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The source of first-cycle capacity loss in LiFePO_4

A.S. Andersson, J.O. Thomas*

Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

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Abstract

The electrochemical extraction of lithium from solid-state synthesised LiFePO_4 has been studied by neutron powder diffraction. A “coffee-bag” type cell of configuration (Li-metal | liq. el. | LiFePO_4) has been charged to 4.1 V, dismantled in a glovebox, and the composite cathode powder sample scraped from the current collector. Two-phase Rietveld refinement gave a triphylite (LiFePO_4) to heterosite (FePO_4) phase-ratio of 18:82. In the absence of significant absorption effects, this ratio is a true representation of the conversion of LiFePO_4 to FePO_4 . Possible mechanisms for lithium extraction/insertion during the first-cycle are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium extraction mechanism; Neutron diffraction; Iron phosphates

1. Introduction

Mechanisms for lithium insertion/extraction into transition-metal oxides are of considerable current interest because of their clear relevance to lithium-polymer and lithium-ion (polymer) battery applications. A special case of this is the potential use of different iron phosphates as active cathode materials in low-cost, rechargeable batteries [1–6]; one of the most promising materials in this class is LiFePO_4 [1]. It shows a very flat voltage curve with a plateau around 3.5 V versus Li/Li^+ and a theoretical capacity of 170 mAh/g.

LiFePO_4 occurs in nature as the mineral triphylite, which has the orthorhombic olivine-type structure (space-group: *Pnma*) with the oxygen atoms arranged in a slightly distorted, hexagonal close-packed arrangement [7,8]. The phosphorous atoms occupy tetrahedral sites, while the lithium and iron atoms occupy octahedral sites. The FeO_6 -octahedra are linked through common corners in the *bc*-plane and the LiO_6 -octahedra form edge-sharing chains in the *b*-direction. One FeO_6 -octahedron has common edges with two LiO_6 -octahedra. PO_4 -groups share one edge with an FeO_6 -octahedron and two edges with LiO_6 -octahedra, see Fig. 1.

Despite its rather compact structure, the cycling capability of LiFePO_4 is remarkably good at low current densities.

Approximately 0.6–0.7 Li^+ ions can be withdrawn from solid-state synthesised LiFePO_4 and reinserted reversibly at a current density of 2 mA/g [1]. It has been suggested by Padhi et al. [1] that the relevant rate-determining step in the cycling process (the factor limiting the rate performance of the material) is lithium diffusion through a diminishing $\text{LiFePO}_4/\text{FePO}_4$ interface as lithium is reinserted into the FePO_4 structure. Since the surface area of FePO_4 is decreasing in this model, the amount of lithium that can pass through the interface is suggested to be insufficient to sustain the current; this leads to a decrease in the reversible capacity at higher current densities. It is therefore, suggested that a larger amount of lithium could be extracted and reinserted reversibly in samples with smaller grain sizes [2]. Preliminary cycling tests at slightly elevated temperatures (40 and 60°C) [9] indicate indeed that the capacity increases with temperature, supporting the notion that it is the diffusion of lithium within each particle that is the limiting step. More recently, LiFePO_4 (particle size ca. 4 μm) has also been prepared by a “new synthetic route” in which a very small amount of some electronically conductive compound is incorporated into LiFePO_4 ; in electrochemical cycling tests made at 80°C (coin-type cells) using a polymer electrolyte, as much as 95–100% of the active material could be utilised, and good cyclability was obtained [10]. The same type of cell also appears to function well at even higher temperatures [11].

In an earlier study [12], we have followed the electrochemical delithiation and subsequent relithiation of LiFePO_4 by in situ XRD and Mössbauer spectroscopy. It

* Corresponding author. Tel.: +46-18-471-3763; fax: +46-18-51-3548.
E-mail address: josh.thomas@mkem.uu.se (J.O. Thomas).

