

# Ionic and electronic transport in single crystalline $\text{LiFePO}_4$ grown by optical floating zone technique

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## Abstract

The present work is devoted to a systematic investigation of ionic and electronic conductivity as well as chemical Li-diffusivity in single crystalline  $\text{LiFePO}_4$  as a function of crystallographic orientation over an extended temperature range. Besides chemical analysis of the elemental ratio of the crystal, we also determined the Fe occupancy on the lithium lattice positions by single crystal X-ray diffraction and synchrotron X-ray radiation followed by Rietveld refinement. AC impedance as well as improved DC polarization/depolarization measurements have been carried out using electronically as well as ionically blocking cells. The activation energies obtained for electronic and ionic conductivities are in the range of 0.55–0.59 eV and of 0.62–0.74 eV, respectively, depending on the orientations. The ionic conductivity is much smaller than the electronic conductivity along all three axes and the electronic conductivity, ionic conductivity and chemical diffusivity of Li ion are found to be effectively two-dimensional (i.e., isotropic in the  $b$ - $c$  plane).

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## 1. Introduction

The olivine type phosphates  $\text{LiMPO}_4$  (e.g.  $M = \text{Fe, Mn, Ni}$ ) exhibit a structure, that is characterized by a framework of metal ( $\text{MO}_6^{n+}$ ) octahedra interconnected with  $\text{PO}_4^{3-}$  tetrahedra [1]. The  $\text{Li}^+$  ions form one-dimensional tunnels in the structure that run parallel to the planes of corner-sharing  $\text{MO}_6$  octahedra, along the [010] direction in the orthorhombic [Pnma] lattice. Within this olivine family, the most significant research activities [2–5] have been focused on the Fe-based member,  $\text{LiFePO}_4$ , due to its advantageous properties as cathode material in Li-based secondary batteries. The main hurdle to use it as a cathode is its very sluggish intrinsic transport. In spite of the pronounced research, the transport properties of the material are only rudimentarily understood. Table 1 shows that the experimental as well as theoretically calculated values for the conductivity activation energies vary greatly from study to study. Variations

of the experimental values can be partly attributed to impurity effects and frozen native defects. In addition,  $\text{LiFePO}_4$  is characterized by a significant anisotropy, and thus orientation effect in the polycrystalline materials can be decisive. Obviously there is a great need to study single crystals. In our institute single crystals have been successfully grown [6] and a first set of transport data were provided in Ref. [7]. These measurements revealed an effectively two-dimensional electronic as well as ionic conductivity (along  $b$ - and  $c$ -axes). Consistent with this also a “two-dimensional” diffusivity was found. Modeling predicted that this material should exhibit two-dimensional electronic conductivity along  $b$ - and  $c$ -axes but one-dimensional  $\text{Li}^+$  ionic conductivity along  $b$ -axis. Three different theoretical calculations [8–10] have been conducted on the diffusion process in  $\text{LiFePO}_4$  and their major conclusion is that the Li ion migration energy is lower along the  $b$ -axis. Recently Ellis et al. [11] have commented that the absolute values of the activation energies calculated theoretically may not be reliable as the models assumed free ion transport and ignored interactions with the framework and localized electron sites. From their

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Table 1  
Reported conductivity activation energies for polycrystalline LiFePO<sub>4</sub>

Method/technique	Activation energy (eV)	References
AC	0.630	[4]
DC	0.390–0.500	[8]
AC	0.155	[19]
DC	0.186	[20]
First principle	0.215	[21]
Mössbauer Spectroscopy	0.775±0.180	[11]
AC	0.66	[22]
Electrochemistry	0.63	[22]
AC	0.502±0.18	[2]
AC	0.38	[23]
Electrochemistry	0.155	[23]

Mössbauer spectroscopy measurement the small polaron carrier mobility is predicted to be “two-dimensional” [11] with motions of Li ions and electrons being correlated.

A further reason for the measured isotropy regarding *b*- and *c*-directions can be a frozen disorder in the cations sublattices impairing the ideal *b*-channel transport considered in Refs. [8–10]. Our initial measurements on the Li<sup>+</sup> ionic conductivity reported in Ref. [7] were restricted to a narrow temperature range due to the low melting point of the electrode component (Li) and the low diffusion coefficient of Li<sup>+</sup> in LiFePO<sub>4</sub>. In DC polarization measurement we could not even reach steady state voltage values in the case of the electronically blocking cell. Therefore, only tentative values for the activation energies for Li<sup>+</sup> conductivity could be given. In this paper we give results using LiAl instead of Li which allows us to overcome these short-comings.

