*Materials Science-Poland, Vol. 24, No. 1, 2006*

# The effect of aluminium on the electrical and electrochemical properties of phospho-olivine – a cathode material for Li-ion batteries

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The structure, electrical and electrochemical properties of phospho-olivine ($LiFePO_4$) doped with aluminium were investigated. Some of the obtained samples had much higher electrical conductivities than the undoped material ($10^{-4}$ S/cm compared to $10^{-10}$ S/cm). It has been stated that the enhanced conductivity is caused by a thin layer of reduced material that has metallic properties (probably iron phosphide), formed on the grain surfaces of phospho-olivine.

Key words: *$LiFePO_4$; phospho-olivine; lithium-ion battery; electrochemical properties*

## 1. Introduction

Contemporary portable electronic devices require very efficient energy supplies, such as Li-ion batteries. Lithium iron phosphate ($LiFePO_4$) with an olivine structure is potentially a very good cathode material for such batteries. Its major advantage is high theoretical capacity, approaching 170 mA·h/g, the voltage of about 3.5 V versus the metallic lithium anode, chemical stability, low price and nontoxicity. Goodenough et al. [1] have reported that it is possible to reversibly insert up to 0.8 mole of lithium per 1 mole of the compound at a current density of 0.05 mA/cm$^2$. In spite of its unquestioned advantageous characteristics, the material will not gain commercial importance unless some drawbacks are overcome. For instance, lithium iron phospho-olivine has low electrical conductivity, which is responsible for the low chemical diffusion coefficient of lithium and low current densities supplied by the battery. It has been reported that the conductivity of $LiFePO_4$ can be improved by doping, e.g.,

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by substituting lithium with Mg, Al, Cr, Ti, Nb, or W [2, 3]. Besides, compounds containing lithium and aluminium have also been tested as anode materials [4].

## 2. Experimental

The materials investigated were prepared from $Li_2CO_3$, $FeC_2O_4 \cdot 2H_2O$, $NH_4H_2PO_4$, and aluminium acetylacetate at high temperatures. The reactants were mixed in stoichiometric proportions in a mortar with addition of propanol. Thermal treatment was performed in two stages under flowing highly pure argon. The first stage, decomposition of the reactants at 350 °C, was continued for 12 h, the second stage, the synthesis at 800 °C, was continued for the next 12 h. After the first stage, the reactants were cooled down to room temperature and again mixed in a mortar. The phase composition of the products was analysed using an X'Pert Pro Philips X-ray diffractometer. Microstructures were examined by scanning electron microscopy (JEOL JSM – 5400 microscope equipped with EDS).

Electrical conductivity was measured by a four-probe ac method, and thermoelectric power was measured by a dynamic method with an increasing temperature gradient. The chemical diffusion coefficient of lithium was measured by GITT [5].

## 3. Results and discussion

The synthesized materials were: $Li_xAl_{0.01}FePO_4$ ($x$ = 0.99–0.97) and $Li_{0.95}Al_{0.05}FePO_4$. These compositions were selected in order to examine the influence of lithium non-stoichiometry on the properties of aluminium-doped phospho-olivine.

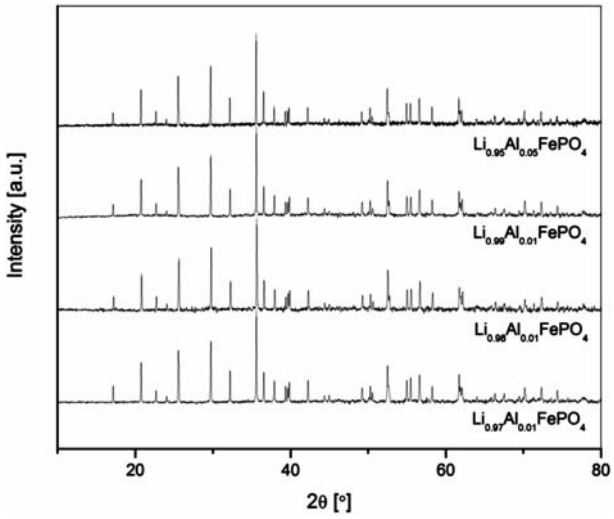


Fig. 1. X-ray diffraction patterns of the investigated samples of phospho-olivines

Figure 1 presents X-ray diffractograms of the investigated samples. The obtained materials are single-phase and consist of tryphyllite ($LiFePO_4$).

