^{57}Fe Mössbauer study of Li$_x$Fe$_{1\text{-}y}$Co$_y$PO$_4$ (y = 0, 0.1, 0.2) as cathode material for Li-ion batteries

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Abstract Lithium iron phosphates LiFe$_{1\text{-}y}$Co$_y$PO$_4$ (y = 0, 0.1, 0.2) exposed to a charging process were studied by ^{57}Fe Mössbauer spectroscopy taking into account XRD and SEM data. Hyperfine parameters of the spectra were determined above and below the magnetic ordering temperature for all the samples. It was shown that the presence of Co impurity atoms in lithium phosphates gives no effect on the hyperfine interaction of ^{57}Fe^{2+} cations. However, Co atoms in the nearest cation environment of Fe atoms lead to a significant change of the hyperfine interactions of ^{57}Fe^{3+} cations. The Co impurity atoms distribution over the positions of the iron atoms in the structure is found not to be statistical, but correlated.

Keywords Mössbauer spectroscopy · Lithium iron phosphate · Cobalt doping · Lithium ion batteries

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1 Introduction

Olivine-type lithium iron phosphate $LiFePO_4$ is a promising material for rechargeable Li-ion batteries with enhanced energy storage capacity, high operating voltage, and good thermal and chemical stability, which is used in lithium ion accumulators [1]. In the process of charging, the extraction of Li atoms from the lattice results in a change of the Fe ion oxidation state (from Fe^{2+} in $LiFePO_4$ to Fe^{3+} in $FePO_4$). One can expect that substitution of Fe atoms by other transition-metal atoms will cause an improvement of the characteristics of the cathode material and in particular will lead to a charge rate increase [2].

In this paper, [57]Fe Mössbauer spectroscopy was used to investigate the effect of cobalt in the structure of cathode materials based on $LiFePO_4$ when exposed to the charging process. In the present study, the focus is on the method of fitting the Mössbauer spectra. The spectra below the Néel temperature were analyzed by the method of reconstruction of the hyperfine field distribution with the diagonalization of the full static Hamiltonian, which includes both the magnetic dipole and electric quadrupole interaction. We hope that this study will help to provide a new insight into charge/discharge processes of doped cathode materials.

2 Experimental

$LiFePO_4$-based composite materials coated with a thin carbon layer were prepared by a sol-gel process:

$$Fe\,(NO_3)_3 \cdot 9H_2O + LiNO_3 + NH_4H_2PO_4 \rightarrow LiFePO_4 + 4NO_2 + NO + 12H_2O.$$

To obtain charged samples, an electrode paste, which is applied to the cathode grid, was prepared using synthesized materials. The resulting electrode was pressed and dried. Then the electrode was placed in a three-electrode ($LiFePO_4$/Li/Li) electrochemical cell where charging was carried out [3]. Cobalt was mixed in the initial constituent materials in the necessary proportion for the synthesis of $LiFe_{1-y}Co_yPO_4$. The voltage for redox couples Co^{2+}/Co^{3+} is much higher than that for the Fe^{2+}/Fe^{3+} couple [4]. Therefore, Co^{2+} ions do not take part in electrochemical processes at potentials corresponding to the charging of $LiFePO_4$. From this point of view, one can assume that doping of the $FePO_4$ sample by these divalent cations can lead to an ion conductivity increase [2]. Lithium transfer in the Fe^{3+} containing phase determines the rate of the charging processes. Therefore, an acceleration of the battery charging process can be expected.

X-ray diffraction (XRD) measurements and data analysis were performed on a Rigaku D/MAX 2200 diffractometer with CuK_α radiation and Rigaku Application Data Processing software. To examine the microstructure of the obtained materials a scanning electron microscope Carl Zeiss NVision 40 was used.

