Structural Evolution of $Li_2Fe_{1-y}Mn_ySiO_4$ (y = 0, 0.2, 0.5, 1) and $LiFeTiO_4$ Cathode Materials for Li-Ion Batteries upon Electrochemical Cycling

Sylvio Indris, Ruiyong Chen, Ralf Heinzmann

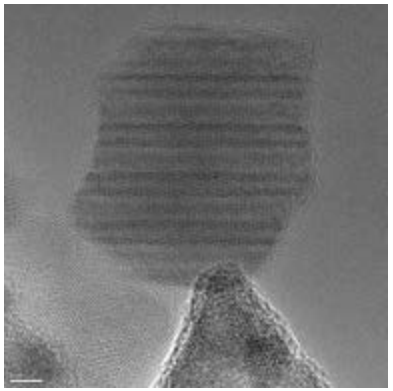
Institute of Applied Materials – Energy Storage Systems
Karlsruhe Institute of Technology

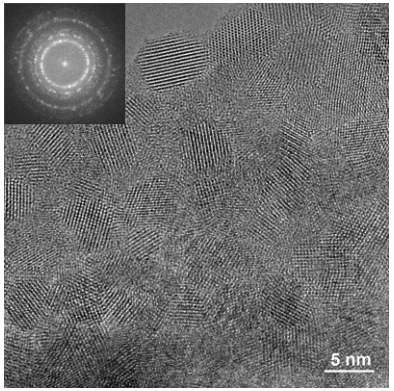
GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung
Projektträger Jülich Forschungszentrum Jülich
Deutsche Forschungsgemeinschaft DFG

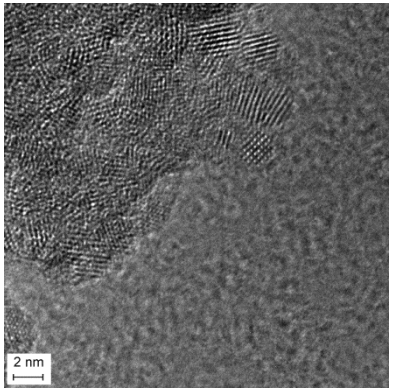
San Diego, February 18th, 2014

Overview: Cathode materials

$LiCoO_2$	0.5 Li per TM	140 mAh/g
$LiMn_2O_4$	0.5 Li per TM	150 mAh/g
$LiFePO_4$	1 Li per TM	170 mAh/g
$Li_2(Fe/Mn)SiO_4$	2 Li per TM ?	330 mAh/g ?
$Li(Fe/Mn)TiO_4$	2 Li per TM ?	290 mAh/g ?

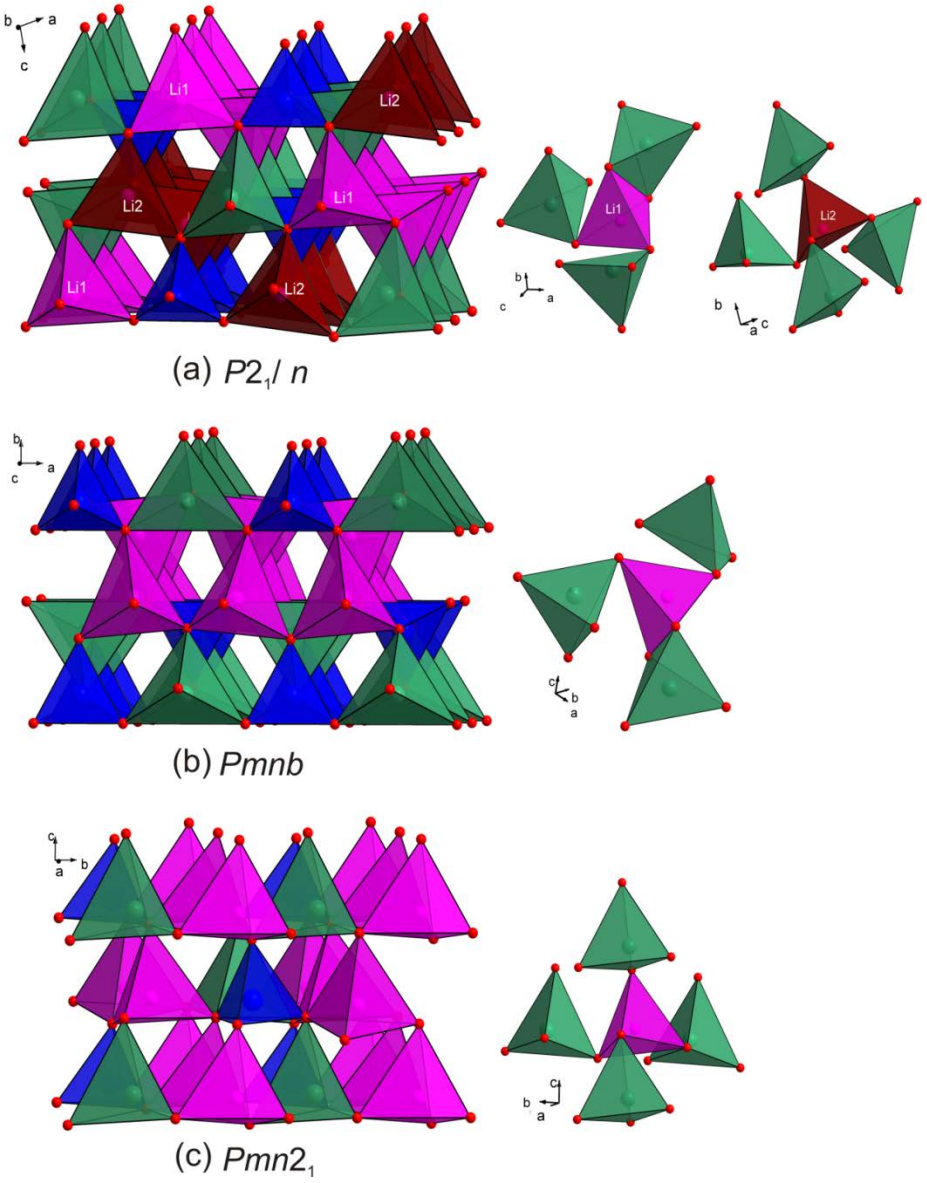






$Li_2Fe_{1-y}Mn_ySiO_4$ / C

- different polymorphs
- sol-gel synthesis
- nanocrystalline powders with carbon coating
- high capacity + high voltage possible (2 Li^+ per TM ?) $\rightarrow$ high energy density
- flexible silicate network



