

Interface Instability Analysis in Solid-State Lithium Batteries Using Advanced *in Situ* Methods

Solid-state lithium batteries are steadily gaining research interest due to their inherently safe design and presumed high energy density and long life cycle. A polymer electrolyte is a key component of current battery technology and can enable the development of next-generation ultra-performant solid-state lithium batteries. Despite the promise of high energy density, the development of polymer-based solid-state lithium batteries is hindered by interfacial challenges such as passivating layer formation and lithium dendrite infiltration^[1-3]. Therefore, a deeper understanding of the interface chemistry and possible failure scenarios is essential for ensuring ideal battery performance. Advanced and *in situ* characterization methods are crucial for comprehending how these interfaces work with cell cycling and identifying responsible factors for cell failure^[4].

Here, by using *in situ* X-ray tomography, combined with XPS, SEM, and AES, we present the structural and chemical evolution of a lithium/PVDF-HFP-based polymer electrolyte interface over prolonged cell cycling at a higher temperature, from the pristine state up to cell failure. The electrolyte membrane, stacked between strips of metallic lithium under pressure, is scanned with this imaging technique while galvanostatic cycling. The *in situ* X-ray computed tomography provides in-depth 3D interface images and, non-invasively with unprecedented accuracy and resolution, displays lithium penetration inside the electrolyte. A 3D reconstruction shows the morphology of the electrolyte after cycling as a result of the lithium infiltration (Figure 1). Post-mortem XPS provides chemical information and shows an accumulation of lithium salts and organic compounds resulting from the degradation of membrane constituents during cycling. Impedance data reveal the degradation is followed by an increase in interfacial resistance. The higher-resolution SEM images and AES provide complementary data to the X-ray data. Together, these techniques contribute to a deeper comprehension of interfacial changes and provide the suggestions needed to overcome failure mechanisms and enhance the electrochemical performance.

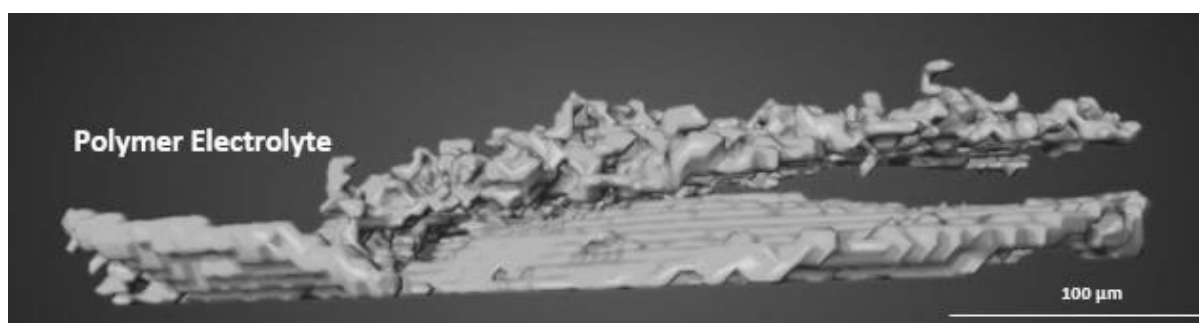


Figure 1: morphology of the electrolyte in a symmetric cell after cycling, as obtained by *in situ* X-ray tomography.

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