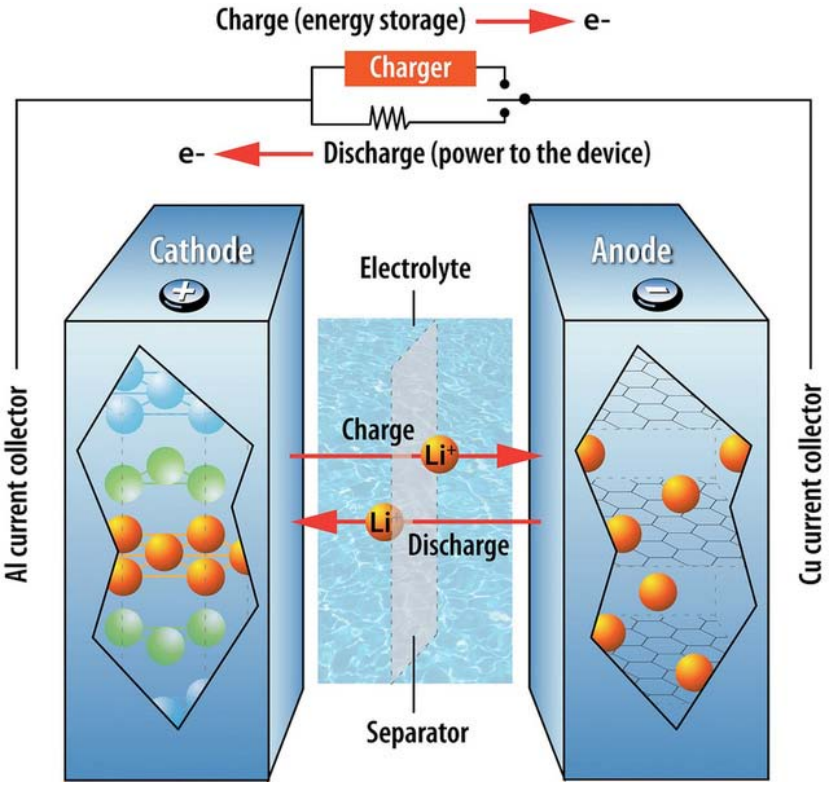
Probing Rechargeable Lithium-ion Battery using Synchrotron techniques

Yongji Tang

Lithium-ion battery



- Research Scope:
  - Cathode : LiMPO4 (M=Fe, Mn)
  - Electrolyte: Lipon, LLZO
  - Anode: MoS_2/G

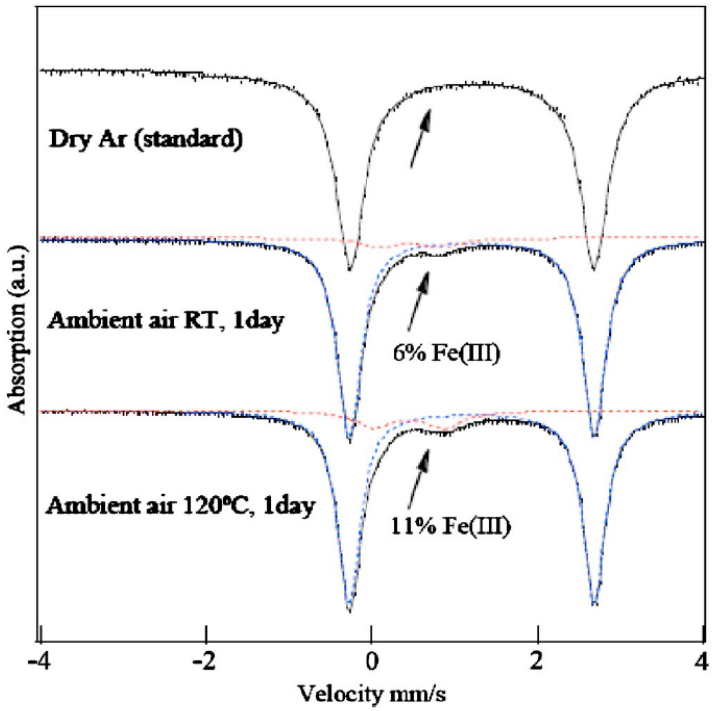
Chemical Stability of $LiMPO_4$ Cathode

- Production, transportation and storage: ambient atmosphere
- Work condition: electrolyte

- LiMPO4, M= Fe, Mn

  Fe: Mossbauer active

  Mn: Mossbauer inactive



Mössbauer spectra of LiFePO4.

