

# ***Ab initio* calculations of the phase stability and electronic properties of $\text{Li}_{2/3}\text{FePO}_4$**

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Charge/discharge of  $\text{LiFePO}_4$  cathode material involves a biphasic reaction between Li-rich  $\text{Li}_{1-x}\text{FePO}_4$  and Li-poor  $\text{Li}_x\text{FePO}_4$  phases. It is thought that phases with intermediate Li content form at the interface to reduce the lattice strain induced by the large volume mismatch between the two main phases [1-2]. Recently, using a spherical aberration-corrected scanning transmission electron microscope we directly observed the interface between Li-rich and Li-poor phases in a chemically delithiated single crystal of  $\text{LiFePO}_4$ . The  $\approx 50$  nm wide interface was found to consist of a mixture of intermediate phases including one with a monoclinic structure and Li content of  $x \approx 2/3$  [3]. In this study, we examined the stability and electronic properties of the  $\text{Li}_{2/3}\text{FePO}_4$  phase using first-principles calculations.

A structure model for monoclinic  $\text{Li}_{2/3}\text{FePO}_4$  was constructed based on previously reported data [2]. Calculations were performed using the VASP code, and the Perdew-Burke-Ernzerhof form of the general gradient approximation was chosen for the exchange-correlation term. The cut-off energy for planewave basis sets was 500 eV. All calculations were spin-polarized and a Hubbard  $U$  potential of 4.3 eV was applied to Fe 3d orbitals.

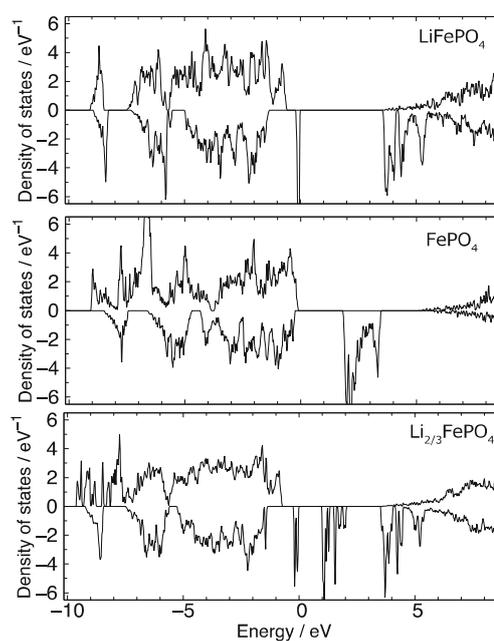
The formation energy of  $\text{Li}_{2/3}\text{FePO}_4$  relative to  $\text{LiFePO}_4$  and  $\text{FePO}_4$  was +2 meV per formula unit.  $\text{Li}_{2/3}\text{FePO}_4$  can thus be considered to be metastable at room temperature.

Fig. 1 compares total densities of states of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$ , and  $\text{Li}_{2/3}\text{FePO}_4$ . The band gaps of  $\text{LiFePO}_4$  and  $\text{FePO}_4$  are 3.5 eV and 2.0 eV, respectively, while that of  $\text{Li}_{2/3}\text{FePO}_4$  is much narrower at 1.0 eV. This suggests that the intermediate phase exhibits faster electronic conduction than the main phases.

## References:

- [1] Y. Orikasa et al., *J. Electrochem. Soc.*, 160, A3061-A3065 (2013).
- [2] S. Nishimura et al., *Angew. Chem. Int. Ed.*, 54, 8939-8942 (2015).
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**Fig. 1.** Calculated total densities of states of  $\text{LiFePO}_4$ ,  $\text{FePO}_4$ , and  $\text{Li}_{2/3}\text{FePO}_4$ . Highest occupied states are set to 0 eV on the horizontal axis in each case, while positive and negative densities correspond to majority and minority spins, respectively.