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Lithium intercalation and deintercalation into lithium–iron phosphates doped with cobalt

Svetlana A. Novikova,[a] Sergei A. Yaroslavtsev,[b] Vyacheslav S. Rusakov,[b] Tatyana L. Kulova,[c] Alexander M. Skundin[c] and Andrei B. Yaroslavtsev*[a,d]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 1279; e-mail: yaroslav@igic.ras.ru*
[b] *Department of Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation*
[d] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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The study of processes occurring during the charge and discharge of a lithium ion battery with a cathode based on $LiFePO_4$ doped with cobalt ions and coated with a thin layer of carbon by means of X-ray diffraction analysis, electrochemical tests and Mössbauer spectroscopy demonstrated that as a result of Co^{2+} incorporation into the $LiFePO_4/C$ cathode material, the charge/discharge rate of the battery increased; cobalt ions are orderly distributed in the structure of the cathode material, both in charged and discharged state, in such a way that the nearest environment of iron contains no more than one cobalt ion.

Progress in the development of rechargeable batteries primarily involves an enhancement of their reliability, response times and capacity. From this point of view, cathode materials based on the lithium–iron double phosphate $LiFePO_4$ with the olivine structure are of interest due to their high capacity (up to 160 mAh g^{-1}) and comparatively low costs.[1–3] The anionic sublattice of this material has high stability. Furthermore, the structures of lithiated ($LiFePO_4$) and delithiated forms ($FePO_4$) are similar. Nevertheless, their mutual solubility is low.[4] As a result, the charging and discharging of $LiFePO_4$ occurs in a narrow voltage range (3.5 V), and the electrolyte components have low oxidizability.[5]

On the other hand, a drawback of $LiFePO_4$ is that it has low electron and mostly ion conductivity,[6] which limits the applicability of a battery with such cathodes to systems that require a high peak output. To improve the properties of the cathode material, it is expedient to obtain nanosized particles coated with carbon and to increase ion conductivity which is considerably lower than electron conductivity.[4]

The aim of this work was to study the processes of defect formation and ordering that occur during the charging and discharging of cells with cathodes based on $LiFePO_4$ doped with cobalt ions.

$LiFe_{1-x}Co_xPO_4/C$ materials were prepared by a sol–gel process described elsewhere.[7,8] The samples contained ~4 wt% carbon. The mean particle size of non-doped $LiFePO_4$ was 50 nm, whereas the particle size in a $LiFe_{0.98}Co_{0.02}PO_4/C$ sample was 250 nm. An increase in the cobalt content to 20% resulted in a comparatively small increase in the particle size to 320 nm.

According to X-ray diffraction data, the synthesis gives a one-phase material corresponding to the orthorhombic $LiFePO_4$ modification. On the other hand, the incorporation of Co^{2+} ions results in a gradual change in unit cell parameters (Figure 1). Cell charging results in the conversion of samples to $FePO_4$. Samples with intermediate iron oxidation states always contain two phases, namely, $FePO_4$ and $LiFePO_4$.

Tests in an electrochemical cell were carried out using the samples of $LiFePO_4$, $LiFe_{0.98}Co_{0.02}PO_4$, $LiFe_{0.95}Co_{0.05}PO_4$, $LiFe_{0.9}Co_{0.1}PO_4$ and $LiFe_{0.8}Co_{0.2}PO_4$. The charging capacity is reduced with increase in the concentration of doping cobalt ions due to a decrease in the concentration of iron ions in the material since the charging processes in these materials are determined by changes in the valence state of these ions.[8] On the other hand, as cobalt ions are incorporated into $LiFePO_4$, the cell charging rate grows noticeably and passes through a maximum. The charging rates of $LiFe_{0.98}Co_{0.02}PO_4$ and $LiFe_{0.95}Co_{0.05}PO_4$ samples increase by a factor of about 3. The charging rate of a cell with a $LiFePO_4$ based cathode is determined by the transfer rate of lithium ions and by the particle size.[4] Therefore, this rate in such materials can be characterised by the specific resistivity of the material calculated from the voltammetric characteristics of cell charging and discharging. The highest charging rate, the highest lithium diffusion coefficient and hence the lowest resistance are observed in the $LiFe_{0.98}Co_{0.02}PO_4$ sample whose specific resistivity decreases by more than an order of magnitude, both during cell charging [from $(9.69\pm0.05)\times10^{10}$ Ohm cm for $LiFePO_4$ to $(5.89\pm0.07)\times10^{9}$ Ohm cm for $LiFe_{0.98}Co_{0.02}PO_4$] and discharging [from $(1.39\pm0.01)\times10^{11}$ Ohm cm for $LiFePO_4$ to $(9.55\pm0.04)\times10^{9}$ Ohm cm for $LiFe_{0.98}Co_{0.02}PO_4$].