R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

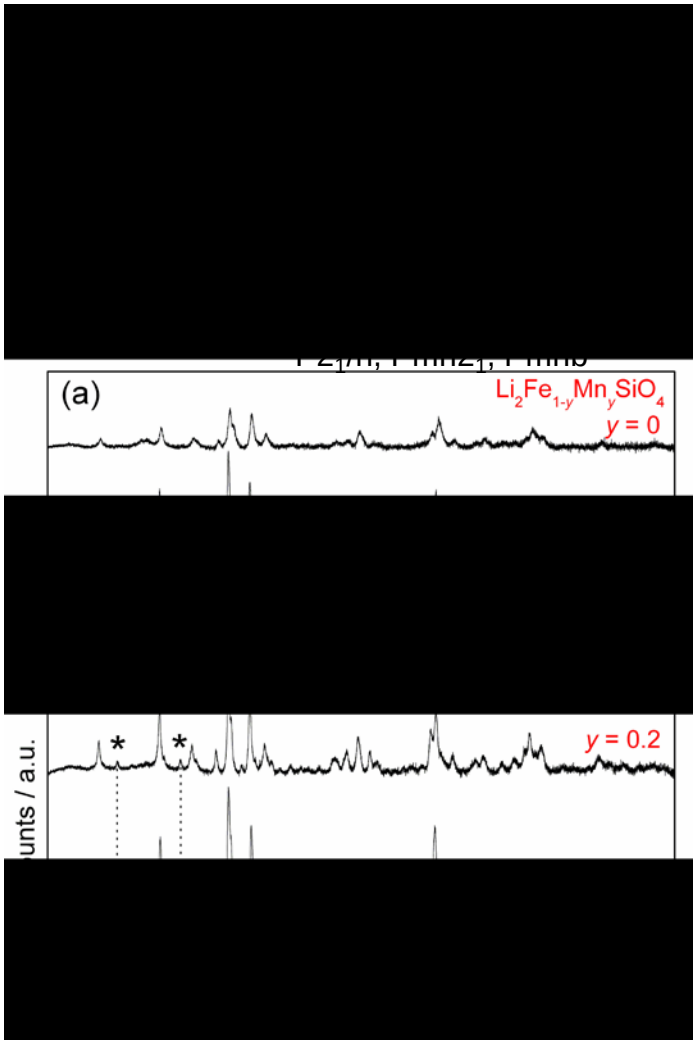
$Li_2Fe_{1-y}Mn_ySiO_4$ / C

Literature (J. Thomas, R. Dominko, …):

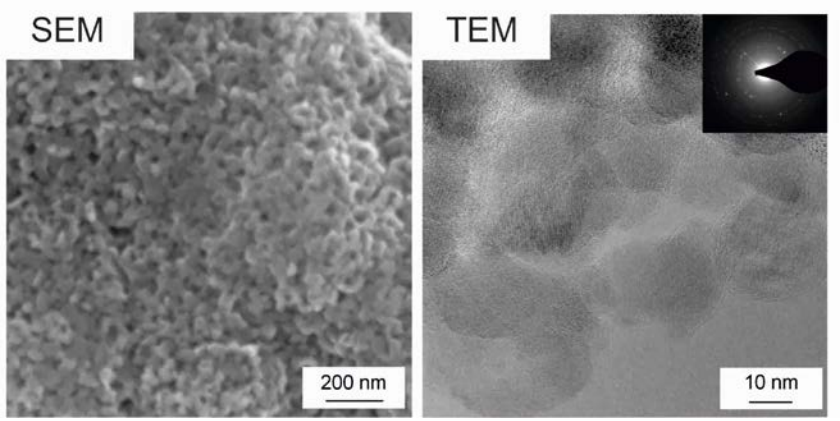
- Crystal structures
- Isolation of polymorphs
- Conversion of polymorphs during cycling
- Formation of polymorphs depends on cycling rate
- Metastable polymorphs
- Conversion during relaxation