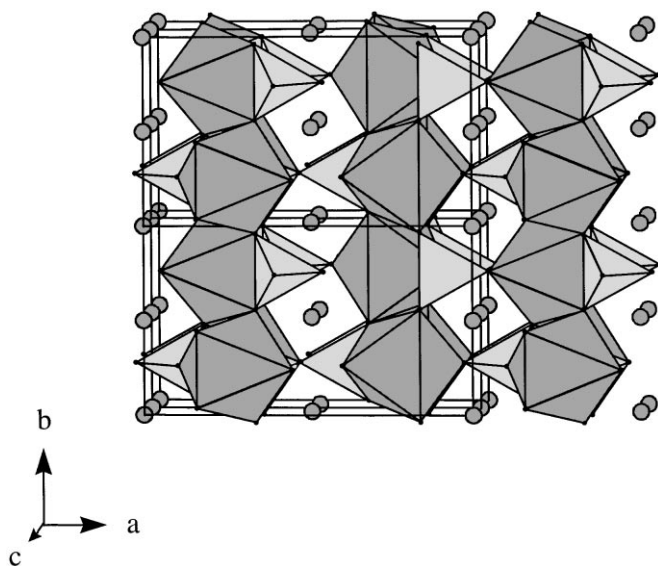


Fig. 1. The structure of LiFePO_4 /triphylite viewed along the c -axis. The P atoms occupy tetrahedral ($4c$) sites (light shading) and the Fe atoms occupy octahedral ($4c$) sites (dark shading). The Li ions (small circles) occupy octahedral ($4a$) sites.

was found that ca. 80% of our LiFePO_4 sample could be utilised at low current densities. Excellent consistency was obtained between the two methods with only a slight discrepancy occurring between the Mössbauer and the electrochemical data. Even this could be attributed to differences in the Mössbauer recoil-free factors originating from slight differences in thermal motion of the Fe atoms in the LiFePO_4 and FePO_4 phases.

The ca. 20% capacity loss during the first-cycle remains to be explained satisfactorily, however. One source of uncertainty in our earlier study was our conceptual picture of the lithium extraction/reinsertion mechanism within a single particle. It is known that X-ray absorption effects can give incorrect values for the degree of conversion, since the X-ray

beam does not penetrate into the core of larger particles. The significance of this effect is investigated here by neutron powder diffraction, where no such absorption effects are present.

2. Experimental

2.1. Synthesis

LiFePO_4 was prepared by the solid-state reaction of stoichiometric amounts of Li_2CO_3 (p.a., Merck), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (>99%, Sigma-Aldrich) and $(\text{NH}_4)_2\text{HPO}_4$ (p.a., Merck) at 800°C , as described previously [9,12]. The phase purity of the material was ascertained by X-ray powder diffraction (Guiner-Hägg film data, Cr $K\alpha_1$ -radiation). Chemical analysis gave the formula $\text{Li}_{0.95}\text{Fe}_{0.97}\text{PO}_{4.11}$.

2.2. Cathode and cell preparation

A large rectangular cathode (approximately $9\text{ cm} \times 18\text{ cm}$) was fabricated by spreading a mix of LiFePO_4 , Shawinigan Black (SB) carbon powder and an EPDM rubber binder (ratio 80:15:5) in cyclohexane onto an Al-foil current collector, which had been pre-coated with a fine deposit of carbon to improve electrical contact. The LiFePO_4 loading was $5\text{--}6\text{ mg/cm}^2$. The electrodes were then dried at 60°C overnight, and again in vacuum at 120°C . A half-cell was prepared by laminating the cathode in an Ar-filled glovebox (<3 ppm H_2O and O_2) against a glass-wool separator soaked in electrolyte and pressed onto a lithium-foil counter electrode. The laminate was vacuum-sealed into a polymer-coated aluminium bag (the “coffee-bag”). The electrolyte used was 1 M LiBF_4 (Tomyama) in EC/DMC 2:1 (Selectipur[®], Merck, Darmstadt, Germany). The cell charge was controlled by a MacPile[™] galvanostat and the current applied was 2.3 mA/g . After charging to 4.1 V (see Fig. 2

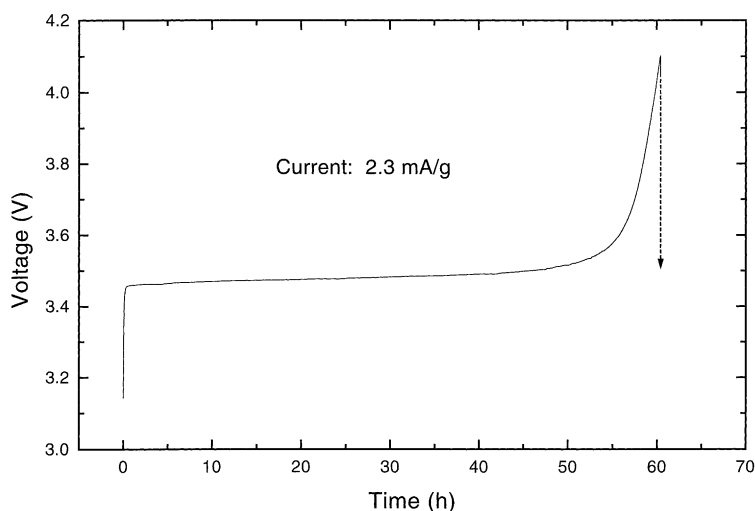


Fig. 2. A typical charging curve for LiFePO_4 .

