

Determining Atomic Structure of Grain Boundaries and Heterostructure Interfaces at Solid-State Electrode/Electrolyte Heterostructures in Lithium Based Oxides

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Improving upon the current generation of lithium-ion batteries requires a holistic understanding of electrochemical and structural/chemical changes due to work-cycles of the electrodes/electrolyte heterostructure. Multiple mechanisms exist for cell degradation, whether this be through structural fatigue in the bulk of the electrodes or via formation of solid electrolyte interfaces (SEIs). With resolutions achievable below 1 Å in aberration corrected transmission electron microscopy (TEM), structural analysis of grains, grain boundaries, as well as interfaces between electrode (LiCoO₂, LCO) and electrolyte (Li₇La₃Zr₂O₁₂, LLZO) as well as formed current induced SEIs is possible on atomic scale. In this work we focus on the atomic structure of grain boundaries of LCO and LLZO, and the interface between LCO and LLZO with the goal of determining the atomistic structure of the boundaries and interfaces that will allow us to build atomistic models for calculating the electronic properties (including barrier heights etc.) for Li transport/diffusion. The observation of defects and interfacial composition down to atomic resolutions is fundamental to understanding the specific characteristics changing the efficiency of lithium-ion movement through the device. Hence, atomic analysis of working and as prepared devices is the key for understanding the processes that lead to SEIs which will ultimately lead to improved design of solid state battery devices.

By combining SEM/EDX/EBSD with HRTEM and STEM/EELS we will present structural and chemical analysis of the electrode/electrolyte grain boundaries in sintered systems as well as the interfaces in thin films heterostructures grown by Pulsed Laser Deposition (PLD). EBSD analysis of the sintered LCO-LLZO system has provided band contrast distinguishing individual grains and phase maps across these samples. Multiple grain boundaries existed within both the electrode and electrolyte and crystal orientations of each grain were mapped. Low-magnification bright- and dark-field TEM has allowed grain boundaries and defects in electrode and electrolyte to be analysed, and suitable dislocation and stacking faults analysis to be done in these complex grain boundaries. Fig 1a, b. Further higher-resolution STEM work has been employed to analyse secondary phases and structure of the defects. The PLD grown heterostructures are less complex in nature, with well-defined grain boundaries within the electrolyte and the electrode. In Fig. 2 is shown a LCO grown film on the Al₂O₃ substrate. The HRTEM and diffraction analysis shows that film is single phases with unique grain boundaries as shown in Fig.2. Further atomistic imaging of these boundaries is ongoing, as well as chemical analysis on sub-nm level using STEM-EELS. Finally, we will also present the chemical and structural stability of the LCO/LLZO interface, with focus on comparing these interfaces in as prepared and under bias structures in *in-situ* conditions.

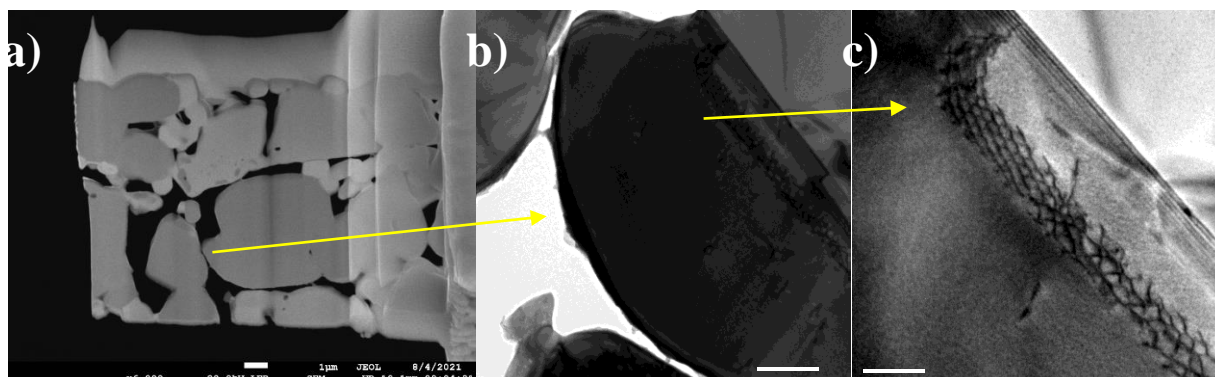


Figure 1: a) SEM of sintered LCO-LLZO system, b) and c) BF-TEM of dislocation system near an LCO grain boundary.

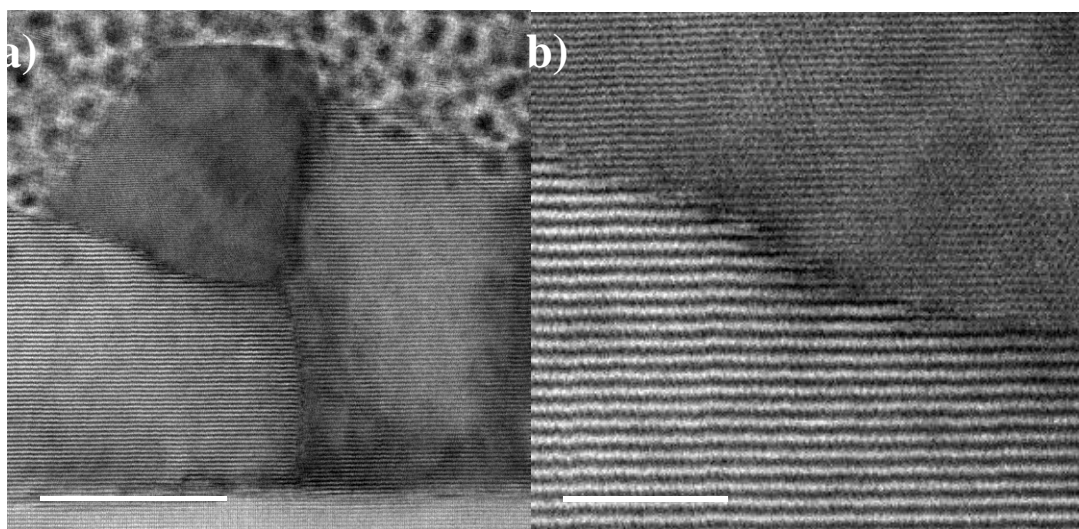


Figure 2: a) HRTEM images of region in the LCO film showing a triple boundary grain. B) HTEM of selected region of the LCO showing the different crystal orientation and structure of the grain boundary indicated in a)