$Li_2Fe_{1-y}Mn_ySiO_4$ / C

XRD

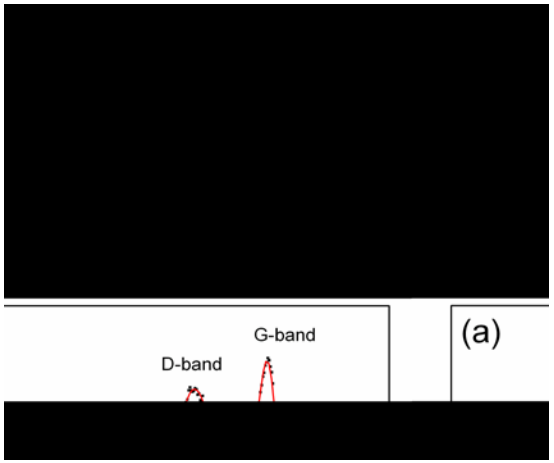


y = 0.2



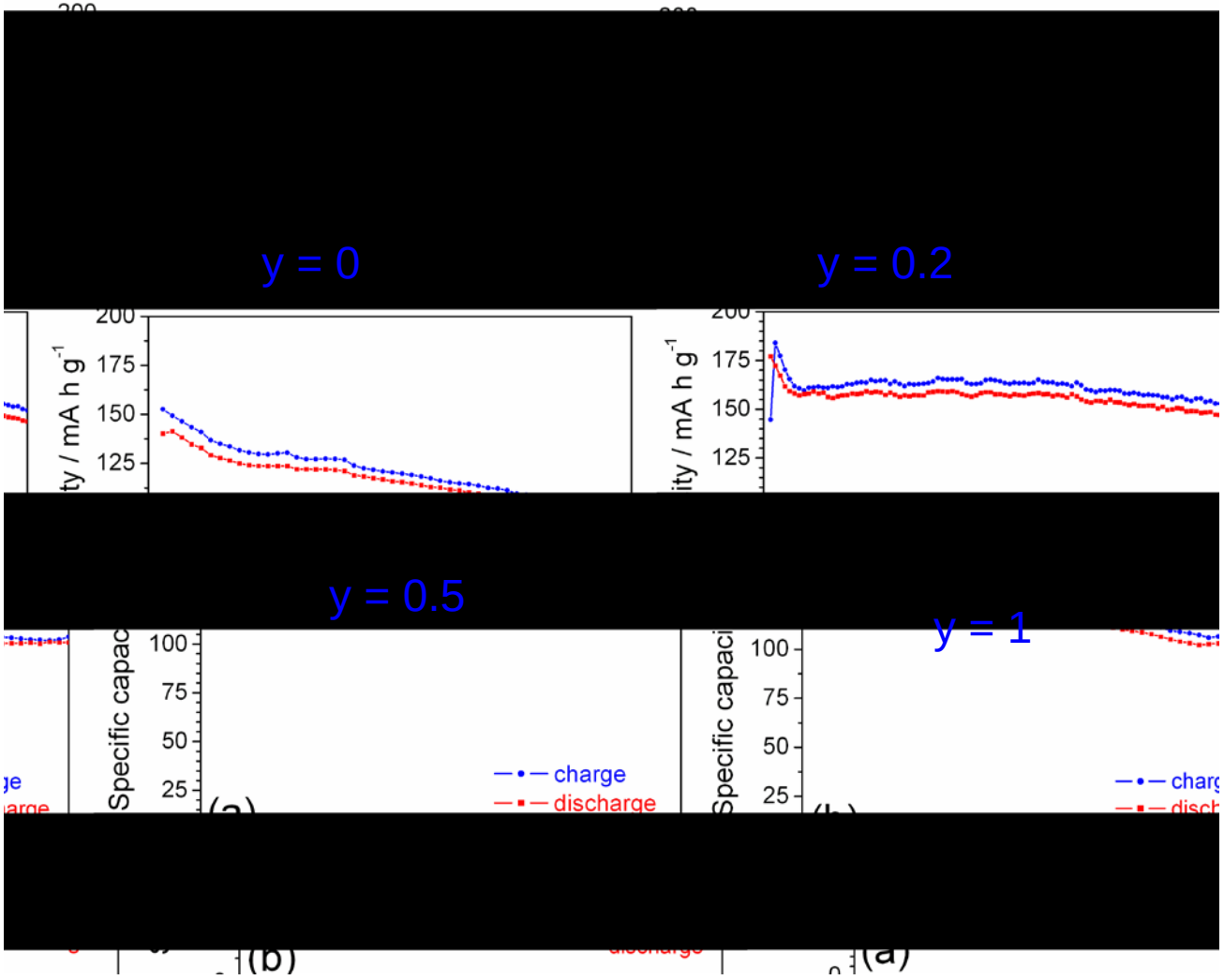
y = 0

Raman



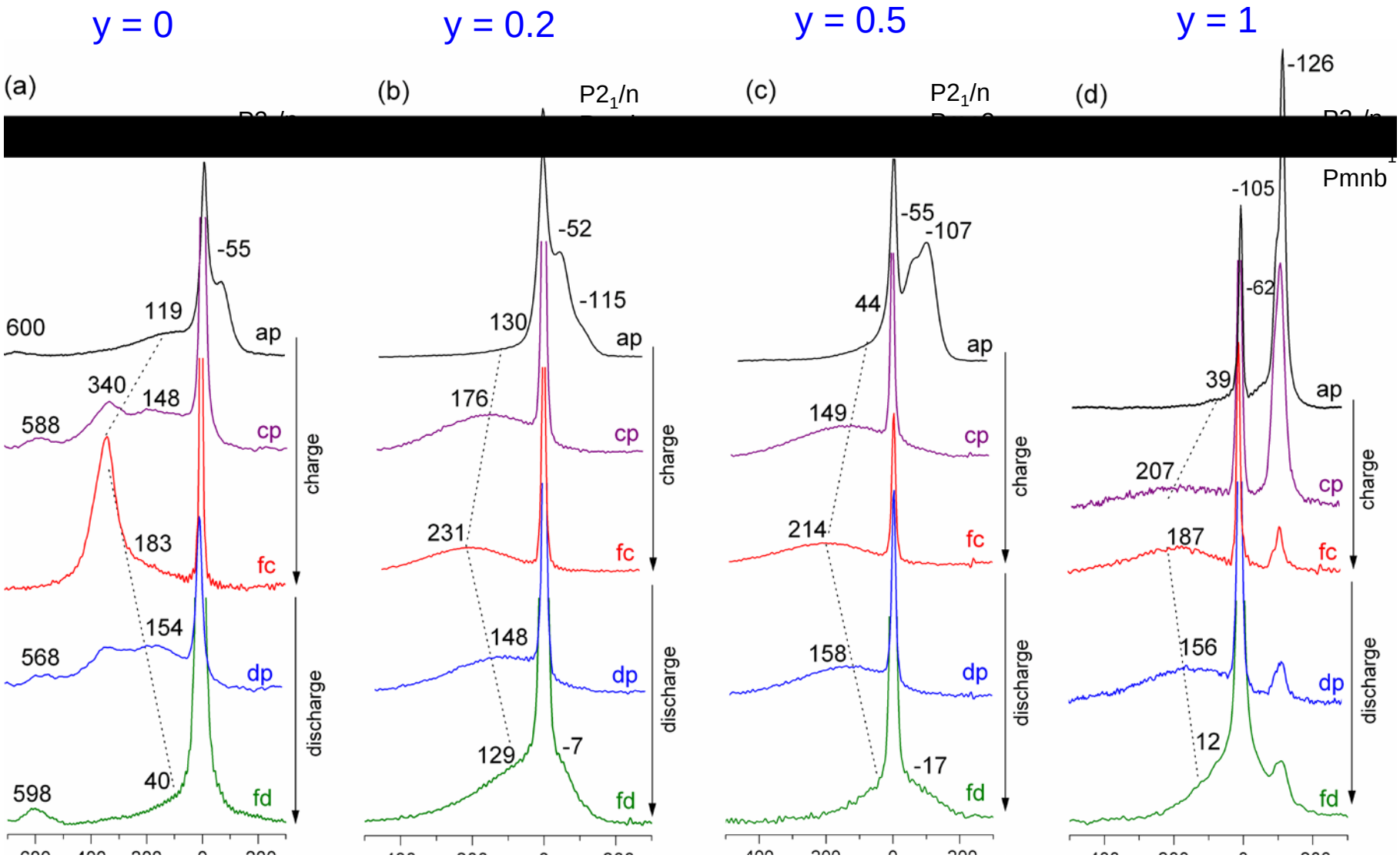
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

