

Direct Observation of Electrochemically Active Fe³⁺/Fe⁴⁺ in LiCo_{0.8}Fe_{0.2}MnO₄ by *in situ* Mössbauer and *in situ* X-Ray Absorption Spectroscopy

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The redox activity of Fe³⁺/Fe⁴⁺ in the spinel LiCo_{0.8}Fe_{0.2}MnO₄ has been tracked in a Li-ion battery via *in situ* Mössbauer spectroscopy and *in situ* X-ray absorption spectroscopy (XAS) during electrochemical cycling. The initial Mössbauer spectrum consists of a doublet with isomer shift IS = 0.330(1) mm/s and quadrupole splitting QS = 0.722(1) mm/s (Fig. 1). These parameters are characteristic of Fe³⁺ in a high-spin state on the octahedral sites of the spinel structure. During the beginning of the charging process vs. Li⁺|Li, a broadening of this doublet can be observed. This corresponds to an increased electric field gradient at the site of the Fe nuclei, i.e. an increase of structural disorder around the Fe ions.

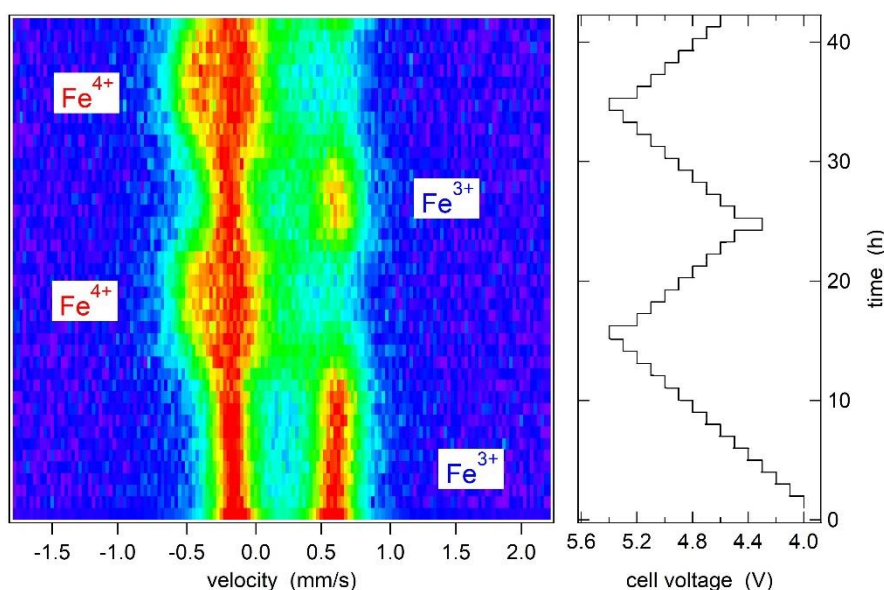


Fig. 1: *In situ* Mössbauer spectra of LiCo_{0.8}Fe_{0.2}MnO₄ acquired during cycling against Li⁺|Li.

During further charging, this Fe³⁺ doublet successively disappears and is replaced by a new narrow doublet with isomer shift of -0.134(6) mm/s. This negative value clearly reveals that Fe⁴⁺ is formed. Further cycling between 5.3 V and 4.3 V reveals that this oxidation is highly reversible.

The XAS spectra (not shown here) acquired during charging of LiCo_{0.8}Fe_{0.2}MnO₄ vs. Li⁺|Li clearly show a shift of the Fe K absorption edge towards higher binding energies and thus an oxidation of Fe³⁺ to Fe⁴⁺. The XAS spectra acquired during discharging show again that this process is fully reversible.

In summary, the reversible formation Fe⁴⁺ was clearly observed by both methods, hence proving the electrochemical activity of Fe at voltages above 5 V vs. Li⁺|Li. This enables future research on new environmentally benign and inexpensive electrode materials with operating voltages above 5 V and thus an increased energy density.