

EXAFS analysis of LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples produced via chemical techniqueM.D. Sharkov^{a,*}, D.V. Agafonov^b, A.V. Bobyl^a, M.E. Boiko^a, E.M. Ershenko^a, S.G. Konnikov^a, K.Ju. Pogrebitsky^a, Y.V. Zubavichus^c^a Ioffe Physico-Technical Institute of the RAS, 26 Politekhnicheskaya, 194021 St. Petersburg, Russia^b St. Petersburg State Institute of Technology (Technical University), 26 Moskovsky pr., 190013 St. Petersburg, Russia^c Kurchatov Institute, National Research Center, 1 Ak. Kurchatova pl., 123182 Moscow, Russia

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ABSTRACT

EXAFS (extended X-ray absorption fine structure) spectra of two triphylite (lithium iron phosphate) samples and a lithium titanate (lithium titanium oxide) sample have been measured and processed. A new method of EXAFS data analysis including a procedure to separate spectrum oscillations based on the variation principle and estimating Fourier window limits has been applied to all the spectra. The volume fractions of impurity phases in the samples are estimated. An assumption is made that the titanate sample contains about 40 vol% titanium oxide in the anatase phase. It is shown that triphylite sample #1 may contain about 1% maghemite (magnetic phase of iron-III oxide) and triphylite sample #2 may include 5–10% iron-III phosphate.

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1. Introduction

Modern rechargeable batteries are frequently based on lithium-containing compounds, e.g., lithium iron phosphate LiFePO_4 (referred to as triphylite) and lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$. When these substances are synthesized by chemical etching they are known to contain some extrinsic phases. These may differ in size, shape, and even physical state, so a triphylite or lithium titanate sample may consist of both perfect crystalline grains and those with amorphous structure. Characterization of samples of this kind requires a technique sensitive to substances in any physical state. This capacity is characteristic of EXAFS (extended X-ray absorption fine structure) spectroscopy.

An EXAFS spectrum is defined as the dependence of the linear X-ray absorption coefficient on the energy of the analyzing monochromatic beam. In this case, the photon energy ranges from one of the absorption edges of the sample substance up to values higher by hundreds of electronvolts [1]. Atoms of a particular type absorb an X-ray photon and are ionized to give a free photoelectron. This electron propagates around the photon-absorber atom and is scattered by its neighbors. The scattered secondary photoelectron waves modify the primary state of the photoelectron, which results in oscillations of the X-ray absorption spectrum for the substance being considered. Typical periods of these

oscillations are related to the distances from the absorber atom to its neighbors. Moreover, Fourier-transformed (FT) EXAFS oscillations correspond to the distribution density of the atomic shell radii for absorber type atoms. Anyway, a special processing procedure is required for obtaining this density function from raw experimental data.

2. EXAFS measurements

Two triphylite samples and one lithium titanate sample were fabricated at St. Petersburg State Technological Institute (Russia). For all the samples, Ti and Fe K-edge EXAFS spectra were measured at the 'Structural Material Science' beamline of the Kurchatov Synchrotron Radiation Center (Moscow, Russia). The spectra were measured in the transmission configuration with two ionization chambers filled with appropriate N_2 -Ar mixtures. The energy scanning procedure was accomplished using a Si (111) channel-cut monochromator crystal. For one of the phosphate samples, hereinafter designated as sample #1, the EXAFS spectrum was measured for the second time three months after the first measurement. For the other sample (hereinafter referred to as sample #2) only a single EXAFS recording procedure was performed.

The recorded Fe K-edge EXAFS spectra of both LiFePO_4 samples are shown in Fig. 1. Fig. 2 represents the Ti K-edge EXAFS spectrum for the titanate sample.

It was found that the phosphate sample #1 has a substantial magnetic moment and thus is assumed to contain some ferromagnetic impurity phases.

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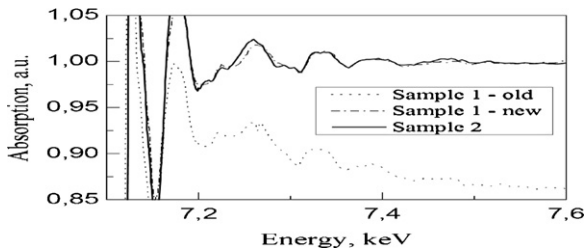


Fig. 1. Fe K-edge EXAFS spectra recorded for the two LiFePO₄ samples.

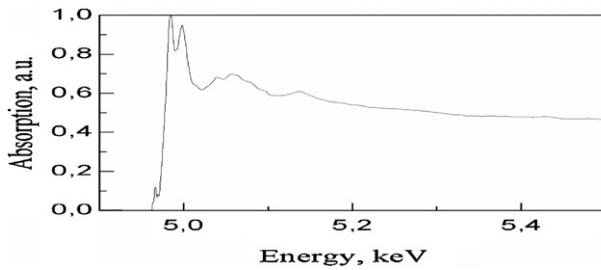


Fig. 2. Ti K-edge EXAFS spectrum recorded for the Li₄Ti₅O₁₂ sample.