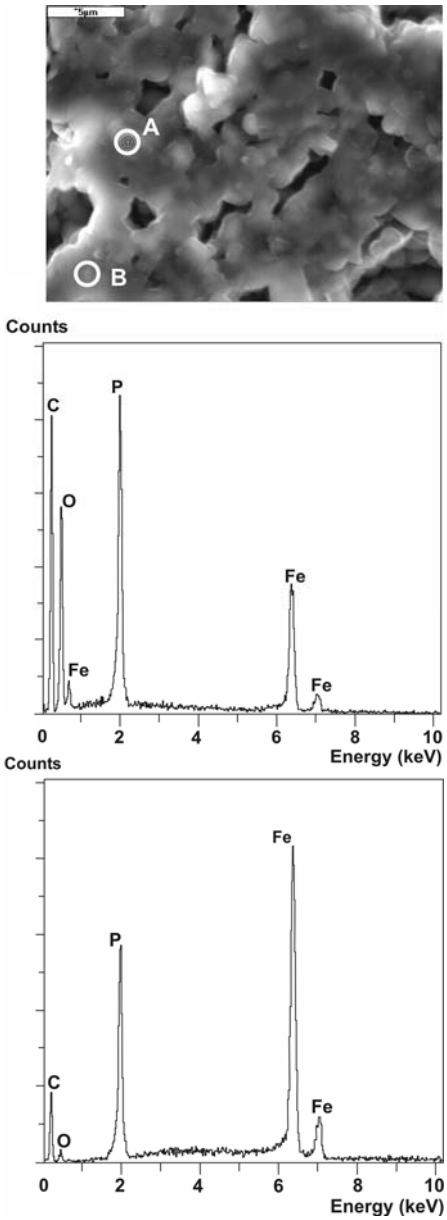


Fig. 2. Point EDS spectra for the sample with composition $Li_{0.99}Al_{0.01}FePO_4$

The analysis of SEM images indicates that the microstructures in all the samples are similar, independent of chemical composition. Examples SEM images of the frac-

tured samples are shown in Figures 2 and 3 (samples with the composition of $Li_{0.99}Al_{0.01}FePO_4$). The distribution of elements in all samples was examined by EDS.

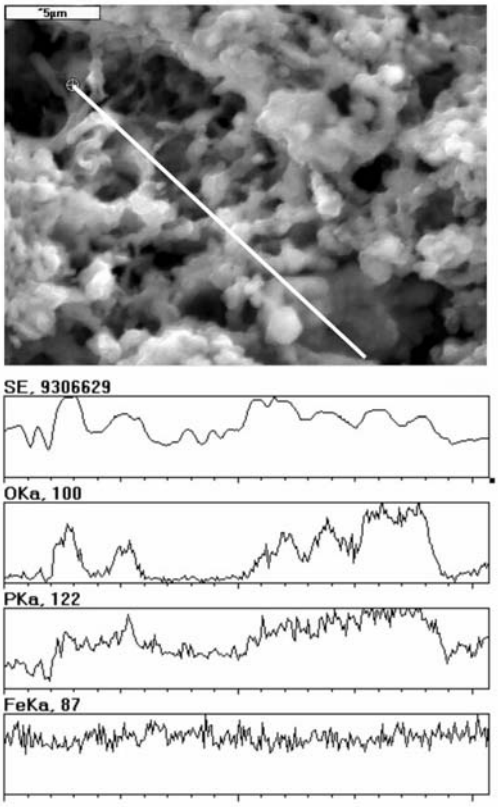


Fig. 3. Line EDS spectra for the sample with composition $Li_{0.99}Al_{0.01}FePO_4$

