

In-situ study of electrochemically-driven phase transitions in $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$

Dorthe B. Ravnsbaek,^{a,*} Kai Xiang,^a Wenting Xing,^a Olaf Borkiewicz,^b Kamila Wiaderek,^b Peter Chupas,^b Karena Chapman^b & Yet-Ming Chiang^a

^a Department of Material Science and Engineering, MIT, 02139 Cambridge, MA, USA

^b Advanced Photon Source, Argonne National Laboratory, 60439 Argonne, IL, USA

The manganese olivine LiMnPO_4 has substantially higher energy density than its iron counterpart, due to a higher voltage plateau at ~ 4.1 V vs. Li/Li^+ compared to 3.45 V for LiFePO_4 . However, LiMnPO_4 exhibits slow charge-discharge kinetics [1] even at nanoscale particle size, which has prevented its commercial use. Interestingly, with even a modest Fe addition, nanoscale $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ (LMFP) exhibits amongst the highest rate capabilities of all the olivines. It has been suggested [2] that this is due to the existence of an intermediate solid solution (here denoted $L_x\text{MFP}$) that reduces the misfit strain by breaking the single phase transition (observed for LFP) into two stages, first a transition of MFP to an intermediate phase $L_x\text{MFP}$, then between $L_x\text{MFP}$ and LMFP [2]. However, at this stage there is still no clear conclusion as to whether the transformations are two-phase first-order reactions or involve formation of solid solutions, which may be metastable. Significant discrepancies are found in the literature between the (x,y) -compositional phase diagrams for $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ determined computationally versus experimentally (by chemical delithiation of large particle powders) [3,4]. Furthermore, previous studies have not been carried out *in-situ* under dynamic electrochemical conditions. The phase evolution dependency on particle size has also not been investigated. This is of importance as the particle size is known to alter the Li-miscibility gap for LFP significantly [5].

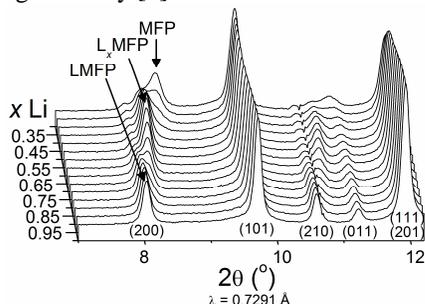


Fig. 1 Section of *in situ* PXD data for $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ measured during charge at 1C plotted as a function of the overall Li-content (x Li) in the sample based on the electrochemical data measured simultaneously.

Here we present a systematic screening of the electrochemical driven phase transitions in a series of $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ ($y = 0.1, 0.2, 0.4, 0.6$ and 0.8) powders with particle size of ~ 50 and 250 nm (based on BET surface area) during charge and discharge at different C-rates as well as selected over- and undervoltages. The screening is carried out using *in* and *ex situ* Synchrotron Radiation Powder X-ray diffraction (SR-PXD) and Pair Distribution Function (PDF) analysis. Furthermore, the materials are investigated using the Potentiostatic Intermittent Titration Technique (PITT).

Figure 1 shows a selected example of a typical set of *in situ* SR-PXD data for $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ measured during charge at 1C. The high quality data allows for Rietveld refinement (>1000 PXD patterns have been refined for this study) and thereby detailed analysis of cell

parameters providing new information about the volume misfits during the formation of non-equilibrium solid solution as well as the structural evolution as a function of both Li- and Mn-content in LMFP olivine phases. These findings will be addressed in the presentation.

Furthermore, from the *in situ* SR-PXD data a series of (x,y) -compositional phase diagrams have been constructed (see example in Figure 2). These illustrate the phase evolution as a function of Mn- and Li-content, as well as elucidate the effects of different electrochemical driving forces and particle sizes. Interestingly, they reveal a strong hysteresis between charge and discharge giving rise to a reduced Li-miscibility gap at the $\text{Fe}^{2+}/\text{Fe}^{3+}$ plateau for materials of lower Mn-content. The origin of the hysteresis as well as the study of local structure using PDF analysis will be discussed in this talk.

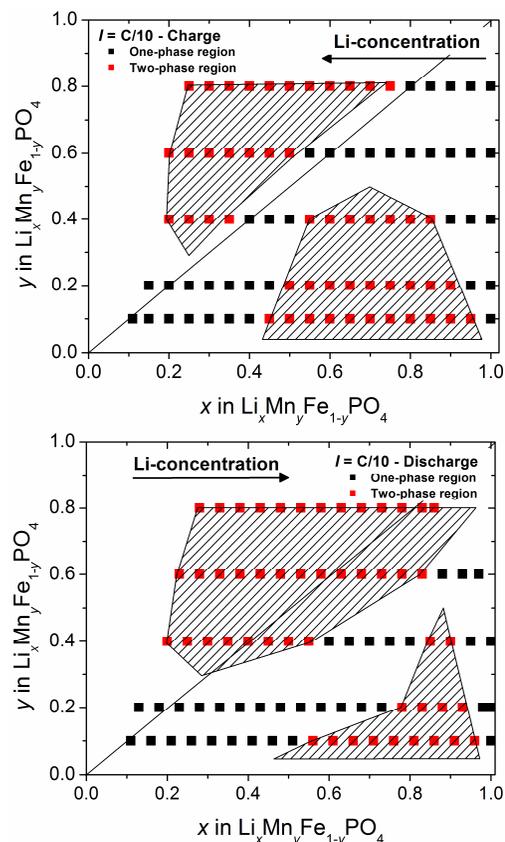


Fig. 2 (x,y) -compositional phase diagrams for $\text{Li}_x\text{Mn}_y\text{Fe}_{1-y}\text{PO}_4$ (~ 50 nm) based on *in situ* PXD measured during charge (upper) and discharge (lower) at C/10. Black and red squares represent single- and two-phase regions, respectively. The lined areas serve as guides-to-the-eye to compare two phase regions.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Award No. DE-SC0002626 and by the Carlsberg Foundation (DBR). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

References

- [1] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] Y.-H. Kao, *Ph.D. thesis*, MIT (2011).
- [3] A. Yamada, Y. Kudo, K.-Y. Liu, *J. Electrochem. Soc.* 148 (2001) A1153.
- [4] R. Malik, F. Zhou, G. Ceder, *Phys. Rev. B* 79 (2009) 214201.
- [5] N. Meethong, H.-Y. S. Huang, W. C. Carter, Y.-M. Chiang, *Electrochem. Solid-State Lett.* 10 (2007) A134.