Solid State Ionics 203 (2011) 33–36

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Thermally-induced cation disorder in $LiFePO_4$

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ARTICLE INFO

Article history:
Received 28 April 2011
Received in revised form 14 July 2011
Accepted 3 August 2011
Available online 11 October 2011

Keywords:
$LiFePO_4$
Lithium cathode
X-ray diffraction
Cation disorder

ABSTRACT

$LiFePO_4$ has a fully ordered olivine structure in samples prepared by solid state reaction below ~800 °C but, with increasing temperature, a small amount of Li and Fe site exchange occurs reaching a value of about 4% just below melting at 975 °C. The disorder is reversible on annealing at lower temperatures and is detected by changes in lattice parameters and in cation site occupancies obtained by Rietveld refinement of X-ray powder diffraction data.

1. Introduction

Following the discovery by Padhi et al. [1] that $LiFePO_4$ is able to reversibly deintercalate Li to give the general formula Li_xFePO_4: $0 \leq x \leq 1$, and thereby function as a high performance cathode for lithium battery applications, there has been great interest in developing this material as a low-cost and environmentally-acceptable alternative to currently-used Co-based cathodes, principally $LiCoO_2$. For satisfactory cathode performance, the active material must be able to deintercalate rapidly both Li^+ ions and electrons and much attention has focussed on doping $LiFePO_4$ to enhance both its ionic and electronic conductivities. The electronic conductivity is usually enhanced by fabricating composites in which the $LiFePO_4$ grains are coated with a more highly conducting material such as carbon [2] or iron phosphide [3]. Attempts to modify the lithium ion conductivity by doping [4] appear to have been largely unsuccessful. By attention to alternative low-temperature synthesis routes [5], nanoparticles of $LiFePO_4$ have been prepared which exhibit modified electrochemical behaviour and give a single-phase Li insertion–deinsertion profile in contrast to the two-phase mechanism that is usually observed.

The olivine structure of $LiFePO_4$ is built of a hexagonal close packed array of oxide ions containing isolated PO_4 tetrahedra and two energetically distinguishable octahedral sites, M1 and M2. Crystallographic studies have shown in stoichiometric $LiFePO_4$, that Li occupies fully the octahedral M1, 4a site and Fe occupies the octahedral M2, 4c site [6–9]. Cation disorder between the M1 and M2 sites is an interesting research area in petrology [10] because it may give insight into the thermal history of the earth's upper mantle where olivine minerals are abundant. In the specific case of $LiFePO_4$, several diffraction studies on materials prepared by low temperature routes have shown a small amount of Li and Fe cation exchange in samples prepared hydrothermally and using wet chemistry [11,12]. A small concentration of Fe on Li sites was visualised in $LiFePO_4$ crystals using dark field scanning transmission electron microscopy, STEM [13,14]. Above ~180 °C, a fully ordered structure occurred in samples that were prepared hydrothermally as well as by direct solid state reaction.

Li–Fe site exchange, also referred to as the anti-site defect, has been shown to be the most favourable defect in $LiMPO_4$: M = Fe,Mn, Ni,Co by computer simulation [15,16]. This intrinsic defect formation can be represented using Kroger–Vink notation:

$$Li_{Li}^{x} + M_{M}^{x} \rightarrow Li_{M}' + M_{Li}^{o} \quad (1)$$

where $'$, ^{x} and ^{o} refer to nominal site charges of −1, 0 and +1.

It is not known whether the cation site exchange is an equilibrium feature of the crystal structure of $LiFePO_4$ below 180 °C or is a metastable effect resulting from low temperature synthesis. Antisite disorder has a deleterious effect on electrochemical properties of $LiFePO_4$ since its Li^+ ion mobility is limited to one-dimensional tunnels [17] parallel to [010]; these tunnels are formed by interconnected FeO_6 octahedra and PO_4 tetrahedra (Fig. 1). Any immobile Fe^{2+} ions effectively block the channels and reduce the possibilities of Li (de) intercalation [9,11]. In addition to possible antisite disorder, there is also evidence that $LiFePO_4$ can be non-stoichiometric with a small excess of Fe and deficiency of Li in samples given a final heat treatment in N_2 at 725 °C [18].

In this paper, we report a study of the temperature dependence of the crystal structure of $LiFePO_4$ and show that a small amount of cation site exchange occurs under equilibrium conditions at high

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doi:10.1016/j.ssi.2011.08.006

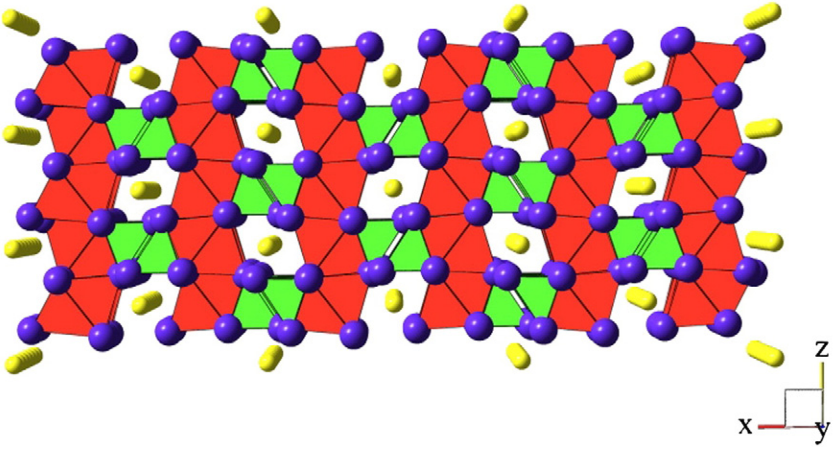

Fig. 1. $LiFePO_4$ structure parallel to (010). Lithium ions are represented as yellow balls and occupy the M1 octahedral site. Iron is octahedrally coordinated in red and green tetrahedra represent the PO_4^{3-} groups.

temperatures which is reversible on subsequent annealing at lower temperature.