The results were also similar. Figures 2 and 3 illustrate EDS spectra for the sample with a composition of $Li_{0.99}Al_{0.01}FePO_4$. Carbon – visible in the plot – was purposely deposited on the surface of samples prior to analysis. These results indicate that the samples are not homogeneous. There are regions with lower concentrations of oxygen and simultaneously higher concentrations of iron and phosphorus, which suggests that the phosphate phase might locally reduce to phosphide, e.g. iron phosphide (the Fe/P ratio observed on the sample surface might result from the presence of FeP and $Fe_2P$). A similar hypothesis has been put forward by Canadian researchers [6] on the basis of EELS and TEM studies. Using a more advanced analytical tool they have stated that the grain boundary region is much richer in phosphorus, iron, and carbon (coming from the decomposition of substrates) than the bulk of grains.

With the selected substrates ($Li_2CO_3$, $FeC_2O_4{\cdot}2H_2O$, $NH_4H_2PO_4$, aluminium acetyl -acetate) and synthesis parameters, it is possible that several reducing agents (Fe, $Fe_x(CO)$, C, CO, $NH_3$) might be present in the reaction environment and partly reduce

$LiFePO_4$ to phosphides. The role of aluminium may be limited to raising lithium non-stoichiometry. As a result, the redox pairs $Fe^{2+}/Fe^{3+}$ form and catalyse the reduction of

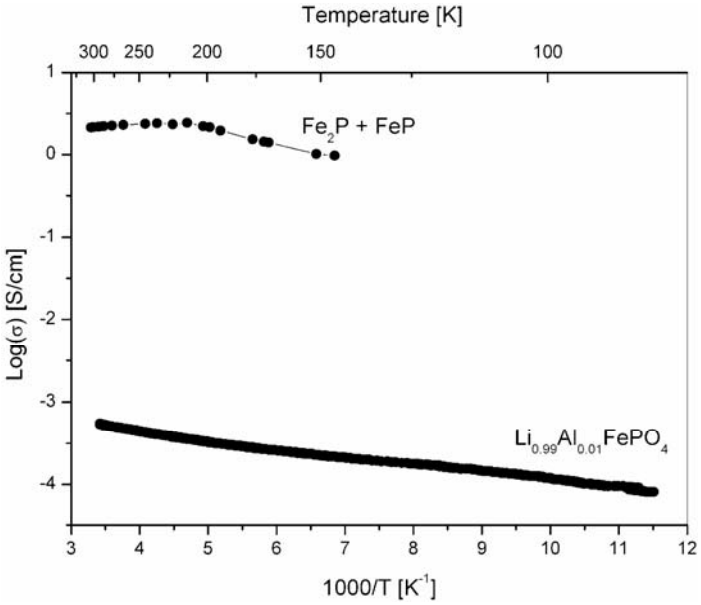


Fig. 4. Electrical conductivity of $Li_{0.99}Al_{0.01}FePO_4$ sample.
For comparison data for a (FeP, $Fe_2P$) mixture are shown

