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Delithiation of olivine – structured $LiFe_xMn_{1-x}PO_4$ cathode materials. Mössbauer studies

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This paper presents the results of applying the ^{57}Fe Mössbauer effect technique to studies of the delithiation mechanism of $Li_xMn_{0.55}Fe_{0.45}PO_4$ olivine samples, and also investigations of the origin of the widely discussed, astonishing high electronic conductivity of tungsten-doped $LiFePO_4$ samples, providing evidence of the presence of a residual, iron-containing and highly conductive phase. The delithiation process is perceived by iron ions as a change of their valence and symmetry of the local surroundings upon lithium extraction. The $Li_xMn_{0.55}Fe_{0.45}PO_4$ compound, which belongs to a novel group of cathode materials for Li-ion batteries, exhibits a single-phase deintercalation region, in contrast to $LiFePO_4$ exhibiting two-phase mechanism of electrochemical lithium extraction/insertion in the entire lithium concentration range, as well as to $LiMnPO_4$, for which the deintercalation process is practically irreversible. The range of deintercalation mechanism in $Li_xMn_{0.55}Fe_{0.45}PO_4$ was found to be exactly related to the content of Fe^{2+} ions in the cathode material. A surface sensitive technique, Conversion Electron Mössbauer Spectroscopy (CEMS), was used to prove the presence of traces of iron phosphides on the grain surfaces of tungsten-doped $LiFePO_4$ samples, pointing to the minor phase as being responsible for the high electronic conductivity of these samples.

Key words: *$LiMn_yFe_{1-y}PO_4$; lithium deintercalation; cathode material for lithium cells; Mössbauer spectroscopy*

1. Introduction

$LiFePO_4$ belongs to the group of $LiFeXO_4$ compounds containing large polyanions $(XO_4)^{y-}$ (where X = S, P, As, Mo, W; $y = 2$ or 3) and has been pointed out already by Goodenough [1, 2] as a promising cathode material for Li-ion batteries. The novel, olivine structured $LiFePO_4$-based group of cathode materials are stable, environmentally benign, and of potentially high stored energy density, but with one serious drawback – insulating properties (electrical conductivity of the order of 10^{-10} S/cm. Advantageous

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operational parameters of a Li-ion battery such as achievable high current density or a fast and fully reversible charge process, require an electronically conductive cathode material. Therefore, efforts have been concentrated on a significant improvement of its conductivity by a selective substitution of Li or Fe in $LiFePO_4$ with other metals. The goal is to overcome the limitations caused by electronic structure and its limiting influence on the transport properties of cathode materials.

The extraction of lithium from $LiFePO_4$ or $LiMnPO_4$ in the charging process of a lithium cell leads to the coexistence of two phases: one with an unchanged initial composition and another with zero lithium content [3, 4]. Moreover, in the case of $LiMnPO_4$, the process is almost irreversible. Substitution of Fe with Mn, yielding $LiMn_yFe_{1-y}PO_4$, substantially changes the nature of the lithium extraction process [5, 6]. For some compositions y, the initial delithiation process ($x = 1$ down to y) commences according to the deintercalation mechanism (related to $Fe^{2+} \to Fe^{3+}$ oxidation):

$$LiMn_yFe_{1-y}PO_4 - xLi^+ - xe^- \to Li_{1-x}Mn_yFe_{1-y}PO_4 \tag{1}$$

which means that a single-phase cathode material is observed with homogenous, gradually falling lithium content. A further lithium extraction ($0 < 1 - x < y$), related to subsequent $Mn^{2+} \to Mn^{3+}$ oxidation and accompanied by a 0.5 V voltage rise in the charge curve, leads to a two-phase system:

$$Li_yMn_yFe_{1-y}PO_4 - xLi^+ - xe^- \to x/y\ Mn_yFe_{1-y}PO_4 + (y - x)/y\ Li_yMn_yFe_{1-y}PO_4 \tag{2}$$

This phenomenon was observed by Yamada et al. [5] who used a chemical method for lithium extraction from $LiMn_yFe_{1-y}PO_4$.

