

## Iron mobility in LiFePO<sub>4</sub> and its consequences for site exchange defect related capacity loss.

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Lithium iron phosphate (LiFePO<sub>4</sub>) has been shown to frequently exhibit a significant amount of iron and lithium inter-mixing (site exchange defects).[1] These defects have been believed to be the source of slow kinetics in such materials,[2] specifically the belief that iron blocks the lithium diffusion path has found widespread acceptance.[3,4]

In this study, using our newly developed force field, atomistic modeling was applied to the investigation of iron mobility in LiFePO<sub>4</sub> and FePO<sub>4</sub>. [5] Surprisingly, the simulation results suggest that anti-site iron ions in FePO<sub>4</sub> experience an activation barrier for the movement along the lithium diffusion channel that is comparable to that of lithium (Figure 1). This puts into question the role of anti-site iron ions in the hindrance of lithium diffusion.

Based on simulation results, we suggest that thermodynamics impede complete delithiation of [Li,Fe][Fe,Li]PO<sub>4</sub>. The presented model describes the iron site to be highly unstable if left unfilled due to a local accumulation of negative charge. For that reason, lithium ions that reside in the iron site cannot participate in the charge storage process. The energy necessary to remove antisite lithium ions has been quantified to 6 eV. Consequently, stoichiometric LiFePO<sub>4</sub> should exhibit a capacity loss of the order of the site exchange defect concentration due to these defects.

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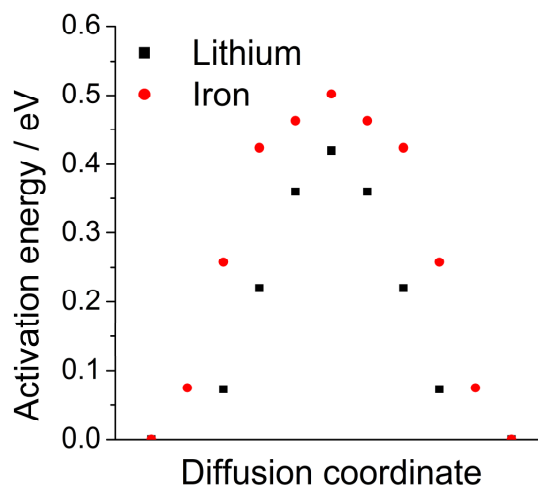


Figure 1. Activation barrier for iron and lithium ions for jumps along the lithium diffusion channel in FePO<sub>4</sub>.

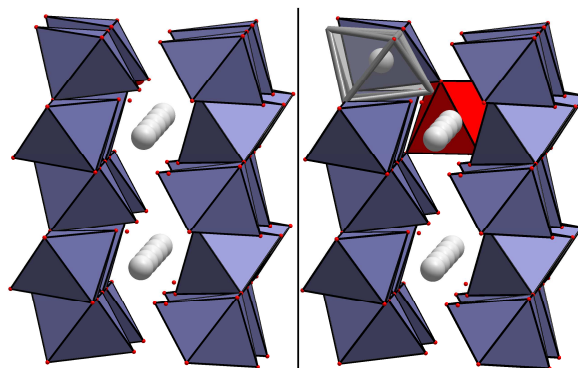


Figure 2. Crystalline LiFePO<sub>4</sub> (left) and LiFePO<sub>4</sub> containing site exchange defects (right). Upon delithiation antisite iron becomes mobile, while antisite lithium is immobilized. (Note: Phosphate groups have been removed for clarity)