Technical Note

In Situ X-ray Approaches in Battery Research

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Introduction: The development of efficient and long lifetime battery solutions is critical to address climate change challenges and to enable more portable consumer devices. To investigate novel battery chemistries and compositions, researchers are increasingly turning to synchrotron facilities to use x-ray techniques to understand the electrochemical and physical processes that take place *in operando* [1-3].

Commonly used x-ray techniques for battery development include:

- **X-ray absorption spectroscopy (XAS)** to provide electrochemical information such as chemical or valence states, bond length, coordination number
- **Micro X-Ray Fluorescence (microXRF)** for elemental composition, migration, and contamination
- **X-ray Diffraction (XRD)** to study the crystal structure and bond lengths of battery materials
- **X-ray Microscopy (XRM)** for failure analysis and to study structural degradation and particle agglomeration in intact batteries and *in operando* pouch cells

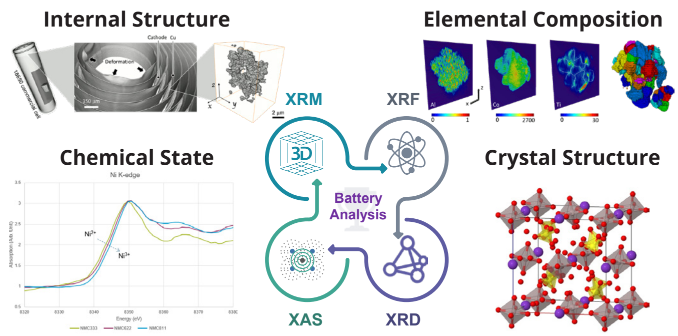

Figure 1: Non-destructive x-ray techniques in battery research.

To date, the vast majority of these studies are done in the synchrotron beam lines because of their high analytical performance (resolution, contrast, and sensitivity), which stems from the energy tunability and high flux of synchrotron x-ray sources. Unfortunately, synchrotron beam time is generally oversubscribed globally and therefore can be challenging, time-consuming, and expensive to obtain.

Sigray Laboratory Solutions for Battery Research

Sigray has developed a suite of groundbreaking lab-based x-ray tools for energy research with performance capabilities approaching that of synchrotron-based approaches. Unique to these systems are patented x-ray sources, x-ray optics, and system geometries that overcome major limitations that have previously bottlenecked laboratory x-ray performance. A growing number of groups at leading universities and companies rely on these systems as standalone tools and/or use them as a complement to synchrotron visits (e.g., pre-screening or validation of experimental fixtures, for instance).

The Sigray suite includes the following x-ray techniques and systems (Fig 2):

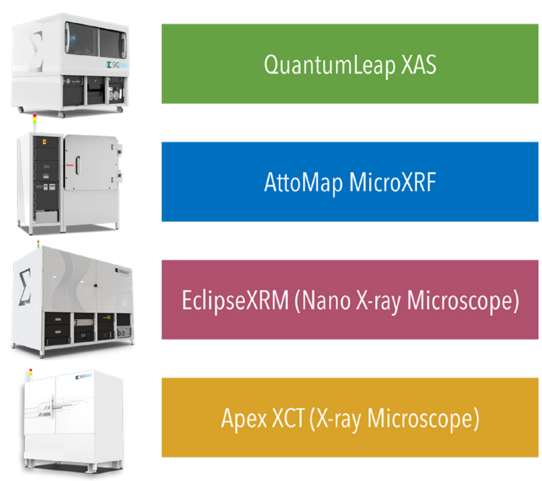

Figure 2: Sigray suite of laboratory x-ray tools for battery research.

1. X-ray Absorption Spectroscopy with QuantumLeap

1.A Technique Overview

X-ray Absorption Spectroscopy (XAS) is a powerful technique to understand the local electronic structure of atoms during an electrochemical process. Unlike X-ray diffraction (XRD), XAS is not limited to crystalline materials and is often used for studying transition metals of importance in battery research.

The principle behind the technique is that absorption of x-rays with energies very close to the binding energy of a core electron in an element (absorption edge) changes nonlinearly. By probing with small increases in x-ray energy around this absorption edge, a relationship between x-ray energy and its absorption can be plotted (Fig 3).

