

## Investigating Strain and Chemistry Evolution of the Solid Electrolyte-electrode Interface via 4D-STEM and EELS

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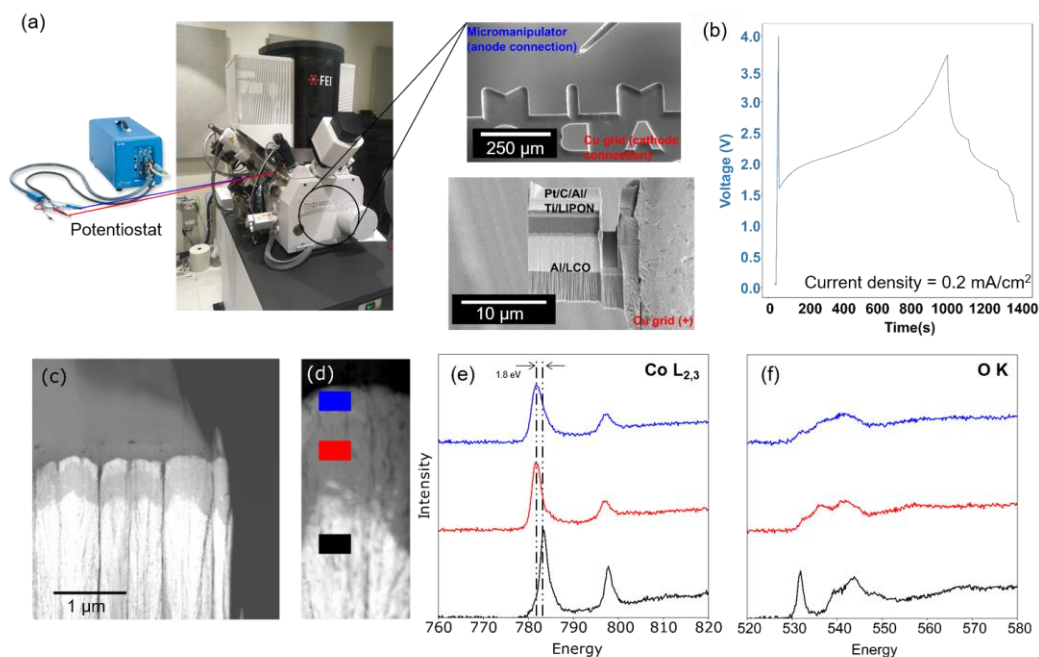
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Functional interfaces within Li-ion battery systems play a dominant role in the performance and safety of these devices as interfacial resistance is assumed to impede Li-ion transport, thereby affecting the capacity and life cycle of the battery system [1]. A model Li-ion battery system for examining interfacial structure-chemistry is LiPON-LiCoO<sub>2</sub>. The solid electrode - solid electrolyte interface contains an inherent, secondary LiCoO<sub>2</sub> interfacial layer between the electrolyte (LiPON) and bulk electrode (LiCoO<sub>2</sub>). This layer undergoes a significant change in chemistry, i.e. Li concentration and Co-O bonding, after biasing [2]. However, limitations in selected area electron diffraction (aperture size) and high resolution imaging (beam damage) are obstacles to the microstructural characterization needed to understand the chemical reactions and phase transformations at this interface.

Four dimensional electron microscopy (4D-STEM) uses a convergent beam that is rastered across a sample for the acquisition of a diffraction pattern at each scan position. These diffraction patterns provide structural information, i.e., strain, orientation, crystallinity, and other material properties [3]. Microstructural maps with 1-2 nm resolution are then generated, and these 4D-STEM datasets enable analysis of localized lattice strain at the relevant, functional length scales.

In this study, the interfaces of an *ex-situ* biased LiPON-LiCoO<sub>2</sub> battery stack and a pristine, as-is LiPON-LiCoO<sub>2</sub> battery stack are investigated with 4D-STEM and electron energy loss spectroscopy (EELS). *Ex-situ* biasing was performed using a focused ion beam (FIB) instrument (Figure 1a). The LiPON-LiCoO<sub>2</sub> battery stack was, separated from the TEM grid, cycled as a micrometer lamella, and then thinned to electron transparency (Figure 1a, 1b, 1c). Spatially resolved EELS across the solid electrode - solid electrolyte interface reveals an approximate 1.8 eV chemical shift of the Co L<sub>2,3</sub> edge, indicative of Li-loss (Figure 1e), and an absent O-K edge pre-peak, indicative of a phase transformation from spinel to rocksalt CoO (Figure 1f) [4,5]. For the pristine and biased battery stacks, 4D-STEM datasets were acquired for the generation of classification maps detailing the variation in microstructure.

Using the microstructural maps generated via 4D-STEM and the electronic bonding spectra acquired by EELS, the phase transformations and chemical reactions across the LiPON-LiCoO<sub>2</sub> battery stack as a function of biasing can be correlated and the structure-chemistry relationship at these interfaces will be discussed in relation to Li-ion transport mechanisms [5].



**Figure 1.** Figure 1: (a) Experimental set-up of ex-situ biasing using a low-current potentiostat as the power source connected to the FIB instrument via an attached port. The anode section of the battery is circuit edited to prevent contact with the copper grid. (b) Charging-discharging profile of the fabricated sample. (c) High angle annular dark field (HAAF) –STEM image of the thinned battery sample. (d) ADF image of region scanned for EELS; the blue box corresponds to the interface between LIPON and LiCoO<sub>2</sub>, the red box corresponds to the dark contrast layer of LiCoO<sub>2</sub>, and the box corresponds the bulk LiCoO<sub>2</sub>. Spectra of the (e) Co L<sub>2,3</sub> edge and (f) O K edge corresponding to boxed regions selected in the ADF image. Co L<sub>2,3</sub> edge shows a 1.8 eV chemical shift, indicative of Li loss. Samples were kept in an inert-environment encapsulation box, glove box, or TEM holder to prevent air and moisture exposure.

## References

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