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## Full Length Article

## Effect of particle size on dc conductivity, activation energy and diffusion coefficient of lithium iron phosphate in Li-ion cells

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## ABSTRACT

Cathode materials in nano size improve the performance of batteries due to the increased reaction rate and short diffusion lengths. Lithium Iron Phosphate (LiFePO<sub>4</sub>) is a promising cathode material for Li-ion batteries. However, it has its own limitations such as low conductivity and low diffusion coefficient which lead to high impedance due to which its application is restricted in batteries. In the present work, increase of conductivity with decreasing particle size of LiFePO<sub>4</sub>/C is studied. Also, the dependence of conductivity and activation energy for hopping of small polaron in LiFePO<sub>4</sub>/C on variation of particle size is investigated. The micro sized cathode material is ball milled for different durations to reduce the particle size to nano level. The material is characterized for its structure and particle size. The resistivities/dc conductivities of the pellets are measured using four probe technique at different temperatures, up to 150 °C. The activation energies corresponding to different particle sizes are calculated using Arrhenius equation. CR2032 cells are fabricated and electrochemical characteristics, namely, ac impedance and diffusion coefficients, are studied.

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## 1. Introduction

Nano materials are expected to play a key role in the performance improvement of rechargeable Li-ion battery technology. Nano materials increase the surface area, leading to higher electrode-electrolyte contact and thus enhance the reaction rate. The solid state diffusion of Li-ions is generally considered to be the rate-determining step of Li-ion batteries. Therefore, the nano structured materials are extensively explored in an effort to enhance the kinetic properties by decreasing the diffusion length to a nanometer scale. Due to the short diffusion length, the nano structured materials show high rate performances [1]. The lithiated olivine phosphates are promising new generation cathode materials for Li-ion rechargeable batteries owing to their numerous advantages such as high energy density, low cost and environmental friendliness. Ever since it is synthesized, the lithium iron phosphate (LiFePO<sub>4</sub> or LFP) became a very promising choice of cathode materials [2]. It exhibits reversible electrochemical lithium insertion/extraction reactions at ~3.4 V (vs. Li/Li<sup>+</sup>) with a theoretical capacity of 170 mAh g<sup>-1</sup> [3]. During lithium-ion extraction and insertion, the active material undergoes a two-

phase transition between LiFePO<sub>4</sub> and FePO<sub>4</sub>, with a flat voltage profile. LiFePO<sub>4</sub> is safer as compared to other metal-oxide cathode materials. Additionally, LiFePO<sub>4</sub> cathode material lies in its tolerance to overcharge/discharge and less prone to thermal runaway [4]. Also, LiFePO<sub>4</sub> has good cycle and thermal stabilities. In spite of its superior performance, LiFePO<sub>4</sub> material has to overcome some barriers for practical applications. Among various issues, the most important concern is its low intrinsic electronic conductivity and slow lithium-ion diffusion across the LiFePO<sub>4</sub>/FePO<sub>4</sub> phase boundary during charge/discharge processes which limit the rate performance of this material. The slow diffusion rate of Li-ion is attributed to a variety of material properties such as large miscibility gap, dimensionality and nature of defect sites [5–9]. Over the past few years, numerous efforts have been made to circumvent the drawbacks mentioned above, including reducing the particle size and homogeneous particle size distribution and supervalent doping [10,11]. An increase by eight orders of magnitude in the electronic conductivity of the olivine-type material is reported by adopting various techniques to increase the conductivity [12–14]. It is generally accepted that the olivine phosphates are wide gap materials in which the charge transport is ascribed by the archetype small polaron hopping rather than band-like transport [15]. The mobile charge carriers can be either electrons or holes in LiFePO<sub>4</sub> systems depending on the lithium addition or withdrawal where the mobile charge carriers occupy Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple. The theoretical in-

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vestigations on the polarons in n-dimensional crystals suggest that the polaron effect enhances as the dimensionality of the system reduces. The activation barrier associated with the hopping is found to be a thermally activated process [16]. The enhancement in electronic conductivity of  $\text{LiFePO}_4$  is due to the lattice strain associated with the reduction of particle size. This becomes prominent at the typical nano scale regime. At nano scale, i.e., particle size of less than 200 nm, there is an enhancement in the polaronic conductivity of about an order of magnitude. The temperature dependence of dc conductivity and nonlinearities in the transport properties of  $\text{LiFePO}_4$  with particle size are due to the interplay between the confinement and lattice strain. The dependence is also due to the effects of strain on the electron–phonon interactions. Finally, the reduction of particle size leads to a shorter hopping distance. The observed conductivity of  $\text{LiFePO}_4$  at room temperature is of the order of  $10^{-10}$ – $10^{-5} \text{ S cm}^{-1}$  [16] with an activation energy ( $E_a$ ) of about 0.65 eV. The limiting factor for the performance of  $\text{LiFePO}_4$  based batteries is related to the material's low electrical conductivity, both ionic and electronic. The ionic component of electrical conductivity is related to the mobility of  $\text{Li}^+$  ions. It is preferential along [010] direction which is characterized by the  $E_a$  of 0.55–0.65 eV when compared to [001] direction with  $E_a = 2.89 \text{ eV}$  and [101] direction with  $E_a = 3.36 \text{ eV}$  [9,17]. It is observed that there exists a relationship between the electronic and the ionic conductivity in  $\text{LiFePO}_4$  [9,16,18,19]. Faster transport of the small polaron generally leads to fast diffusion of lithium cations, which hints at their mutual connection. Therefore, high electrical resistivity may be considered responsible for the low values of lithium diffusion coefficient,  $D$ . Values of  $D$  reported in the literature fall over a wide range from  $10^{-16}$  to  $10^{-11} \text{ cm}^2\text{s}^{-1}$ , and their poor reproducibility indicates the strong influence of the method of preparation of material [9].