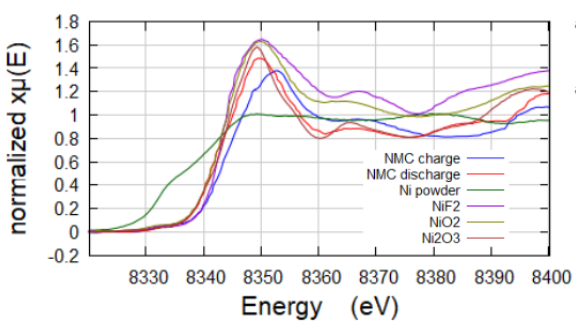

Figure 3: *Example of QuantumLeap spectra, in which absorption of x-rays are plotted as function of their energy. Shown are 6 spectra of Ni: charged and discharged NMC batteries and reference foils (Ni, NiF_2, NiO_2, Ni_2O_3).*

1.B System Overview

Sigray QuantumLeap XAS is the first laboratory system that provides synchrotron-like XAS capabilities with sub-eV resolution with acquisition times within minutes, and the only commercial XAS with access to both transmission-mode XAS (for concentrated samples) and **fluorescence-mode XAS** (low concentrations of 5% wt or lower). The system combines patented x-ray components, such as Sigray's ultrabright multi-target x-ray source, with patented system designs and acquisition routines. QuantumLeap's breakthrough design enables it to be the only laboratory system to enable high energy resolution acquisition at low Bragg angles (for more details, refer to Sigray's technical White Paper on Quantum Leap).

1.C Applications in Battery Research

QuantumLeap products span the energy range of 2.1 to 25 keV, covering a vast majority of the elements of interest in battery research, including sulfur and all transition metals (nickel, manganese, cobalt, zinc).

Li-Ion Batteries (LIBs): Because it is the only system with fluorescence-mode XAS, QuantumLeap has become instrumental in the development of NMC-type Li-Ion battery materials, in which the goal is to minimize the weight percentage of Mn and Co to improve their cost. Such samples cannot be analyzed using conventional transmission-mode laboratory XAS because the high weight percentage of Ni and concentrations of Mn and Co do not provide adequate signal-to-noise (SNR). Fig 4 show spectra of Co and Mn in a Ni-dominant NMC, acquired using QuantumLeap in f-XAS mode.

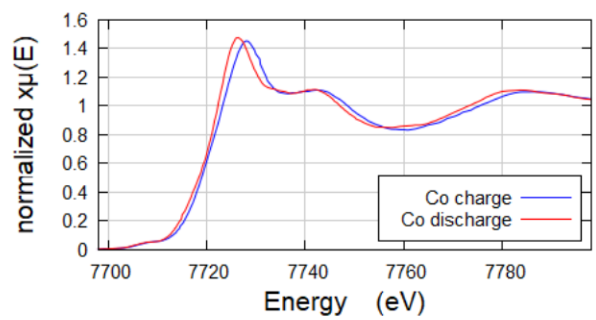

Figure 4A: *24 hours after discharge of low concentration 3-5 wt.% Co in Ni-dominant NMC battery*

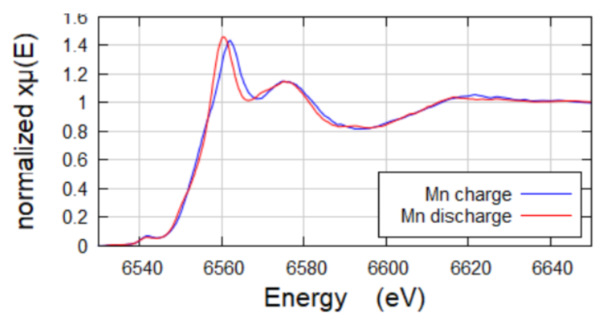

Figure 4B: *18 hours after discharge of 2 wt.% Mn in Ni-dominant NMC*

Intact Pouch Cells: Keeping the electrode material within an intact pouch cell prevents environmental-induced chemistry changes and, importantly, enables *in situ* and repeated studies. However, intact pouch cells are highly absorbing to intact pouch cell batteries, even challenging ones with low x-ray transmission of <1% (Fig 5 shows ~0.2-0.3% transmission data).