$Li_2Fe_{1-y}Mn_ySiO_4$ / C



R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

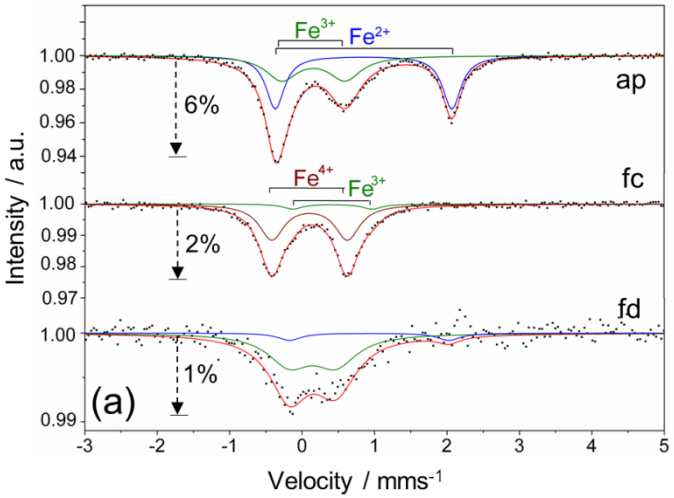
$Li_2Fe_{1-y}Mn_ySiO_4$ ^7Li MAS NMR Fe^{2+} , Mn^{2+} ↔ Fe^{3+} , Mn^{3+}



R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

$Li_2Fe_{1-y}Mn_ySiO_4$ Fe Mössbauer spectroscopy

y = 0

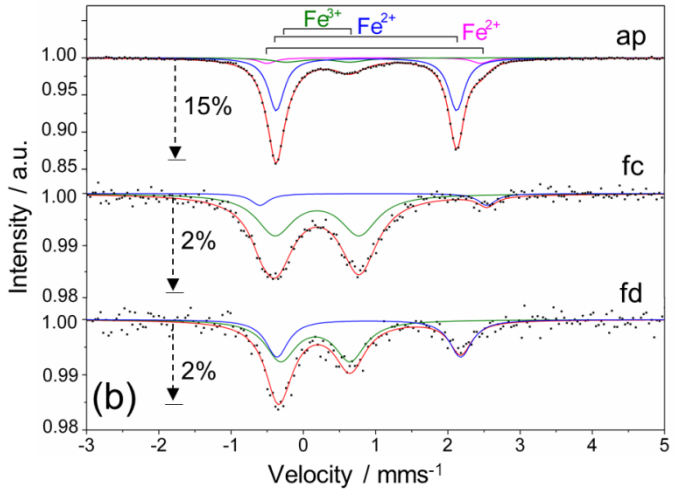


charge

discharge

$Fe^{2+} \leftrightarrow Fe^{3+}$

y = 0.2



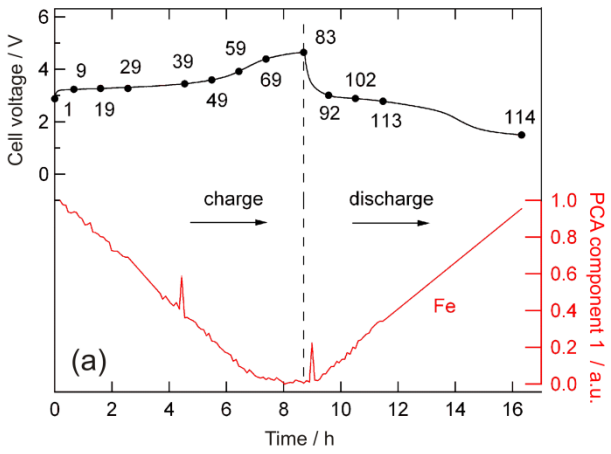
charge

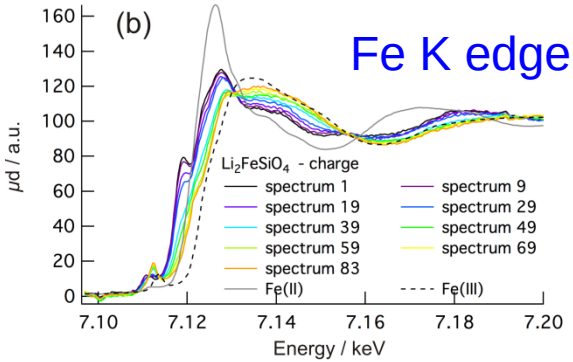
discharge

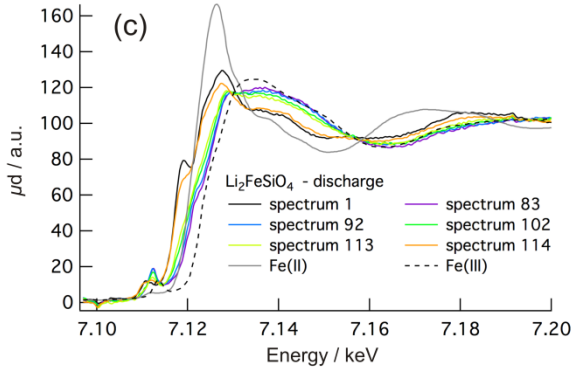
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