In this work, the results of ^{57}Fe Mössbauer spectroscopy performed on samples obtained by electrochemical lithium extraction in $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ cells are presented, as are the CEMS results obtained for tungsten-doped and pristine $LiFePO_4$ samples.

2. Experimental details

The $LiMn_{0.55}Fe_{0.45}PO_4$ samples were synthesized by a high-temperature (750 °C) reaction from Li_2CO_3, $MnCO_3$, $FeC_2O_4 \cdot 2H_2O$ and $NH_4H_2PO_4$; the samples were XRD-confirmed to be single-phase with an orthorhombic olivine structure (*Pmna*). The substitution of smaller Fe^{2+} ions by larger Mn^{2+} ions leads to an evident increase of all cell parameters.

The tungsten-doped samples were obtained by high-temperature solid-state reaction of Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$, and H_2WO_4 under a flow of purified argon.

The lithium-deficient $Li_xMn_{0.55}Fe_{0.45}PO_4$ samples were obtained by the electrochemical extraction of lithium in $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ cells with a lithium metal anode, Selectipur LP71 electrolyte (EC:DEC:DMC 1:1:1, 1M $LiPF_6$, from Merck), and composite cathode material. Due to the high resistance (> 10^7 Ω/cm) of the cathode material samples, an electronically conductive additive (graphite) was required to assure proper cell operation. The added graphite formed a highly electronically conductive matrix, in which low-conductive grains of $LiMn_{0.55}Fe_{0.45}PO_4$ were sited.

In the case of the $LiMn_{0.55}Fe_{0.45}FePO_4$ materials, the Mössbauer effect measurements were performed at 300 K with a spectrometer working in constant acceleration mode in transmission geometry with a $^{57}Co(Rh)$ source. The Conversion Electron Mössbauer Spectroscopy (CEMS) measurements for tungsten-doped $LiFePO_4$ samples were done with a $^{57}Co(Cr)$ source. The presented isomer shifts are given relative to the sources. The effect is set to be 100% for the background CEMS spectra as commonly done for the sake of comparing with transmission spectra.

3. Results and discussion

$Li_xMn_{0.55}Fe_{0.45}PO_4$. Figure 1 presents the OCV curve of the $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ cell. The accompanying OCV curves of the $Li/Li^+/Li_xMnPO_4$ and $Li/Li^+/Li_xFePO_4$ cells are shown for comparison. The jump in the OCV curve for the $Li_{0.55}Mn_{0.55}Fe_{0.45}PO_4$ cathode material can be ascribed to the difference in redox potentials between Fe^{2+}/Fe^{3+} (~3.5V) and Mn^{2+}/Mn^{3+} (~4.0V) [1]. The lower voltage range reflects the iron content of $LiMn_yFe_{1-y}PO_4$, while the higher one corresponds to the manganese concentration. The dashed vertical line positioned at $x_{Li} = 0.55$ separates sections where iron and manganese ions are oxidized.

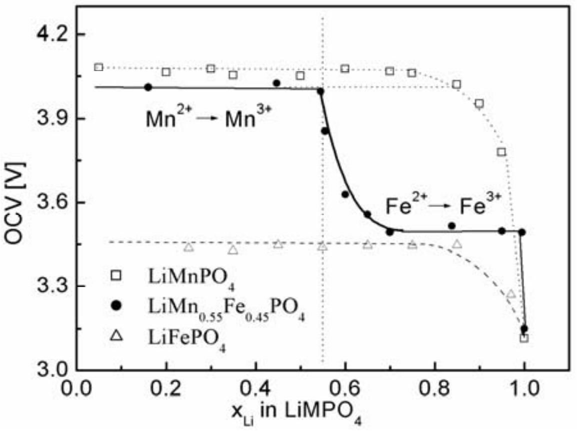

Fig. 1. OCV curves of $Li/Li^+/Li_xMnPO_4$, $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ and $Li/Li^+/Li_xFePO_4$ cells. The dashed vertical line placed at $x_{Li} = 0.55$ separates regions where iron and manganese ions are oxidized in the $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ cell. The lines connecting points are only to guide the eyes