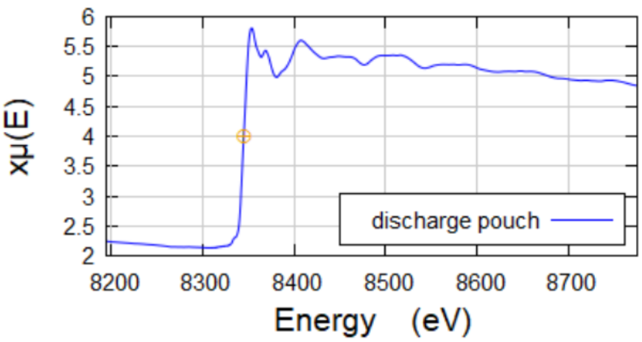

Figure 5: *High quality (K=10.5) EXAFS of a discharged pouch cell battery. Transmission of x-rays through the sample was only ~0.2-0.3%*

2. Micro X-ray Fluorescence with AttoMap

2.A Technique Overview

MicroXRF is an ultrahigh sensitivity approach for elemental mapping and quantification. X-ray Fluorescence occurs when x-rays excite atoms within a sample, promoting inner shell electrons to the outer shells or emitting them from atoms. The atoms will eventually relax, resulting in outer shell electrons falling into the holes left behind by the inner shell electron. This relaxation produces an x-ray. Because the distances between outer shells and inner shells is characteristic to each element, measurement of the x-ray energies emitted by the sample gives not only the elements contained within the illuminated region, but also the quantity.

2.B System Overview

Sigray AttoMap microXRF provides **unprecedented sensitivity** to detect heavy and even light elements (e.g., C, O, N) that are too low concentration to be measured using electron-based techniques such as SEM-EDS and EPMA or other microXRF systems. Its performance is enabled by patented innovations: Sigray's patented x-ray energy tunable source and high efficiency double paraboloidal x-ray optics. The instrument provides fast, non-destructive chemical mapping at <5 μm resolution and acquisition times down to 2 ms per point. A major advantage of the Attomap is its ability to tune X-ray incident energy to elements of interest to maximize fluorescence cross section. This ability to switch energy can increase sensitivity > 1000X (Fig 6).

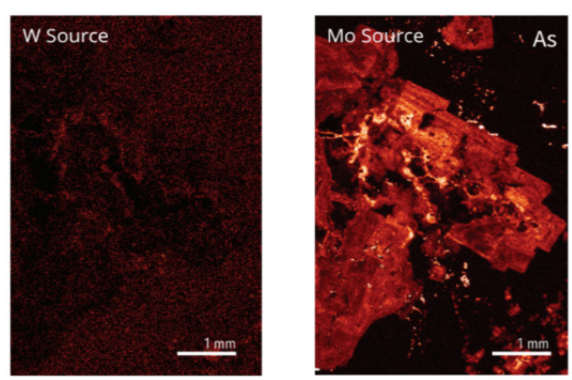

Figure 6: *Sigray AttoMap features a patented x-ray source with multiple x-ray targets (each target produces a different x-ray spectra). Arsenic from the same sample is shown using two different x-ray targets: tungsten and molybdenum to illustrate the major gains in sensitivity possible.*

2.C MicroXRF and Battery Research

Attomap provides high sensitivity detection levels down to sub-ppm levels for transition elements commonly used in battery research. Elements can be automatically quantified using Fundamental Parameters (FP) models, and the AttoMap software features automated peak fitting (Fig 7) for rapid identification of elemental composition.

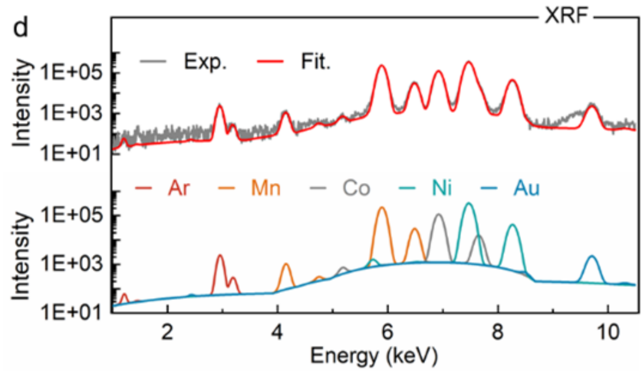

__Figure 7:__ Identification and quantification of elemental composition in a microns-scale spot of an NMC battery using AttoMap's intuitive software. Relative weight percent or absolute amounts can be calculated using models or standards.