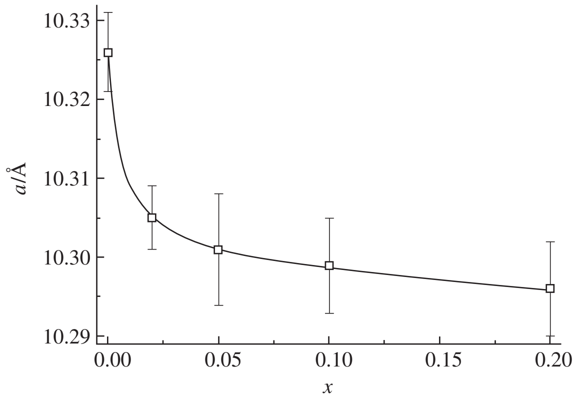

Figure 1 Effect of cobalt content *x* on the unit cell parameter *a* of $LiFe_{1-x}Co_xPO_4$.

Strictly speaking, this effect had to be expected for the charging process only, since each incorporated cobalt ion in the delithiated form ($Li_xFe_{1-x}Co_xPO_4$) should match one lithium ion in an interstice that serves as the charge carrier in this process. The diffusion coefficient of lithium directly depends on the concentration of defects and should raise with the cobalt content at initial doping stages. However, as the cobalt content is increased further, this effect is hindered by defect association processes. During discharge, the sample resistance is determined by transfer in the $LiFe_{1-x}Co_xPO_4$ phase. From general considerations, the concentration of carriers in it should not depend on the cobalt concentration. Obviously, the rate of the transfer processes is determined by defect formation and ordering processes in doped samples. To describe them, we studied the Mössbauer spectra of these materials at 5 K. According to Lee and Kim,[9] the Néel points are about 60–120 K for $FePO_4$ and 20–50 K for $LiFePO_4$, below which the Mössbauer spectra of $LiFePO_4$ and $FePO_4$ are characterized by hyperfine magnetic structures. In this case, $LiFePO_4$ has a spectrum with hyperfine parameters characteristic of divalent iron ions: isomer shift $\delta = 1.351\pm0.003$ mm s^{-1}, quadrupole splitting[†] $\Delta E_Q = 3.04\pm0.02$ mm s^{-1}, magnetic hyperfine field $H_{hf} = 123.1\pm0.4$ kOe, and resonance line width $\Gamma = 0.243\pm0.004$ mm s^{-1} [Figure 2(*a*)]. The hyperfine spectral parameters of $FePO_4$ are characteristic of trivalent iron ions, namely, $\delta = 0.543\pm0.004$ mm s^{-1}, $\Delta E_Q = -1.57\pm0.03$ mm s^{-1}, $H_{hf} = 501.1\pm0.2$ kOe, and $\Gamma = 0.211\pm0.009$ mm s^{-1} [Figure 2(*b*)]. At the same time, a small fraction of iron with the other valence remains in each sample.