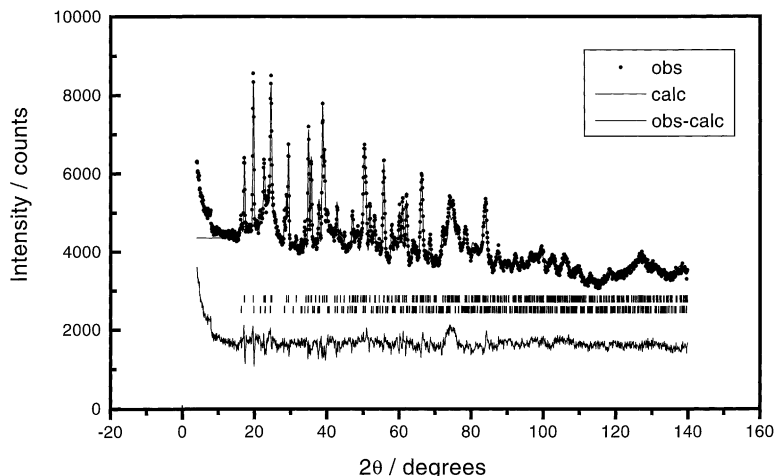


Fig. 3. The result of the Rietveld refinement of ND-data ($\lambda = 1.470 \text{ \AA}$) on a cathode charged up to 4.1 V. The experimental profile (dotted line), the calculated profile (solid line) and the difference between the observed and calculated profile (at the bottom) are shown. Regions excluded from the refinement due to problems with describing the background: $4.0\text{--}10.0^\circ$ in 2θ .

for a typical curve), the cell was dismantled in the glovebox, and the cathode rinsed in DMC and dried at 60°C overnight in vacuum. The entire composite cathode material was scraped carefully from the current collector and investigated by neutron powder diffraction at the medium-flux steady-state R2 reactor in Studsvik, Sweden, using an array of 35 detectors arranged at ca. 4° intervals in 2θ .

3. Results and discussion

A two-phase refinement was performed on the neutron diffraction data (Fig. 3) to determine the relative amounts of the two-phases present. The weight percentage of phase (p) in a mixture of m phases is given by the relation:

$$w_p = \frac{n_p(ZMV)_p}{\sum_{i=1}^m n_i(ZMV)_i},$$

where M_i is the formula weight of the phase i involving Z_i formula units/cell of volume V_i [13], n_i the refined scale factor for the i th phase.

In this present two-phase refinement, 19 parameters were refined: 2θ zero-point, two scale-factors, atomic co-ordinates for FePO_4 , and one half-width parameter, w (constrained to be the same for both phases), three isotropic thermal displacement parameters (B) for FePO_4 (one for each atom type) and one overall B for LiFePO_4 . The cell parameters used are those obtained earlier from X-ray data, and were not refined [12]. The atomic co-ordinates for LiFePO_4 were constrained to the values from Streltsov et al. [8] (Table 1). The two-phase refinement gave the amounts of FePO_4 and LiFePO_4 in the charged cathode to be 82 and 18%, respectively. The amount of charge passed through the cell corresponded to ca. 0.80 Li^+ /formula unit. The structural data obtained for FePO_4 in this refinement are given in Tables 1 and 2.

Table 1
Parameters obtained from two-phase Rietveld refinements of the ND-data^{a,b,c}

	LiFePO ₄				FePO ₄			
	x	y	z	B	x	y	z	B
Li	0	0	0	1.7 (3) ^d	–	–	–	–
Fe	0.28222	0.25	0.97472	1.7 (3) ^d	0.2781 (5)	0.25	0.949 (2)	0.34 (6)
P	0.09486	0.25	0.41820	1.7 (3) ^d	0.0917 (10)	0.25	0.388 (2)	1.0 (2)
O ₁	0.09678	0.25	0.74279	1.7 (3) ^d	0.1193 (8)	0.25	0.706 (2)	1.06 (6) ^d
O ₂	0.45710	0.25	0.20602	1.7 (3) ^d	0.4370 (9)	0.25	0.167 (2)	1.06 (6) ^d
O ₃	0.16558	0.04646	0.28478	1.7 (3) ^d	0.1675 (6)	0.0461 (9)	0.246 (2)	1.06 (6) ^d
n	1.56 (2)				0.30 (2)			
R_{Bragg} (%)	17.3				11.0			

^a Values for which standard deviations are given have been obtained in this work (the cell parameters are taken from X-ray data and were not refined here).