Martin J F et al. Electrochem. Solid-State Lett. 2008;11:A12-A16

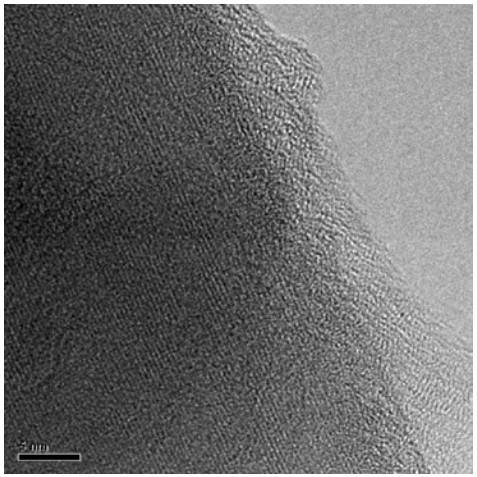
Stability of LiMPO4 in air

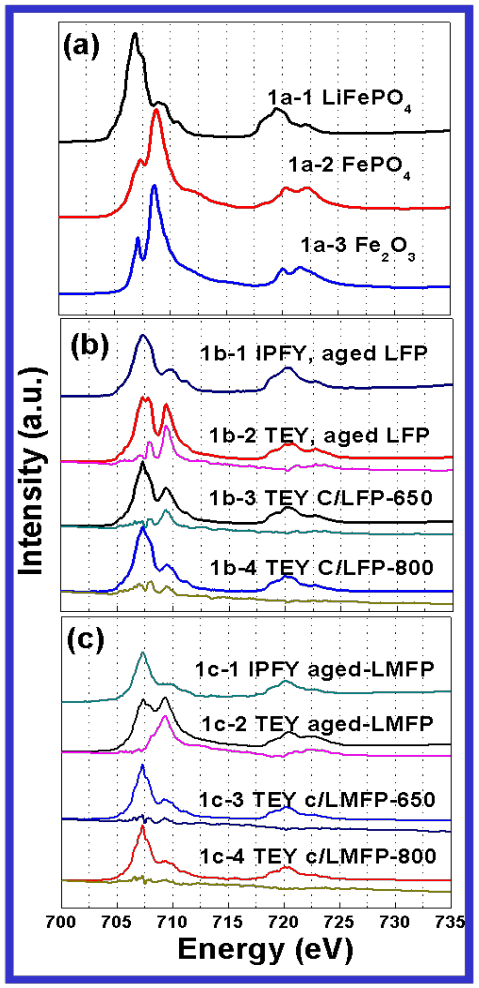
Experimental:

LiFePO4, LiMnFePO4, LiMnPO4

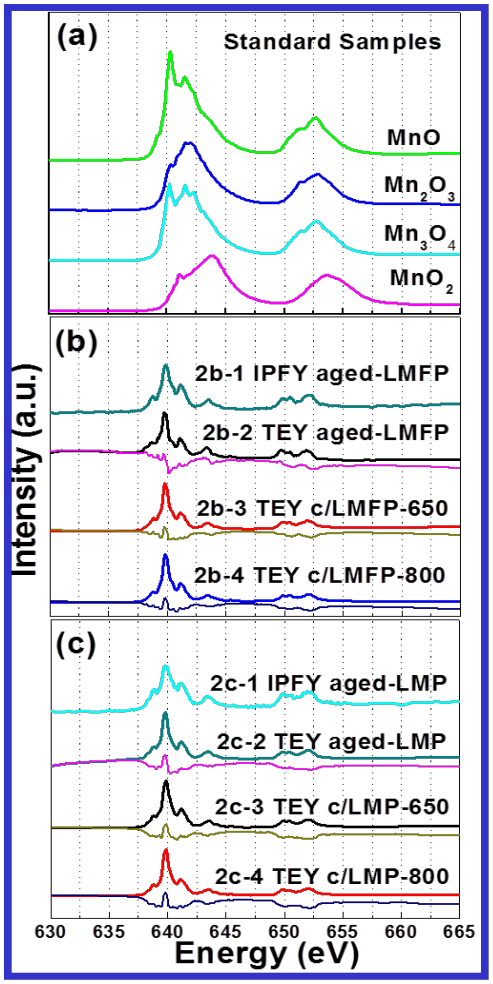
Exposed to ambient air for 6 months

Post-treatment #1: Carbon coating at 650 oC
Post-treatment #2: Carbon coating at 800 oC





