

# Lithium ion conductivity in single crystal $\text{LiFePO}_4$

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## ABSTRACT

Although extensively studied as a potential Li rechargeable battery cathode in its powder form, very little is known about the anisotropy of the ionic and electronic transport properties in  $\text{LiFePO}_4$  as it may be manifested in single crystal studies. Here, we report on the conductivity of lithium ions along three principal axis directions in single crystal  $\text{LiFePO}_4$  as a function of temperature by AC impedance spectroscopy. Despite the apparent quasi-two dimensional nature of the crystal structure, suggestive of facilitated inplane diffusion, we show that Li diffusion in  $\text{LiFePO}_4$  is, to a large extent, confined to one dimension through tunnels along *b*-axis (using the *Pnma* symmetry group notation), implying oriented powders in batteries may improve the performance of this material as a cathode in rechargeable batteries. Our results may also explain the numerous failed attempts to enhance the ionic conductivity by introducing divalent and trivalent substitutions to  $\text{Li}^+$  that, although produce vacancies in the Li sheets, may concurrently impede the diffusion in the tunnels.

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## 1. Introduction

Lithium iron phosphate ( $\text{LiFePO}_4$ ) has been one of the most promising cathode materials for the second generation lithium rechargeable battery by virtue of its improved safety, low environmental cost [1–4], and high theoretical current capacity (170 mAh/g [5]). However, the poor conductivities (both ionic and electric) are major drawbacks which generally cause capacity losses at higher charge–discharge currents, keeping  $\text{LiFePO}_4$  from being a commercially viable cathode material [6,7]. Recently, several research groups made efforts to overcome these problems by carbon-coating  $\text{LiFePO}_4$  particles [8,9], doping transition metal ions [1], and reducing particle size [10,11]. However, these approaches have not addressed systematically the intrinsic conductivities of the cathode material itself. Moreover, even the conductivity improvements did not show improvements in the battery performance. In order to determine the limiting factors for the charge transport in this compound, a better understanding of the lithium and electron conduction mechanisms in  $\text{LiFePO}_4$  is needed.

First-principles calculations predict that lithium ions have a one-dimensional diffusion channel along *b*-axis in all members of the  $\text{LiMPO}_4$  group [12–14]. In the first study, *c*-axis was predicted to have the highest lithium diffusivity, but, this study used the *Pbnm* symmetry group for which *c*-axis is equivalent to *b*-axis in the *Pnma* symmetry. The calculated lithium diffusion activation energy along *b*-axis was found in the range from 0.215 eV [12,13] to 0.66 eV [14] for

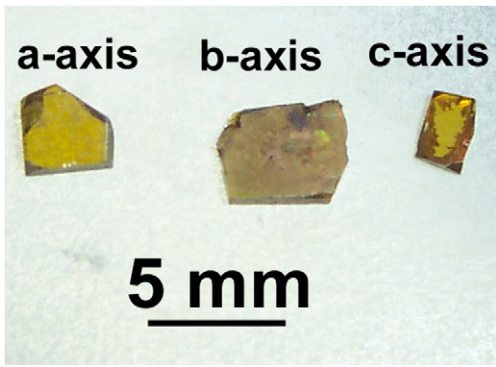
$\text{LiFePO}_4$  using either *ab initio* methods or first-principles calculations. The experimental values for the activation energy of  $\text{LiFePO}_4$  measured from sintered powders, however, are spread over a wide range from 0.156 eV to 0.63 eV [1,15–18]. The controversies regarding the activation energy and whether the enhancement in the electronic conductivity for cation-doped  $\text{LiFePO}_4$  is truly due to the substitution of  $\text{Li}^+$  by the cations or due to the grain-boundary impurities [19] indicate that the ionic conductivity and electronic conductivity in  $\text{LiFePO}_4$  are still not fully understood. To resolve these controversies, conductivity studies of pure and the cation-doped  $\text{LiFePO}_4$  single crystals, which are free of grain-boundary impurities, are required.

Recently, large  $\text{LiFePO}_4$  single crystals of  $100 \text{ mm}^3$  in size have been grown successfully by the flux growth method. Herein, we report the ionic conductivities of single crystal  $\text{LiFePO}_4$  along the three principal axes directions at various temperatures and the lithium ionic diffusion activation energies along the three axes are also calculated.

## 2. Experimental method

Single crystals  $\text{LiFePO}_4$  were grown by the flux method as detailed in Ref. [20]. A large single crystal about 0.5 g in weight was oriented and cut into three plates with large facets normal to the three principal axis direction, as shown in Fig. 1. The orientation is within  $0.5^\circ$  error from the principal axes. The thickness of the thin plates is about 0.8 mm with thickness/area ratios of 1.11, 0.485, and  $1.16 \text{ cm}^{-1}$  with the facets normal to the *a*-axis, *b*-axis and *c*-axis, respectively. The crystal structure and composition of the single crystals have been measured by X-ray diffraction and neutron diffraction [20,21].

