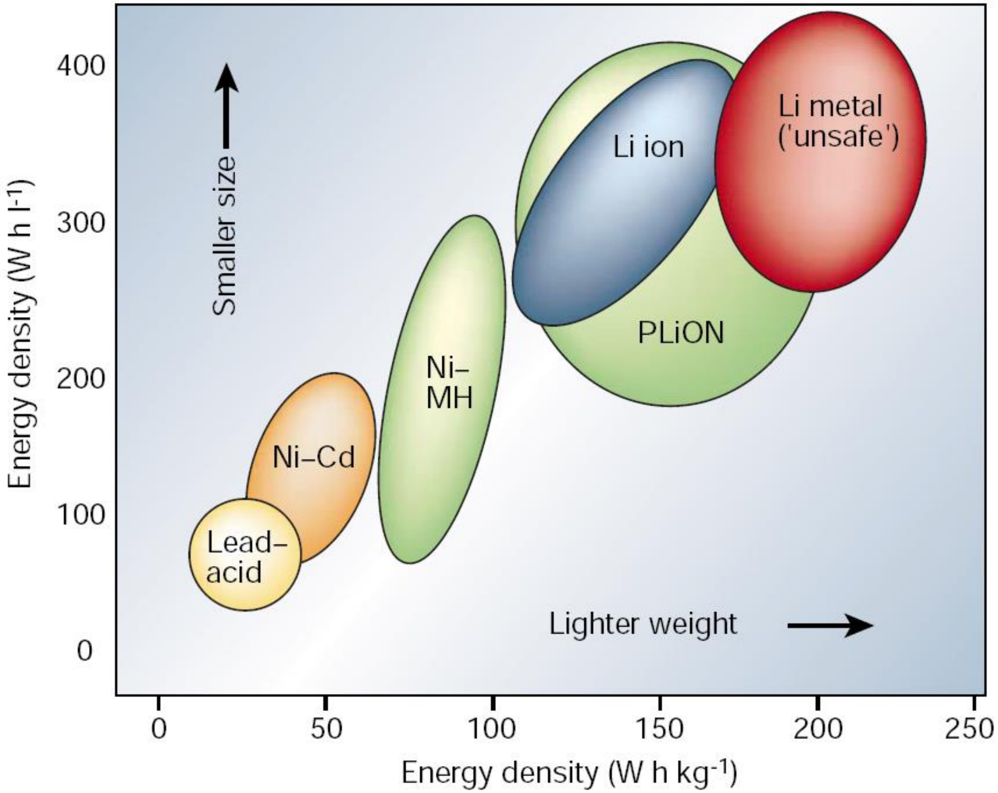
New Electrode Materials for Li-Ion Batteries: Insertion Mechanisms and Li Ion Mobility

Sylvio Indris

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

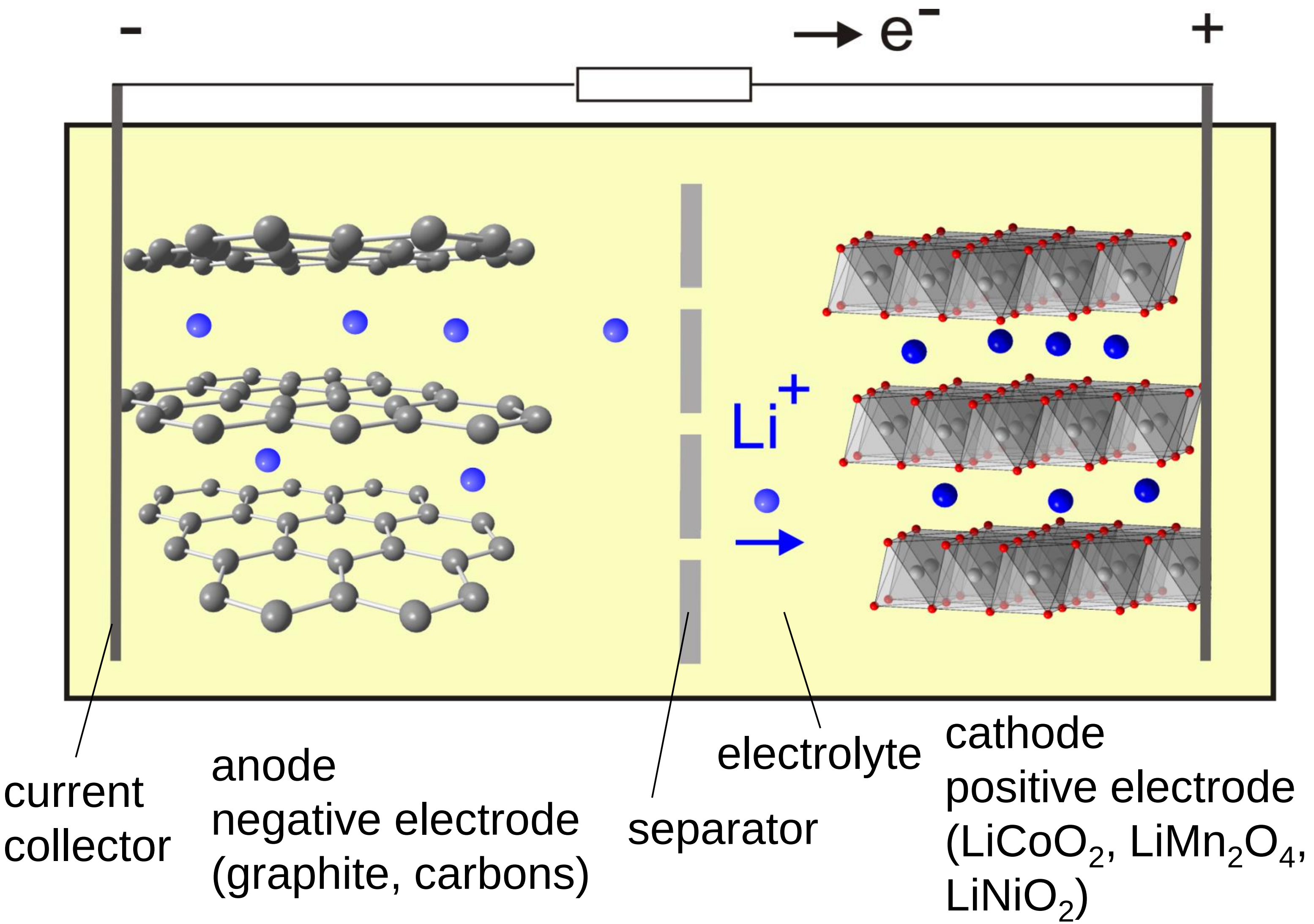
Hannover, May 19th, 2014

Li ion batteries: high energy density → smaller devices



Tarascon et al., Nature 414 (2001), 359

Li ion batteries: principle (here: discharging)



$LiC_6 \leftrightarrow Li^+ + e^- + 6\ C$

$2\ Li_{0.5}CoO_2 + Li^+ + e^- \leftrightarrow 2\ LiCoO_2$

$2\ Li_{0.5}CoO_2 + LiC_6 \leftrightarrow 2\ LiCoO_2 + 6\ C$

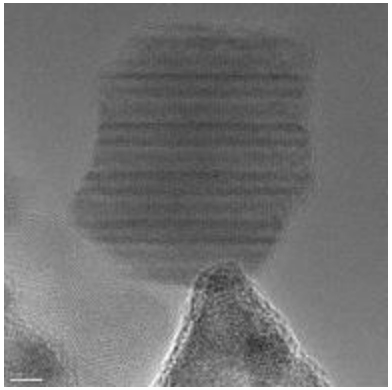
$\Delta_R G^{\ominus} = -U_0 \cdot n \cdot F$

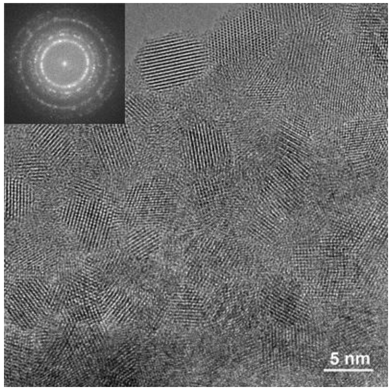
Overview: Electrode materials

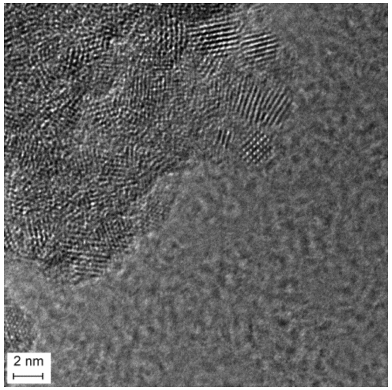
- anodes
  - $Li_4Ti_5O_{12}$
  - TiO_2
  - SnO_2, $(Ti/Sn)O_2$, $(Al/Sn)O_2$, $(Mg/Al/Sn)O_2$ …
  - ZnO
  - $MnFe_2O_4$, $MgFe_2O_4$, …
  - $Y_2Ti_2O_5S_2$, …

- cathodes

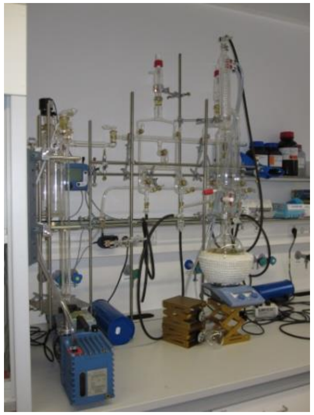
$Li(Co/Ni/Mn/Al)O_2$	0.5 Li per TM	140 mAh/g
$Li(Ni/Mn)_2O_4$	0.5 Li per TM	150 mAh/g
$Li(Fe/Mn/Co)PO_4$	1 Li per TM	170 mAh/g
$Li_2(Fe/Mn)SiO_4$	2 Li per TM ?	330 mAh/g ?
$Li_2(Fe/Mn)TiO_4$, …	2 Li per TM ?	290 mAh/g ?







