

Mössbauer spectroscopy study of defects in hydrothermally synthesized LiFePO_4 cathode material

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Abstract Hydrothermally synthesized LiFePO_4 has been prepared with different synthesis times in order to study defects in the crystal structure and their evolution. The Mössbauer spectra can be interpreted as due to three components, Fe^{2+} in LiFePO_4 , Fe^{2+} in unreacted precursor material which resembles the Mössbauer spectrum of Fe^{2+} in vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and Fe^{3+} . The Fe^{3+} contribution differs from room temperature oxidation of the precursor material, and can partly be due to charge compensating defects in the LiFePO_4 structure. With increasing synthesis time, the latter two contributions virtually disappear from the spectra.

Keywords LiFePO_4 · Mössbauer spectroscopy · Defects

1 Introduction

Ever since the suggestion of the use of LiFePO_4 as cathode material for Li ion batteries [1] the compound has received immense interest. LiFePO_4 is cheap and non-toxic, and it shows good electrochemical properties such as high energy density, good cyclability, and high stability.

LiFePO_4 is already used in commercial Li-ion batteries, but much effort still goes into developing new synthesis methods to reduce the cost of the batteries. Hydrothermal synthesis has proven itself as a cheap, environmentally benign and easily scalable way of

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producing inorganic materials [2]. However, when synthesized hydrothermally at low temperatures, LiFePO_4 shows disappointing electro-chemical properties due to defects in the crystal structure. It is believed that the transition metal partly occupies the Li M1 sites, and thereby blocks the Li-ion diffusion pathway [3, 4].

Samples of LiFePO_4 have been synthesized with different reaction times in order to study the defect development with time. Combined neutron/X-ray diffraction studies and Mössbauer spectroscopy give detailed information on the site occupancy of the structure [5]. In this contribution we describe the Mössbauer findings in some detail.

The main conclusions from the combined Rietveld analysis (see [5] for details) are that the samples synthesized for 40 min show Fe ($\sim 7.5\%$) and vacancy ($\sim 10\%$) occupancy on M1 site (Li site) of the structure, decreasing to $\sim 2\%$ after 7 h synthesis. The crystallinity increases from $\sim 80\%$ for the sample synthesized for 40 min to $\sim 97\%$ for the sample synthesized for 7 h. The studies show that the presence of defects in the crystal structure is directly related to coexistence with the amorphous phase.

In Ref. [5], the ferrous part of the Mössbauer spectra were analysed in terms of a single distribution of quadrupole split components. In this contribution, we have added Mössbauer data of the amorphous phosphate precursor, which gives a new interpretation of the previously published Mössbauer data [5].

2 Samples and experimental methods

The precursors for the hydrothermal synthesis were prepared by mixing aqueous solutions of H_3PO_4 , FeSO_4 and LiOH , (molar ratio 1:1:4) forming a thick green gel. The synthesis was performed in Teflon lined steel autoclaves at $170\text{ }^\circ\text{C}$ for 40 min, 2 h and 7 h. The hydrothermal synthesis was done quickly after formation of the precursor material to avoid oxidation of ferrous iron. Mössbauer spectroscopy of a sample of precursor gel was measured separately, where oxidation could not be avoided. For details on the sample preparation, see Ref. [5].

Each synthesized sample was characterized by neutron and X-ray Rietveld refinement as well as X-ray and neutron pair distribution function (PDF) analysis, crystallinity determination, Mössbauer spectroscopy, ion coupled plasma (ICP) studies and scanning electron microscopy (SEM).

Mössbauer spectra were recorded at room temperature in transmission geometry using 5–10 mCi source of ^{57}Co in rhodium matrix. Isomer shifts and velocities are given relative to the centre of the spectrum of $\alpha\text{-Fe}$ at room temperature.

3 Results and analysis

Time dependent spectra of the precursor material are shown in Fig. 1. The spectra have been analysed simultaneously in terms of two components labelled Fe(II) and Fe(III) in Fig. 1. Fe(II) is assigned to high spin Fe^{2+} and simulated with a distribution of quadrupole splittings based on linear segments in the distribution function [6]. Here two segments proved to be sufficient to describe the data. Coupling between isomer-shift and quadrupole splitting was assumed. Fe(III) is assigned to high-spin Fe^{3+} and was analysed as a simple Lorentzian doublet.