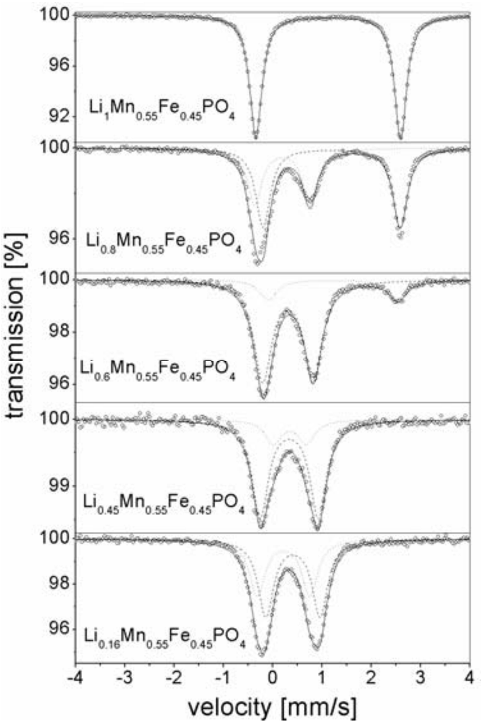

Fig. 2. Mössbauer spectra of $Li_xMn_{0.55}Fe_{0.45}PO_4$ samples obtained by deintercalation in a $Li/Li^+/Li_xMn_{0.55}Fe_{0.45}PO_4$ cell. The dashed lines represent the fitted components (quadruple doublets), while the solid lines are their sums

In the case of the starting $LiMn_{0.55}Fe_{0.45}FePO_4$ cathode material, only one quadruple doublet with a natural linewidth, originating from a single-valence state of iron (Fe^{2+}) occupying a unique crystallographic site, was necessary to fit the observed absorption pattern in the Mössbauer transmission spectrum (Fig. 2). For the subsequent electrochemically deintercalated samples, $Li_xMn_{0.55}Fe_{0.45}FePO_{4,}$ the spectra were unambiguously fitted with two doublets with different isomer shifts (IS) and quadruple splittings (QS), indicating the presence of Fe^{2+} and Fe^{3+} ions with a relative ratio r varying with and matching the lithium content x ($r = x - 0.55/0.55$, $1 \geq x \geq 0.55$). As expected, the spectrum of $Li_{0.45}Mn_{0.55}Fe_{0.45}FePO_4$ consists of components originating only from Fe^{3+}, as at this stage only Fe^{3+} ions are present in the sample. Further deintercalation results in a successive oxidation of Mn^{2+} and, as a consequence, changes in the local symmetry of the iron site, which is confirmed by an increasing quadruple split of the doublets in the Mössbauer absorption pattern.

$Li_{0.98}W_{0.01}FePO_4$. Metallic conductivity of $LiFePO_4$ achieved by doping [7] has attracted great attention and intensified studies on the influence of dopants on the electrical conductivity of this material. Some following attempts of this substitution reported in literature [8], however, yield unclear results due to the observed negligible and rather random influence of the dopant type and its concentration on conductivity. One of the possible explanations of the observed increase in conductivity considers the formation of a nano-sized, conductive path, created by iron phosphides on the phosphate grains.

