

Elucidating Ionic Mobility in Multivalent Spinel Oxides

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With lithium-ion batteries seemingly reaching their developmental limits, researchers are exploring new chemistries to obtain the higher energy densities needed for electric vehicles to become more competitive for universal market adoption. Batteries based on Mg chemistries could achieve these goals. Oxides with a spinel structure are predicted to provide a favorable combination of properties to function as attractive magnesium cathodes; however, traditionally, Mg²⁺ intercalation suffers from sluggish mobility. Theory has predicted the energy barriers for the Mg²⁺ hops between tetrahedral sites via the vacant octahedral sites are low enough to enable sufficient room temperature transport. Experimental studies have shown potential Mg²⁺ migration at comparable timescales. While the activation barriers could be extracted, the path followed by the Mg²⁺ cation during a hop remains to be elucidated.

To better understand the trajectories for multivalent ion mobility in spinel oxides, variable temperature neutron diffraction and pair distribution function (PDF) are used to examine the average and local structure. Reverse Monte Carlo (RMC) profiling is then used to map the ionic pathways via large-box modeling of the crystal structure. Further contrast is provided by studying similarly structured samples where hopping is predicted to face higher activation barriers than Mg and, thus, show slower migration. Insight into how ion mobility is achieved in spinel structured oxides will better inform the design of new battery cathode host structures and electrolytes to help push Mg batteries into commercialization.