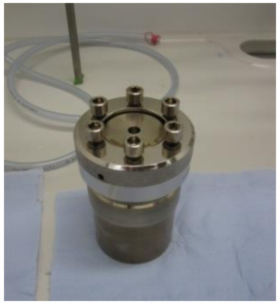
Synthesis

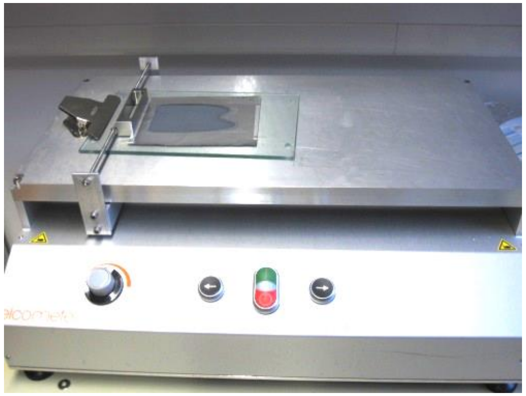


Synthesis of Nanoparticles, Nanostructures and Nanocomposites:

- coprecipitation methods
- sol-gel synthesis
- hydrothermal/ solvothermal synthesis
- solid-state reaction
- electrospinning

→ electrode film preparation

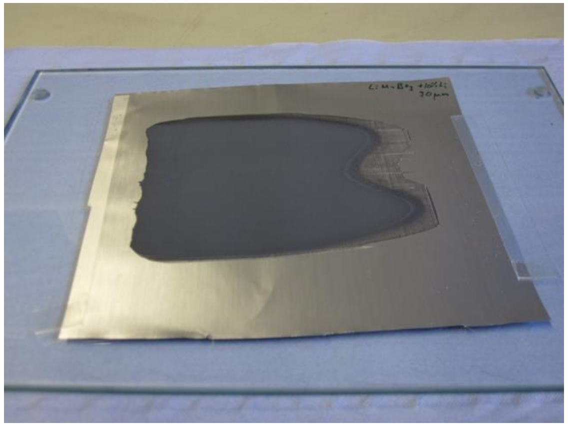




Important Parameters

Application (e.g EV)	Li-Ion Battery	Electrode Material
- range capability	- charge capacity measured in mAh/g - cell voltage	- amount of Li inserted light elements for host - redox potentials in anode, cathode
- fast charging / accelaration	- power density	- fast Li diffusion
- long lifetime (>10 years)	- cycling behaviour	- reversibility of reaction high-rate behavior
- price / toxicity / safety	- price / toxicity / safety	- price / toxicity / safety
→ Field test	→ Battery tests	→ NMR, *in situ* methods

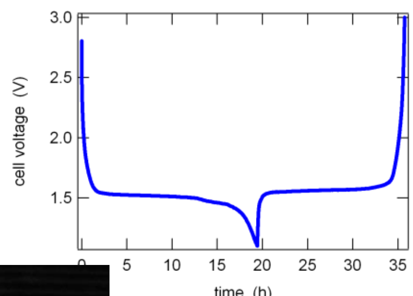
Different cell types:

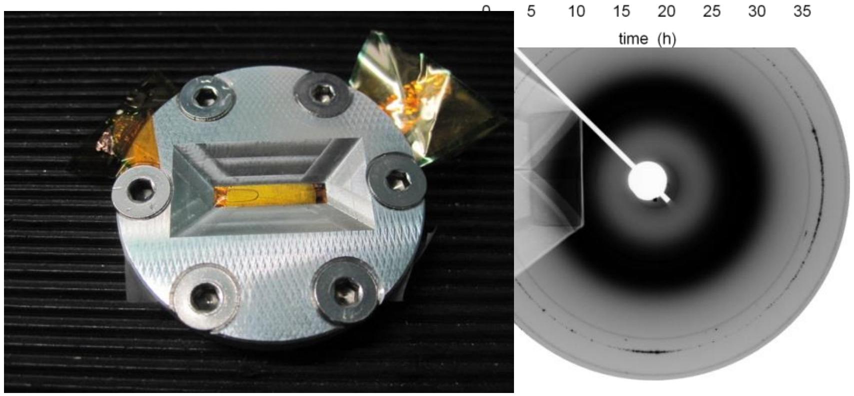


swagelok cells

coin cells (CR2032)

transmission cells
In situ XRD / XAS
at ANKA
(+ Mössbauer)





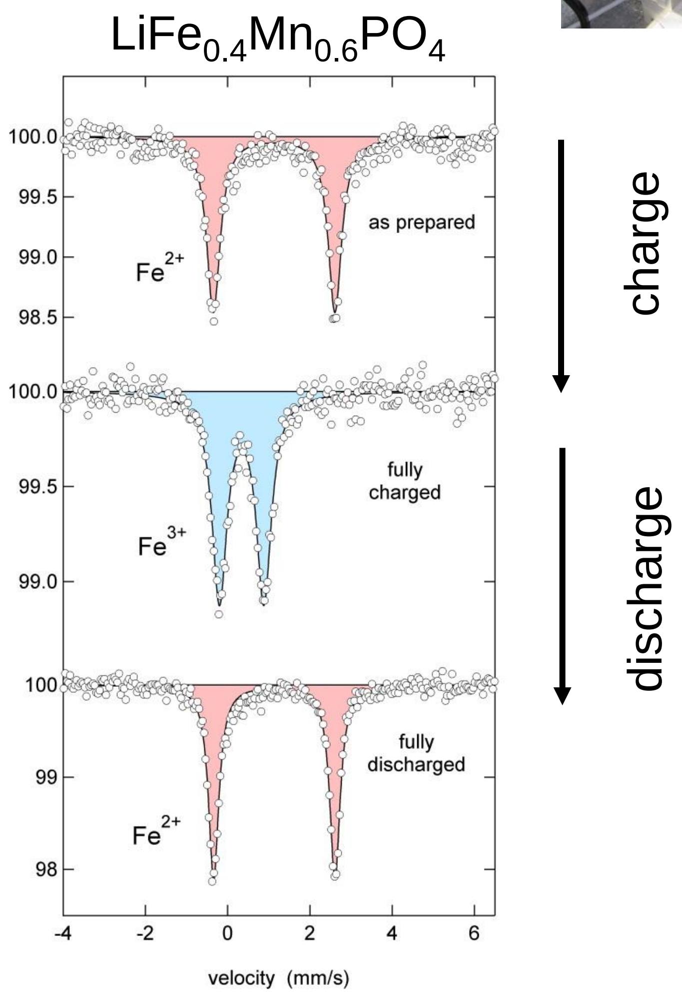
pouch cells
(*in situ* NMR)

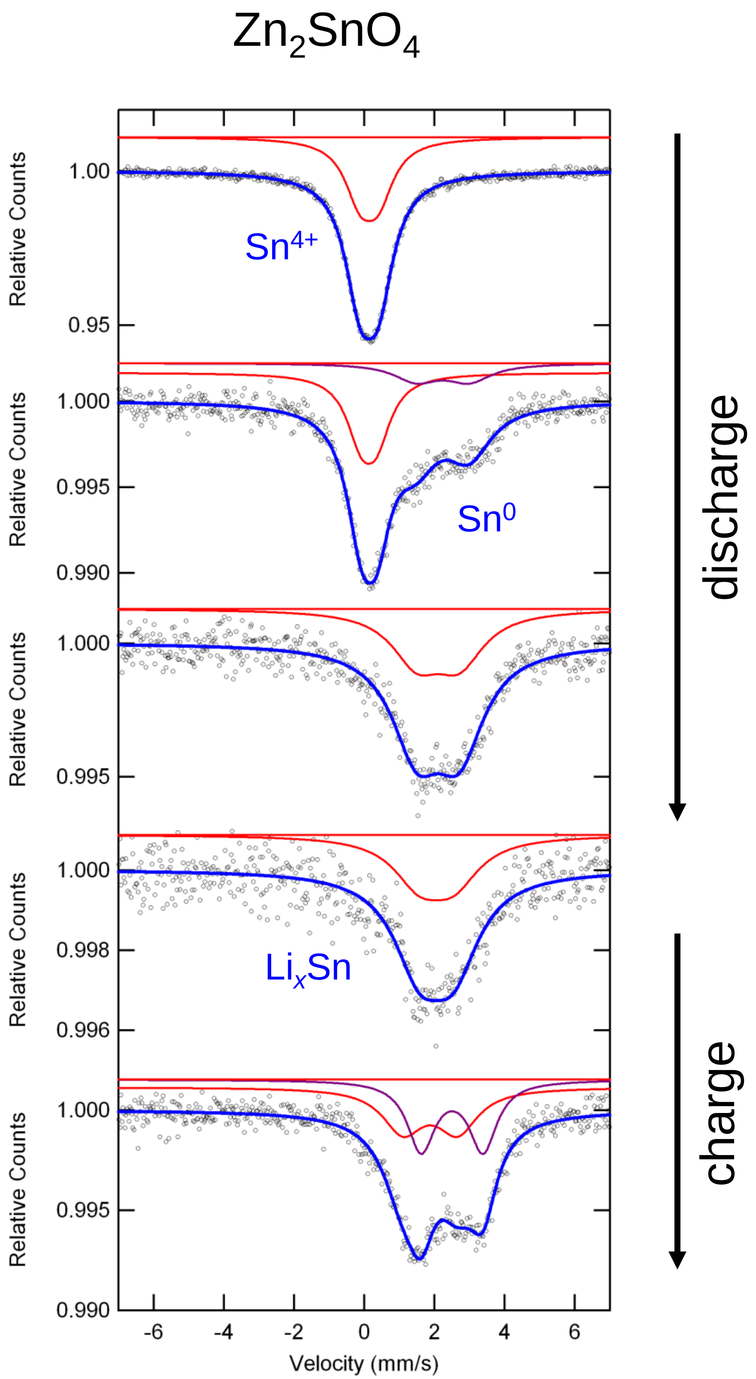
Overview: Experimental Methods

Standard sample characterization XRD, SEM, TEM, …	long-range structure, morphology
Battery tests	cell performance
Solid State NMR spectroscopy (MAS, VT, PFG, *in situ*, relaxometry)	local structure (element-specific), dynamics
Fe + Sn Mössbauer spectroscopy (*ex situ*, *in situ*)	short-range structure, oxidation states
In situ XRD measurements	long-range structure
In situ XAS measurements	local structure (element-specific), oxidation states
Impedance Spectroscopy	interfaces, degradation
In situ SEM	morphology

Mössbauer spectroscopy

changes of local structure
and charge state
of Fe or Sn during
reduction and oxidation

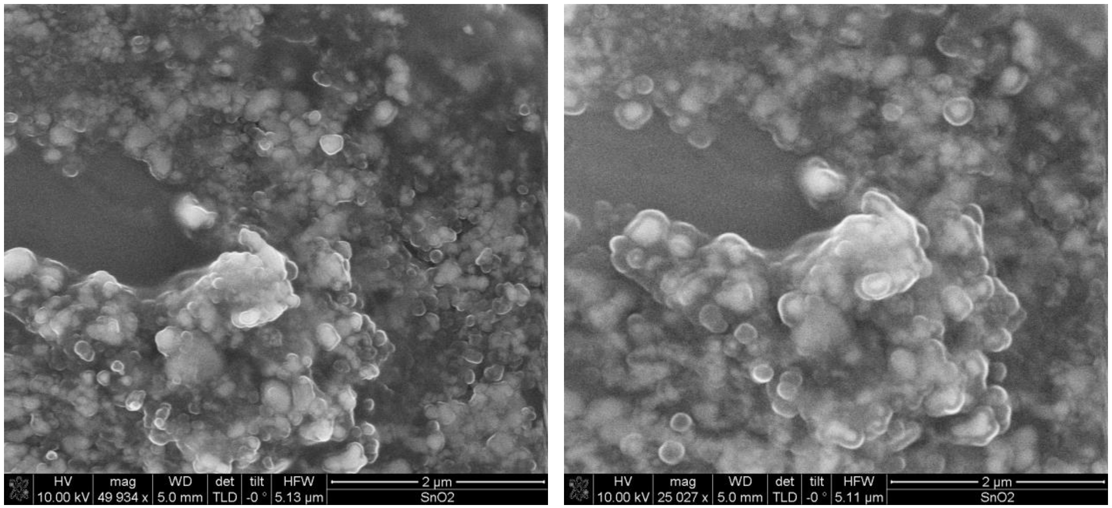




In situ SEM

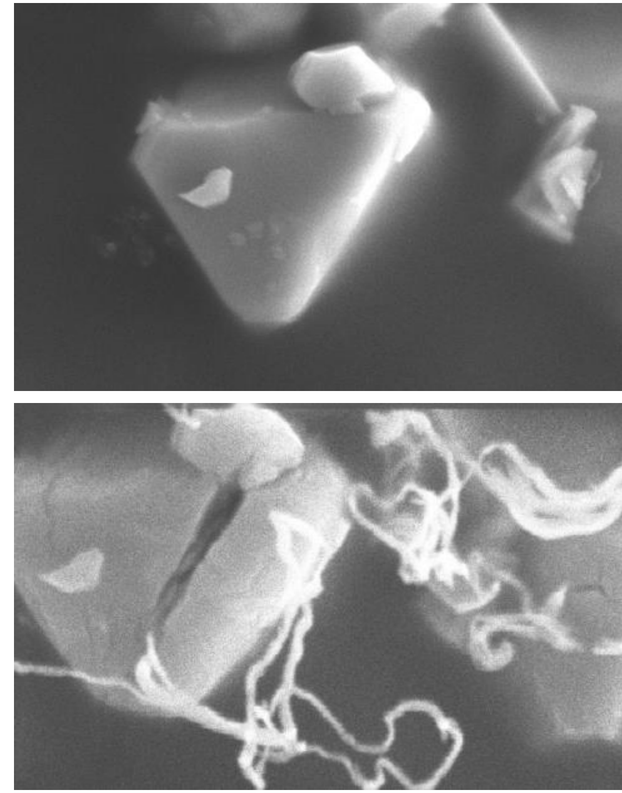
(together with R. Mönig, KIT-IAM)

SnO_2



- Particles grow and develop surface layers.
- Mass contrast detected by backscattered electrons shows that coating has lower Z than SnO_2 particle; consistent with the assumption that Li_2O forms at surface of particles.