In order to shine light on the above discussed disagreement between the experimentally obtained results and theoretical prediction on lithium ion conductivity and diffusion, we check the anti-site substitution of Li and Fe in the lattice position by single crystal X-ray diffraction and synchrotron X-ray radiation followed by Rietveld refinement.

## 2. Experimental

Single crystals of LiFePO<sub>4</sub> are grown in an optical floating zone furnace with 4 × 300 W halogen lamps installed as infrared radiation sources. Details of the preparation are given elsewhere [6]. Crystallographic orientation is achieved using Laue X-ray photography and additionally confirmed by powder and single crystal X-ray diffraction (STOE, IPDS2). Inductively-coupled-plasma (ICP) optical emission spectroscopy (SPECTRO CIROS) was employed to determine the chemical composition of LiFePO<sub>4</sub>. X-ray photoelectron spectroscopy with an Axis Ultra instruments and EPR spectroscopy (X-band, Bruker ER 041 Microwave Bridge) has been used to identify impurities. Details are given elsewhere [7].

Two types of cell configurations were employed to derive the transport properties. For the ionically blocking cell, Ti/LiFePO<sub>4</sub>/Ti, titanium metal films were evaporated onto the polished surfaces with a thickness of 200 nm. The total conductivity was measured by High Resolution Dielectric Analyzer

in the frequency range from 10<sup>7</sup> to 5 × 10<sup>-3</sup> Hz (see also Ref. [7]).

For electron blocking cell LiAl/Li/LiFePO<sub>4</sub>/Li/LiAl, LiFePO<sub>4</sub> was contacted by LiI (Aldrich, 99.99%) pellets. LiAl pellets served as terminal contacts. The contact resistance was minimized by heat treatment at 200 °C for 20 h. The transport measurements were performed inside a hermetically seal air tight quartz tube cell under dry argon atmosphere. The cell assembly was done under controlled atmosphere (water content <1 ppm; O<sub>2</sub> content <1 ppm).

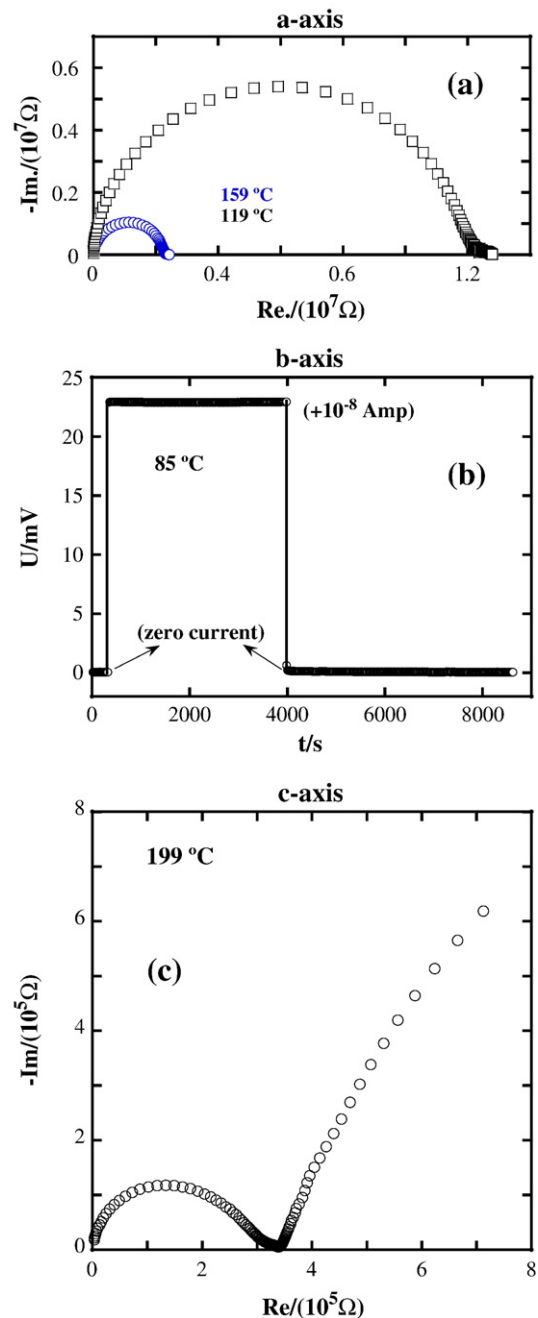


Fig. 1. (a) Impedance spectrum of the symmetric cell, Ti/LiFePO<sub>4</sub>/Ti, (b) step function galvanostatic DC polarization measurement of the same cell and (c) impedance spectrum of the symmetric cell, LiAl/Li/LiFePO<sub>4</sub>/Li/LiAl.

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