

^7Li MAS NMR study of the lithium iron phosphate system for Li-ion batteries

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Lithium iron phosphate has over the last decade become one of the new emerging materials for Li-ion batteries. Most often, battery materials are paramagnetic and studying them with Nuclear Magnetic Resonance spectroscopy appears of first interest. Indeed, NMR, as a local probe, is very sensitive to the presence of single electrons close to the nucleus under observation, thanks to the dominating interaction; the Fermi-Contact shift. In particular, in paramagnetic materials, some spin density is transferred from the transition metal ion to the nucleus probed by mechanisms described in literature [1]. These delocalization and polarization effects induce positive and negative Fermi contact shifts respectively.

Lithium iron phosphate phase (Fig. 1) (Pnma symmetry) [2] possess a single environment for the transition metal ion, for Li and P, and three environments for O. Fe^{2+} ions with ($t_{2g}^4 e_g^2$) electronic octahedral configuration are present.

Lithium iron phosphate phase was electrochemically oxidized and then characterized by ^7Li NMR (Fig. 2) with Hahn Echo sequences. A spectrum fit was done in each case and we were able to distinguish different NMR peaks.

To understand and assign the signals observed for all the phases, we have examined the possible spin transfer mechanisms occurring in delithiation process, taking into account Li environment (Fe^{2+}). The use of DFT calculations of the Fermi contact coupling constant A^i , directly linked to the NMR shift (and then giving its sign and size), further assists us in the spectral analysis.

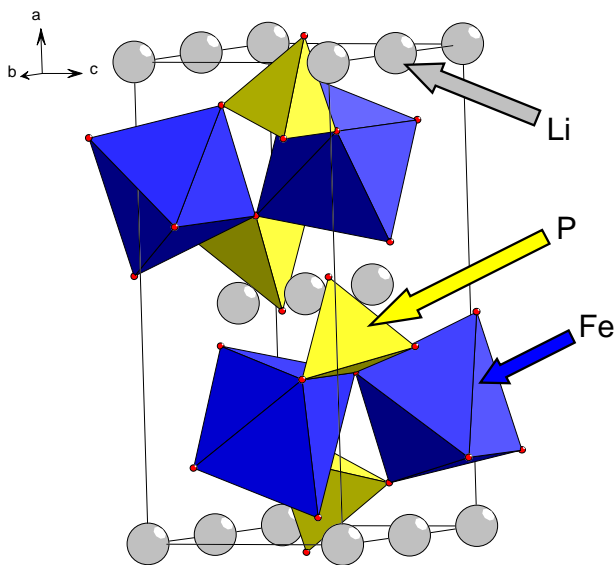


Fig. 1: Structure of LiFePO_4 based on coordinates from [2].

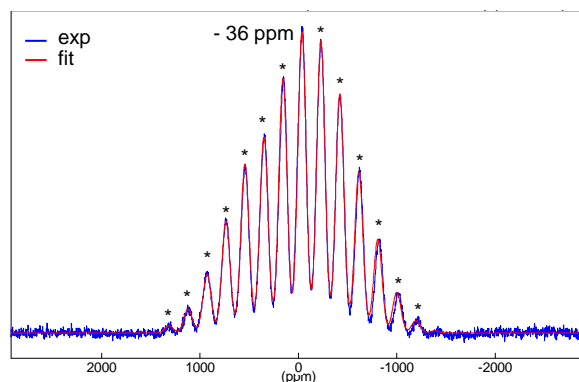


Fig. 2: ^7Li MAS NMR spectra of LiFePO_4 at 155 MHz (Hahn echo) with a spinning rate of 30 kHz. Blue line correspond to experimental spectrum and red line to the fit.

Acknowledgements

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References

- [1] D. Carlier, M. Ménétrier, C.P. Grey, C. Delmas, and G. Ceder, *Phys. Rev. B Condens. Matter Mater. Phys.* (2003), 67, 1741031-17410314.
- [2] A. Nytén and J. O. Thomas, *Solid State Ionics* (2006), 15, 1327-1330.