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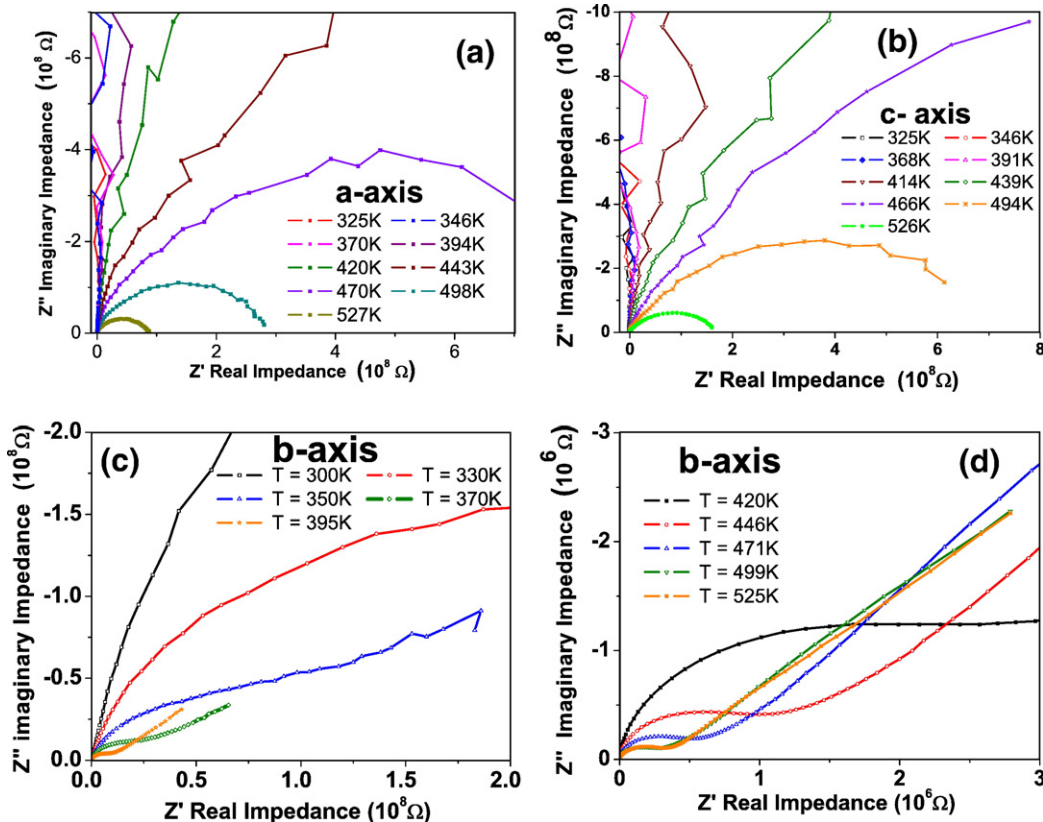
**Fig. 1.** Photographs of the single crystals thin plates with the *a*, *b*, and *c*-axes normal the gold-coated surfaces, respectively. The gold coating on crystal *c* is partly peeled off when the picture was taken after AC impedance measurements.

The single crystal plates were mechanically polished and coated with gold on the wide surfaces using physical vapor deposition technique with average thickness of about 250 Å. The gold coating on the edges was carefully removed to prevent current shortage. The gold-coated single crystal plate was placed in an airtight sample chamber filled with Ar and then connected to a Solarton 1260 Impedance Gain-phase Analyzer to measure the magnitude and phase angle of the impedance of the sample simultaneously. The measurements were performed under sinusoidal voltage (peak height 0.5 V) across the sample in 1 to 10 MHz frequency range. The sample temperature was controlled to within ±1 K by placing the heater around the sample chamber.

**3. Results and discussion**

The complex impedance along the three principal axes is plotted in the complex plane with real versus imaginary as indicated (the so-called Cole–Cole plot). Fig. 2 shows the experimental results of the impedance of the three crystals at different temperatures, as indicated. The impedance spectra along *b*-axis are separately shown in Fig. 2 (c, d) due to the very different scale at low temperatures from those at high temperatures. As can be clearly seen in Fig. 2(a, b), the impedance data along *a*- and *c*-axis are very similar. At temperatures below 400 K, the impedances are almost lines perpendicular to the *x*-axis, a clear signature that the crystals are insulators (both ionic and electronic) with extremely weak conductivity (exceeding the conductivity range of the AC impedance). With the increase of temperature, semicircles are gradually formed. At 500 K, almost perfect semicircles are observed along both *a*-axis and *c*-axis and the semicircles become smaller at *T*=526 K.

The impedance plots along *b*-axis are very different from those along *a*-axis and *c*-axis. A partial semicircle forms even at room temperature *T*=300 K. By increasing the temperature, more segments of the semicircle are observed. At 370 K, inclined spikes appear gradually at the low-frequency end. The first semicircle at high frequency is due to bulk ionic conduction and the spikes at low frequency are usually due to the secondary ionic carrier [24], grain-boundary diffusion in the powder samples [25] or the surface ion diffusion [26]. We believe that the spikes at low frequencies in this case are due to electrode surface effects at high temperatures which was also observed in other single crystal impedance measurements [22–24,26].



**Fig. 2.** Complex impedance plots for voltages applied across the (a) *a*-axis, (b) *c*-axis and (c, d) *b*-axis crystallographic directions. Due to the very different scale, the impedances along *b*-axis at low temperature (c) and those at high temperature (d) are shown separately.

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