Unique to the AttoMap is its strength in trace-level detection (e.g., sub-0.01%) of important low Z elements such as Al, Mg, Na, F, S, P, and organics (C, O, N). This is achieved using a tilted goniometer stage and a high vacuum enclosure with 10E-5 Torr. The ability to tilt the sample stage in the Attomap also allows elemental analysis to vary from deep to shallow interaction volumes.

AttoMap's high sensitivity is advantageous to:

- **Monitor and track cross contamination** such as Fe particles during battery manufacturing and quality control (QC) processes [8]
- **Quantify the migration of transition elements** across electrodes as a function of charging cycle [10]
- **Inspect chemical composition** and the ratio of elements in NMC batteries

Sigray has developed a correlative workflow to first identify the location of potential impurities using transmission X-ray microscopy, followed by AttoMap microXRF to identify the chemical composition of these impurities. Shown in Fig 8 is a transmission x-ray image of a lithium cathode of an NMC battery, and the distribution of Ni, Mn, and Co in the battery (labeled "Baseline"). AttoMap was used to identify three micron-scale particulate impurities seen on the x-ray image.

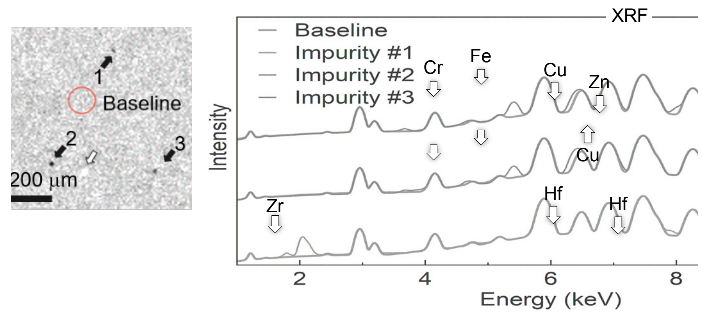

__Figure 8:__ Correlative study using x-ray imaging followed by microXRF on the AttoMap to quantify the distribution of Ni, Mn, and Co in an NMC battery and to identify particulate impurities (Fe, Cr, Cu, Zn, Zr, and Hf) produced during battery production [8].

3. X-ray Microscopy with EclipseXRM and Apex XCT

3.A Technique Overview

X-ray microscopy (XRM) is a powerful tool for the analysis of the structure of materials at various length scales, ranging from microns to nanometers. The approach measures the absorption of x-rays to form images of the internal structures of intact samples. Because x-rays are non-destructive, XRM is often used to observe microstructural changes after or during charging cycles.

3.B System Overviews

Sigray offers the two leading XRM models: EclipseXRM and Apex XCT. EclipseXRM is a breakthrough nanoCT system that scans a range of intact and cut battery samples at world-leading 300 nm spatial resolution (Fig 9). The system uses a patent-pending geometry that allows the highest resolution imaging on the market, even for samples placed in large *in situ* cells. In contrast to the EclipseXRM, Sigray's Apex XCT is specifically designed for planar samples (including pouch cell batteries) and can image such samples at 0.5 μm resolution within minutes.

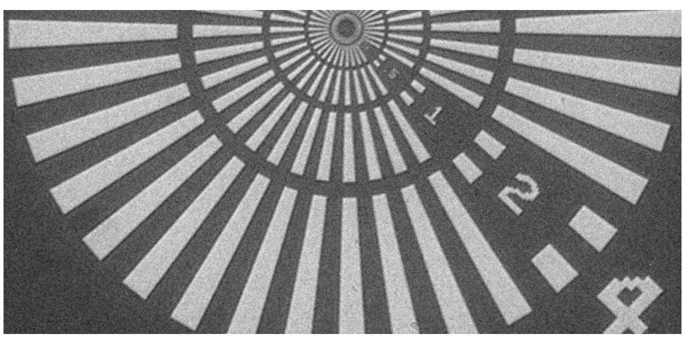

Figure 9: *Spatial resolution on the EclipseXRM is 300nm (inner spoke on target is 200nm). This is almost half that of the leading x-ray microscope competitor and results in finding defects (cracks, voids) and features that would otherwise be invisible.*

3.C X-ray Microscopy and Battery Research

Lithium ion batteries (LIBs) are complex electrochemical systems with hierarchical multiscale structures in which physical and chemical processes take place simultaneously. For a quantitative understanding of structural changes, repeated imaging of a battery between charging cycles or *in operando* is essential.