Fe L-edge



Mn L-edge

Chemical Stability of LiMPO4 in Electrolyte

- Commercial Electrolyte: $LiPF_6$ in EC/ DMC
- Thermal decomposition*:

$$LiPF_6 = LiF + PF_5$$

$$PF_5 + H_2O = POF_3 + 2\ HF$$

Mechanisms**:

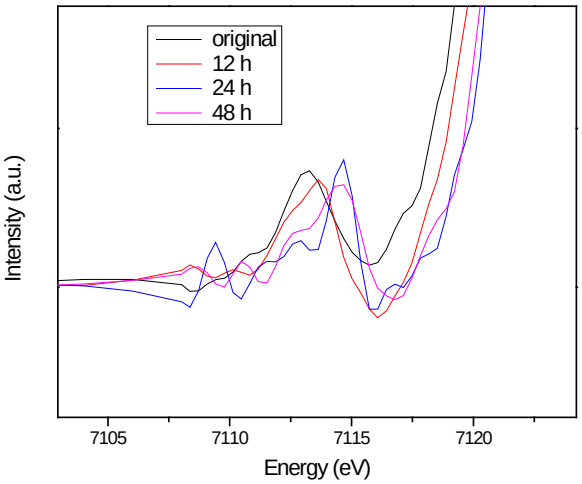
$$LiFePO_4 + 2HF = LiH_2PO_4 + FeF_2$$

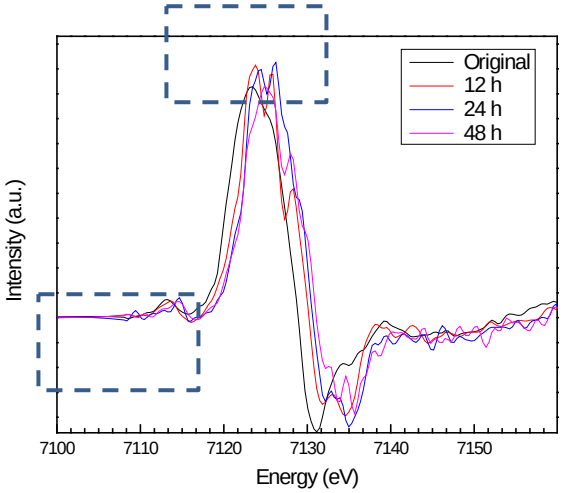
Or: $LiFePO_4 + 3HF = LiF + FeF_2 + H_3PO_4$

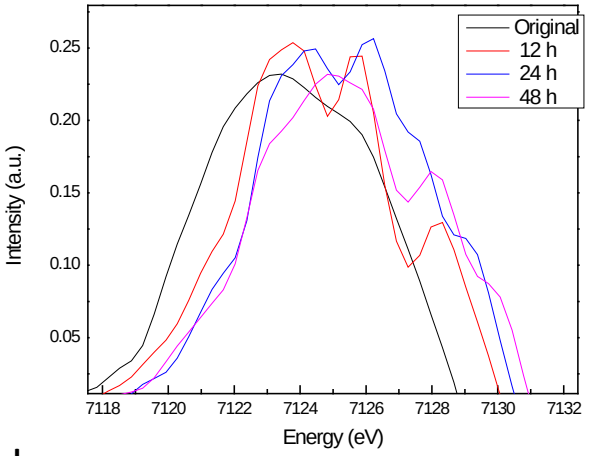
Results in reduced capacity

•S.F. Lux et al. Electrochemistry Communications 14 (2012) 47–50
•* M. Koltypin, L.F. Nazar et al, Journal of Power Sources 174 (2007) 1241–1250