$CuCr_2Se_4$



- Particles grow and break apart
- formation of Cu metal whiskers

$\rightarrow$ Cu-Li exchange mechanism

D. Chen et al., *J. Power Sources* **196**, 6382 (2011).

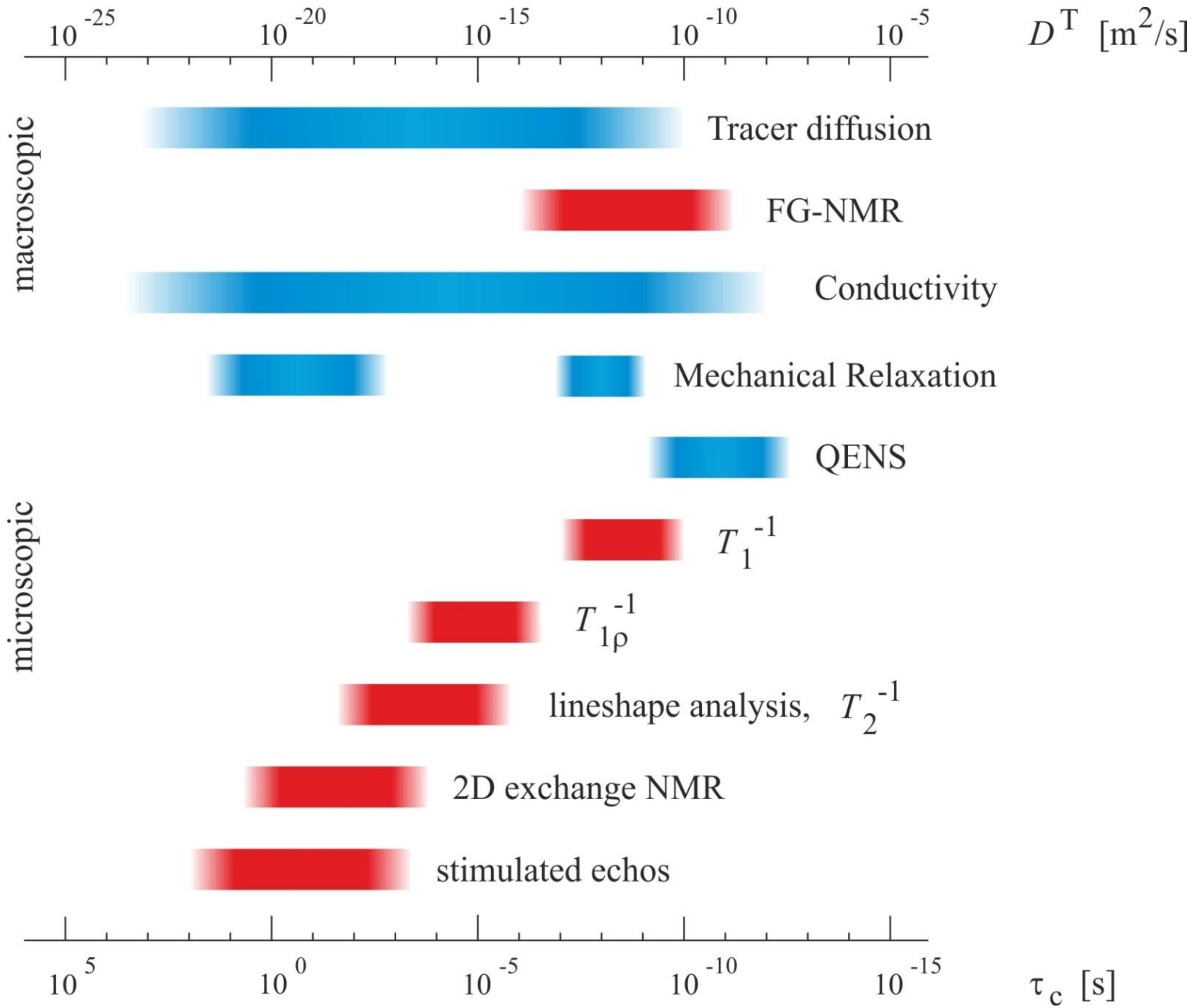
W. Bensch et al., *Phys. Chem. Chem. Phys.* **14**, 7509 (2012).

MAS NMR spectroscopy ^{7}Li, ^{6}Li, ...

200 MHz spectrometer	small magnetic field (4.7 T)
1.3 mm rotors, 67 kHz rotation	very fast sample spinning

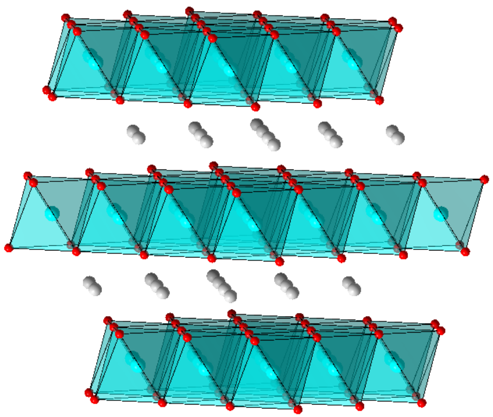
- number of Li sites
- identification of Li sites (comparison with reference materials)
- exchange rates between sites (2D NMR)
- mobilities of different Li species (temperature dependence)
- direct measurement of diffusion coefficient (field gradients, ...)

Ion Dynamics in Condensed Matter

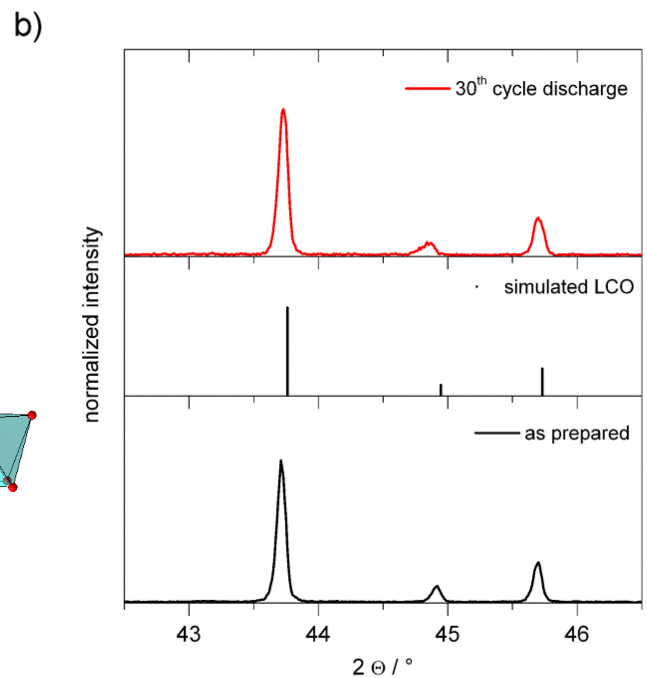


$LiCoO_2$: NMR at different charge states/cycle numbers

$LiCoO_2$ ($R\bar{3}m$)

