Towards Visualization of Atomic-Level Transport in Ion Conductors: Characterizing Structural Dynamics with Advanced Electron Microscopy and Data Science

The ability to design structures that can regulate and control the ionic functionalities of electroceramics for applications in a wide range of devices requires a fundamental understanding of transport pathways. Ionic transport typically takes place in the presence of a wide range of defects including dopant species, dislocations, precipitates, grain boundaries, and surfaces. The ability to elucidate the relationship between local structure and transport remains an ongoing challenge for both experimental and computational techniques. Modern transmission electron microscopy (TEM) allows the structure and composition of electroceramics to be characterized down to the atomic level. However, the dream of *in situ* electron microscopy is to characterize the transport and reactivity functionalities with high spatial resolution. Can transport/diffusion processes be directly observed at the atomic level? What does such a statement even mean?

Molecular timescales are typically in the picosecond range and atomic level information is available with advanced computational methods like *ab initio* molecular dynamics(Kang, Vincent et al. 2022). But large-scale complex systems with processes involving correlated atomic motions remain computationally inaccessible. Experimental ultrafast approaches to high resolution TEM can yield time resolutions of picoseconds, at least for cyclic processes, but the associated spatial resolution is limited to 2 nm (Zhang and Flannigan 2019). Bridging this spatiotemporal gap is an ongoing challenge in the field. An emerging new generation of electron detectors have greatly improved sensitivity and readout rates allowing atomic resolution information to be captured on the millisecond time scale. While this remains far from molecular timescales, it does make it possible to consider looking for repetitive atomic dynamic processes, such as diffusion pathways, that may be matched to millisecond temporal resolution(Lawrence, Levin et al. 2020, Lawrence, Levin et al. 2021). The rate of structural dynamics can be manipulated and matched to the system readout speed through temperature control. For example, a process with an activation energy of 0.6 eV will manifest about 1000 jumps per second at room temperature. This lies within the range of activation energies for oxygen migration pathways in many oxygen ion conductors.

Here we use aberration corrected *in situ* transmission electron microscopy equipped with cutting edge detector technology to explore ionic transport and diffusion in oxides with a focus on cerium dioxide and strontium titanate. Oxygen transport is easier to detect, at least in comparison to say, lithium transport, because of the larger anion size and the significant perturbation of the cation sublattice during transport. However, even at millisecond time resolutions, the signal per frame gets very small for atomic resolution analysis with moderate electron dose rate. To compensate for this, we have developed convolutional neural networks to denoise data sets (Marcos-Morales, Leibovich et al. 2023). With oxygen transport, local short-lived structural changes can be rather subtle to detect. Consequently, novel sophisticated image processing techniques must be employed to characterize the nature of the structural dynamics (Thomas, Crozier et al. 2023). This presentation will review what is currently possible in measuring atomic resolution structural dynamics in electroceramics and how the field is likely to evolve over the near future.

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