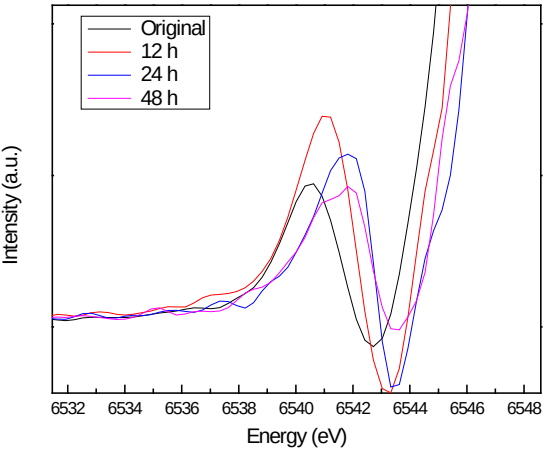
LMFP aged in electrolyte

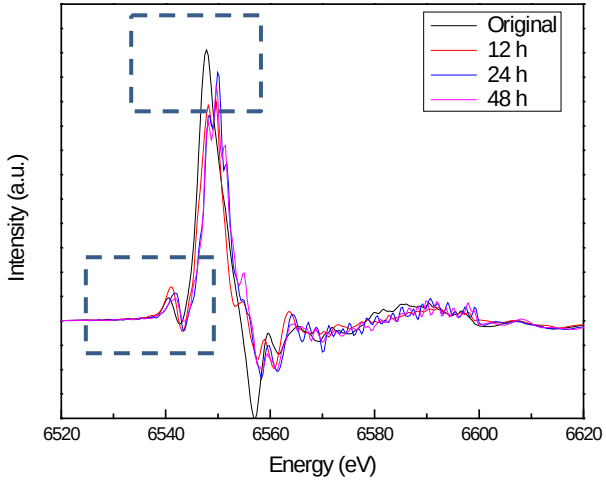


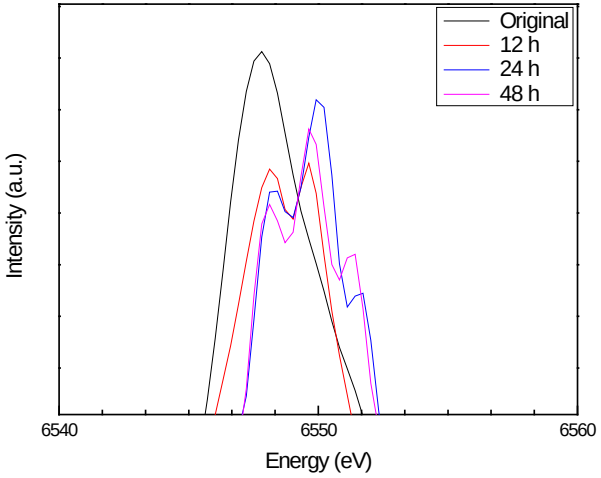




First Derivative of Fe K-edge







First Derivative of Mn K-edge

Ageing of LiFePO4 in electrolyte

Proposed Mechanisms in literature*:

$LiFePO_4 + 2HF = LiH_2PO_4 + FeF_2$

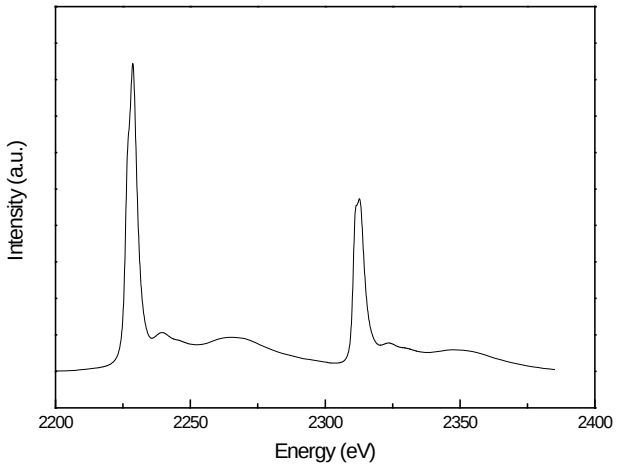
Or: $LiFePO_4 + 3HF = LiF + FeF_2 + H_3PO_4$

Our study show Fe and Mn change to higher chemical states, suggesting a different mechanism.