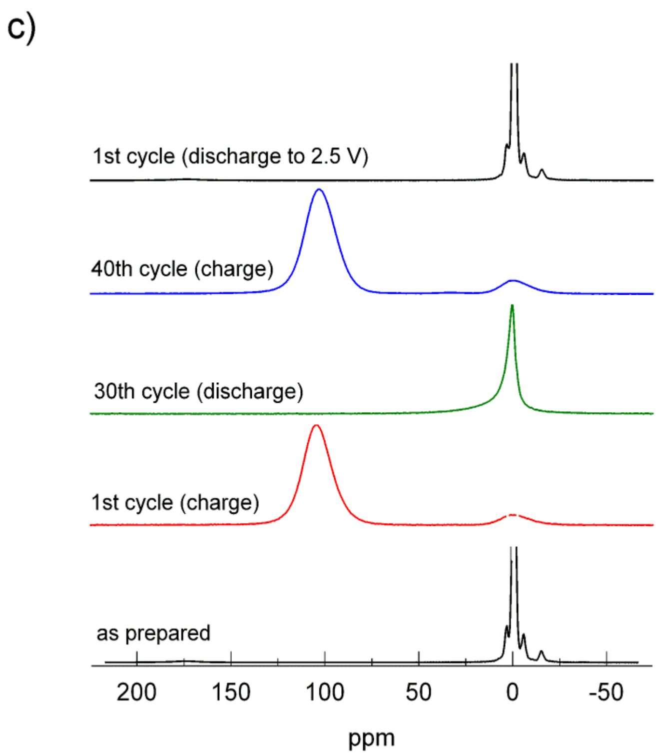


XRD



long-range structure

^{7}Li MAS NMR



local structure

$Co^{(3+)}$: $3d^6$

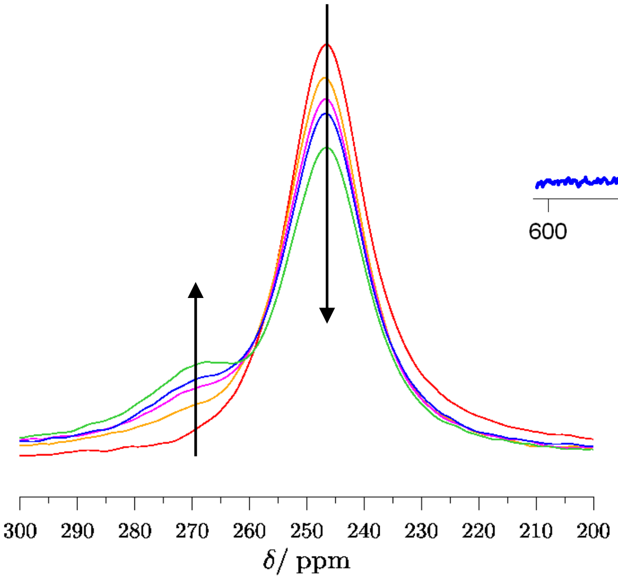
$Co^{(4+)}$: $3d^5$

N. Schweikert et al., *Solid State Ionics* **226** (2012), 15.

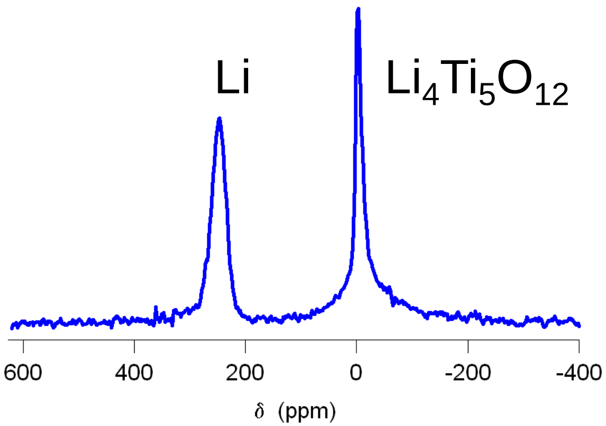
In situ NMR Spectroscopy

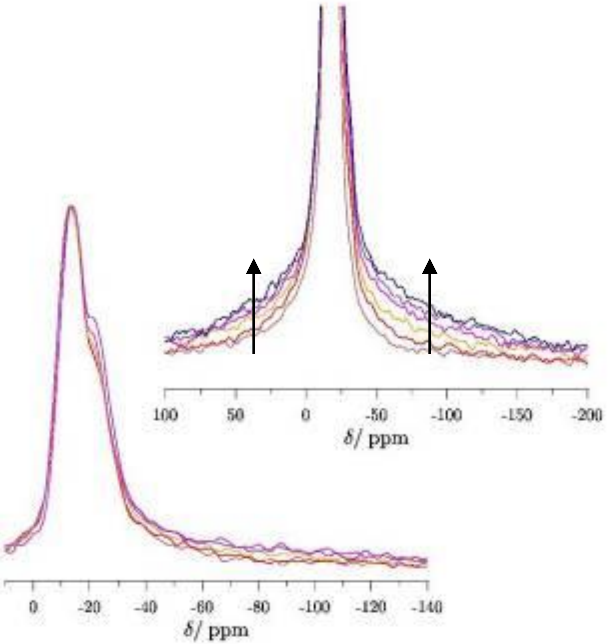
- *in situ* observation of changes in local structure around specific probe nuclei
- elucidation of reaction mechanisms
- observation of side reactions

NMR probe with *in situ* cell

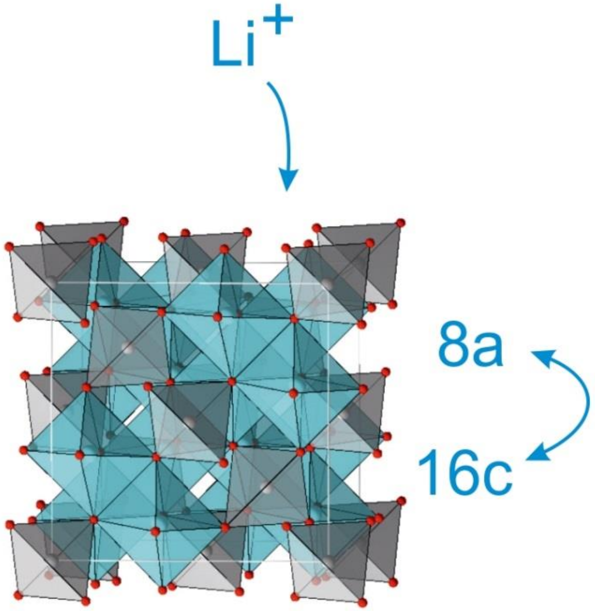


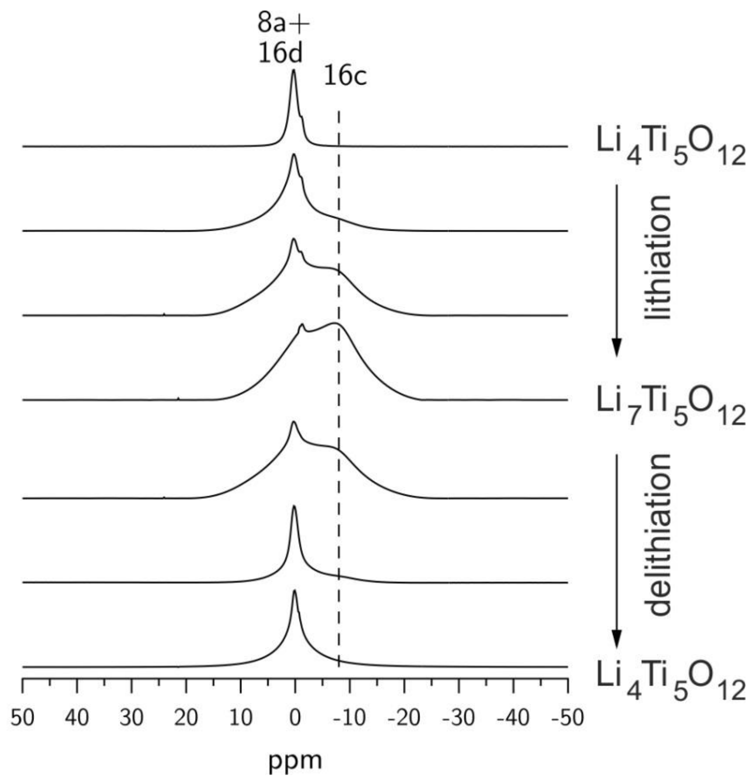
^{7}Li NMR spectrum of complete Li battery





Ex situ ^{7}Li MAS NMR Spectroscopy: $Li_{4+x}Ti_5O_{12}$ (x = 0 … 3)





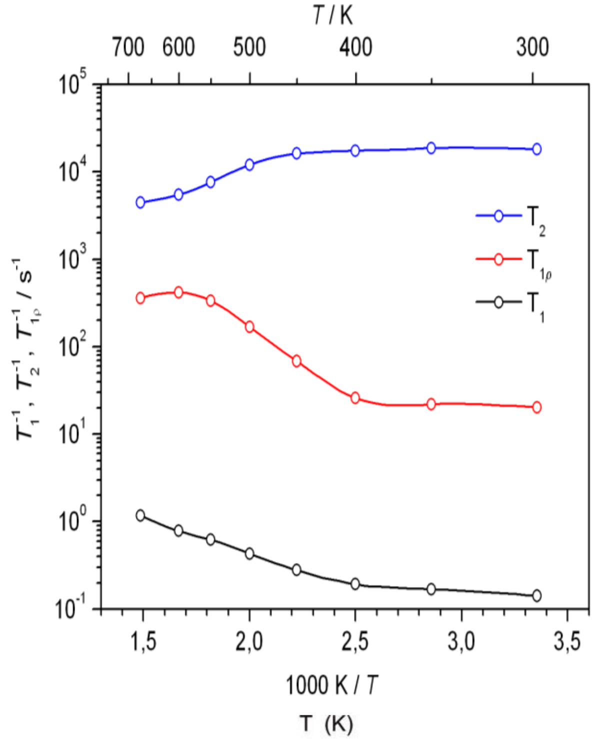
Rearrangement of Li ions:

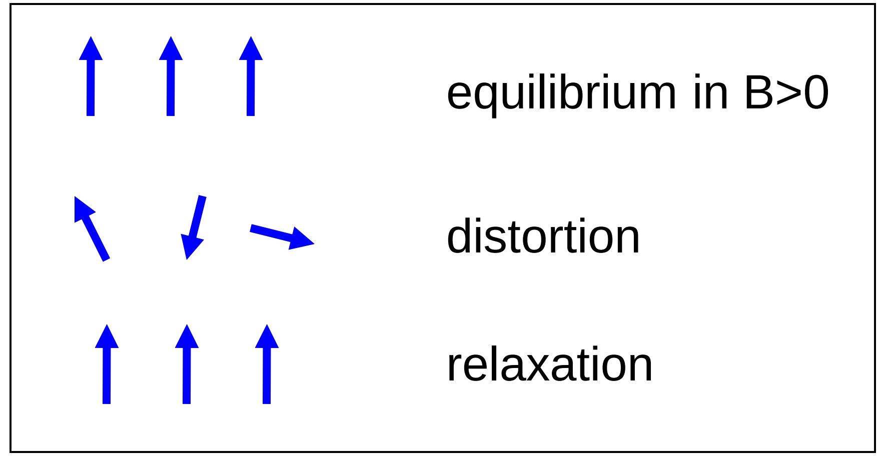
Li^{+} → Li(16c)

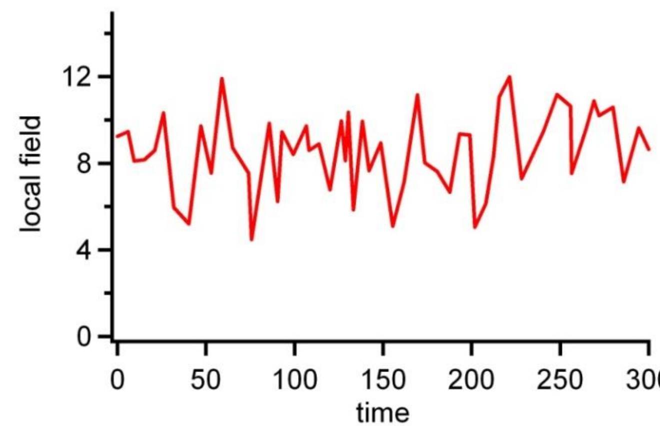
Li(8a) → Li(16c)

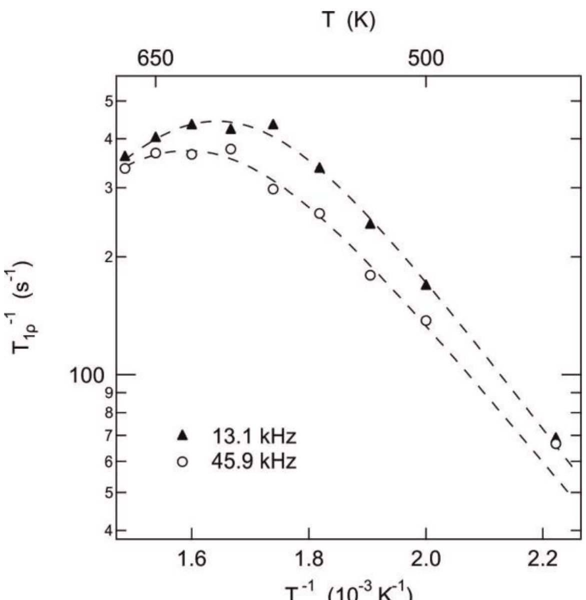
H. Hain et al., *Solid-State Nucl. Magn. Reson.* **42** (2012), 9.

