

MAS NMR Studies of Olivine LiFePO_4

Young Joo Lee, Marca Doeff, Jeffrey A. Reimer, and
Elton J. Cairns

Ernest Orlando Lawrence Berkeley National
Laboratory, and Department of Chemical
Engineering, University of California at Berkeley,
Berkeley, CA 94720

LiMPO_4 materials with the olivine structure are of current interest for use in rechargeable Li batteries. The polyanion PO_4 groups provide bridges between the layers and stabilize the structure even in the fully charged state.¹ Among the various olivine compounds, LiFePO_4 and $\text{Li}[\text{Fe},\text{Mn}]\text{PO}_4$ show the promising characteristics, which are extremely dependent on synthesis methods.

The ^7Li NMR spectra of various LiFePO_4 samples showing a range of capacities and cycling stabilities, were obtained. A single resonance at -14 ppm is observed for all the materials, which indicates only one local environment for the lithium cations without the presence of a significant amount of defect sites. It is noteworthy that there is no correlation between the electrochemical performance and the structure, implying that the ability of the intercalation/deintercalation of these materials mainly depends on other factors such as the particle size and morphology. The ^7Li NMR spectra of LiFePO_4 samples which were charged to different stages are shown in Figure 1. Here, the extent of the charging is calculated based on the capacity measured (~ 140 mAh/g) during the charging. As the charging proceeds, a single resonance is seen without a significant change in the peak position. For example, the resonance of the 60 % charged material shifts to -17 ppm, compared to the resonance of the 0 % charged electrode at -22 ppm. Since 60 % charging corresponds to $\text{Li}_{0.5}\text{FePO}_4$, the electrode has Fe^{2+} and Fe^{3+} in equal amounts. Previously, we observed the resonance at -8 ppm for LiFePO_4 and 68 ppm for LiMnPO_4 .² Since Fe^{3+} has the same electronic configuration as Mn^{2+} , $\text{Li}_{0.5}\text{FePO}_4$ is expected to give rise to a resonance at 30 ppm, which is not consistent with our observation. Thus, it appears that the lithium cations that remained in the structure have the same environment as LiFePO_4 . This raises the question of the deintercalation mechanism of the shrinking core model vs. the mosaic model³ and more work is under way to clarify the situation.

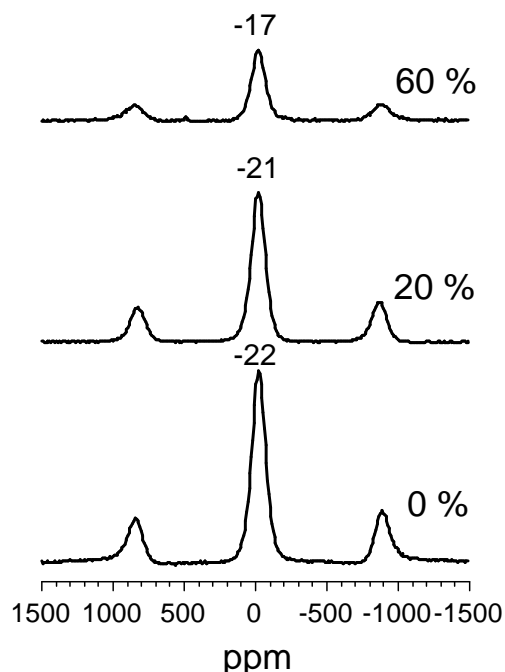


Fig. 1. ^7Li MAS NMR spectra of LiFePO_4 at different stages of charging. All the spectra were acquired with an echo sequence at a frequency of 25.50 MHz and spinning speeds of 22 kHz. The spectra are plotted with an absolute intensity scale normalized to the amount of sample.

References

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