

# In situ XANES and EXAFS Study of $\text{Li}_{2-x}\text{NiTiO}_4$ cathode material for Li-ion batteries

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In-situ x-ray absorption spectroscopy (XAS) was used to obtain direct information on Ni valence state and local environment of Ni cations in the crystal structure of  $\text{Li}_{2-x}\text{NiTiO}_4$ . The material, recently synthesized in our laboratory via a patented citrate-precursor method [1], possesses almost all the desired properties to become perfect cathode material for high energy density Li-ion batteries in the future. The in-situ XAS measurements allowed detailed monitoring of structural changes and changes of Ni oxidation state in the electrode material during Li-ion extraction and insertion in the process of charging and discharging of the battery.

Ni K-edge absorption spectra of the  $\text{Li}_{2-x}\text{NiTiO}_4$  cathode material samples were measured at room temperature in transmission detection mode at beamline E4 of HASYLAB, using a Si(111) double-crystal monochromator with about 1.5 eV resolution at 8 keV. Higher-order harmonics were effectively eliminated by a flat Au coated mirror and by detuning the monochromator crystals to 60% of the rocking curve maximum, using the beam-stabilization feedback control. The beam was focused by a toroidal Au coated mirror. The beam size on the sample was 6 mm x 1 mm. The intensity of the x-ray beam was measured by three consecutive 10 cm long ionization detectors filled with Ar at the pressure of 90 mbar, 600 mbar and 770 mbar; respectively. The absorption spectra were measured within the interval [-250 eV to 1000 eV] relative to the Ni 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 Ni metal foil (Ni K-edge 8333.0 eV) placed between the second and the third ionization chamber. Absolute energy reproducibility of the measured spectra was  $\pm 0.03$  eV.

The samples were prepared in the form of half-batteries with the total absorption thickness ( $\mu\text{d}$ ) of about 2 above the investigated Ni K-edge. The half battery was mounted on a sample holder 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 (520 minutes) and discharging (535 minutes) of the battery with a current density corresponding to C/6. The measuring time for each spectrum was 30 minutes, so that 37 XANES and EXAFS spectra were collected.

Absorption spectra of some reference nickel compounds with known Ni valence state and structure (Ni acetate, NiO) were recorded for comparison. The reference samples were prepared from micronised powders of the Ni compounds homogeneously mixed with micronised BN powder and pressed into homogeneous pellets with the total absorption thickness of about 1.5 above the Ni K-edge.

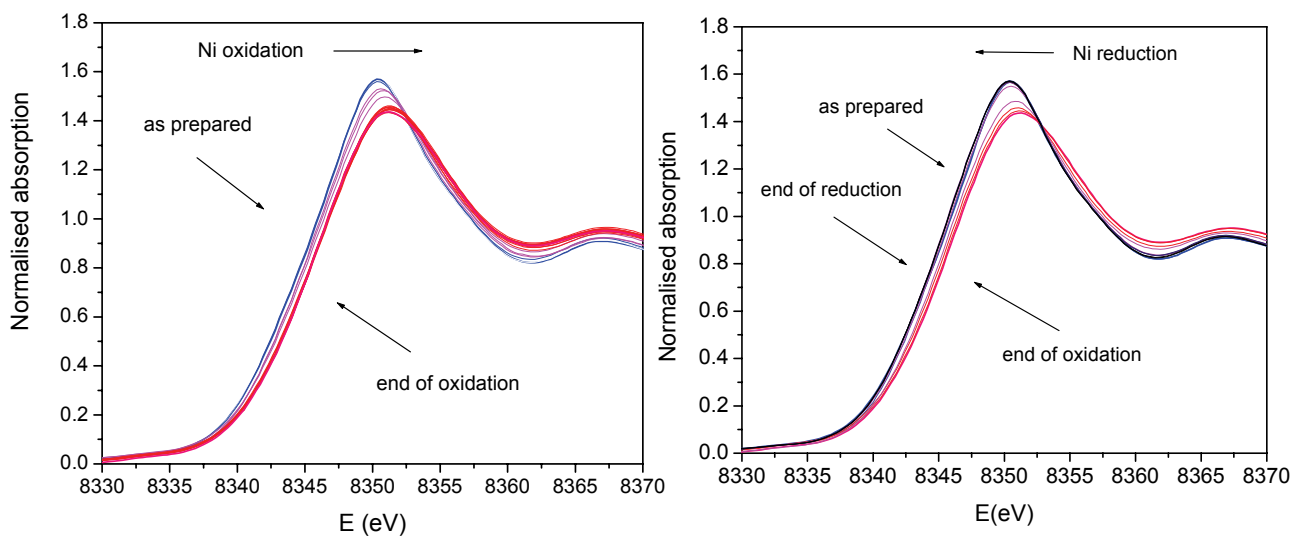


Figure 1: Normalized Ni K-edge XANES spectra of  $\text{Li}_{2-x}\text{NiTiO}_4$  sample during the process of charging (oxidation) (left) and discharging (reduction) (Right).

Ni K-edge XANES spectra from the series obtained during first charge/discharge cycle are shown in Fig. 1. A gradual shift of the edge to higher energies is clearly visible during first 230 minutes of battery charging (fig 1 left). In the process of battery discharging (Fig 1 right) a gradual shift of the edge back to the initial energy value is detected. The results therefore indicate that the changes of Ni valence state and symmetry are reversible in one cycle.

The Ni-K edge EXAFS spectra from the series obtained during the first charge/discharge cycle reveal the contributions of individual shells of atoms around Ni. The spectra show significant structural changes only in the nearest oxygen coordination shell around Ni 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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### References

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