EclipseXRM: X-ray microscopy is unique as it has the power to carry out hierarchical 3D imaging at multiple length scales. EclipseXRM enables imaging of intact batteries at zoomed-out overviews (coarser resolution) and zoomed-in (0.3 μm) detailed views of defects and microstructures. Examples of multiple resolution scans from Sigray PrismaXRM (the previous generation version of EclipseXRM) are described in Ref [7] and shown in Fig 10. High resolution images clearly indicate delamination and deformation of current collectors as the primary failure mechanisms of a 18650 LIB.

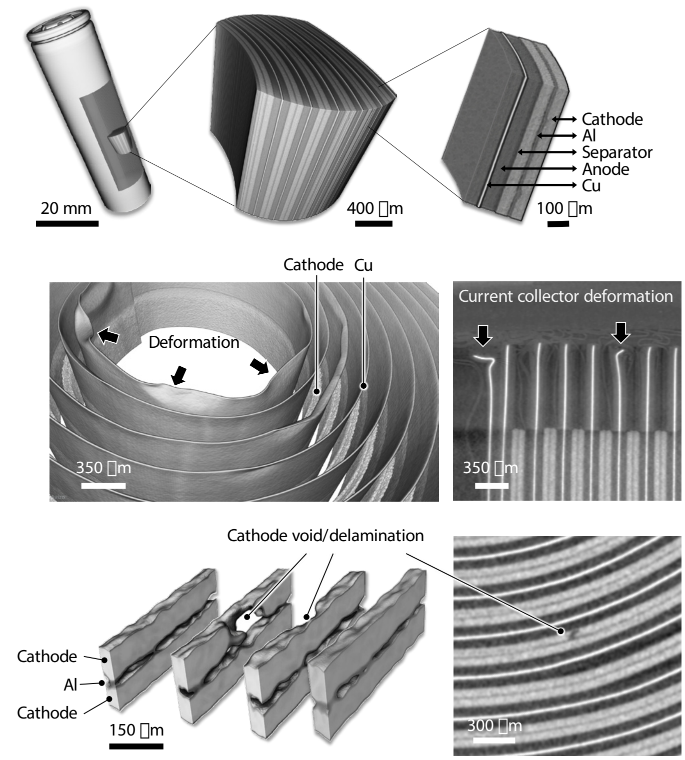

Figure 10: *Hierarchical multiscale 3D imaging of intact battery to details of its internal structures and defects, for example, deformation of current collector to voids and delamination [7].*

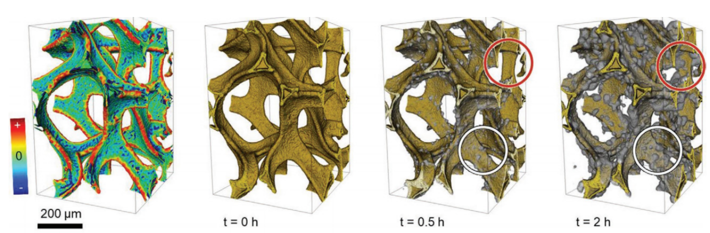

Figure 11: *In situ x-ray tomography of a Zn aqueous battery [9].*

EclipseXRM's high resolution (300nm) capabilities provide crisp and sharp images of electrode particles and their degradation mechanisms in unpackaged battery materials (Fig 12) and intact coin cells (Figs 13 & 14).