Ex situ NMR Spectroscopy: $Li_{4+x}Ti_5O_{12}$ relaxation rates





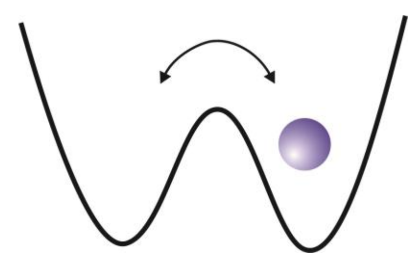




maximum:
$\omega_L \approx \tau^{-1}$

spin dynamics → Li ion dynamics

- maximum: jump rate ≈ 10^4 s^{-1}
- flank: activation barrier ≈ 0.3 eV

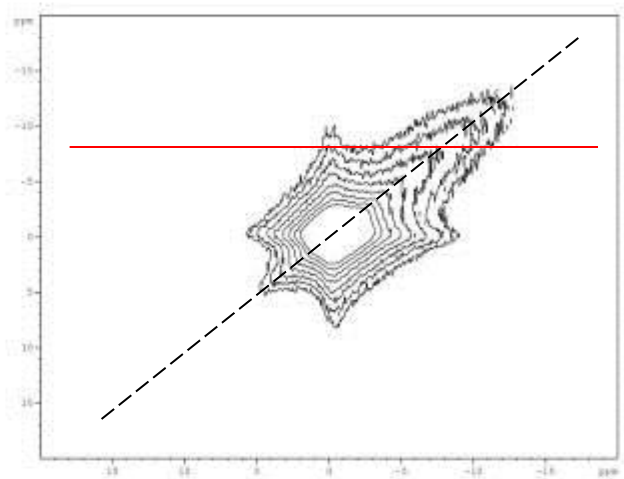


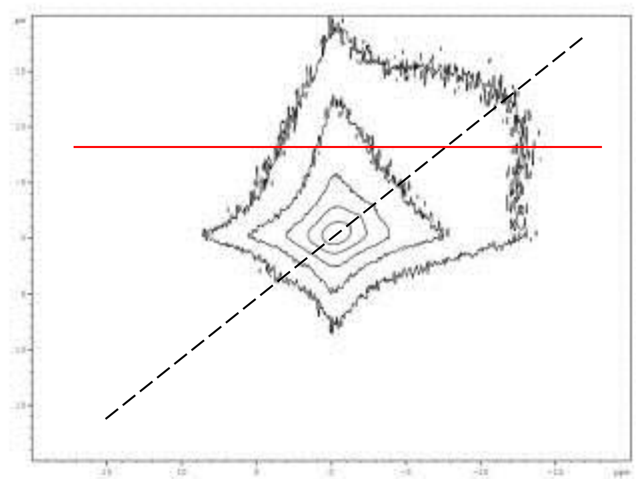
H. Hain et al., *Solid-State Nucl. Magn.* Reson. **42** (2012), 9.

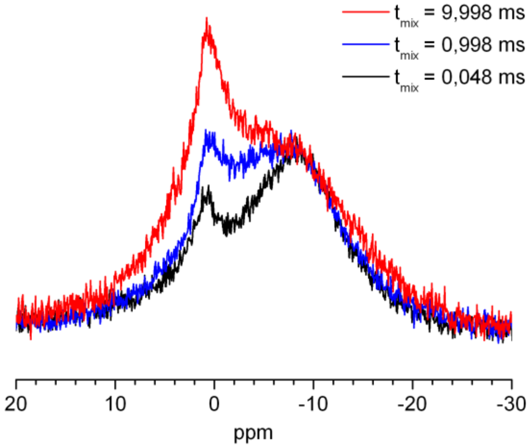
<u>2D ^{7}Li MAS NMR:</u> $Li_{4+x}Ti_5O_{12}$

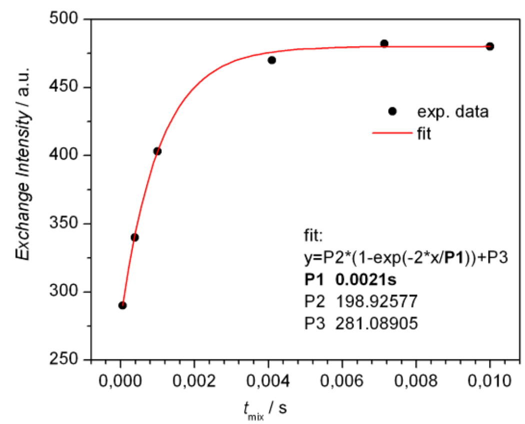
^{7}Li : 93 %
^{6}Li : 7 %

jump rates between specific sites, here: 16d ↔16c ?





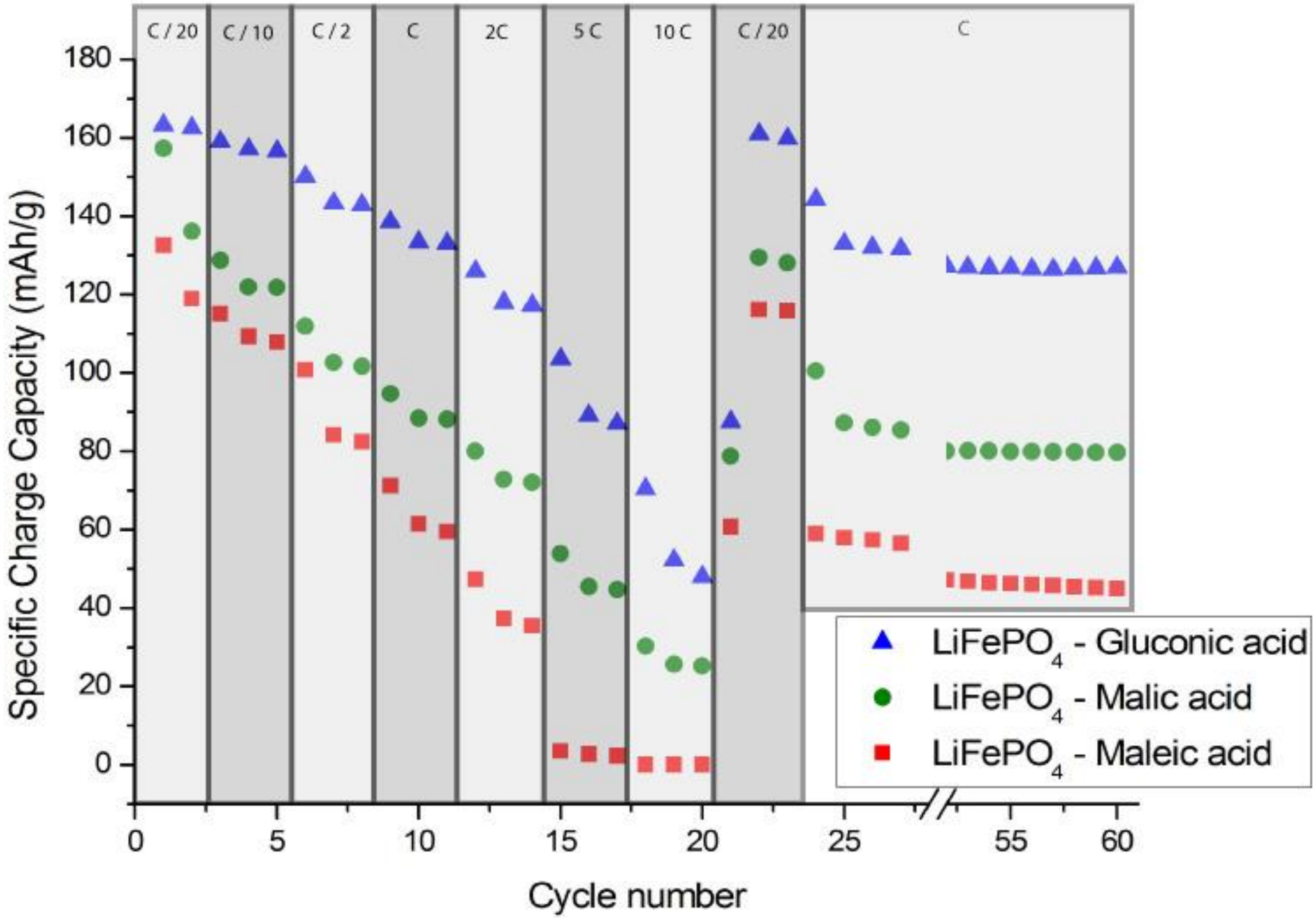




2.1 ms

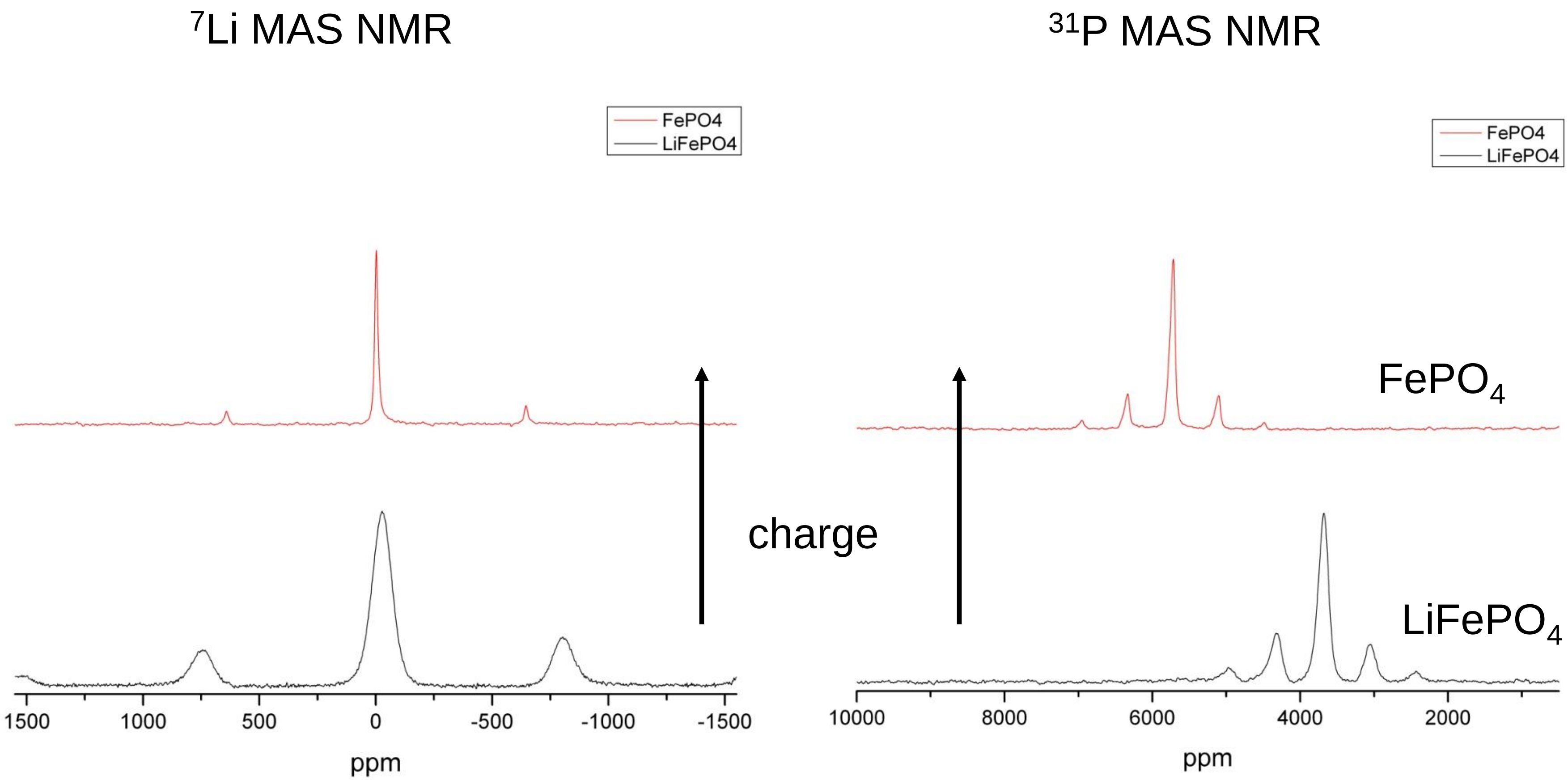
H. Hain et al., *Solid-State Nucl. Magn.* Reson. **42** (2012), 9.

