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Lithium-ion batteries – state of art
Novel phospho-olivine cathode materials

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This work is a brief review of physicochemical properties of modern cathode materials for Li-ion batteries. These intercalated transition metal compounds of layered, spinel or olivine-type structure exhibit a correlation between their microscopic electronic properties and the efficiency and mechanism of lithium intercalation. The recently reported metallic-type conductivity of doped phospho-olivine $LiFePO_4$, being a novel promising cathode material, is discussed in more detail, and some fundamental arguments are presented against the bulk nature of the observed high electronic conductivity.

Key words: *Li-ion battery; cathode material; phospho-olivine;* $LiFePO_4$*; intercalation*

1. Introduction

The enormous technological progress and common use of portable electronic devices call for batteries with high energy densities per unit mass and volume, a high number of charge-discharge cycles, safe operation, non-toxicity and low price. In the widely used technologies of reversible Ni–Cd and NiMH batteries, no further improvements can be anticipated. A prospective technology under intensive development is that of reversible lithium batteries (Li-ion batteries). These are based on the reversible intercalation of lithium into the transition metal compounds M_aX_b (X = O, S). The effectiveness of intercalation in a $Li_xC_6/Li^+/Li_{1-x}M_aX_b$ cell, where the anode reaction is

$$C_6 + xLi^+ + xe^- \leftrightarrow Li_xC_6 \qquad (1)$$

and the cathode reaction is

$$Li_1M_aX_b \leftrightarrow Li_{1-x}M_aX_b + xLi^+ + xe^- \qquad (2)$$

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depends on the transport properties of ions and electrons in both electrode materials and on the availability of sites for Li^+ ions, as well as on the density of electron states near the Fermi level in both materials [1, 2]. The graphite anode does not limit the useful parameters of such batteries. Potential improvements in the operation of the Li-ion batteries can be sought after in the cathode material.

In today's Li-ion batteries, $LiCoO_2$ cathodes have been replaced by other materials, such as $LiCo_{1-y}Ni_yO_2$ and $LiMn_2O_4$. These cathodes have a number of limitations. With $LiCoO_2$ it is possible to use merely half of its theoretical capacity, because the electrochemical deintercalation/intercalation process is reversible only within a limited compositional range, i.e. $LiCoO_2$–$Li_{0.5}CoO_2$, resulting in a low capacity of 130 mAh/g. Moreover, $LiCoO_2$ is toxic and relatively expensive. On the other hand, the capacity of $LiNiO_2$ is higher than the capacity of $LiCoO_2$, but its thermal stability is lower and the compound cannot be used in Li-ion batteries for safety reasons. The delithiation of $LiNiO_2$ leads to the exothermic oxidation of the liquid organic electrolyte. Therefore, the development of solid electrolytes (e.g., polymeric ones), which might replace the commonly used EC/DMC-$LiPF_6$, is a very important research direction. This would extend the service life of Li-ion batteries and increase their safety of operation. In the case of manganese spinel, $LiMn_2O_4$, capacity losses are observed on cycling and battery parameters degrade at elevated temperatures.

2. Iron oxide-based cathode materials

Some investigations under way are focused on cathode materials based on iron oxides. The interest in iron compounds arises from the fact that iron is cheap, abundant in the earth crust, and friendlier to the environment than cobalt, nickel, or manganese. Unfortunately, the iron-containing layered compound $LiFeO_2$, isostructural with $LiCoO_2$ and $LiNiO_2$, appears to be metastable. The stability of ABO_2 oxides with layered structures of the α-$NaFeO_2$ ($R3m$) type can be estimated from Pauling's rule [3], according to which the r_B/r_A ratio should be less than 0.86. In the case of $LiCoO_2$ and $LiNiO_2$, this ratio is 0.77 and 0.78, respectively. For $LiFeO_2$, $r_{Fe^{3+}}/r_{Li^+}$ equals 0.88, and the structure is unstable. Another important reason, which excludes $LiFeO_2$ from being applied in batteries, is the unfavourable position of the redox potentials of iron in relation to those of lithium [4] (Fig. 1). The Fe^{3+}/Fe^{4+} potential is too distant from that of Li/Li^+ and located beyond the electrochemical window of the electrolyte, which cannot guarantee the neutrality of the electrolyte versus the cathode. On the other hand, the Fe^{3+}/Fe^{2+} potential is too close to that of Li/Li^+, which results in a voltage of the cell that is too low. Such behaviour is related to the high-spin configuration of Fe^{3+} and strong interactions between d electrons.

