

In situ XANES and EXAFS Study of $\text{Li}_{2.1}\text{Fe}_{0.9}\text{Si}_{0.9}\text{P}_{0.1}\text{O}_4$ cathode material for Li-ion batteries

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We recently synthesized new nanocrystalline $\text{Li}_{2.1}\text{Fe}_{0.9}\text{Si}_{0.9}\text{P}_{0.1}\text{O}_4$ materials with partial exchange of P on Si site in P21/n space group. Prepared material is potentially interesting as cathode material for high energy density Li-ion batteries. The in-situ XAS measurements were used for detailed monitoring of structural changes and changes of Fe oxidation state in the electrode material during in the process of charging and discharging of battery (lithium extraction and insertion).

Fe K-edge absorption spectra of the $\text{Li}_{2.1}\text{Fe}_{0.9}\text{Si}_{0.9}\text{P}_{0.1}\text{O}_4$ cathode material sample were measured at room temperature in transmission detection mode at beamline C of HASYLAB, using a Si(111) double-crystal monochromator with about 1 eV resolution at 7 keV. Higher-order harmonics were effectively eliminated by a flat Ni coated mirror and by detuning the monochromator crystals to 60% of the rocking curve maximum, using the beam-stabilization feedback control. The beam size on the sample was 5 mm x 1 mm. The intensity of the x-ray beam was measured by three consecutive 10 cm long ionization detectors, the first filled with N₂ at the pressure of 900 mbar, the second filled with 210 mbar of Kr and the third 310 mbar of Kr. The absorption spectra were measured within the interval [-250 eV to 1000 eV] relative to the Fe K-edge. In the XANES region, equidistant energy steps of 0.3 eV were used, while for the EXAFS region, equidistant k-steps ($\Delta k \approx 0.03 \text{ \AA}^{-1}$) were adopted, with an integration time of 1s/step. In all experiments the exact energy calibration was established with simultaneous absorption measurement on 5-micron thick Fe metal foil (Fe K-edge 71123.0 eV) placed between the second and the third ionization chamber. Absolute energy reproducibility of the measured spectra was $\pm 0.05 \text{ eV}$.

The sample was prepared in the form of half-battery using EC:DEC 0.4M LiTDI electrolyte. The battery was sealed in a coffee bag. The total absorption thickness (μd) of the sample was about 2.6 above the investigated Fe K-edge, with Fe K-edge jump of about 2. The half battery was mounted on a sample holder in vacuum between the first and the second ionization detector. The XAS spectra were measured initially on as-prepared sample, then in continuous repetitions during the first cycle of charging (621 minutes) and discharging (693 minutes) of the battery with a current density corresponding to C/20 and voltage range of voltage range 4.2V to 1.2V. The measuring time for each spectrum was 30 minutes, so that 50 XANES and EXAFS spectra were collected.

Fe K-edge XANES spectra from the series obtained during first charge/discharge cycle are shown in Fig. 1. As prepared sample was partly oxidized, containing 19.1% of Fe^{3+} , as determined with Moesbauer spectroscopy. A gradual shift of the edge to higher energies is clearly visible during battery charging (Fig. 1 left). In the process of battery discharging (Fig. 1 right) a gradual shift of the edge back towards the initial state, but not reaching it. The results therefore indicate that the changes of Fe valence state and symmetry are not completely reversible after the first cycle.

In XANES analysis the ratio of $\text{Fe}_{3+}/\text{Fe}^{2+}$ is precisely determined using the linear-combination-fit method, as reported in our previous XANES analyses of similar cathode materials [1 - 4].

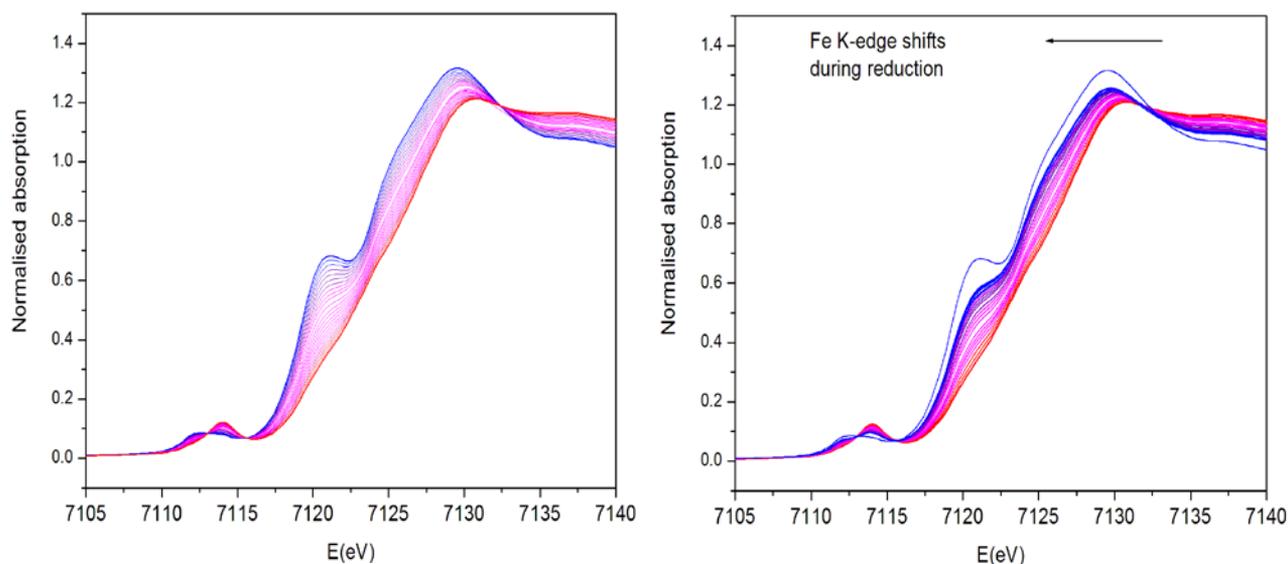


Figure 1: Normalized Fe K-edge XANES spectra of $\text{Li}_{2.1}\text{FeP}_{0.1}\text{Si}_{0.9}\text{O}_4$ sample during the process of charging (oxidation) (left) and discharging (reduction) (right). The spectrum of as prepared sample is plotted for comparison.

The Fe-K edge EXAFS spectra from the series obtained during the first charge/discharge cycle reveal the contributions of individual shells of atoms around Fe. The spectra show significant structural changes only in the nearest oxygen coordination shell around Fe cations during oxidation. During the first cycle of reduction the structural changes are not completely reversible. The cathode material does not return to the structure of the as-prepared sample.

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