$Li_2Fe_{1-y}Mn_ySiO_4$ *in situ* XAS

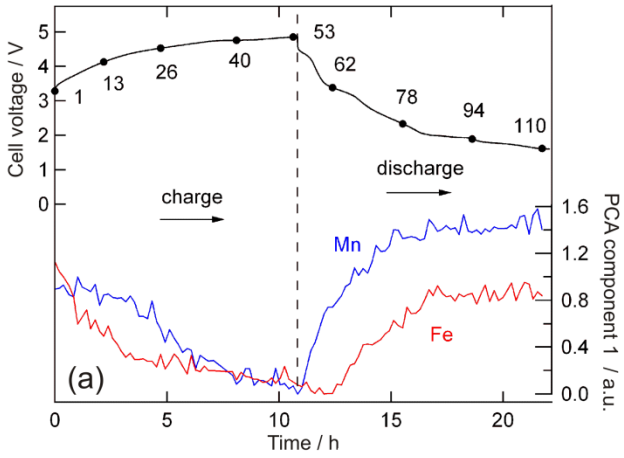
y = 0

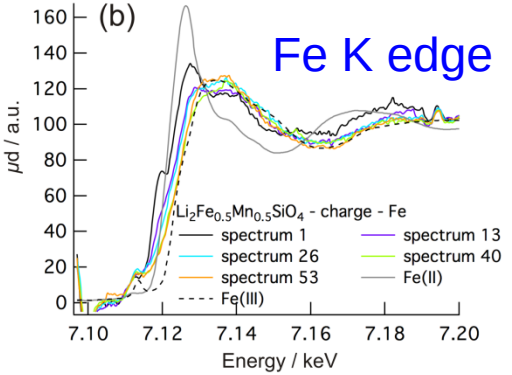


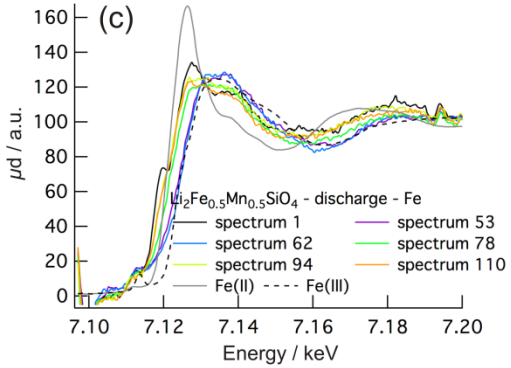


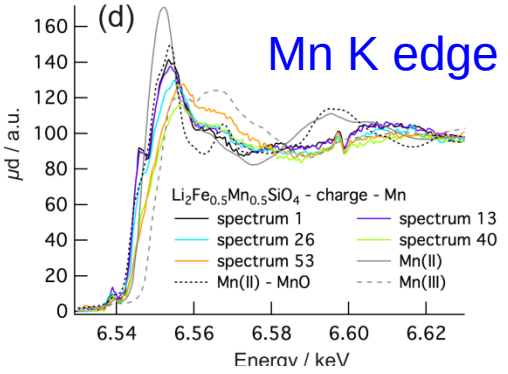


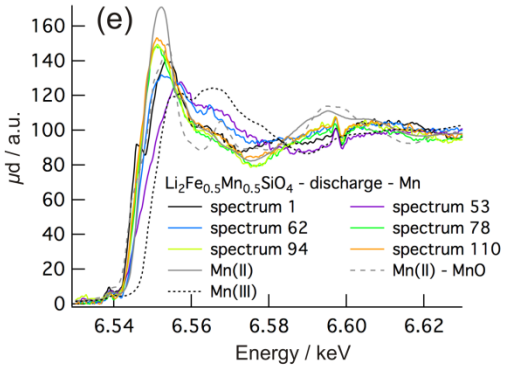
y = 0.5









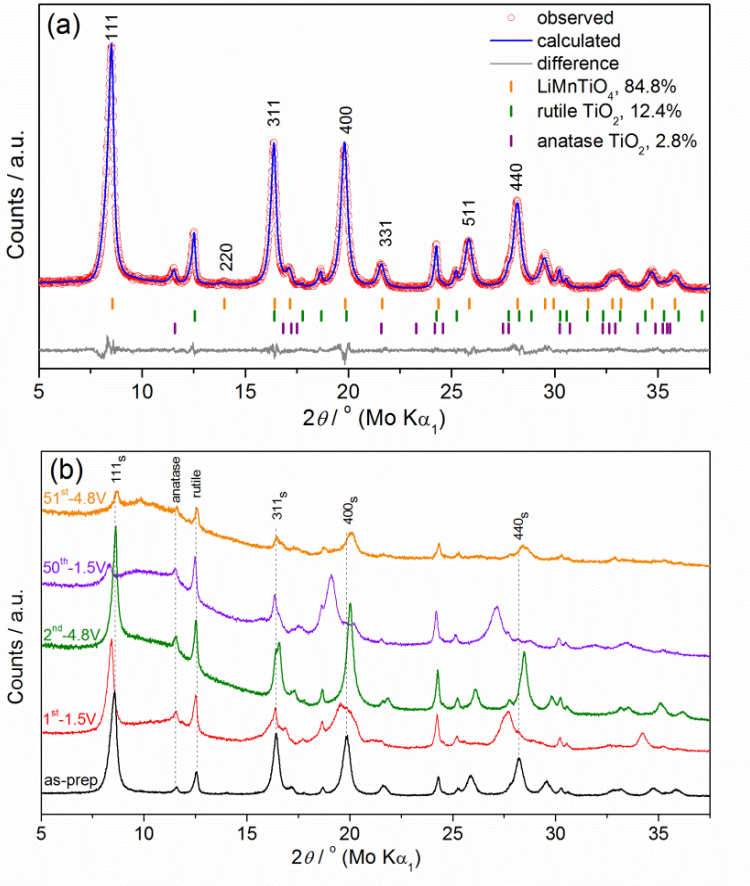


R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