Doping with cobalt does almost not change the Mössbauer spectrum of $LiFe_{0.9}Co_{0.1}PO_4$ *versus* $LiFePO_4$. Much greater changes are observed in the spectrum of $Li_{0.1}Fe_{0.9}Co_{0.1}PO_4$ [Figure 2(*c*)], where the resonance lines are broadened considerably, and splitting into two components is distinctly observed at Doppler velocities of –4 and 8.5 mm s^{-1}. This is caused by the fact that this spectrum is a superposition of two subspectra, the first of which has a relative intensity of 54.5±1.4% and totally matches the spectrum of undoped $FePO_4$, whereas the second one has the hyperfine parameters $\delta = 0.567\pm0.004$ mm s^{-1}, $\Delta E_Q = -0.44\pm0.02$ mm s^{-1}, $H_{hf} = 517.7\pm1.5$ kOe, $\Gamma = 0.412\pm0.005$ mm s^{-1} and an intensity of 45.5±1.4%. The environment of each iron ion in similar structures of $LiFePO_4$ and $FePO_4$ contains four ions of the same kind having common vertices of the coordination polyhedra. If cobalt ions are randomly distributed in iron positions, 65.61% of iron ions in $Li_{0.1}Fe_{0.9}Co_{0.1}PO_4$ should have only iron ions as the nearest neighbours, 29.16% should have one cobalt atom, 4.86% should have two cobalt ions, while 0.36 and 0.01% should have three or four cobalt ions, respectively. Thus, depending on the quality of the Mössbauer spectrum, we can obtain a few subspectra with an intensity ratio of ~66 : 29 : 5 for the three most intense ones. If clusters were formed, the difference in the intensities of the subspectra would only increase. The intensity ratio of ~55 : 45 can only be observed in case of ordered distribution of cobalt that should only be located in iron ion environments. The predominating component in the spectrum of a $Li_{0.2}Fe_{0.8}Co_{0.2}PO_4$ sample corresponds to iron ions having one cobalt ion in the coordination environment, but there are still no iron ions with two neighbouring cobalt ions.

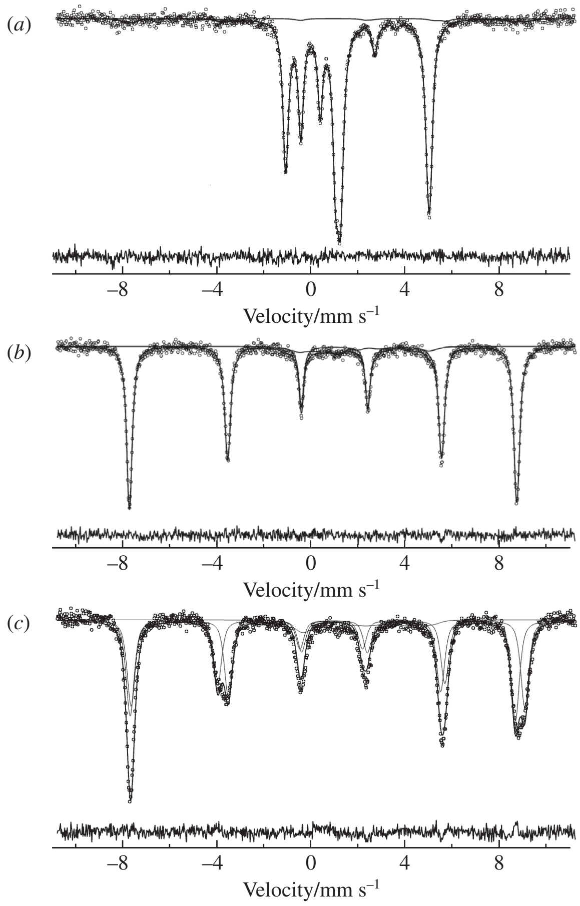

Figure 2 Mössbauer spectra of (*a*) $LiFePO_4$, (*b*) $FePO_4$ and (*c*) $Li_{0.1}Fe_{0.9}Co_{0.1}PO_4$ at 5 K. The dots represent the experimental intensities, and the lines show their decomposition into components.

Thus, the Mössbauer spectroscopy data unambiguously indicate that the distribution of cobalt ions in the structure is ordered. This is unexpected. Due to the low mutual solubility of the $LiFePO_4$ and $FePO_4$ phases,[4] it could be expected that, during charging, cobalt ions would be concentrated in the centres of cathode material particles where the $LiFePO_4$ phase remains. However, it does not occur in reality. This effect may be favoured by a low mobility of cobalt ions and their ordering in the sample. For this reason, it can be assumed that the increase in the ion conductivity of samples in the phase corresponding to the charged state ($Li_xFe_{1-x}Co_xPO_4$) is due to interstices filling of the of the $FePO_4$ structure with lithium ions. On the other hand, the increase in the discharge rate determined by processes that occur in the $LiFe_{1-x}Co_xPO_4$ phase may result from local structure distortions due to differences in the ionic sizes of cobalt and iron, structural ordering or facilitation of lithium intercalation owing to the presence of some original amount of lithium ions in the $Li_xFe_{1-x}Co_xPO_4$ structure.

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[†] The quadrupole splitting was found taking into account the asymmetry of the electric field gradient tensor and given with the sign which actually refers to that of the main component of this tensor.