^b Atomic co-ordinates for LiFePO_4 are from Streltsov et al. [8]: a (\AA) = 10.3290 (3); b (\AA) = 6.0065 (2); c (\AA) = 4.6908 (2).

^c Starting atomic co-ordinates for FePO_4 were taken from Eventoff et al. [14]: a (\AA) = 9.8142 (2); b (\AA) = 5.7893 (2); c (\AA) = 4.7820 (2).

^d B -values constrained to be the same.

Table 2

Interatomic distances (in Å) for LiFePO_4 [8] and FePO_4 (this work, neutron powder diffraction data)

	LiFePO_4	FePO_4
$\text{LiO (1)} \times 2$	2.171 (1)	–
$\text{LiO (2)} \times 2$	2.087 (1)	–
$\text{LiO (3)} \times 2$	2.189 (1)	–
FeO (1)	2.204 (2)	1.945 (7)
FeO (2)	2.108 (2)	1.874 (10)
$\text{FeO (3)} \times 2$	2.251 (1)	2.143 (6)
$\text{FeO (3')} \times 2$	2.064 (2)	2.040 (5)
PO (1)	1.524 (2)	1.545 (12)
PO (2)	1.538 (2)	1.540 (13)
$\text{PO (3)} \times 2$	1.556 (1)	1.551 (8)

These numbers are in very good agreement with what has been obtained earlier with X-ray diffraction and Mössbauer spectroscopy [12]. The two-phase refinement of the in situ XRD data of a charged cell gave an apparent content of 83% FePO_4 and curve fitting of the in situ Mössbauer spectroscopy data gave 82% FePO_4 (Fig. 4).

There is, thus, a general consensus that we have a ca. 15–20% capacity loss in all our studies; we now consider what is the most likely source of this loss. The two most critical factors are:

- the lithium extraction/reinsertion mechanism within a single active LiFePO_4 particle. This is clearly related to the synthesis technique used, which will have a critical bearing on the transport of lithium-ions and electrons into and out of the individual particle;

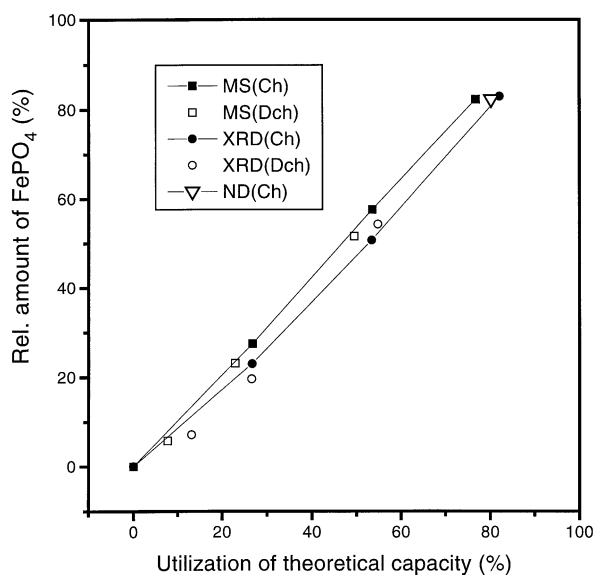


Fig. 4. The relative amount of FePO_4 vs. charge passed as obtained from Mössbauer data (circles) and XRD data (squares) (from [12]) and Rietveld refinement of ND-data (this work). For clarity, a line is drawn to connect successive points on the charge cycle.

- the electrode morphology: a range of factors combine to influence the performance of the electrode (particle-size and -shape distribution, SB/binder components, particle contact, etc.).

These two factors are clearly coupled. Given that this present ND result eliminates the possibility of “hidden” unconverted regions at the centres of larger particles, two possible models can be proposed for the mechanism for lithium extraction/insertion within a given particle in the LiFePO_4 system (Fig. 5).