Mössbauer spectra have been recorded by using a conventional spectrometer MS-1101E of electromechanical-type with the constant acceleration mode and absorption geometry in the temperature range 4.8–300 K. The time dependence of the Doppler rate has a "triangular" shape. The spectra corresponding to the ascending and descending areas of the "triangle" have been registered in 1024 channels. A [57]Co (Rh) γ-ray source was used. Calibration has been done using an α-Fe foil as reference sample. Low temperature spectra have been recorded by cooling the sample with the help of a helium cryostat SHI-850-5 from JANIS RESEARCH. The recorded spectra were fitted with hyperfine parameter distributions by the SpectrRelax software [5].
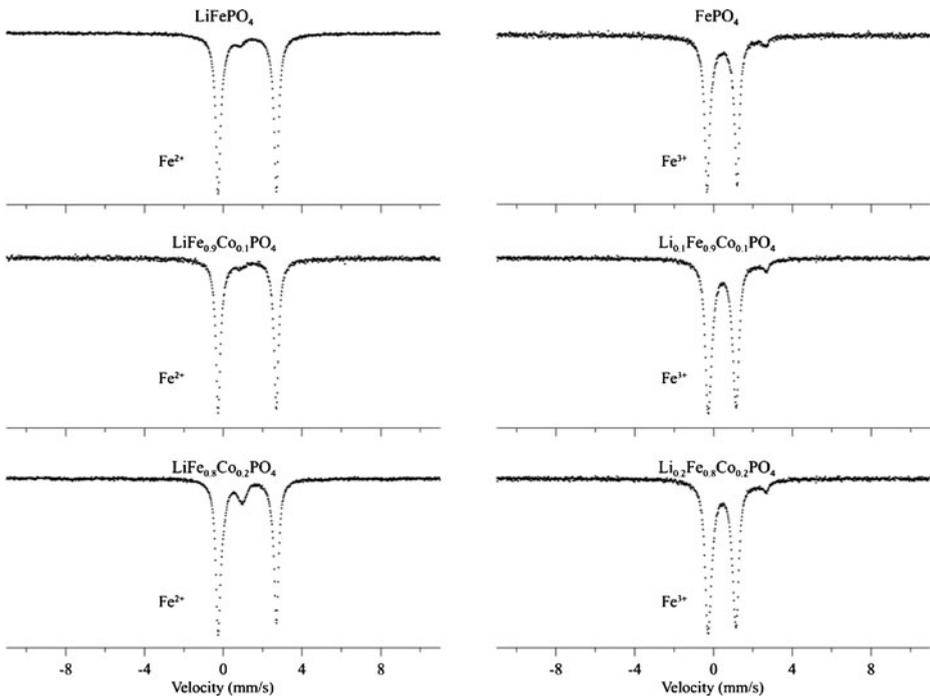
Fig. 1 Mössbauer spectra of $Li_xFe_{1-y}Co_yPO_4$ with different relative content of Co measured at room temperature

3 Results and discussion

According to X-ray data all investigated materials ($LiFe_{1-y}Co_yPO_4/C$ for y values from 0 to 0.2) crystallize in orthorhombic modification, s.g. *Pnma*. All unit cell parameters of the structure of the synthesized materials decrease with increasing the relative content of Co^{2+} ions [6].

Electron microscopy data show that the average particle size in the $LiFePO_4/C$ composite is about 50 nm while Co^{2+} incorporation results in the growth of the particle size up to 320 nm for the $LiFe_{0.8}Co_{0.2}PO_4/C$ sample [6].

According to the general statements the conductivity should increase only for the charging process. The lithium transfer trough the $LiFe_{1-y}Co_yPO_4$ phase determines the conductivity in the discharging process. In this phase the charge carrier concentration shouldn't depend on the cobalt concentration. But noticeable discharge rate increases were observed for doped samples too. In order to understand the nature of these processes the Mössbauer spectra of the cobalt containing $LiFePO_4$-based materials were investigated.