It seems that the problems associated with structural instability and the unfavourable position of the redox potentials of iron versus lithium can be overcome by using a new series of iron compounds, e.g. $LiFeXO_4$, proposed by Goodenough [5], whose large polyanions $(XO_4)^{y-}$ (X= S, P, As, Mo, W; $y = 2$ or 3) might stabilize the structure. The presence of such polyanions $(XO_4)^{y-}$, with a strong covalent X–O bond,

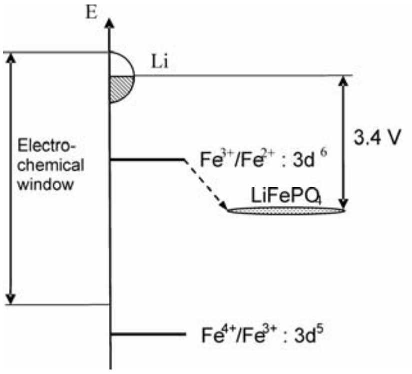

Fig. 1. Energy diagram showing the Fe^{4+}/Fe^{3+} and Fe^{3+}/Fe^{2+} potentials in the cathode materials based on iron in octahedral coordination

stabilizes the anti-bonding state, Fe^{3+}/Fe^{2+}. The Fe–O bond becomes less covalent due to the induction effect in the Fe–O–X system, which raises the electrode potential. The stronger the X–O bond, the weaker the Fe–O bond and the higher is the cell voltage. A shift of the Fe^{3+}/Fe^{2+} potential in $LiFePO_4$ (Fig. 1) results in a high voltage (3.4 V) of the $Li/Li^+/Li_xFePO_4$ cell.

3. Phospho-olivine – a new cathode material

$LiFePO_4$ with the olivine structure belongs to the family of NASICON-type compounds (NASICON – sodium super-ionic conductor), known to be fast ionic conductors and used as solid electrolytes in electrochemical cells. In $LiFePO_4$, the hexagonal close-packed lattice of oxygen has two-dimensional channel network being potential fast diffusion paths for lithium ions. Structural limitations (in the FeO_6 octahedra joined by corners, the Fe–Fe distances are larger than 4 Å, while in simple oxides M–M distances do not exceed 3 Å), however, make the material practically an insulator. Its electrical conductivity at room temperature is extremely low compared to typical cathode materials and equals 10^{-10} S·cm^{-1}. Thus, the observed LiFePO4 delithiation is not really a diffusional deintercalation process, described by the following equation:

$$LiFePO_4 - xLi^+ - xe^- \longleftrightarrow Li_{1-x}FePO_4 \tag{3}$$

which yields a homogeneous material with varying lithium content. The data reported in the literature [6] and our own studies [11] indicate that lithium extraction from $LiFePO_4$ in the discharge cycle leads to the decomposition of the cathode material into two phases, of which one contains lithium and the other is lithium-free:

$$\mathrm{LiFePO_4} - x\mathrm{Li^+} - x\mathrm{e^-} = x\mathrm{FePO_4} + (1 - x)\mathrm{LiFePO_4} \tag{4}$$

and a similar reverse reaction (discharging cycle):

$$\mathrm{FePO_4} + x\mathrm{Li^+} + x\mathrm{e^-} = x\mathrm{LiFePO_4} + (1 - x)\mathrm{FePO_4} \tag{5}$$

The reversibility of the charge–discharge processes is related to the great similarity of the structures of $LiFePO_4$ and $FePO_4$ (the same space group), which have a volume difference of only 6,81%. The described behaviour of the cathode material is not at all beneficial – only the grain surfaces of the cathode are effectively used and the current density of the cell is low. The reason for reactions (4) and (5) to occur is low electronic conductivity. Some attempts have been made to improve microscopic conductivity by the grain refinement of $LiFePO_4$, coated with carbon during synthesis. The applied procedures do not, however, increase the electronic conductivity within the grains and therefore affect neither the chemical diffusion coefficient of lithium nor the current density.