LiFePO$_4$: coating with C from different precursors



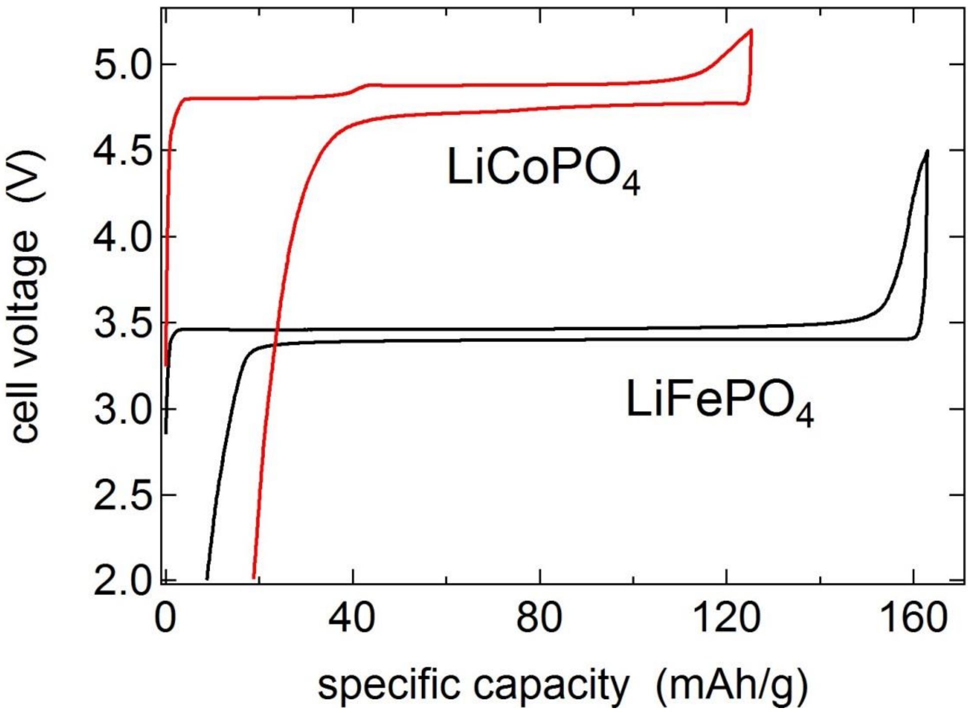
Hydrothermal synthesis → nanostructures: nanoparticles with C coating !

$\underline{LiFePO_4}$:

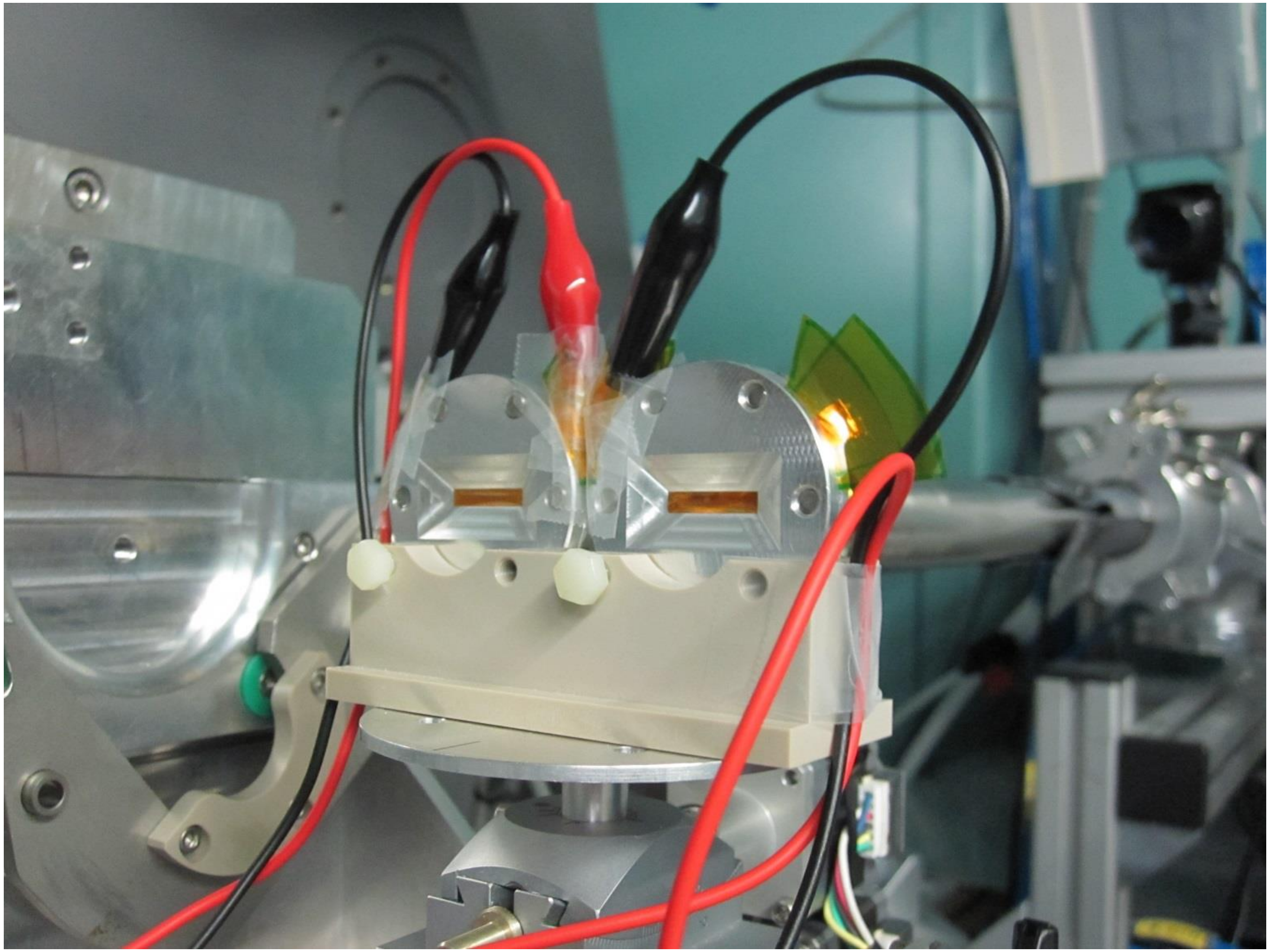


2 phase mechanism (1 step)

<u>$LiFePO_4 \leftrightarrow LiCoPO_4$</u> :