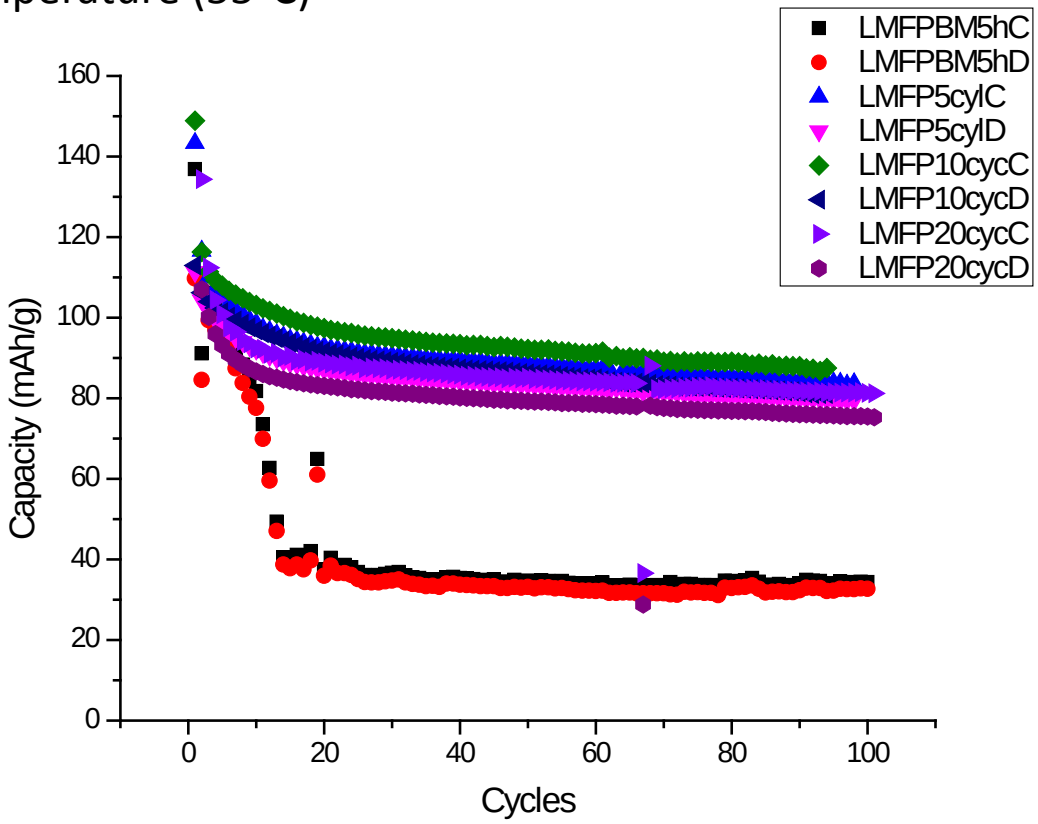
* M. Koltypin, L.F. Nazar et al, Journal of Power Sources 174 (2007) 1241–1250

ALD ageing-protective coating on LMFP

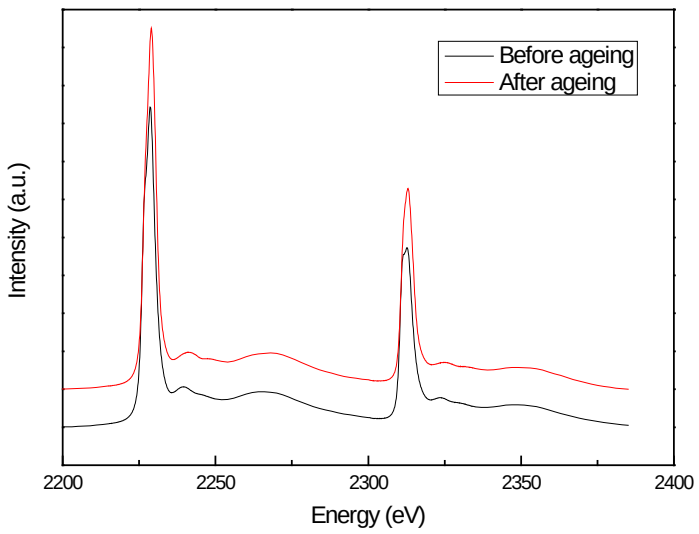
ALD ZrO2 coating (5, 10 and 20 cycles)
Charge/discharge at Elevated Temperature (55°C)



