Structure, defects and thermal stability of delithiated olivine phosphates

Scientific Achievement

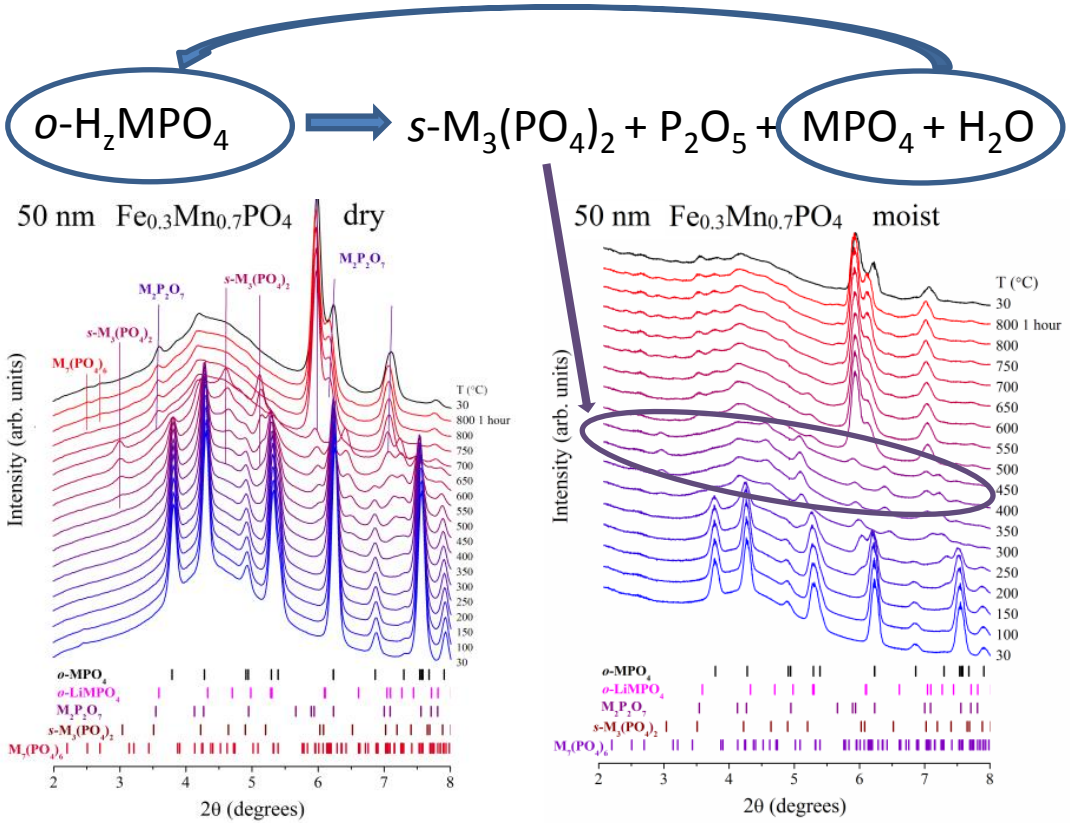
We have revealed that water catalyzes the conversion of Mn-rich olivine (Fe,Mn)MPO_4 to sarcopside $(Fe,Mn)_3(PO_4)_2$ upon heating.

Significance and Impact

Controversial data on thermal stability of delithiated Mn-rich olivines used as cathodes in Li-ion batteries is explained by detrimental role of water uncontrollably reacting with sample upon air exposure. Dry samples are stable up to 400 °C, which is safe for most applications and will allow greater energy storage than the common $LiFePO_4$.

Research Details

We investigated structural changes upon heating of delithiated olivine phosphates under variety of conditions using in-situ x-ray diffraction at NSLS. This was complemented by thermal gravimetric analysis with mass spectrometry and calorimetry. Li and H NMR also gave key information about the reactions.



In-situ high-temperature synchrotron diffraction of dry and moist $Fe_{0.3}Mn_{0.7}PO_4$ indicating that moisture exposure compromises thermal stability

G. M. Nolis, F. Omenya, R. Zhang, B. Fang, S. Upreti, N. A. Chernova, F. Wang, J. Graetz, Y.-Y. Hu, C. P. Grey, M. S. Whittingham – J. Mater. Chem. (2012) *22, 20482*

This work was performed at Binghamton University, Stony Brook University, Cambridge University and Brookhaven National Laboratory