3. Complementary investigations

Both the triphylite samples were also subjected to an X-ray diffraction (XRD) analysis. Fig. 3 presents both the XRD data sets measured for the phosphate samples #1 and #2, respectively.

The XRD data were recorded with a Bruker D8-DISCOVER instrument at the Ioffe Institute (St. Petersburg, Russia). Monochromatic Cu K α X-ray beams (with a wavelength of 1.54 Å) passed through a Ge (2 2 0) four-fold channel-cut monochromator crystal were used in the diffraction experiments.

The experimental rocking curves have a certain saw-tooth profile. This shape is characteristic of two-dimensional structures (graphene, adsorbate layers, carbon nanotubes, etc.). In addition, the diffraction peaks for both the samples are substantially broader than the standard instrumental XRD peaks. Situations of this kind are typical of powder-like and dispersed media.

Fig. 3 demonstrates the possible presence of a compound with a spinel lattice in the phosphate sample #1, with the presence of a noticeable fraction of this compound in sample #2 being hardly probable. Unfortunately, the diffraction data give no way of exactly determining the fraction of a particular spinel-latticed substance in sample #1 (although this spinel may, in fact, impart magnetic properties to sample #1).

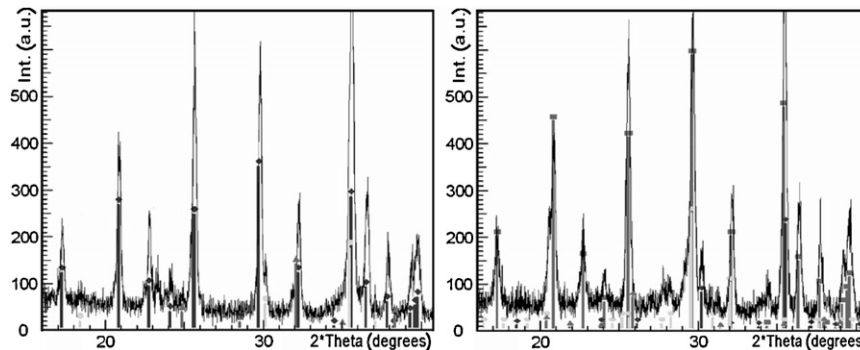


Fig. 3. XRD data for the LiFePO₄ samples #1 (left) and #2 (right).

4. Data processing technique

A new EXAFS processing method developed by some of the authors [2] was applied to all the spectra described in this paper. The method includes a procedure for extracting EXAFS oscillations with the help of the variation principle and a rough estimation of the Fourier window limits which, nevertheless, can diminish the effect of the experimental noise on the results obtained in analyses of the spectra.

A special functional is constructed in order to extract the oscillating part from an EXAFS spectrum under consideration. This functional must take the minimum value for the sought-for smooth part of the spectrum, required to calculate the oscillations. The functional consists of integral terms responsible for the smoothness of the sought-for function, its closeness to the spectrum itself, and zero value of the integral of the smooth part subtracted from the spectrum, taken over the processing range. The functional-minimization task can be transformed to the Euler–Lagrange equation having in the given case the form:

$$\left(\frac{d^2}{dE^2} - C^2 \right) \mu_0 = C^2(A - \mu),$$

where E is the photon energy, μ is the EXAFS spectrum with the smooth part μ_0 , and A and C are the processing parameters interrelated by the condition that the integral of the function $\mu(E) - \mu_0(E)$ is zero. A couple of first-order boundary conditions complement the task to make it unambiguous. The optimal value of C is to be chosen as approximately the reciprocal of the oscillation period μ [3].

A series of analyses of how the EXAFS processing results depend on the Fourier window limits have been made for spectra of the reference metals (V, Cr, Co, Cu, Zr, Ag) [3]. It was found that the most correct EXAFS processing results are obtained when the lower Fourier window limit is taken to be 40–80 eV and the window width is between 300 and 600 eV. Wider windows lead to a more pronounced noise contribution to the Fourier-transformed oscillations.

5. Results and discussion

The Fourier-transformed EXAFS oscillations for the Ti K-edge EXAFS of Li₄Ti₅O₁₂ and the three Fe K-edge spectra of LiFePO₄ are presented in Figs. 4 and 5, respectively.

The EXAFS spectrum of lithium titanate was converted to a pseudo-density curve describing the distribution of interatomic distances in the next way. The edge energy was found from the peak position of the first derivative of the spectrum, $d\mu/dh\nu$. This widely employed approach yielded a value of 4.977 keV for the edge [1,4]. The oscillations of the spectrum were separated by the method based on the variation principle and described in Section 3 of this

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