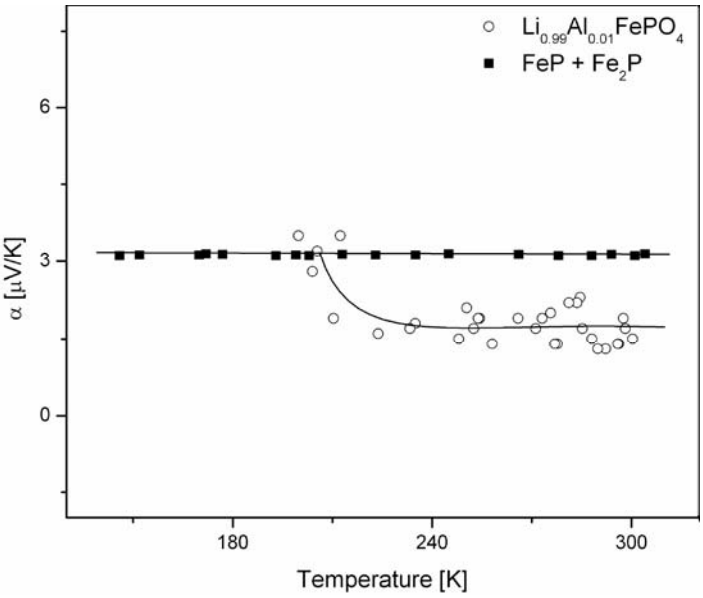


Fig. 5. Thermoelectric power of $Li_{0.99}Al_{0.01}FePO_4$ sample.
For comparison data for a (FeP, $Fe_2P$) mixture are shown

phosphate. During the synthesis, this process occurs locally and does not disturb the overall stoichiometry of the sample, which according to XRD analysis does not contain any foreign phases.

The consequences of the mentioned processes are important for the electrical properties of the materials obtained. The electrical conductivity varied from $<10^{-7}$ to about $10^{-4}$ S/cm at room temperature. The conductivity could not be correlated with chemical composition. Figures 4 and 5 present the conductivity and thermoelectric power of $Li_{0.99}Al_{0.01}FePO_4$ (the sample with the highest conductivity). For comparison, the characteristics of the material received by a complete reduction of phospho-olivine to $Fe_2P$ and FeP are also given [7]. Depending on whether a continuous conductive path is formed during synthesis or merely local precipitates, the conductivity may change by several orders of magnitude. This is probably the reason for inconsistent results obtained in different laboratories [2, 8] and for the irreproducibility of synthesis carried out under the same experimental conditions.

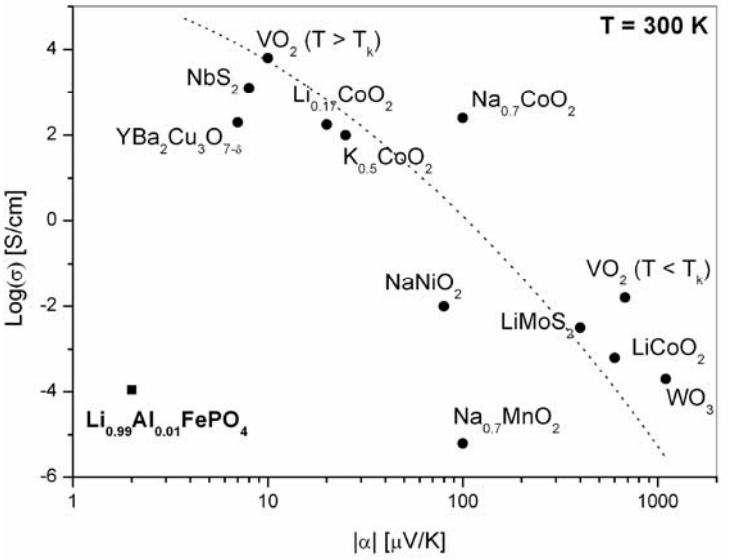


Fig. 6. Comparison between electrical conductivity and thermoelectric power for different transition metal compounds

It is interesting to note the non-typical electronic properties, i.e. a very low thermoelectric power (characteristic of metals) at room temperature of about 3 μV/K and at the same time a relatively low room-temperature conductivity of about $10^{-4}$ S/cm. The results obtained for many transition-metal compounds by Molenda et al. [9–12] indicate a corrrelation between conductivity and thermoelectric power. As follows from Figure 6, the properties of $LiFePO_4$ do not obey this relation. To explain this behaviour, it is suggested that a thin layer of iron phosphides with low resistivity creates a percolation path on the surface of the grains of the material, which has a much

higher resistivity ($LiFePO_4$). The low electrical conductivity may be caused by a low thickness of this layer, and thermoelectric power – independent of size effects – assumes values characteristic of the component responsible for this parameter.

