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# A New Cryo-FIB-TEM Approach for Damage-free Characterization of Garnet Electrolytes in Solid-state Batteries

Hongkui Zheng, Jiang Cui and Kai He

Clemson University, Clemson, South Carolina, United States

In the past few years, solid-state batteries (SSBs) have attracted increasing attention for being used as an alternative to the current Li-ion batteries (LIBs) due to their advantages in safety and potential for high-density cell packing. The key to the transition from LIBs to SSBs lies in the use of solid-state electrolytes to substitute the organic liquid electrolytes that are dominant in commercial LIBs, making the electrochemical operation safe and stable even at high voltages [1]. Among many types of inorganic and polymeric solid-state electrolytes that have been previously studied, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte is considered promising because of its outstanding stability against Li, wide electrochemical window, and relatively high ionic conductivity. However, several problems still exist in the use of garnet electrolytes, such as poor Li wettability, Li dendrites through electrolytes, and side reactions with air to form lithium carbonate ($Li_2CO_3$), which deteriorate the Li/LLZO interfacial properties [2]. To address these issues, it is critical to characterize the interfacial structures between Li and solid electrolyte and understand how they affect the electrochemical properties and battery performance.

Transmission electron microscopy (TEM) is a powerful tool to characterize the garnet-type LLZO solid electrolyte. However, there are practical problems that limit such experiments, mainly due to the radiation damage induced by high-energy electron beam and the unwanted side reactions with the chemically reactive ambient atmosphere (i.e., oxygen, nitrogen, and moisture), while this issue becomes more challenging when involving Li metal, which is more sensitive to both electron beam and environment. The electron-beam damage can be reduced below an acceptable threshold by lowering the acceleration voltage and/or cooling sample to the cryogenic condition, so-called cryo-EM, which has proven to be effective for preventing Li from electron-beam or focused ion beam (FIB) damage [3-5]. Moreover, protecting air-sensitive materials during sample transfer is also viable via specially designed sample holders. Here, we present a new cryo-FIB-TEM approach that combines cryo-FIB with cryo-TEM and further integrates with a fully compatible sample transfer between glove box, FIB, and TEM during sample preparation and observation. This new workflow allows the air-sensitive sample to be secured inside an Ar-filled enclosure during transfer procedures and stay at cryo conditions during FIB or TEM operations, in which the air protection-cryo holder is essential to make the whole process possible (Figure 1). Implementing this method in Hitachi NB5000 FIB/SEM and H-9500 TEM [6], we highlight a damage-free reconstruction of the 3D model of Li/LLZO interface by FIB sectioning tomography, which visually illustrates the detailed microstructures of grain boundaries and micropores, as shown in Figure 2. Further investigation using low-kV and cryo-TEM is also readily applicable based on this approach, from which we can evaluate the effect of voltage and cryo temperature on damage resistance of specific sensitive materials. Overall, the new damage-free protocol for cryo-FIB-TEM approach can be universally applied to the characterization of a broad range of sensitive materials and soft matters in general.

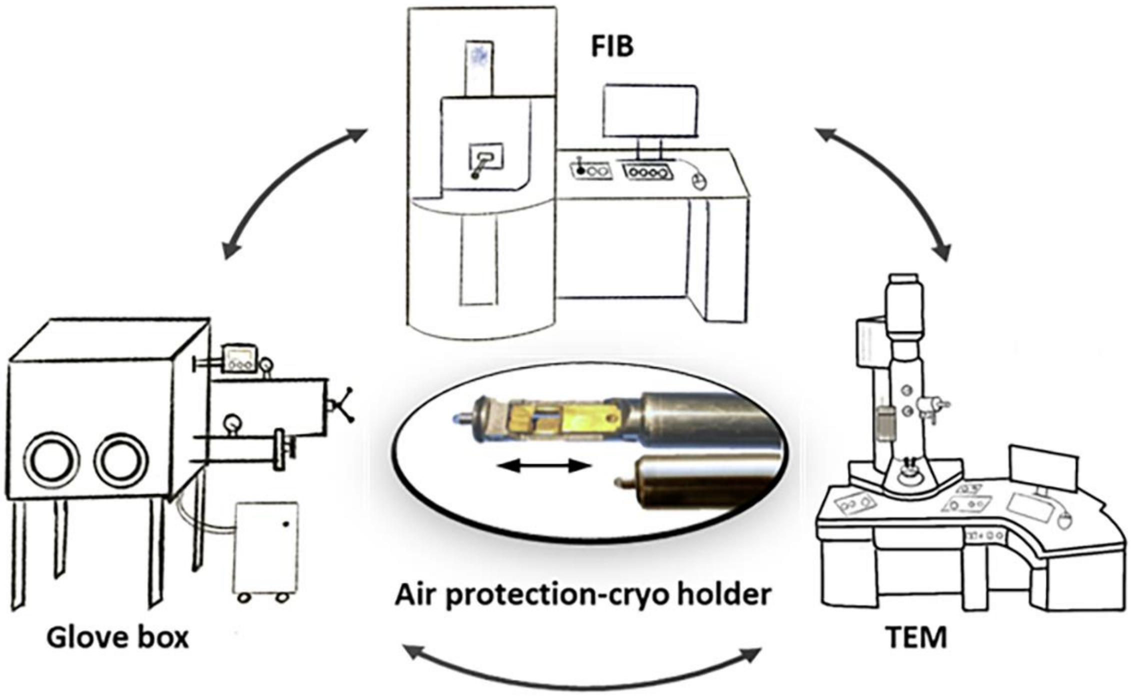


**Figure 1.** Schematic illustration of the cryo-FIB-TEM workflow enabled by specially designed air-protection cryo holder.

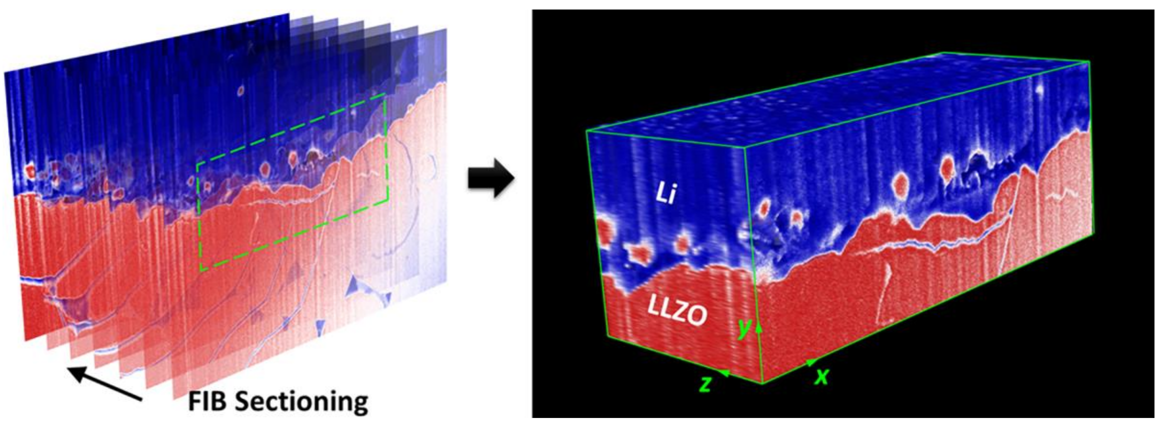


**Figure 2.** Cryo-FIB sectioning tomography and the reconstructed 3D model showing Li/LLZO interface.

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