ESRF	**Experiment title:** Understanding failure mechanisms in solid-state batteries at the cathode/electrolyte interface using XRD-CT and XCT	**Experiment number:** MA 5627
Beamline: ID15A	**Date of experiment:** from: 06/06/2023 to: 06/12/2023	**Date of report:** 09/09/2023
Shifts: 12	**Local contact(s):** Marco Di Michiel	*Received at ESRF:*

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Report:

Solid state batteries (main experiment)

X-ray diffraction computed tomography (XRD-CT) and absorption contrast X-ray computed tomography (XCT) were measured on solid-state Li-ion batteries in discharged and charged states. The compared conditions were: solid-state electrolyte (baseline Li_6PS_5Cl [LPSC] vs modified LPSC) and cathode (baseline transition metal oxide [TMO] cathode vs coated-TMO). Specific chemistries and 2θ values have been omitted until publication. XRD-CT measurements provided for spatially resolved determination of parasitic reaction products, heterogeneous lithiation of the cathode particles, and other quantities (Figure 1). The shift in 2θ of one of the cathode peaks, used as a proxy for lithiation of the cathode, was found to be quite heterogeneous depending on factors such as: cathode particle aggregation, overall state-of-charge of the battery, solid-electrolyte used, and coated vs uncoated cathode (Figure 2). Data analysis, segmentation, and interpretation is still ongoing. We anticipate the results to inform design rules for future development of low pressure, high-energy density all-solid-state batteries for

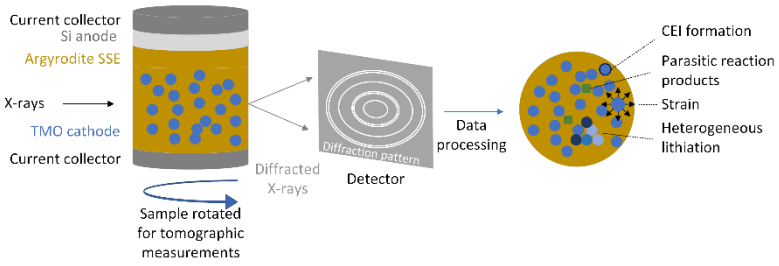

Figure 1: Schematic of XRD-CT measurement and local properties that can be probed with the resulting data.

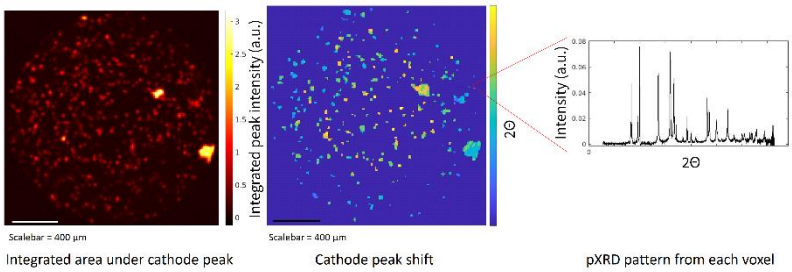

Figure 2: From left: integrated area under the cathode peak, cathode peak shift, and the powder XRD pattern from a single voxel. The cathode peak shifts as the cathode is lithiated.

applications including electric vehicles and grid-scale energy storage. We expect to publish these results within 8 months.

Co-free cathodes (preliminary data)

XRD-CT and XCT were performed on *ex situ* chunks of Co-free, Li- and Mn-rich (LMR) cathodes in both the pristine state and after a high-voltage activation induces an irreversible phase change in the material. These data were collected during the allotted time for proposal MA5627. The results show the ability to clearly distinguish the pre- and post-activation phases in this cathode and offer the potential to distinguish non-activated regions within the cathode bulk by fitting the peak centers at each voxel to known peaks for both phases (Figure 3) . With these data, we can correlate crystallographic and microstructural features to battery performance to help inform and guide the design of optimized Li-ion batteries. This analysis will help pave the way towards abundant and locally sourced Co-free Li-ion batteries for future electric vehicle implementation.

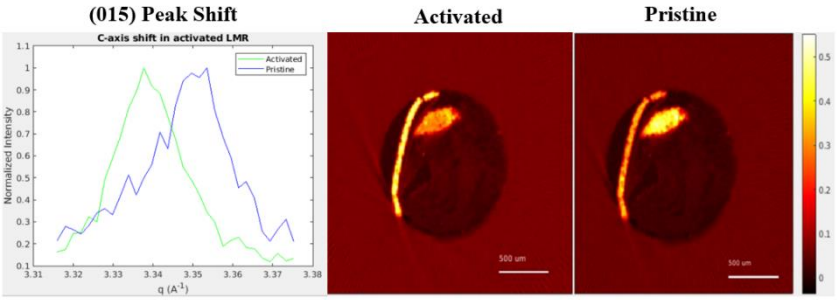

Figure 3: Spatial visualization of the lattice change in two ex situ cathode chunks. The skinny chunk is post-activation and the other is pristine. The (015) XRD peak shifts to lower q after activation (left) due to repulsive Coulombic forces between anion layers in the crystal structure. Normalized, integrated peak intensities for the activation peak (q = 3.32-3.35 A^{-1}) (middle) and the pristine peak (q = 3.34-3.37 A^{-1}) (right).

Lead pipe corrosion control treatments (preliminary data)

XRD-CT and XCT were collected for one sample of lead pipe scales during the allotted time for proposal MA5627 to determine the efficacy of using these imaging techniques for pipe scale analysis. Results show that the methods can distinguish between different phases (e.g. hydrocerrusite, lead, quartz) (Figure 1) and should provide an accurate 3D reconstruction of the heterogeneous pipe scales. Pipe scales are materials that form coatings on the inside of pipes as chemical compounds and minerals in water react with corroding pipes. The purpose of the scales is to passivate the surface of the pipe wall. These results will inform the nature of lead pipe scales by providing insight into the morphology and mineralogy and the mechanisms of scale formation which to our knowledge has not been studied with these methods. Traditional pipe scale analysis techniques fail to provide a 3D resolved microstructural analysis and involve labor intensive sample preparation as well as subsampling errors.

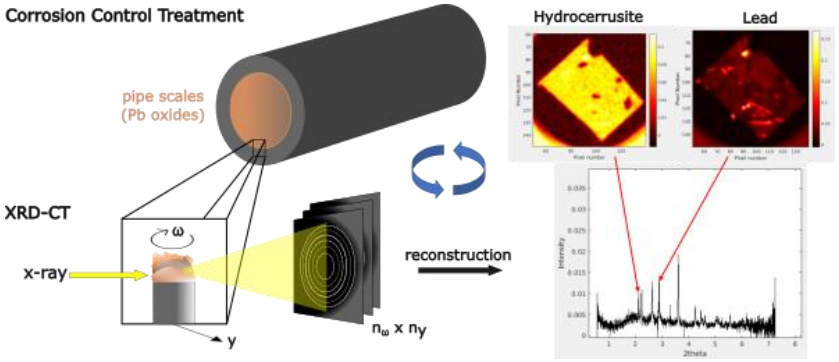

Figure 4: Overview of corrosion control treatment strategy and x-ray characterization before and after treatment. Two phases present in the scale layers have been reconstructed from one XRD-CT slice.