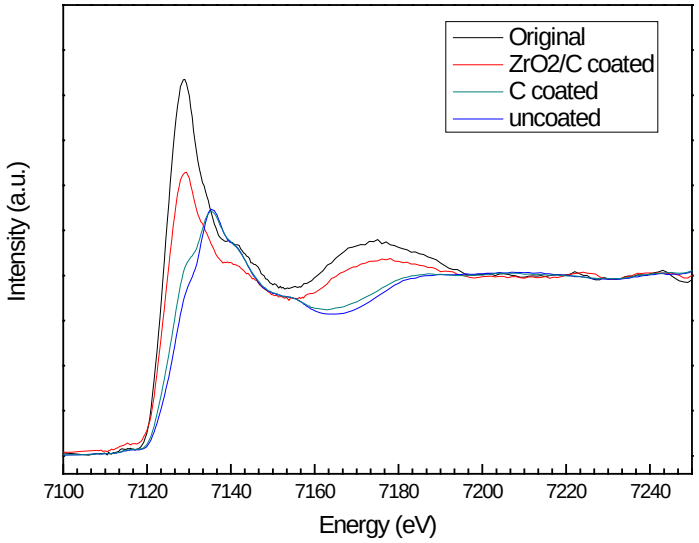
Zr $L_{3,2}$-edge XANES



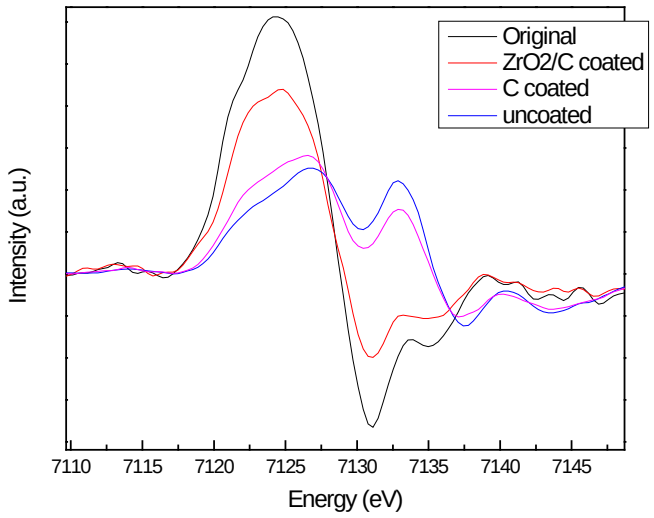
Charge/discharge performance

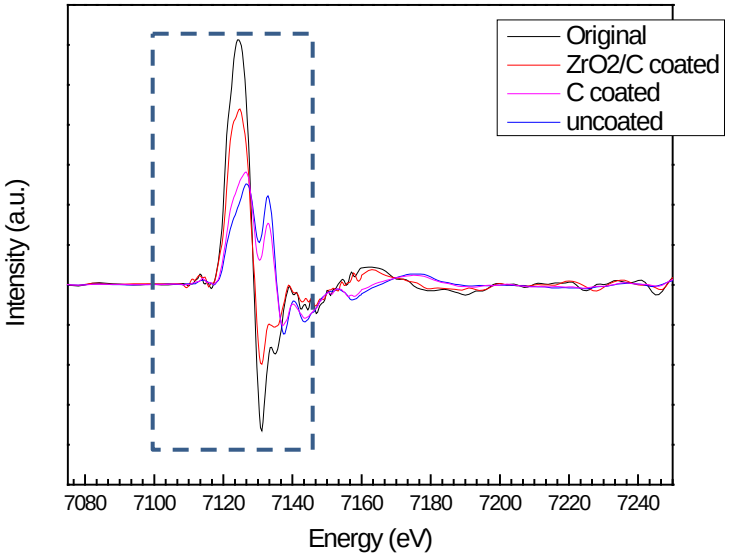


ZrO2 L-edge



Fe K-edge





First derivative

Thanks for your attention!