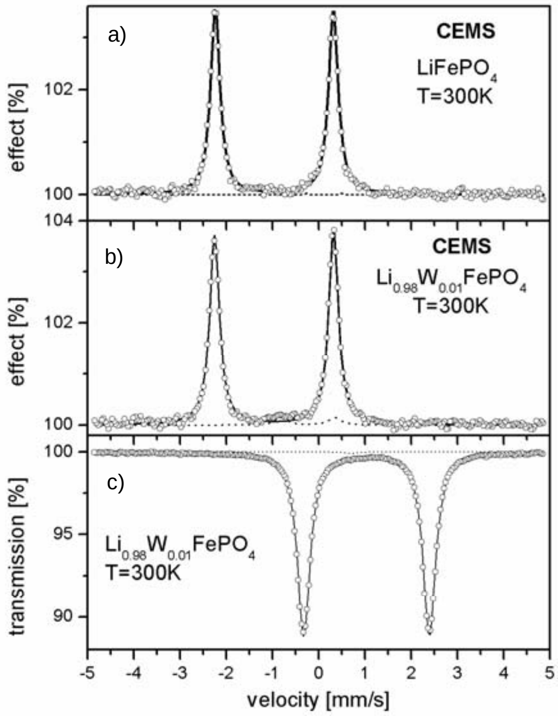

Fig. 3. CEMS spectra of pristine $LiFePO_4$ (a) and tungsten-doped $Li_{0.98}W_{0.01}FePO_4$ samples (b), together with a classical, "transmission" spectrum of the same doped sample (c)

In the case of the tungsten-doped $Li_{0.98}W_{0.01}FePO_4$ sample, which is found to be electronically conductive, only one quadruple splitted (QS) doublet, originating from a single valence state of iron (Fe^{2+}), was necessary to fit the observed absorption pattern in the transmission spectra (Fig. 3c). The CEMS technique, however, being a rather "surface sensitive" method, yields a slightly asymmetric pattern for the same sample (Fig. 3b), which was unambiguously fitted with two doublets with different isomer shifts (IS) and quadruple splittings (QS), indicating the presence of another phase containing iron. The isomer shifts of the component point to Fe_2P as the supplementary phase. A comparison of the relative contributions to the spectra enables the estimation of the content of the minor phase at a 4% level. A similar CEMS measurement, but carried out for an undoped and non-conductive $LiFePO_4$ sample (Fig. 3a), exhibits a symmetrical spectrum, and an attempt to fit it with two components, as in the previous case, fails since the second component vanishes. Therefore, the high conductivity of doped $LiFePO_4$ samples should be ascribed to the formation on a surface iron phosphide layer, which creates a conductive path over the whole sample. The iron phosphide on the surface of the grains may originate from the presence of internal reducing agents, since during the synthesis process species like Fe, $Fe_x(CO)_y$, C, CO and NH_3 are released. For this reason, the real influence of the dopant seems to restrict only to the assumed lithium deficiency during the synthesis of the doped compound, which leads to the presence of a Fe^{2+}/Fe^{3+} redox couple, catalysing the reduction of $LiFePO_4$ into Fe_2P and forming a thin conductive layer over the sample.

4. Conclusions

Among a large number of papers devoted to the novel phospho-olivine cathode materials, only few [5, 6] take advantage of Mössbauer spectroscopy, which enables the direct and quantitative observation of the Fe^{3+}/Fe^{2+} pair in the $Li_xMn_{0.55}Fe_{0.45}PO_4$ cathode material upon lithium deintercalation and its variation with changing lithium content. The measured spectra yield information on the valence states of iron atoms and on the variation in the symmetry of their local surroundings.

In the case of the tungsten-doped $Li_{0.98}W_{0.01}FePO_4$ sample, the spectra obtained by CEMS prove the presence (4%) of another phase (Fe_2P) containing iron. Since an analogous measurement carried out for the undoped (and non-conductive) $LiFePO_4$ sample indicates no presence of the foreign phase, the high conductivity of doped $LiFePO_4$ samples should be ascribed to occurrence of a highly conductive phase on the surface of $LiFePO_4$ grains.

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