Abstract: Next generation lithium-ion batteries will take on a wide variety of roles to meet the increased requirements from growth in consumer electronics, electric vehicles, and utility storage for integrating intermittent renewable (solar and wind) power sources. The cost per watt-hour of commercial batteries have shown incremental improvement due to improved manufacturing design, though drastic increases in energy and power density are needed to satisfy projected demand. Solid-state electrolytes (SSE) are explored due to their potential to improve energy and power density through enabling alkali metal anodes, while mitigating safety and temperature stability concerns associated with conventional liquid electrolyte lithium-ion batteries. However, there are still significant scientific and engineering hurdles before the full potential of SSEs can be realized: primarily performance degradation from chemical and mechanical interfacial instability.

We enable the use of solid-state thin film battery materials and devices as a model system for fundamental studies of bulk and interface properties because of their well-defined geometry and controlled chemical composition, eliminating any effects from polymeric binder or conductive agents. In this thesis, we explore the structural, mechanical, and electrochemical properties of thin film electrolytes amorphous lithium lanthanum titanate (a-LLTO) and lithium phosphorous oxynitride (LiPON) along with the fabrication of thin film batteries with various electrode chemistries. Using these devices we develop focused ion beam (FIB) as a technique to fabricate electrochemically active nanobatteries that enables in situ analysis in a FIB or transmission electron microscope (TEM) to couple local structural, morphological, and chemical phenomena. Further, one key advantage of SSEs is the potential to use a lithium metal anode. However, characterization of Li and Li/electrolyte interfaces is limited due to its intrinsic high chemical reactivity, low thermal stability, and low atomic number, making it prone to contamination and melting. Therefore, we demonstrate the ability of cryogenic focused ion beam (cryo-FIB) to process and characterize electrochemically deposited Li and Li metal based solid-state thin film devices.