaics imaged features such as cracks and pockmarks and Spectral Mosaics visualized elemental and chemical-state distribution. These results showed that a protective coating was effective at creating uniformly dispersed layers and mitigating harmful degradation side reactions during cycling. Combined, the unique capabilities offered on PHI XPS systems offer an effective method to image and analyze very heterogeneous battery materials to understand where degradation occurs, in order to improve stability and long-term performance.