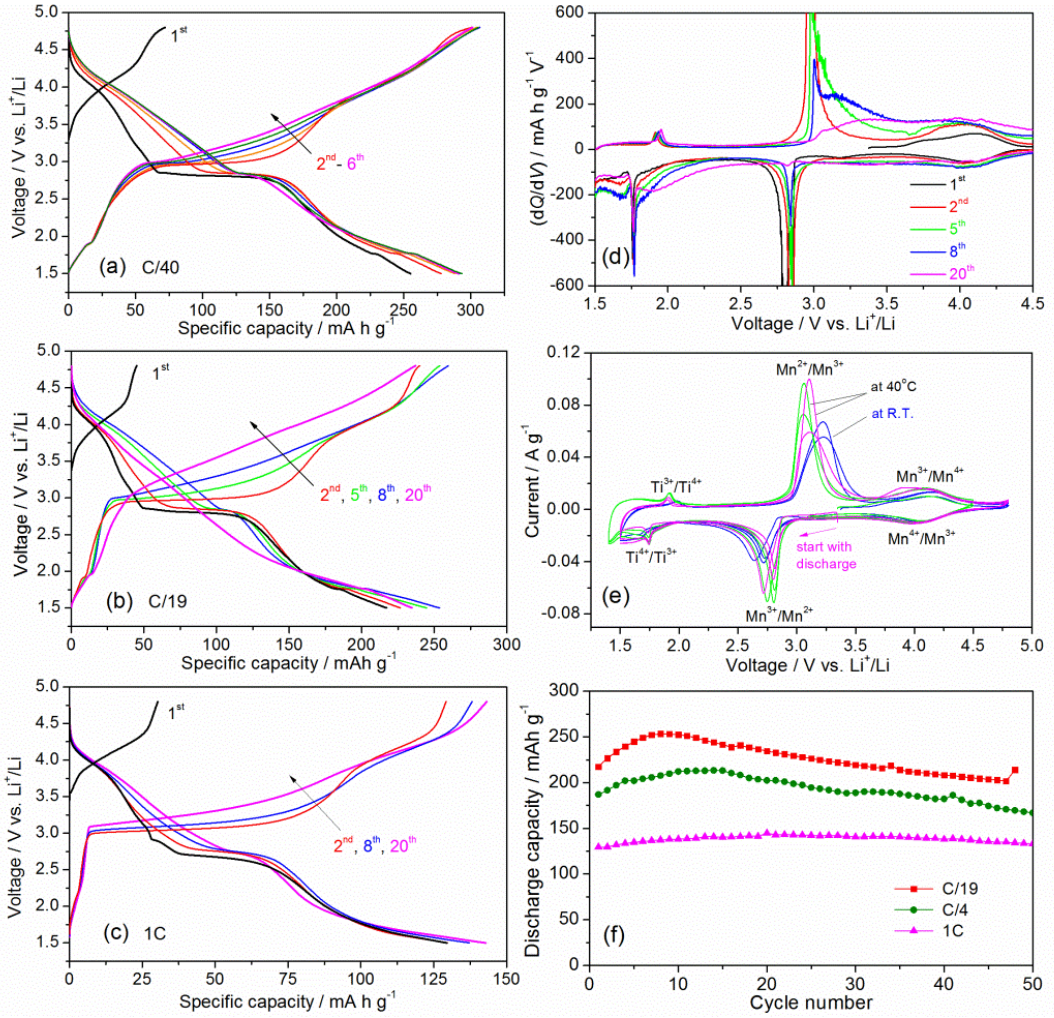
$LiMnTiO_4$

$LiMn^{3+}Ti^{4+}O_4 \leftrightarrow LiMn^{3+}Mn^{4+}O_4$

XRD



cycling

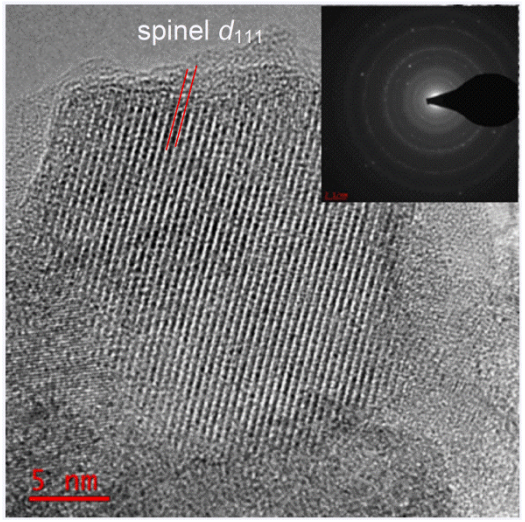


1.6 Li

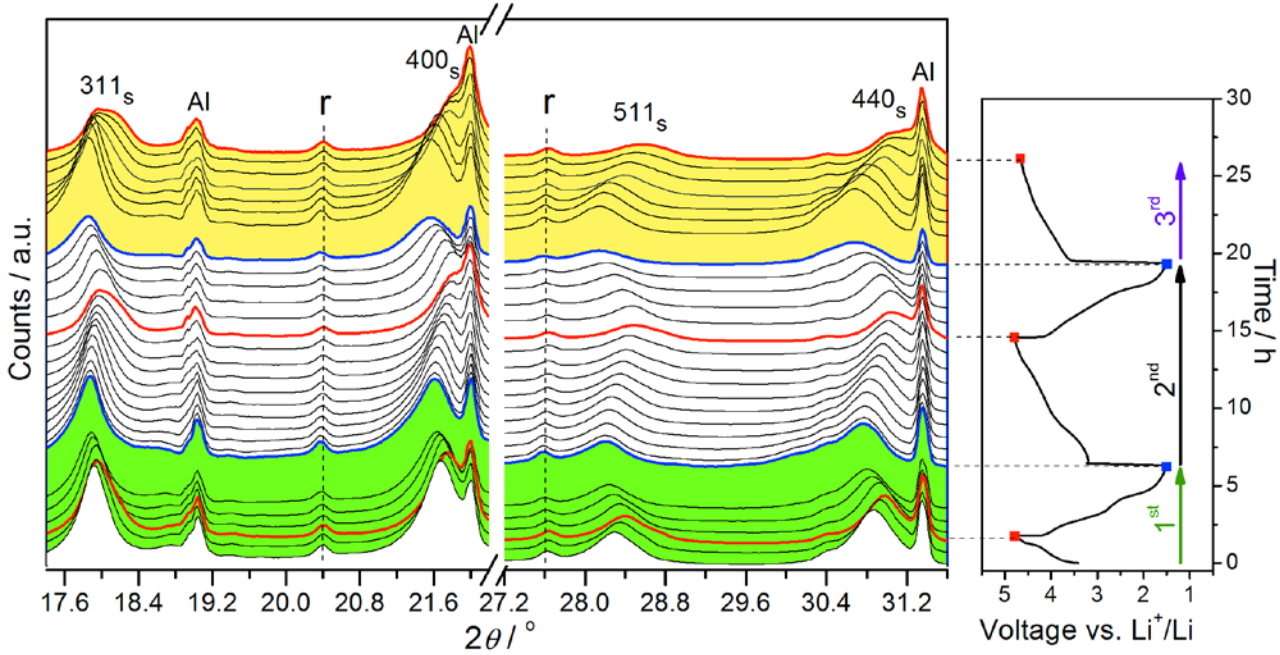
$Li_{0.4...2.0}MnTiO_4$

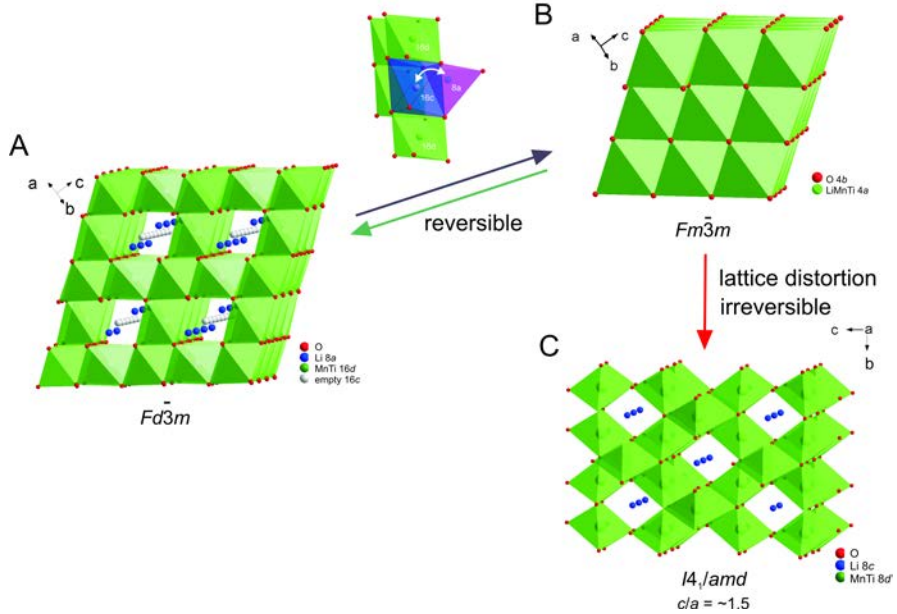
$LiMnTiO_4$

TEM



in situ XRD





Conclusions