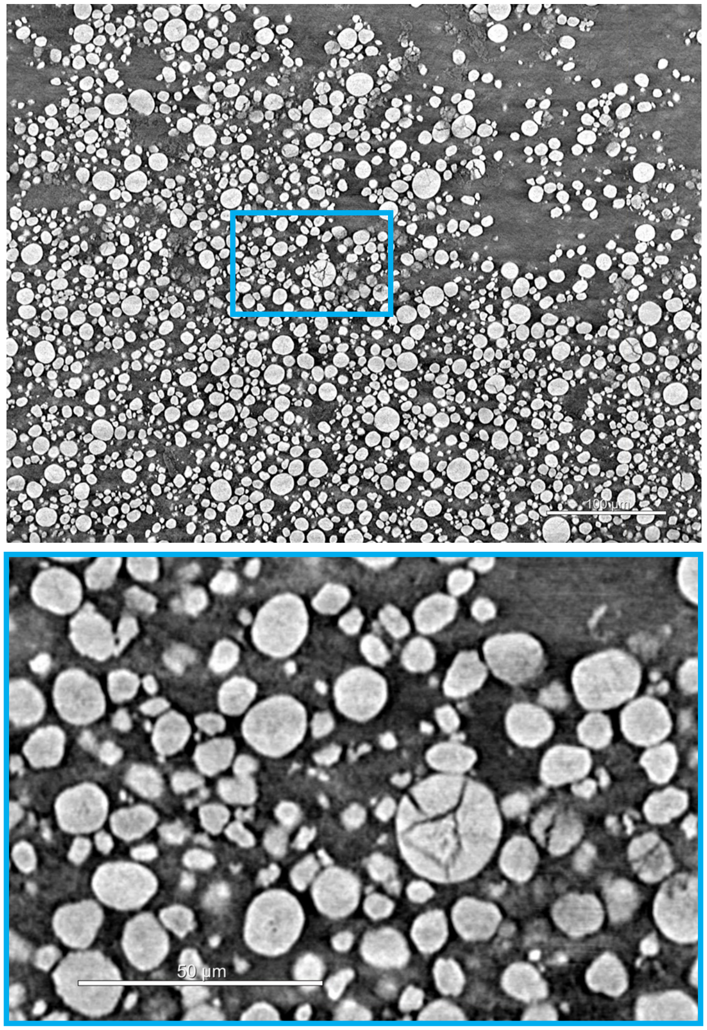

Figure 12: *Top: full field of view and bottom: a cropped (zoom-in) of cracked NMC cathode particles at 0.21 µm voxel. Courtesy Prof. Ming Tang, Rice University.*

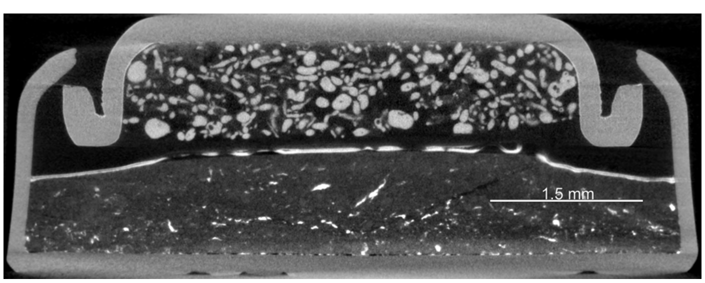

Figure 13: *Commercial LICB LR626 coin cell (vertical cross-sectional view)*

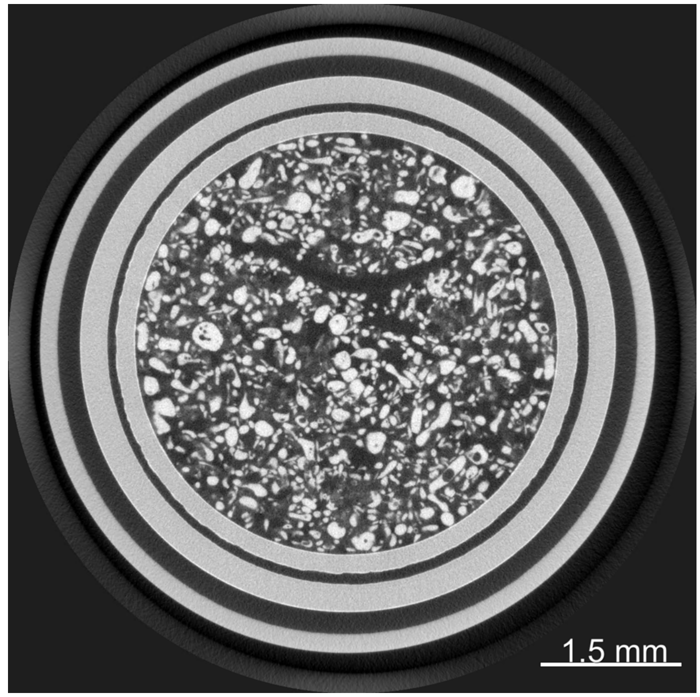

Figure 14: *Commercial LICB LR626 coin cell (horizontal cross-section)*

Examples of the full range of battery defects that can be imaged using the EclipseXRM are shown in Fig 15.