The Mössbauer spectra of undoped samples obtained at room temperature can be described by two quadrupole doublets, which refer to the Fe^{3+} and Fe^{2+} states (Fig. 1). The spectra do not appreciably change with the addition of cobalt impurity atoms. With increasing the relative content of cobalt, the Mössbauer parameters of the Fe^{2+} subspectrum change only insignificantly, while the parameters of the Fe^{3+} subspectrum change to a greater extent (see Table 1). We did not determine hyperfine parameters for all local positions of ^{57}Fe atoms, as there are only small changes in the spectra. Further measurements were carried out at temperatures below the Neel point ($T < T_N$).

Table 1 Ranges of the Mössbauer hyperfine parameters, derived from the analysis of $Li_xFe_{1-y}Co_yPO_4$ at room temperature where δ is isomer shift, ΔE is quadrupole splitting

Samples	State	δ(mm/s)	ΔE(mm/s)
$LiFe_{1-y}Co_yPO_4$	Fe^{2+}	1.18–1.22	2.92–3.02
$Li_yFe_{1-y}Co_yPO_4$	Fe^{3+}	0.43–0.48	2.28–3.04
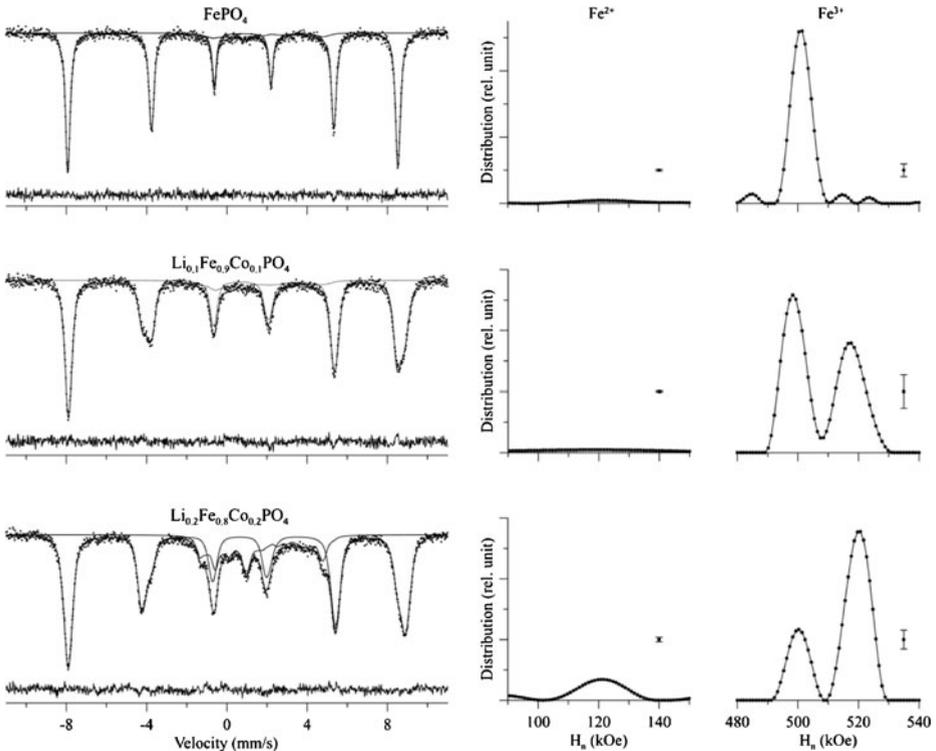
Fig. 2 Mössbauer spectra of $Li_xFe_{1-y}Co_yPO_4$ with different charge state and different concentration of Co measured at 5 K and corresponding distributions of the hyperfine magnetic field $p(H_n)$

Mössbauer spectra recorded at 5 K are more informative than those recorded at room temperature. A change in the ratio of the subspectrum intensity for ferrous and ferric atoms was observed during charging for all the samples. Cobalt incorporation vastly changes the subspectra of Fe^{3+}, some lines become broadened and some of them split up (Fig. 2), while the subspectra of Fe^{2+} (Fig. 3) do not noticeably change. The spectra at 5 K were fitted with two sets (Fe^{2+}/Fe^{3+}) of eight PseudoVoigt absorption lines by diagonalizing the 4×4 magnetic and quadrupole Hamiltonian matrix to get relative line positions and intensities. At the same time, a reconstruction of the hyperfine field distributions in the presence of a linear correlation between all of the hyperfine parameters of the spectrum was carried out.