Structural changes during electrochemical cycling observed by

XRD
^{7}Li MAS NMR spectroscopy
Fe Mössbauer spectroscopy
in situ XAS

highly reversible oxidation/reduction $Fe^{2+} \leftrightarrow Fe^{3+}$
$Mn^{2+} \leftrightarrow Mn^{3+}$

conversion of poylmorphs / changes in cation arrangem.

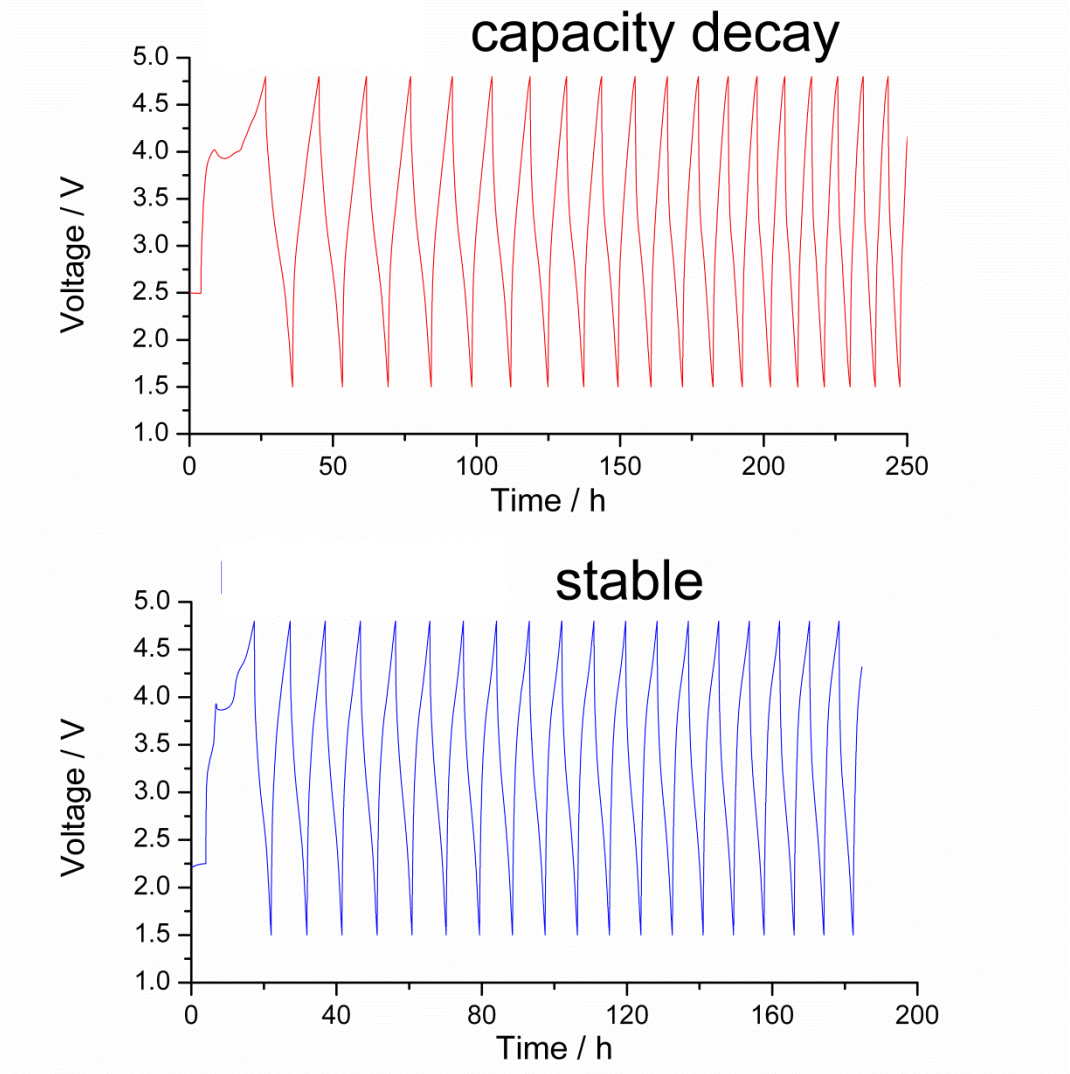
high degree of structural disorder after cycling