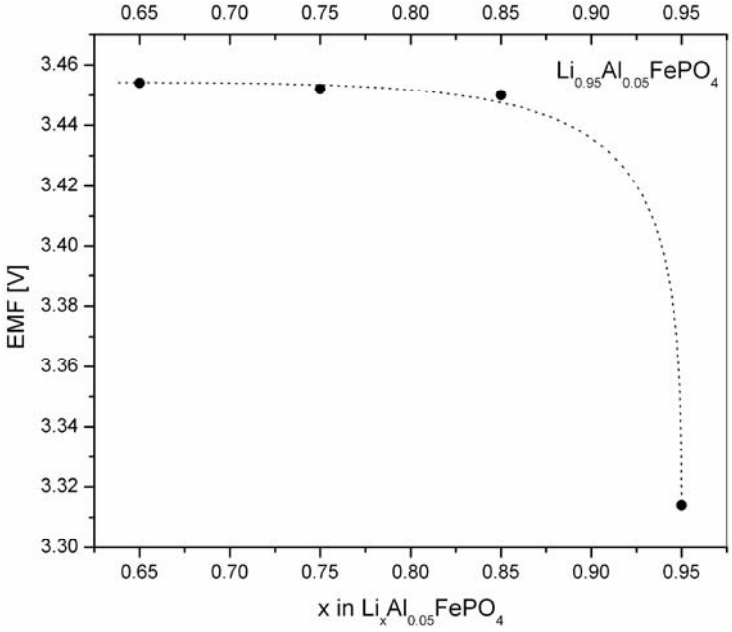


Fig. 7. EMF of the Li / $Li^+$ / $Li_{0.95}Al_{0.05}FePO_4$ cell as a function of lithium concentration

Figure 7 shows the EMF of a $Li/Li^+ \mid Li_{0.95}Al_{0.05}FePO_4$ cell as a function of lithium concentration. Except for the initial sudden jump, there are no variations in EMF during the charging cycle. Such behaviour can be explained by a two-phase operation mechanism of the cathode material:

$$LiFePO_4 - xLi^+ - xe^- \rightarrow (1-x)LiFePO_4 + xFePO_4 \tag{1}$$

The coexistence of the two phases, $LiFePO_4$ and $FePO_4$, in equilibrium during the whole process maintains a constant value of the voltage. This statement is supported by XRD analysis of the cathode material based on the conductive phospho-olivine with an initial composition of $Li_{0.99}Al_{0.01}FePO_4$ after 50% delithiation (Fig. 8). Two phases can be identified in this diffractogram, one with the structure of tryphyllite, $LiFePO_4$, and another with the structure of heterosite, $FePO_4$. The two-phase mechanism has been previously reported for undoped phospho-olivines with low bulk conductivities [1], but in the samples obtained in this work, with conductivities of about $10^{-4}$ S/cm, the diffusional mechanism of deintercalation has been anticipated.

The chemical diffusion coefficients of lithium in the obtained materials measured by GITT were very low ($10^{-12}$–$10^{-17}$ $cm^2/s$), close to that of pure phospho-olivine $LiFePO_4$ [13].

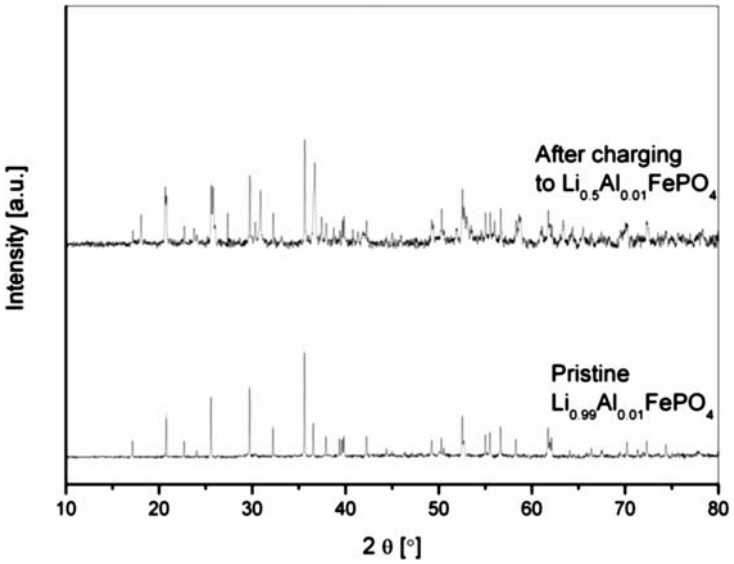


Fig. 8. X-ray diffraction patterns of the cathode material based on the conductive phospho-olivine with the initial composition $Li_{0.99}Al_{0.01}FePO_4$ before and after 50% delithiation