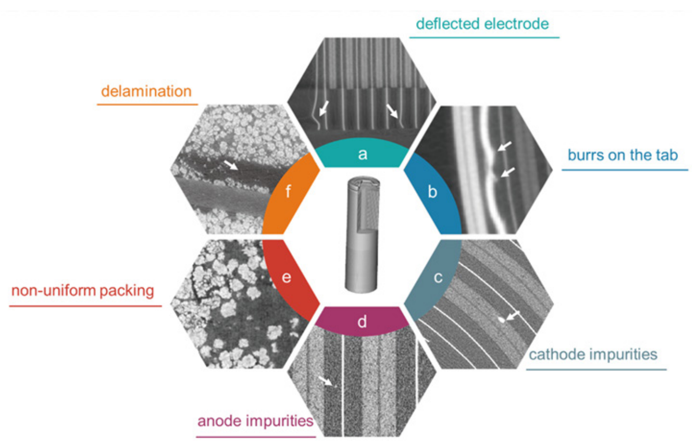

Figure 15: *Examples of degradation mechanisms imaged by EclipseXRM on intact batteries and battery components.*

Apex XCT: Pouch cell batteries have high aspect ratios and often are difficult to image using conventional x-ray imaging approaches at high resolutions beyond 10s of microns [10]. The Apex XCT's patented scanning geometry is ideal for planar samples, enabling submicron resolution on intact pouch cell batteries and at high throughputs of down to single digit minutes. Ref [11] describes the use of Apex XCT for *in situ* quantification of NMC particle sizes (Fig 16) and for characterization of battery failures (Fig 17) on pouch cell batteries.

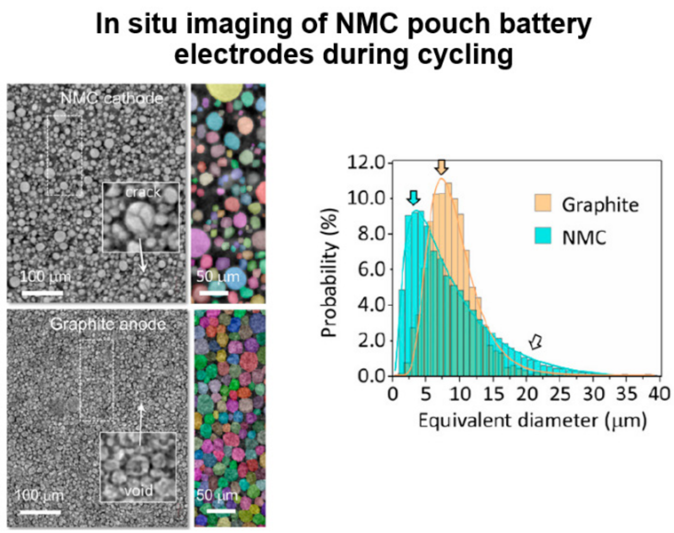

Figure 16: *In situ characterization of pouch battery particle sizes during cycling using Apex XCT. Note that cracks in NMC cathode particles and voids in graphite anodes were observed (insets).*

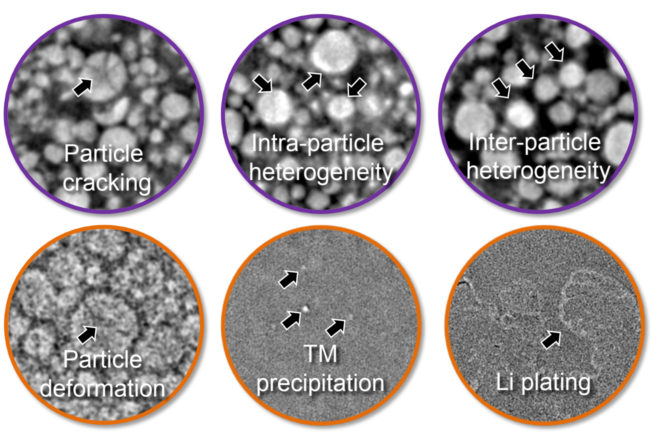

Figure 17: *In situ characterization of multiple structural degradation mechanisms of batteries during cycling, including: particle deformation, particle cracking, transition metal precipitation, Li plating, and dendrite formation and growth using Apex XCT.*

Conclusion

Advances in battery research depend on a multi-technique approach to develop comprehensive understanding of chemical and structural battery degradation mechanisms. Synchrotron x-ray techniques have been critical in significant discoveries, but the lack of accessibility slows the pace of research. Sigray has developed a suite of spectroscopy and imaging laboratory tools for 24 hours a day, 7 days a week access to synchrotron-like capabilities to accelerate battery research.

References

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