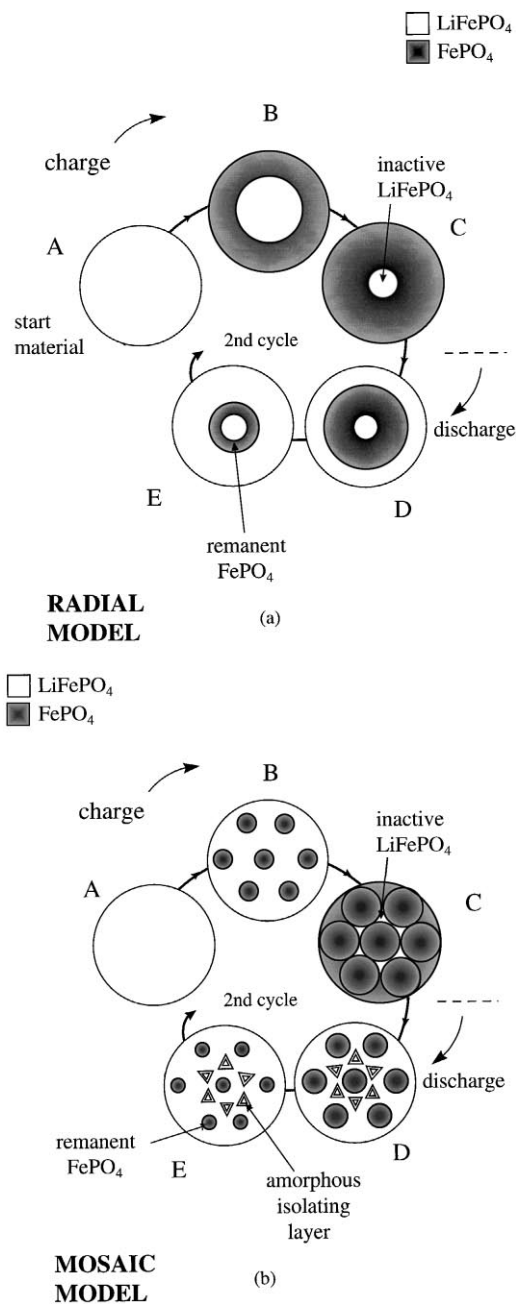


Fig. 5. Schematic representations of two possible models for lithium extraction/reinsertion into a single particle of a LiFePO_4 : a “radial model” (a); and a “mosaic model” (b). See text.

One model (the “radial model”: Fig. 5a) envisages a radius-dependent process in which the $\text{LiFePO}_4/\text{FePO}_4$ interface moves inward through each particle as the outer region converts to FePO_4 (B: Fig. 5a). During this process, lithium-ions and electrons have to move out through the newly formed FePO_4 phase. The essential source of capacity loss in this model is, thus, the unconverted LiFePO_4 at the centre of the larger particles (C: Fig. 5a), since it is not possible to extract all lithium-ions and electrons efficiently. When lithium re-insertion takes place from the outside of the particle inwards (D: Fig. 5a), a new annular $\text{LiFePO}_4/\text{FePO}_4$ interface moves quickly through the particle, and approaches the unconverted LiFePO_4 region at the centre of the particle. This region does not recombine with the inactive LiFePO_4 ; instead, an annular region of FePO_4 is left trapped around the LiFePO_4 core (E: Fig. 5a).

An alternative model (the “mosaic model”: Fig. 5b) invokes a mosaic character within each particle. The idea here is that lithium extraction/reinsertion can occur at many sites within a given particle (B: Fig. 5b). The source of capacity loss is the trapped, isolated zones of inactive LiFePO_4 formed as these separate lithium-extracted regions impinge on one another (C: Fig. 5b). On discharge, lithium re-enters the major part of these FePO_4 regions, leaving only the cores as unconverted FePO_4 . At the same time, the inactive LiFePO_4 regions are left entrapped by a thin coating of some amorphous material, formed during the initial charging process as the FePO_4 regions grew (from B to C) and finally coalesced.

Note that, to be consistent with our observations, the volumes of inactive LiFePO_4 (the labelled regions in Fig. 5a and b) should be ca. 15–20% of the total original volume of LiFePO_4 in both models, and the region of remnant FePO_4 ca. 7%. Our data is not capable of distinguishing these two models, although a slight intuitive preference must be given to the “mosaic model”, especially since it is intrinsically particle-size independent. In reality, it can be expected that some superposition of the essential features of the two models will apply, such that the “mosaic” features of the latter model will have some form of “radial” distribution.

Clearly, the limiting process is (in both models) a combination of low lithium-ion diffusion rate and low electronic

conductivity in the FePO_4 phase, which prevents the full conversion of LiFePO_4 to FePO_4 , and back again. This is indeed supported by the fact that the addition of some unidentified “electronically conductive material” is able to enhance the kinetics and the degree of material utilisation dramatically [10,11].

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