Conductivity Assessment in Doped Lithium Iron Phosphate Olivines

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For lithium-ion application into hybrid-electric vehicles (HEVs), among other considerations, cost is an issue of increased priority. Use of $LiFePO_4$ as the cathode material for lithium-ion batteries presents an opportunity to lower cost due to low raw materials cost and relative ease of synthesis. The key issue with this material is that bulk conductivity is low. Recent work by Chiang et. al. has suggested that conductivity can be improved by up to 8 orders of magnitude through the use of metal doping.[1]

At TIAX, modeling studies of $LiFePO_4$ have been employed in order to gain understanding of this material's conductivity and to find methods for improving conductivity. Density-of-states calculations like that shown in Figure 1 help explain conductivity performance and offer a method for screening the effect of chemical changes, such as doping, on the conductivity.

We used the full-potential linear augmented plane wave method (FLAPW) to understand the underlying physics of conductivity of doped $LiFePO_4$ material. A common mechanism for improved conductivity involves dopants with the valence electron count different from substituted atoms. This changes the concentration of conduction electrons. Our work shows that the conductivity in $LiFePO_4$ is mostly governed by electron hoping between magnetic Fe ions. Therefore, an alternative mechanism is required to explain the results reported in the literature.

In conjunction with modeling, laboratory experiments have investigated the effect of cation doping on $LiFePO_4$. XRD measurements [Fig. 2] aid in confirming synthesis of materials and can be used to monitor structural effects of added dopants. Results confirm the ability of dopants to improve conductivity however the magnitude of this improvement remains under investigation.

Since our modeling work has identified alternate mechanisms for improving conductivity in $LiFePO_4$, experimental verification of these are underway. By using modeling, key parameters have been identified which determining the opportunities for enhanced conductivity in $LiFePO_4$. They also raise the possibility for multiple explanations as to the mechanism of enhancing conductivity in $LiFePO_4$.

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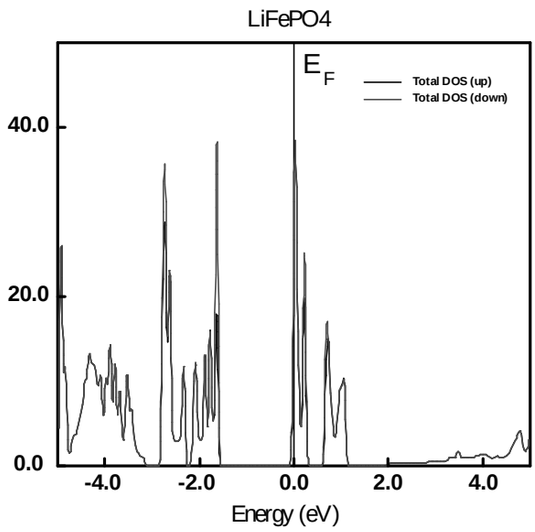

Figure 1. Density-of-states calculation for $LiFePO_4$.

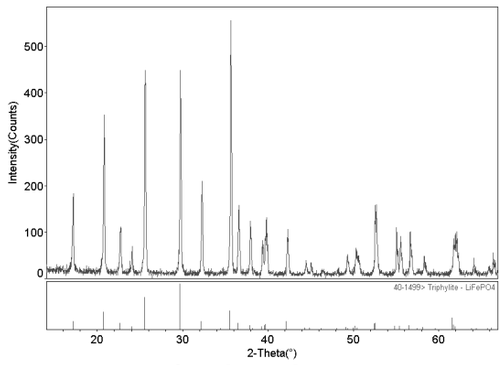

Figure 2. XRD of synthesized $LiFePO_4$.

[1] Chung, S.-Y.; Bloking, J. T.; Chiang, Y.-M.; *Nature Materials*, v. 1, 123, 2002.