In spite of this, $LiFePO_4$ has some important advantages: the highest theoretical capacity of all known cathode materials (170 mAh/g), and the highest thermal stability, which guarantees safety of use and stable capacity after numerous work cycles. The most challenging issue in the search for a cathode material based on phospho -olivine is to get a mixed ionic-electronic conductivity, which should activate the diffusional mechanism of the deintercalation/intercalation process of reaction (3).

The first reports by Chiang [7] on the metallic-type conductivity of $LiFePO_4$, achieved by doping, evoked great interest and intensified studies on the influence of dopants on the electrical conductivity of this material.

Chiang [7] obtained a spectacular increase in electrical conductivity – by a factor of 10^7 – by introducing Nb^{5+}, Zr^{4+}, or Mg^{2+} ions into the lithium sublattice. Activation energies were of the order of 0.05 eV at room temperature. Figures 2 and 3 present the results of electrical conductivity and thermoelectric power measurements of phospho -olivine samples doped with W^{6+}, Ti^{4+}, and Al^{3+}. Conductivities of 10^{-2}–10^{-3} S/cm, together with low activation energies ranging from 0.02 to 0.1 eV, can be interpreted as metallisation at the border of carrier localization. The low absolute value of thermoelectric power – about 10 μV/K – and the lack of its dependence on temperature are characteristic of the metallic state. The described behaviour might be related to the formation of a narrow dopant band. Such a semiconductor–metal transition upon doping is known as a Mott's-type transition [8]. At some critical concentration, N_c, the electron wave functions of the dopant overlap, which leads to the formation of a dopant conduction band. Systematic analyses of the electrical properties of phospho-olivine doped with different concentrations of W, Ti or, Al, however, raise doubts about the bulk conductivity mechanism. The basic objections originate from a minor and rather random influence of the dopant type and concentration on conductivity. Moreover, an inhomogeneous distribution of the dopant (EDS) also leads to the same "metallic" behaviour of the material, and even for the highly conductive samples the deintercalation proceeds by a two-phase mechanism as in the case of pure $LiFePO_4$.

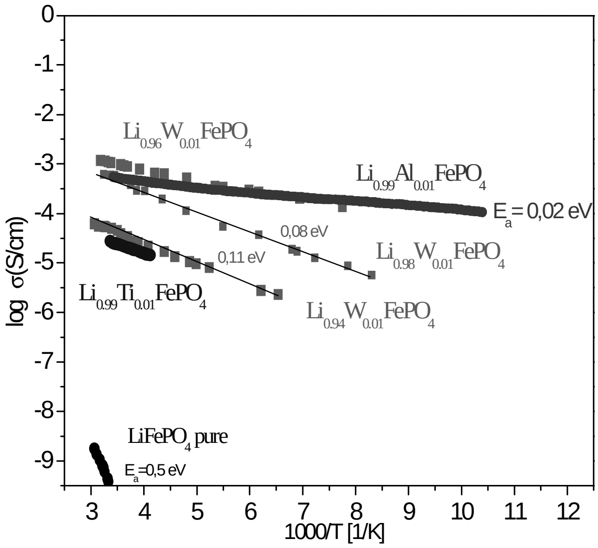

Fig. 2. Electrical conductivity of the pristine phospho-olivine samples and doped with W^{6+}, Ti^{4+} and Al^{3+}

