

In Situ and Operando Imaging of the Evolution of Battery Materials and Interfaces

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It is critical to understand and control reaction mechanisms in next-generation battery materials to guide engineering of materials for optimal performance [1]. Here, I discuss my group's efforts using *in situ* transmission electron microscopy (TEM) and *operando* X-ray tomography to investigate reaction mechanisms in battery materials across length scales. First, I will present our work using *operando* X-ray tomography to reveal interfacial dynamics in solid-state batteries [2]. Specifically, the evolution of the interface between lithium metal and the sulfide electrolyte $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ was investigated with X-ray synchrotron computed microtomography. Owing to the high ionic conductivity of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ ($>10^{-3} \text{ S cm}^{-1}$), we were able to electrochemically test symmetric $\text{Li}/\text{Li}_{10}\text{SnP}_2\text{S}_{12}/\text{Li}$ cells at the relatively high current density of 1 mA cm^{-2} while simultaneously collecting 3D images of the cell. Interphase growth and the formation of interfacial voids were observed throughout the electrochemical experiments. Segmentation and detailed image analysis enabled quantitative analysis of these phases, which were coupled to electrochemical measurements to establish links between interphase growth and void formation to cell failure. We ultimately found that the loss of interfacial contact area caused by void formation at the lithium interface is primarily responsible for failure, with current constriction effects exacerbating the voltage polarization in the cell due to the formation of isolated contacting regions with highly localized current flow. Next, I will discuss our *in situ* TEM experiments that reveal reversible void nucleation and growth during lithiation and delithiation of antimony (Sb) alloy nanocrystals [3]. Sufficiently small Sb alloy nanocrystals were found to form single voids during dealloying with lithium rather than undergoing shrinkage, as in larger particles. This effect is due to a mechanically stiff outer oxide shell that retains its shape, as indicated by a chemo-mechanical model of the transformation process. Importantly, the voiding behavior translated to improved electrochemical behavior in battery cells due to the lack of surface dimensional changes of the materials. Finally, I will briefly discuss *in situ* investigations of the effect of intercalated species on thermal stability of nanoscale materials [4]. Together, these studies highlight the importance of detailed understanding of reaction mechanisms across length scales, which can be used to guide the development of batteries with improved performance.

References

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