ELECTRONIC CONDUCTION AND REACTION WITH LITHIUM OF DOPED $LiFePO_4$ OLIVINE TYPE CATHODE MATERIALS

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Novel group of cathode materials, olivine structured $LiFePO_4$ based, are stable, “green” and of high energy density, but with serious drawback - insulating properties (10^{-10}Scm). Practically advantageous operational parameters of a battery, like high current density, require electronically conductive cathode material. The efforts are concentrated on significant improvement of conductivity by selective doping of $LiFePO_4$ with other metals (e.g. Zr, Nb, W). Overcoming limitations caused by electronic structure and its influence on transport properties, enables tailoring of the cathode properties. $LiFePO_4$ based materials, with conductivity enhanced by factor 10^7 and of metallic character, were obtained series of tungsten doped samples $Li_{1-x}W_yFePO_4$. The phase composition of these samples were investigated by Moessbauer effect measurements at 300K with a spectrometer working in constant acceleration mode in transmission geometry (spectrum in Fig.1) or as CEMS (Conversion Electron Moessbauer Spectroscopy – spectra in Figs.2 & 3) with the 57Co(Cr) and 57Co(Rh) sources respectively. In the case of the tungsten doped, $Li_{0.98}W_{0.01}FePO_4$ high electronically conductive sample, in the transmission spectra (Fig.1) only one quadruple splitted (QS) doublet were necessary to fit the observed absorption pattern originating from single valence state of iron (Fe^{+2}). Spectrum obtained for the same sample, but by the CEMS technique, which is rather “surface sensitive” method, exhibits slightly asymmetric pattern (Fig.2) which was unambiguously fitted with two doublets of different isomer shifts (IS) and quadruple splitting (QS) indicating presence of another phase containing iron. The value of its IS points to presence of Fe_2P. Comparison of the relative contributions to the spectrum enables estimating the content of the minor phase at about 4%. Similar CEMS measurement, but performed for undoped non-conductive $LiFePO_4$ sample (Fig.3), shows symmetrical spectrum and an attempt to fit it with two components, as in the previous case was, fails as the second component vanishes.

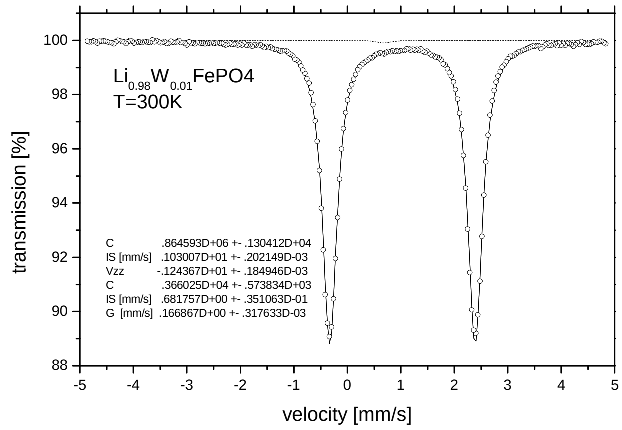

Fig.1

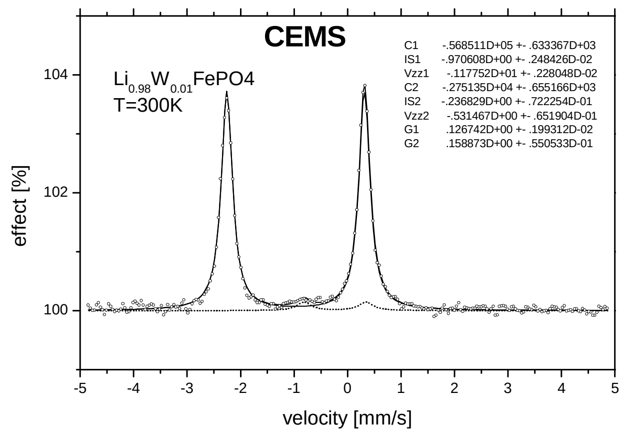

Fig.2

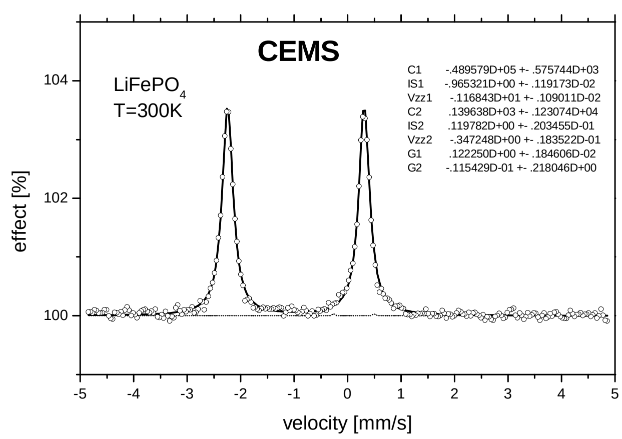

Fig.3

In the presented work the actual composition of the obtained doped $LiFePO_4$ samples and the nature of electronic conduction of the cathode materials with relation to the nature of cathodic reaction is discussed.