Substitution of Co atoms for Fe in the structure of $FePO_4$ leads to the appearance of another peak in the hyperfine field distribution (Fig. 2). This is caused by the fact that the subspectra of Fe^{3+} consist of the superposition of two subspectra. The first one totally
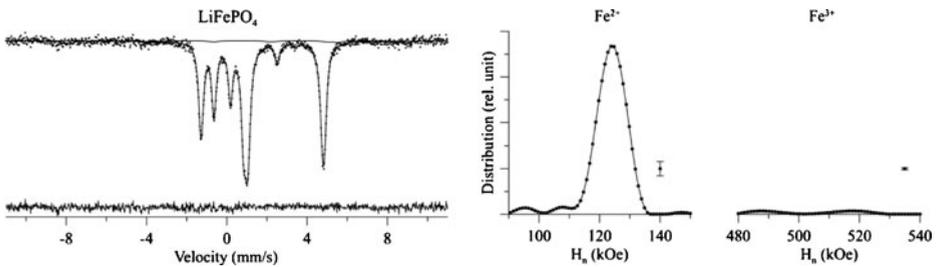
Fig. 3 Mössbauer spectra of LiFePO$_4$ measured at 5 K and corresponding distributions of the hyperfine magnetic field p(H_n)

matches the spectrum of undoped FePO$_4$ (Table 2), where Fe^{3+} is in a position surrounded by four Fe atoms in the nearest cation environment (4Fe), whereas the second one significantly differs as cobalt atom appear instead of iron atom in the nearest cation environment (3Fe1Co). Increasing the concentration of cobalt results in the change of the relative intensity of the two configurations: Fe^{3+}(4Fe) and Fe^{3+}(3Fe1Co) (Fig. 2). Spectra of partially (not completely) charged samples consist of a superposition of three states of the iron atom: Fe^{2+}, Fe^{3+}(4Fe) and Fe^{3+}(3Fe1Co). As can be seen from the hyperfine magnetic field distributions for Fe^{3+} (Fig. 2), the positions of the iron configurations (4Fe) and (3Fe1Co) are well resolvable, and no other states were observed. The hyperfine parameters of the subspectra for the two states of Fe^{3+} significantly differ (Table 2). Substitution of Fe by Co atom in the nearest environment of Fe^{3+} cation increases the isomer shift ($\Delta \delta = 0,05 \div 0,08$ mm/s), the quadrupole coupling constant ($\Delta(e^2qQ) \cong 2,2 \div 2.8$ mm/s) and the magnetic hyperfine field ($\Delta H_n = 20 \div 22$ kOe). The parameters of the Fe^{2+} subspectrum, on the other hand, are almost independent of the relative content of cobalt (Table 2).