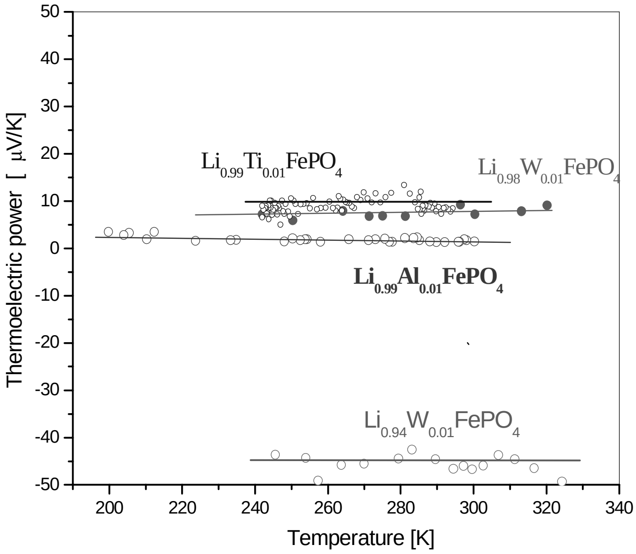

Fig. 3. Thermoelectric power measurements of the phospho-olivine samples doped with W^{6+}, Ti^{4+} and Al^{3+}

Results obtained by Nazar et al. [9], who by using a specific synthesis route arrived at phospho-olivine samples with lithium deficit $Li_{1-x}FePO_4$ and also stoichiometric $LiFePO_4$ with metallic-type conductivity, give strong arguments against the hypothesis about dopant atoms contributing to bulk metallic conductivity. Even if it is assumed that the obtained stoichiometric samples have a slight lithium deficit, and consequently a mixed valency of iron, the presence of the Fe^{2+}–Fe^{3+} pair cannot account for the observed high electronic conductivity, since the iron–iron distance (~4 Å) in the olivine structure is too large. In numerous M–O oxides, metallic-type conductivity appears when the M–M distances are smaller than 3 Å. Therefore, what is the reason for the observed increase in conductivity by as much as seven orders of magnitude? Two possibilities should be considered: the appearance of conductive paths formed by residual carbon from the organic precursors used in synthesis, or by iron phosphides on phosphate grains. Traces of iron phosphides (estimated as ~4%) were observed by surface sensitive CEMS [11] or TEM [9]. Such a composite material consists of highly resistive grains and conductive surface of grains lined with iron phosphides, which play the role of conductive paths within the whole sample. The origin of iron phosphides on the surface of grains may be associated with the presence of internal reducing agents such as Fe, $Fe_x(CO)_y$, C, CO, and NH_3, which are released during synthesis from substrates such as $FeC_2O_4 \times H_2O$, $NH_4H_2PO_4$, and Li_2CO_3. As a result, a partial reduction of phosphates to phosphides may take place. For this reason, the real influence of the dopant seems to be restricted only to the assumed lithium deficit of the doped compound, which leads to the presence of the Fe^{2+}/Fe^{3+} redox couple, which in turn catalyses the reduction of $LiFePO_4$ to Fe_2P and forms a thin conductive layer over the sample.

Investigations aimed at improving the transport properties of phospho-olivine [12] indicate that the desired electronic-ionic mixed conductivity can be achieved by substituting a different transition metal for iron, generating a transfer of electrons from one ion to another. As an illustration, Mn^{+2} ($3d^5$) in Fe^{+2} ($3d^6$) sites in phospho-olivine $LiFe_{0.4}Mn_{0.6}PO_4$ introduces 0.6 moles of holes localized on manganese, and activates electronic conductivity through charge transfer between Fe and Mn. Charge transport becomes easier owing to the markedly increased concentration of effective carriers, whereas the Fe–Mn distance in $Li_xFe_{0.4}Mn_{0.6}PO_4$ remains the same as the Fe–Fe distance in $LiFePO_4$, i.e. 4 Å. Pure $LiFePO_4$, with all iron ions at the oxidation state Fe^{+2}, is an insulator. Charge carriers are created by lithium nonstoichiometry, which produces Fe^{3+} (electron holes), their concentration being, however, as low as 0.001 moles. It has been stated that at a composition of $Li_xFe_{0.4}Mn_{0.6}PO_4$ lithium deintercalation proceeds according to a diffusional mechanism. Similar observations have been reported by Yamada [10] for the chemical delithiation of phospho-olivine. This problem is discussed thoroughly in Refs. [11] and [12].

4. Conclusions

In the case of the discussed phospho-olivine cathode material, the formation of phosphides on grain surfaces during synthesis can be regarded as an *in situ* formation of a composite material.

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