Effect of particle size reduction on conductivity, activation energy and diffusion coefficient of  $\text{LiFePO}_4/\text{C}$  is studied in this paper using commercial  $\text{LiFePO}_4$  powder of 5  $\mu\text{m}$  particle sizes. The micron size particles of cathode material were reduced to nano level by ball milling for different durations in a liquid medium. This reduction in the particle size was confirmed by X-ray powder diffraction, particle size analyzer and scanning electron microscopy. The samples with different particle sizes were pelletized, and their dc resistivities were measured from ambient to 150 °C by four-probe setup, and the activation energies were calculated using Arrhenius equation. CR2032 cells are fabricated from un-ball milled  $\text{LiFePO}_4/\text{C}$  of 5  $\mu\text{m}$  particle size and the material ball milled for 15 h, which was found to have maximum conductivity. Lithium foil was used as anode. These cells were characterized for ac impedances and diffusion coefficients by electrochemical impedance spectroscopy, and the effect of particle size on these parameters is discussed.

## 2. Experimental

Commercial  $\text{LiFePO}_4/\text{C}$  powder with 10% carbon content (LFP-0, 99.99% purity, MTI, USA) was wet ball milled (Planetary ball mill model Retsch PM 100) with toluene as the milling medium. Ball milling was carried out at a speed of 400 rpm with a ball-to-powder ratio of 10:1 for different durations of 5 (LFP-5), 10 (LFP-10), 15 (LFP-15) and 20 hours (LFP-20) to obtain particles of nano size. The obtained samples were further structurally characterized by X-ray powder diffraction, particle size analyzer and scanning electron microscopy (SEM) using PANalytical x'pert pro X-ray Diffractometer, HORIBA scientific nanopartica SZ-100, nano particle analyzer, and Zeiss Auriga FIB system with Bruker XFlash detector 5030 for SEM respectively.

The four probe method was used to measure the resistivity of LFP powders. The samples with different particle sizes were pelletized and sintered at 700 °C for 8 hours. Pellets of 10 mm diameter and 1.5 mm thickness were used to measure resistivities. The four

probe setup has four individually spring loaded probes which are collinear and equally spaced. This technique involves bringing the four equally spaced probes into contact with the material of unknown resistance. The probe array is usually placed in the center of the material. The outer probes are used for passing constant current through the sample. The electric current carried through the two outer probes sets up an electric field in the sample. The two inner probes measure potential difference using a high impedance voltmeter.

The whole arrangement is mounted on a suitable stand and the leads are provided for the voltage measurement. The experimental setup consists of a probe arrangement, sample, oven up to 200 °C, constant current generator, oven power supply and digital panel meter to measure voltage and current. In the present work, constant current sources model nos. CLS-01 and LCS-02 and digital voltmeter DMV-001 connected to a constant temperature chamber/oven (SES Instruments, India) were used for the measurement of resistivity.

Each sintered pellet was kept under the four probes carefully so that all probes rest on the pellet to make proper contact. At room temperature, the resistivity was measured for each pellet. The temperature was increased up to 150 °C with an increment of 10 °C and from the measurements; the resistivity  $\rho$  and conductivity  $\sigma$  are calculated corresponding to each temperature. The activation energies were calculated using the following Arrhenius equation [20] and compared with respect to their particle size.

$$\sigma = A \exp(-E_a/kT) \quad (1)$$

where,  $\sigma$  = Conductivity (S/cm),

$E_a$  = Activation energy (eV)

$T$  = Temperature (°K)

$k$  = Boltzmann's constant

80 wt% of ball milled  $\text{LiFePO}_4/\text{C}$ , 5 wt% of acetylene black and 15 wt% poly vinylidene fluoride (PVdF) in *N*-methyl-2-pyrrolidone (NMP) solution was considered to prepare the cathodes. CR 2032 hardware with lithium metal foil as anode (99.9% purity, MTI, USA) was used to fabricate coin cells in half cell configuration [21]. The cells were charged up to 4.2 V and discharged to 2.7 V at room temperature initially for five cycles. The electrochemical characteristics, namely, ac impedance and diffusion coefficient are studied.

## 3. Results and discussion

The particle sizes obtained from the distribution graph of LFP-5, LFP-10, LFP-15 and LFP-20 are  $350 \pm 7 \text{ nm}$ ,  $183 \pm 3.6 \text{ nm}$ ,  $112 \pm 2.2 \text{ nm}$  and  $107 \pm 2.1 \text{ nm}$  respectively. A typical particle size distribution of LFP-15 is shown in Fig. 1. Particle size of the commercial  $\text{LiFePO}_4$  powder [GELON LIB GROUP, CHINA, Batch no: 120105] is of 3–5  $\mu\text{m}$  size.

As can be observed from the microstructure and the surface morphology (from SEM), the particles are broken down to smaller size with increasing time of ball milling. The ball milling yields considerably smaller particles of irregular shape with inhomogeneous particle size distribution. Particle size obtained from the micrograph of LFP-15 is approximately 100 nm which is in close agreement with that obtained from the particle size analysis. SEM micrographs of LFP-0 and LFP-15 are shown in Fig. 2.

The variation of the conductivity with temperature is plotted in Fig. 3, as a typical case. Natural logarithm of conductivity,  $\ln(\sigma)$  vs. reciprocal of the temperature,  $1/T$  plotted in Fig. 3 shows an increase in the dc conductivity with increasing temperature. The product of slope of plot and Boltzmann constant gives activation energy [20].

Table 1 shows the variation of resistivity and the conductivity values obtained using four probe technique with ball milling time. It can be seen from Table 1 that grinding of material from 0 to 20

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