stabilization possible by doping

$Li_2Fe_{1-y}Mn_ySiO_4$

Outlook

y = 0.5

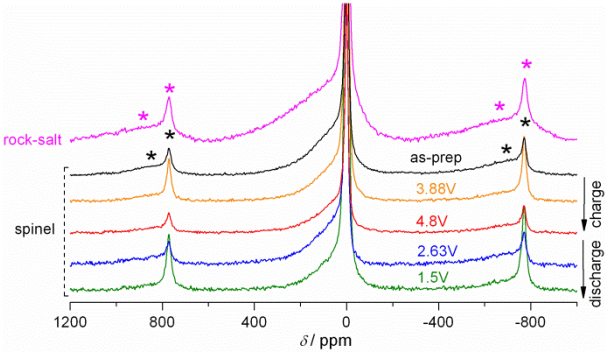


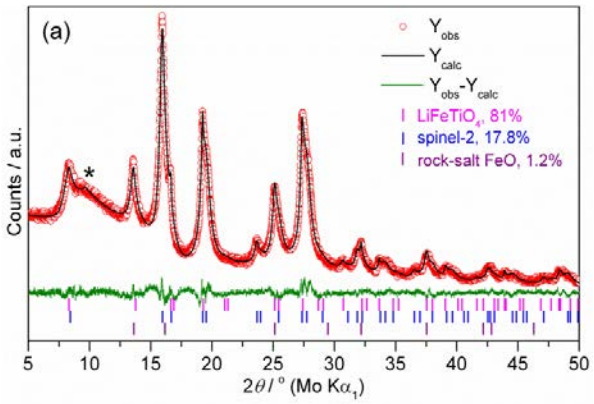
Overview: Experimental Methods

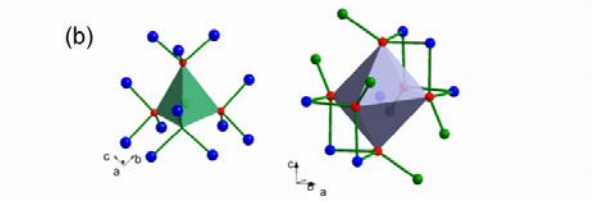
Standard sample characterization XRD, SEM, TEM, …	long-range structure, morphology
Battery tests	cell performance
In situ XRD measurements	long-range structure
In situ XAS measurements	local structure (element-specific), oxidation states
Solid State ^{7}Li NMR spectroscopy (MAS, VT, PFG, *in situ*)	local structure (element-specific), dynamics
Fe Mössbauer spectroscopy (*ex situ*, *in situ*)	short-range structure, oxidation states

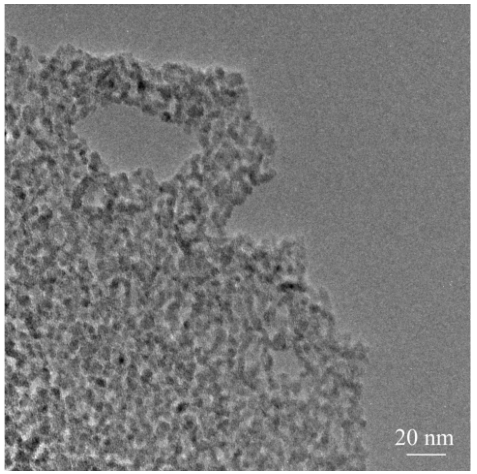
$LiFeTiO_4$

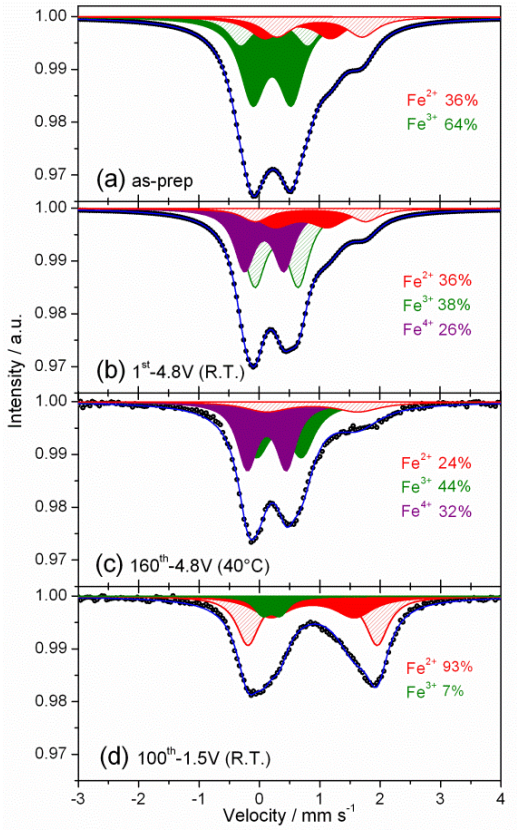
(together with M. Knapp, M. Yavuz)

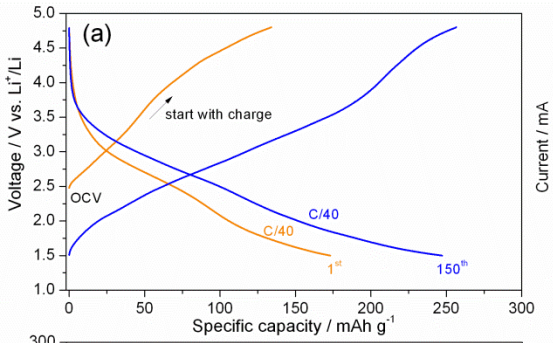


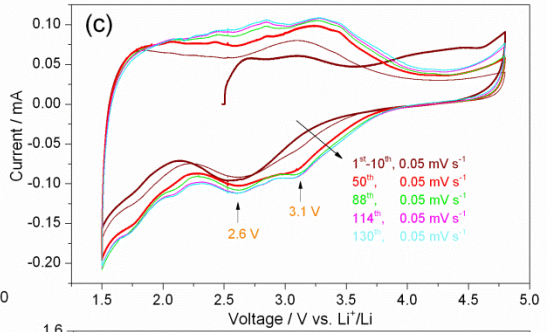


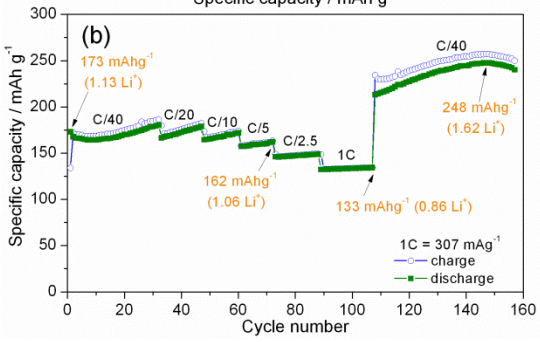


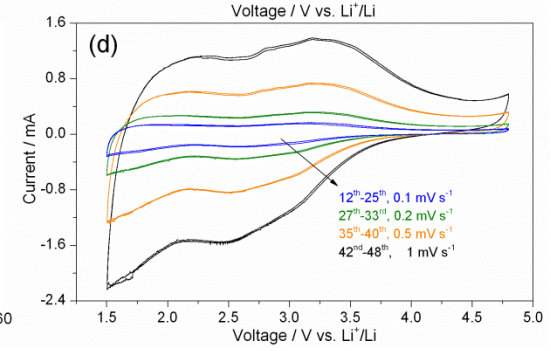












R. Chen, S. Indris, *EP* 13401030, 2013.