If a random cobalt ion distribution is assumed in the Li$_{0.1}$Fe$_{0.9}$Co$_{0.1}$PO$_4$ structure, it can be easily calculated that 65.61 % of the iron ions in Li$_{0.1}$Fe$_{0.9}$Co$_{0.1}$PO$_4$ should have only iron ions as the nearest neighbours (4Fe), 29.16 % should have one cobalt and three iron ions (3Fe1Co), and 4.86 %, 0.36 % and 0.01 % should have 2, 3 or 4 cobalt ions, respectively (2Fe2Co, 1Fe3Co, 4Co). In that case we might be able to observe several subspectra depending on the Mössbauer spectrum quality. For a random cobalt ion distribution the ratio of the intensities of the two most intense subspectra should be equal to ≈ 2.25. The observed ratio of the intensities however is much less and ≈ 1.20. Such a result can only explained if an ordered distribution of cobalt atoms exists so that in the nearest Fe^{3+} ion environment there is no more than one cobalt atom (Fe^{3+}(3Fe1Co)). The concentration of the Fe^{3+}(3Fe1Co) sites increases with cobalt content increase (Fig. 2). In the Li$_{0.2}$Fe$_{0.8}$Co$_{0.2}$PO$_4$ spectra the ratio of the Fe(4Fe) and Fe^{3+}(3Fe1Co) line intensities corresponds to ≈ 0.37. In the case of a random cobalt ion distribution it should be 1:1 and the subspectrum of Fe^{3+}(2Fe2Co) should have an intensity about 40 % of Fe^{3+}(4Fe) subspectrum. But we did not observe at all Fe^{3+} ions which are surrounded by two Fe and two Co atoms (2Fe2Co) in spectrum (Fig. 2).

Thus the analysis of the Mössbauer spectra of the investigated phosphates with different Co content allows to conclude that the partial substitution of cobalt atoms for iron in LiFePO$_4$ structure results in only one additional Fe^{3+}ions position appearance, which is attributed to three Fe and one Co atom in the nearest cation environment of Fe^{3+}(3Fe1Co).

Table 2 Values of the Mössbauer hyperfine parameters, derived from the analysis of the hyperfine field distributions for $Li_xFe_{1-y}Co_yPO_4$ at 5 K, where δ is the isomer shift, e^2qQ is the quadrupole coupling constant and H_n is the magnetic hyperfine field

Sample	State	δ(mm/s)	e^2qQ(mm/s)	H_n(kOe)
$LiFePO_4$	Fe^{2+}	1.35 ± 0.01	5.53 ± 0.02	123.1 ± 0.4
$LiFe_{0.9}Co_{0.1}PO_4$	Fe^{2+}	1.35 ± 0.01	5.57 ± 0.03	123.9 ± 0.6
$LiFe_{0.8}Co_{0.2}PO_4$	Fe^{2+}	1.35 ± 0.01	5.58 ± 0.02	122.9 ± 1.4
$FePO_4$	Fe^{3+}(4Fe)	0.54 ± 0.01	-2.73 ± 0.04	501.1 ± 0.2
$Li_{0.1}Fe_{0.9}Co_{0.1}PO_4$	Fe^{3+}(4Fe)	0.52 ± 0.01	-2.97 ± 0.08	497.6 ± 0.8
	Fe^{3+}(3Fe1Co)	0.57 ± 0.01	-0.77 ± 0.16	517.7 ± 1.5
$Li_{0.2}Fe_{0.8}Co_{0.2}PO_4$	Fe^{3+}(4Fe)	0.49 ± 0.01	-3.19 ± 0.11	499.8 ± 0.8
	Fe^{3+}(3Fe1Co)	0.57 ± 0.01	-0.40 ± 0.07	520.8 ± 0.4

4 Conclusion

Lithium iron phosphates $LiFePO_4$, $LiFe_{0.9}Co_{0.1}PO_4$ and $LiFe_{0.8}Co_{0.2}PO_4$, exposed to a charging process were studied by ^{57}Fe Mössbauer spectroscopy. Hyperfine parameters of the spectra were determined above and below the magnetic ordering temperature for all the samples. From this the following facts were established:

1) The presence of impurity Co atoms in lithium phosphates:

   - gives no effect on the hyperfine interaction of ^{57}Fe nuclei for Fe^{2+} cations;
   - Co atoms in the nearest cationic environment of Fe atoms lead to a significant change of the hyperfine interaction of ^{57}Fe for Fe^{3+} cations.

2) The Co impurity atom distribution on the positions of the iron atoms in the structure is not statistical, but correlated.

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