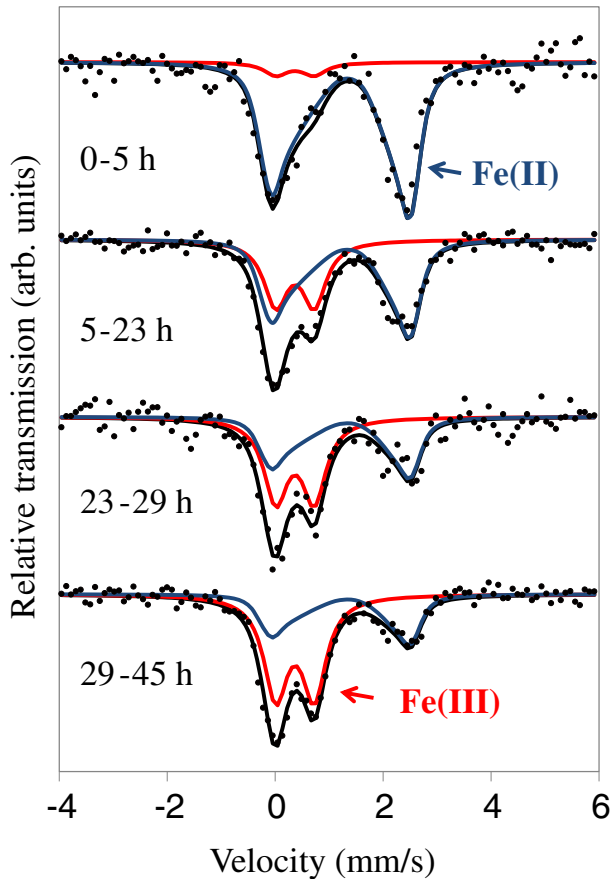


Fig. 1 Room temperature Mössbauer spectra obtained in the time intervals indicated from the preparation of the precursor materials. *Solid lines* show the fitting components and their sum

Table 1 Hyperfine parameters obtained from simultaneous analysis of the Mössbauer spectra in Fig. 1

	Fe(III)	Fe(II)
δ (mm/s)	0.37(1)	1.24(8)
ΔE_Q (mm/s)	0.74(2)	2.2(2)
Γ (mm/s)	0.52(2)	0.26(3)

For Fe(II) average hyperfine parameters are given. The coupling parameter between quadrupole splitting and isomer-shift of Fe(II) was found $d\delta/d\Delta E_Q = -0.07(2)$

In the first measurement (0–5 h) the spectrum is dominated by the Fe(II) component, and gradually the sample oxidizes and the spectra become dominated by the Fe(III) component. The hyperfine parameters are given in Table 1.

The area fraction of Fe(II) was found to decrease with a simple exponential dependence with half of the original Fe(II) area remaining after 23(2) hours.

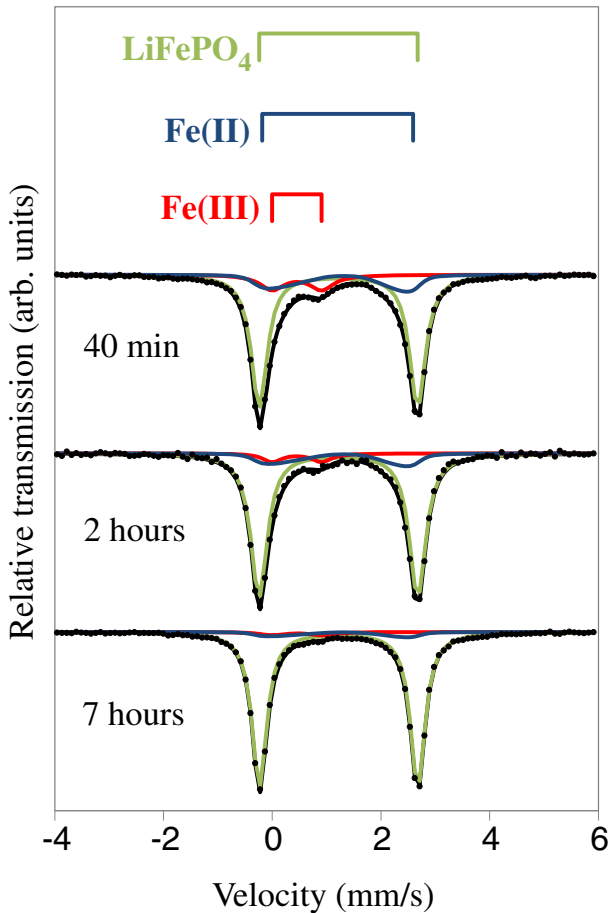


Fig. 2 Room-temperature Mössbauer spectra obtained on LiFePO_4 samples synthesized for different synthesis times as indicated. The *solid lines* show the fitting components indicated with a bar diagram at top

The Mössbauer spectra of the hydrothermally treated samples are shown in Fig. 2. The spectrum obtained from the sample synthesized for 40 min clearly shows sign of a component due to Fe^{3+} , seen as a feature at ~ 0.9 mm/s belonging to the right leg of a quadrupole doublet. This feature is less prominent in the spectra from samples with longer synthesis time.

The spectra are dominated by component(s) due to ferrous Fe. In the Mössbauer spectrum of the sample obtained after 40 min synthesis, the lines due to ferrous Fe shows a clear asymmetry; the line at ~ 2.65 mm/s is broader on the left hand side, and the line at ~ -0.25 mm/s is broader on the right hand side. This asymmetry suggests the presence of Fe environments that give rise to ferrous doublets with lower quadrupole splitting than the dominating component.