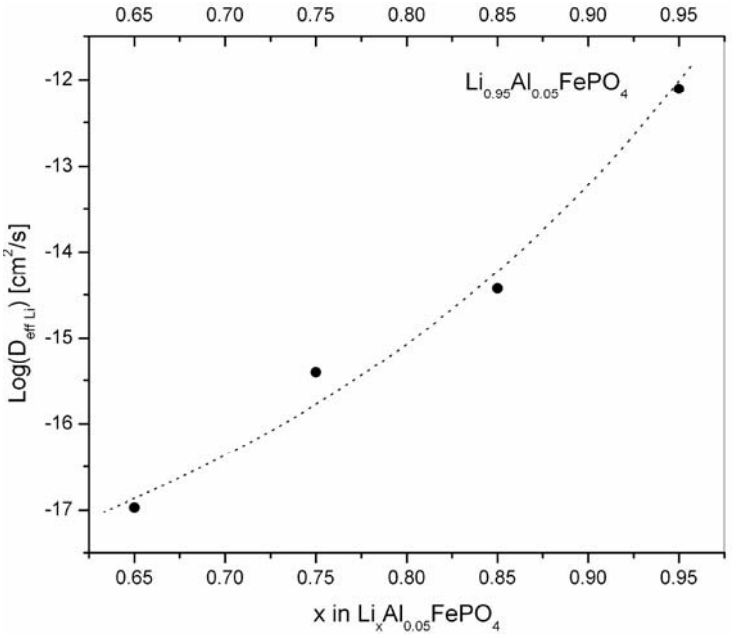


Fig. 9. Dependence of the chemical diffusion coefficient of lithium as a function of lithium concentration in the cathode material $Li_{0.95}Al_{0.01}FePO_4$

Figure 9 shows an example of the dependence of the lithium chemical diffusion coefficient on lithium concentration in the cathode material $Li_{0.95}Al_{0.05}FePO_4$. Should

the conductive samples of doped phospho-olivine have some bulk conductivity, the increasing electronic conductivity would enhance the mobility of the lithium ions. This, however, is not the case. The quasi-metallic conductivity is related to the phosphide layer that covers the non-conducting phospho-olivine grains. Aluminium doping, in spite of the apparently metallic type of conduction, did not change the mechanism of lithium intercalation/deintercalation during the operation cycle of the cell, i.e. it did not activate the diffusional mechanism of intercalation. This is another strong argument against the bulk metallic properties of aluminium-doped phospho-olivine.

## 4. Conclusions

The distribution of elements in the obtained samples is not uniform. EDS reveals regions with lowered concentrations of oxygen, which indicate the partial reduction of $LiFePO_4$ to iron phosphides.

EMF variations for $Li\,|\,Li^+\,|\,Li_xAl_{0.01}FePO_4$ cells and X-ray diffractograms of the conductive cathode material after partial delithiation allow the conclusion that the reaction taking place in the charging cycle of the cell proceeds according to a two -phase mechanism. In the cathode material, which has a relatively high conductivity, the diffusional mechanism of lithium does not operate, meaning that aluminium as a dopant does not improve the bulk electronic properties of $LiFePO_4$. It catalyses the reduction of phosphate and the formation of a thin surface layer composed of iron phosphides.

**Acknowledgements**

The work supported by the Polish Committee for Scientific Research under the grant No. 4T08A 020 25.

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*Received 10 December 2004*
*Revised 17 February 2005*