2. Experimental

$LiFePO_4$ powders were synthesised by solid-state reaction. Stoichiometric amounts of Li_2CO_3 (99.99% pure, dried at 180 °C), $NH_4H_2PO_4$ (99.9% pure) and $FeC_2O_4{\bullet}2H_2O$ (99% pure) were weighed out, ground together into a paste with acetone in an agate mortar, dried and placed in a gold foil boat inside a horizontal tube furnace which was hermetically sealed to allow an atmosphere of flowing N_2. In the presence of oxygen, sample oxidation occurred as shown by the ready detection of powder X-Ray Diffraction, XRD, lines of secondary phases including Fe_2O_3 and $Li_3Fe_2(PO_4)_3$. The samples studied here showed no evidence of the presence of such oxidised phases and therefore the atmosphere during synthesis was oxygen free.

The samples were fired initially at 400 °C for 3 h and 600 °C for 3 h to decompose oxalates and carbonates, respectively. After cooling to room temperature, samples were reground, pressed to form pellets and heated at higher temperatures for 12 h in N_2 using ramps of 5 °C/min. After reaction, pellets were crushed and phase purity was investigated using a STOE STADI P X-ray powder diffractometer, in transmission mode, Mo Kα_1 radiation ($\lambda = 0.7092$ Å). Indexing of the XRD patterns was carried out using WinX^{pow} software. Peak calibration used Si external standard. Structural models were tested by refinement of the XRD data using the General Structure Analysis System, GSAS [19].

3. Results and discussion

Phase-pure samples of $LiFePO_4$ were synthesised successfully by solid state reaction at temperatures in the range 650–800 °C. Heating in N_2 was necessary to avoid oxidation of Fe. Lattice parameter data are summarised in Table 1 for a sample synthesised at 685 °C, reheated at and quenched from 975 °C and then subsequently reannealed at 880 °C. Heating at 975 °C caused an expansion in all three parameters of the orthorhombic unit cell which was largely reversed on subsequent anneal at 880 °C. Literature data for $LiFePO_4$ are also included in Table 1 and are generally similar to those for the samples both synthesised at 685 °C and subsequently annealed at 880 °C.

Table 1
Lattice parameters of $LiFePO_4$ after different heat treatments.

Heat treatment	a/Å	b/Å	c/Å	Volume/Å^3
Synthesis at 685 °C	10.3287(4)	6.0078(2)	4.6936(2)	291.25
Synthesis at 685 °C followed by heating at 975 °C	10.3535(4)	6.0179(2)	4.7008(2)	292.88
Synthesis at 685 °C followed by heating at 975 and 880 °C	10.3346(2)	6.0102(1)	4.6935(1)	291.52
Ref. 8	10.3377(5)	6.0112(2)	4.6950(2)	291.76
Ref. 9	10.3447(9)	6.0033(5)	4.6964(4)	291.66

During the initial stages of Rietveld refinement of XRD data, it appeared that some Li/Fe site exchange had occurred in the sample quenched from 975 °C. Since it is not possible to simultaneously refine site occupancies and thermal parameters of a given site using XRD data, thermal parameters for the Li and Fe sites were obtained first using the 685 °C data set for which there was no evidence of cation site exchange. These parameters were then fixed and used for all data sets and the Li/Fe cation site occupancies were allowed to refine. These thermal parameters were similar to those obtained by refinement of neutron diffraction data [20]. It was assumed that the samples had the stoichiometric $LiFePO_4$ composition and that overall cation site occupancies were full.

Results of Rietveld refinement of X-ray powder diffraction data for the three samples are summarised in Tables 2–4, with a profile plot showing the experimental, calculated and difference profiles for one sample in Fig. 2. Satisfactory refinement was obtained for all three samples. It is clear that the sample synthesised at 685 °C had full cation order to within 3 esds, as did the sample that was given a final anneal at 880 °C. However, the sample heated at 975 °C which was found to be just below the melting temperature, showed ~4% anti-site disorder with partial site exchange of Li and Fe between 4a and 4c sites. This amount of cation site exchange is well outside the error range (±3 esds) of the site occupancies (Table 3). In addition, XRD profiles and difference profiles for two models, with and without cation interchange between octahedral sites, are shown as Supplementary Fig. 1. Without cation exchange, the difference profile is

Table 2
Structural parameters of $LiFePO_4$ reacted at 685 °C.

Atom	Site	x	y	z	Occupancy (%)	100×Uiso (Å^2)
Li	4a	0	0	0	99.4(2)	1.28
Fe	4a	0	0	0	0.6(2)	1.28
Fe	4c	0.2821(1)	0.25	0.9738(4)	99.4(2)	0.46
Li	4c	0.2821(1)	0.25	0.9738(4)	0.6(2)	0.46
P	4c	0.0957(3)	0.25	0.4181(7)	100	1.05(13)
O	4c	0.0940(8)	0.25	0.7479(13)	100	1.98(31)
O	4c	0.4518(9)	0.25	0.2131(10)	100	0.98(24)
O	8 d	0.1644(6)	0.0415(8)	0.2800(7)	100	1.06(21)

Space group Pnma, $\chi^2 = 3.91$ Rwp = 3.96% Rp = 3.05%