There are several ways to describe this asymmetry. In [5] the asymmetry was described with a single quadrupole splitting distribution. Bini et al., [7] observed similar asymmetry in the Mössbauer spectra of microwave-hydrothermal LiFePO_4 , and the asymmetry was

Table 2 Hyperfine parameters and spectral areas found from the analysis of synthesized samples of LiFePO₄

Spectral comp.	Synt. time	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)	Area (%)
LiFePO ₄	40 m	1.218 (4)	2.913(4)	0.36(1)	73(2)
	2 h	1.217(4)	2.918(8)	0.37(1)	82(2)
	7 h	1.222(4)	2.913(4)	0.33(1)	91(2)
Fe(II) ^a	40 m	1.24(8)	2.2(2)	0.26(3)	15(1)
	2 h				12(2)
	7 h				6(1)
Fe(III)	40 m	0.45(2)	0.91(2)	0.42(6)	12(1)
	2 h				6(1)
	7 h				3(1)

^aSame average parameters as in Table 1

described with the inclusion of two additional quadrupole split components interpreted to be due to structural defects in the LiFePO₄ structure.

Here, however, we find that this feature is adequately described using a dominating doublet assigned to Fe²⁺ in LiFePO₄, (marked “LiFePO₄” in Fig. 2) and Fe(II) identical to the ferrous component found in the Mössbauer spectra of the precursor material. This method is the most simple in terms of interpretation and number of fitting variables.

Additionally, the spectra were analysed with a quadrupole doublet marked Fe(III) assigned to high-spin Fe³⁺. As this component is only well visible in the Mössbauer spectrum obtained of the sample synthesized for 40 min, the same hyperfine parameters were used in the simultaneous analysis of the data obtained for samples synthesized for 2 and 7 h. Hyperfine parameters and spectral areas are gathered in Table 2.

The isomer-shift and quadrupole splitting of Fe²⁺ in LiFePO₄ show negligible dependence on synthesis time, but the line-width is narrowest for the sample synthesized for 7 h. The hyperfine parameters are in reasonable agreement with reported hyperfine parameters of Fe²⁺ in LiFePO₄ [7, 8], although the quadrupole splitting obtained here is significantly lower.

4 Discussion

From PDF data of the precursor (not shown) and previous diffraction studies [9–11] Fe²⁺ seem sitting in amorphous phosphate structure that could resemble vivianite (Fe₃(PO₄)₂·8H₂O). The Mössbauer spectrum of vivianite [12] resembles the Mössbauer spectrum of Fe(II) obtained here, i.e. broader absorption at the left hand side, and the average parameters obtained (Table 1) are consistent with the average parameters from Ref. [12] supporting this suggestion.

Within the spectral resolution, it is not possible to conclude that the Fe(II) component observed in the samples (Fig. 2) differs significantly from the Fe(II) component of the precursor material (Fig. 1). There could be differences, but undetectable due to the strong overlap of the component due to Fe²⁺ in LiFePO₄. It should be emphasized that the assumption that they are identical is the simplest explanation of the experimental data.

The hyperfine parameters of Fe(III) are different in the case of oxidized precursor material (Table 1) and synthesized samples (Table 2). In the latter case, accurate determination of the hyperfine parameters of Fe(III) is hampered by overlap of the left hand leg of the

Fe(III) doublet with the dominating ferrous components. However, the right hand leg which is not significantly overlapping with other components is not found at the same position in the two cases; 0.74(2) mm/s in the Mössbauer spectra of oxidized precursor material and 0.91(2) mm/s in the Mössbauer spectra of synthesised samples, demonstrating that the Fe³⁺ environment is not identical in the two cases.

This can be partly explained as due to Fe³⁺ in the LiFePO₄ structure. Charge compensation due to Li vacancies in the structure [5] can account for ~2 % of the as Fe³⁺. It is, however, not possible to conclude that the environment of Fe³⁺ in the unreacted precursor material of synthesized samples is identical with Fe³⁺ environments formed by oxidation at room temperature of Fe²⁺ in the precursor material.

5 Conclusions

Mössbauer spectroscopy on precursor and hydrothermally synthesized samples of LiFePO₄ for different times has been performed. The Mössbauer spectra of the hydrothermally synthesized samples can be analysed in terms of three contributions due to (1) Fe²⁺ in LiFePO₄, (2) Fe²⁺ indistinguishable from Fe²⁺ in the amorphous phosphate precursor, resembling the spectrum of vivianite (Fe₃(PO₄)₂·8H₂O) and (3) Fe³⁺ which is different from simple oxidation of the precursor material and could have contribution from charge compensating Fe³⁺ in the LiFePO₄ structure. With increased synthesis time, the latter two contributions virtually disappear and the line-width of the doublet due to Fe²⁺ in LiFePO₄ decreases, indicating formation of defect reduced LiFePO₄.

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