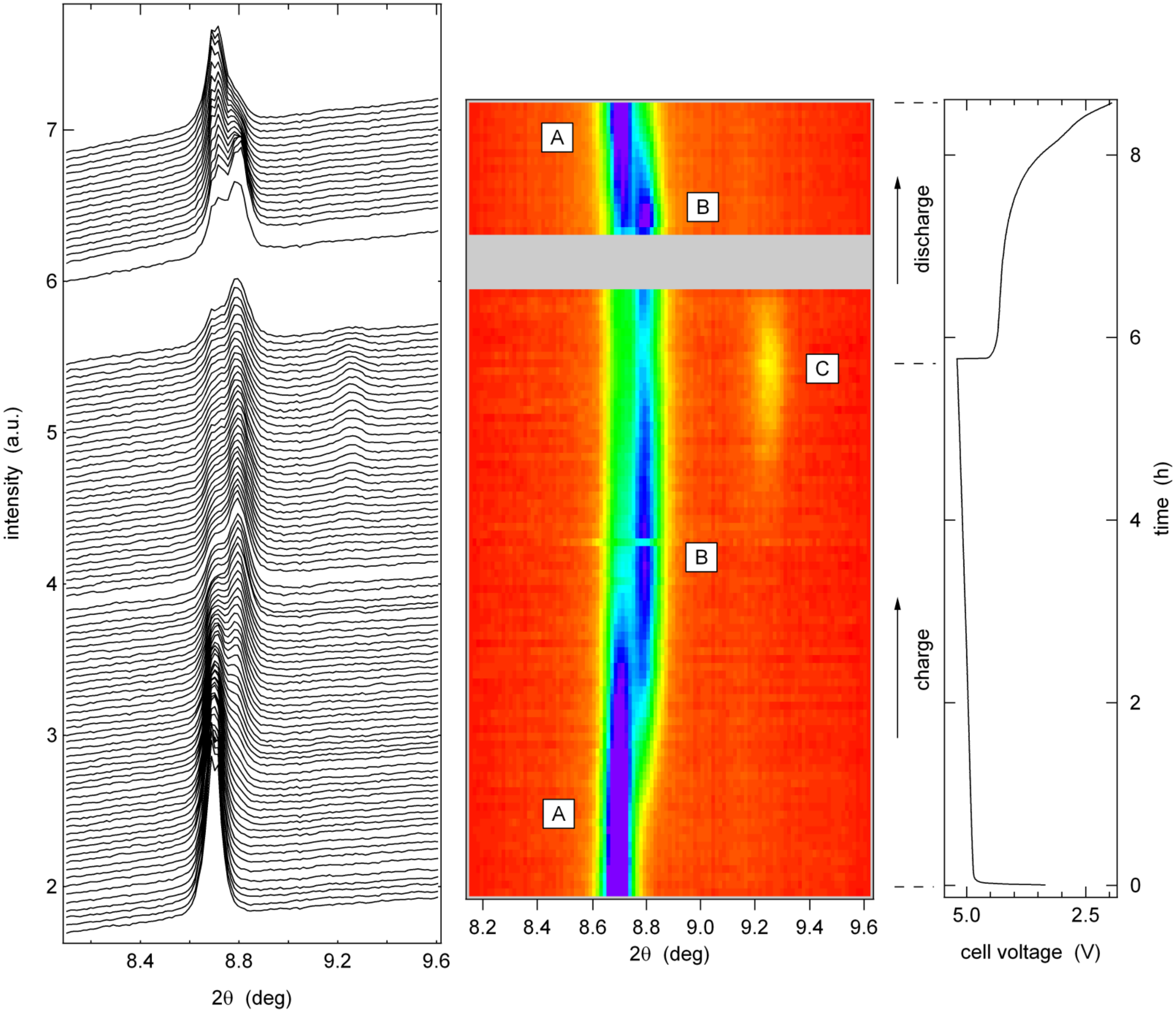


$\underline{LiCoPO_4}$: *in situ* XRD



30 – 200 sec per scan

$LiCoPO_4$:   *in situ* XRD



LiCoPO$_4$

Li$_{0.7}$CoPO$_4$

CoPO$_4$

Li$_{0.7}$CoPO$_4$

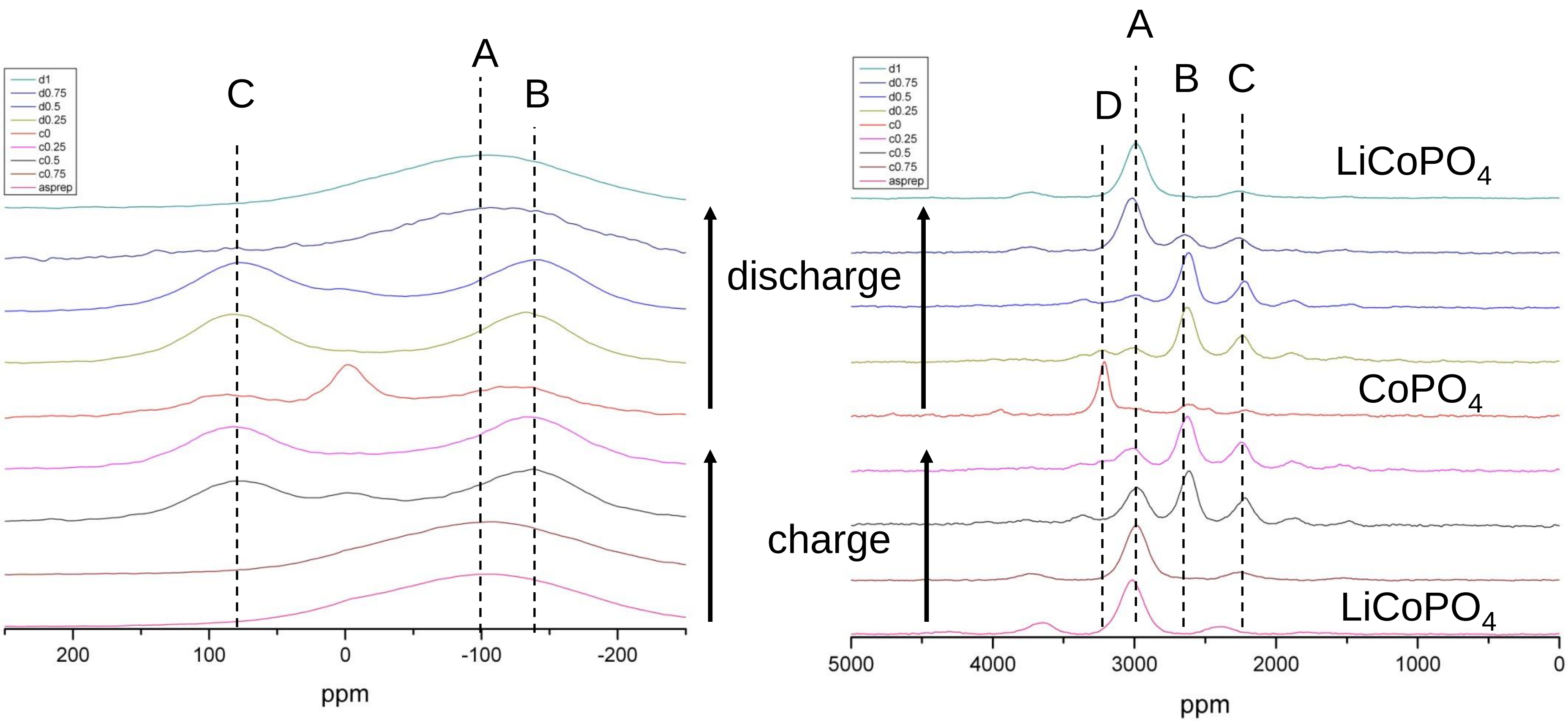
LiCoPO$_4$

2-step mechanism + intermediate phase   (≠ Fe)

$LiCoPO_4$:

^{7}Li MAS NMR

^{31}P MAS NMR



2 step reaction

intermediate phase: $Li_{0.7}CoPO_4$

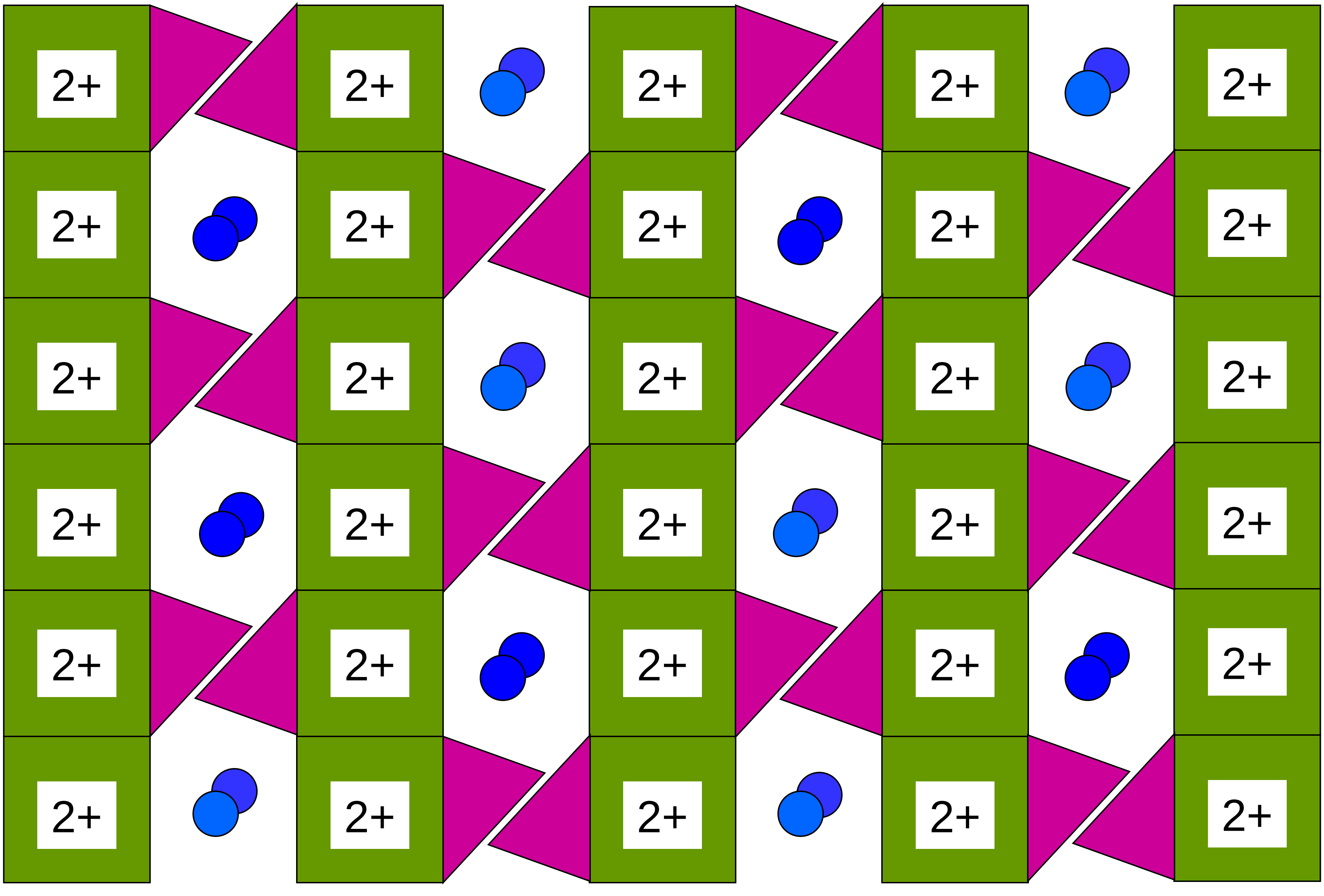
2/3 3/4

2 Li environments (1:1)

2 P environments (2:1)

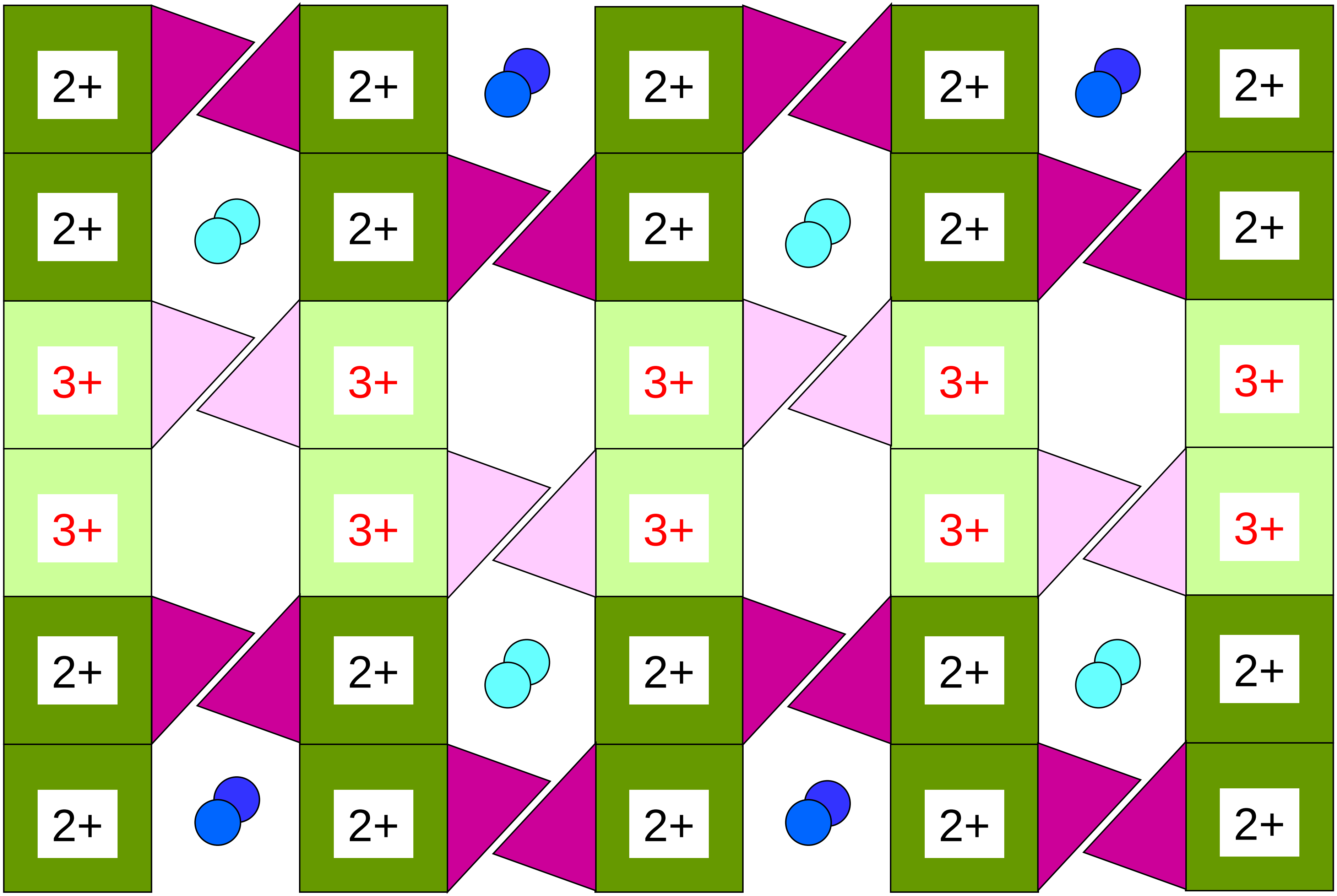
$LiCoPO_4$

view along c axis



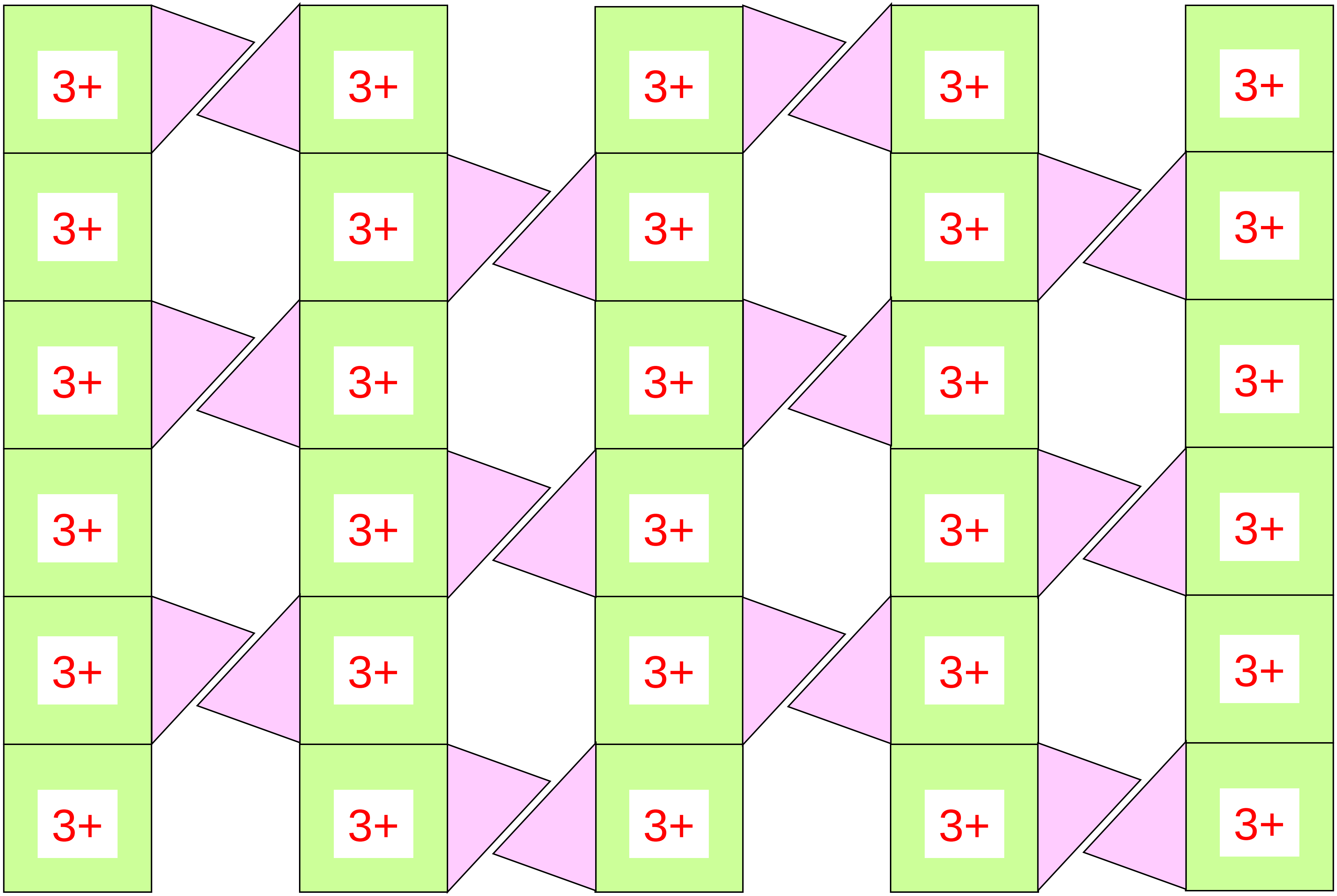
$Li_{2/3}CoPO_4$

view along c axis

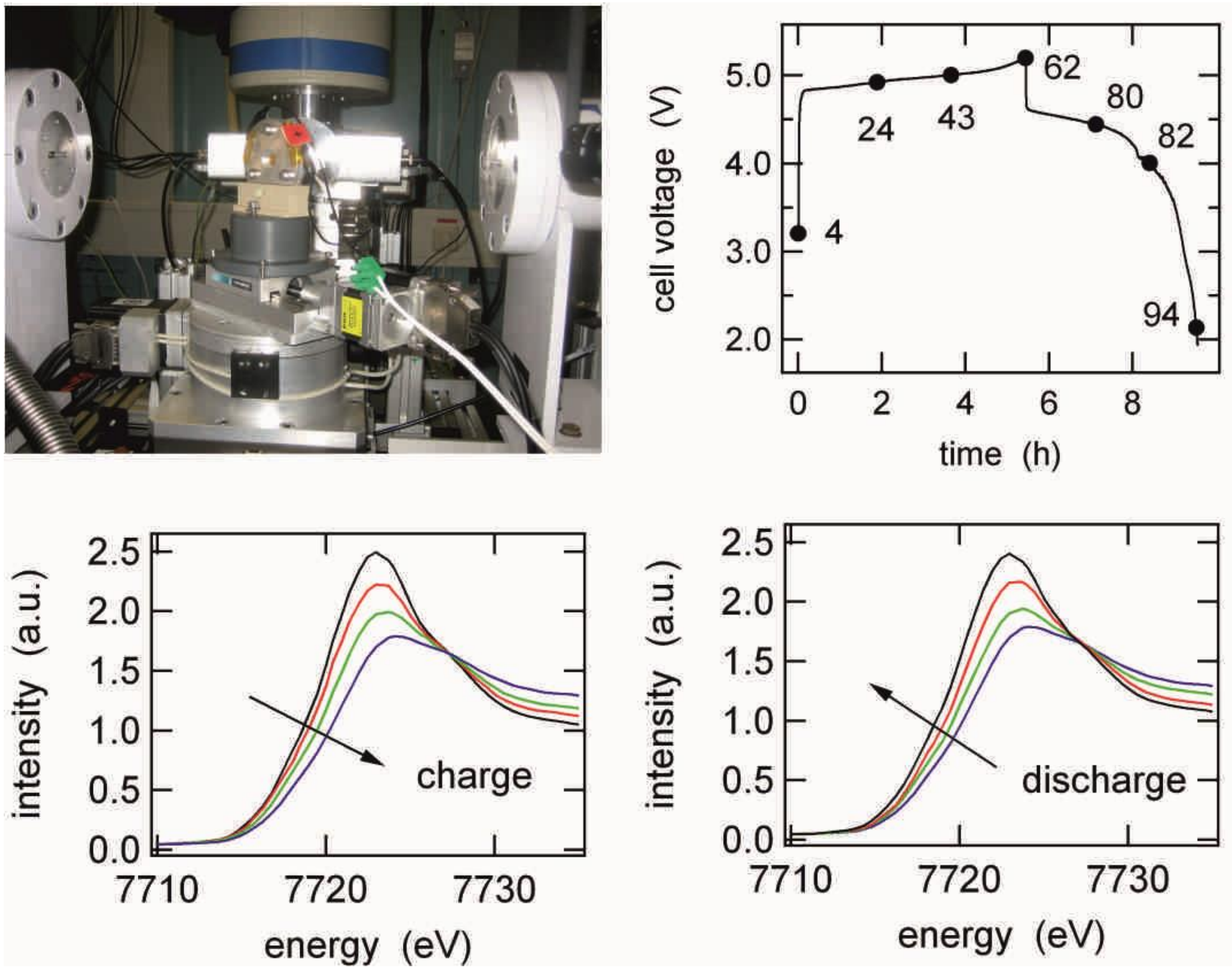


$CoPO_4$

view along c axis



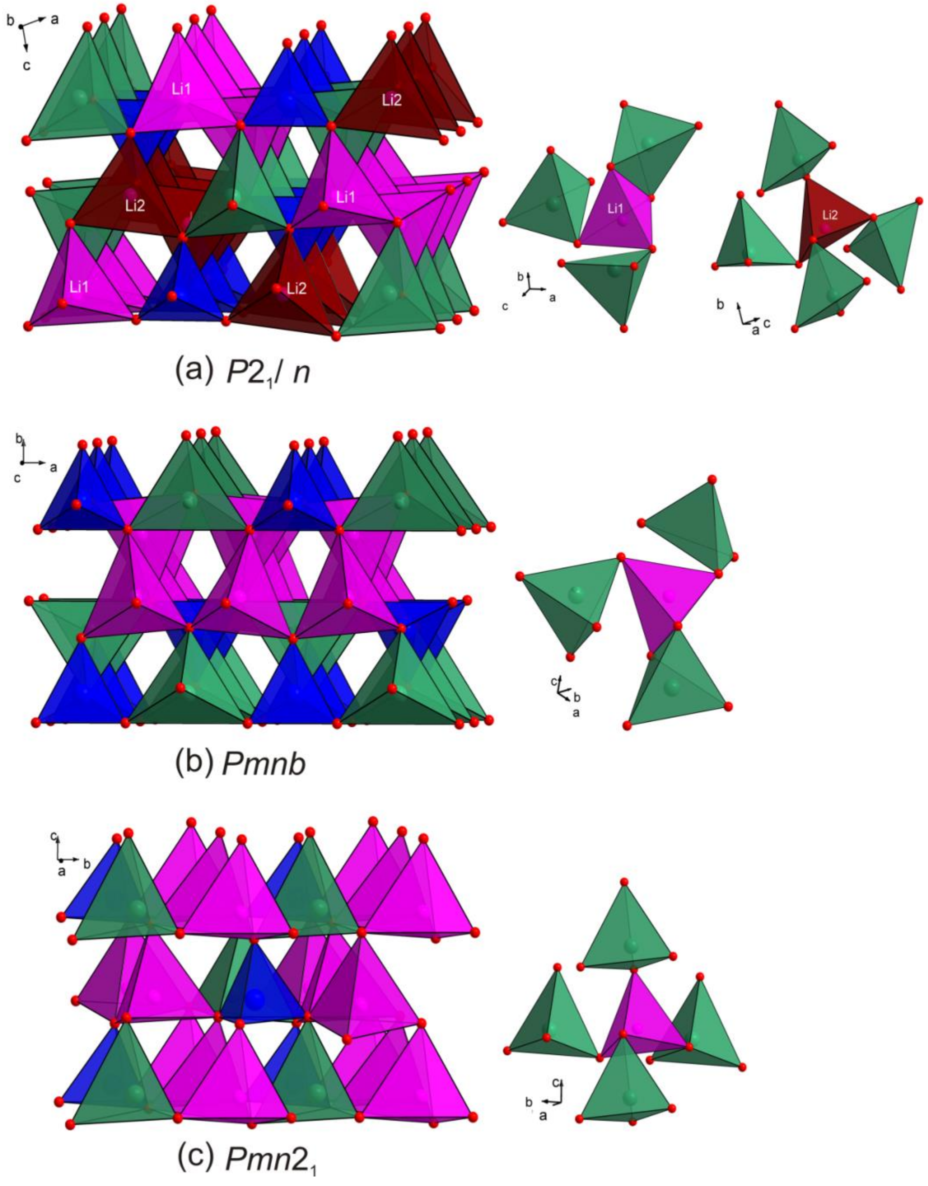
LiCoPO$_4$: *in situ* XAS on Co K edge



highly reversible oxidation/reduction of $Co^{2+/3+}$

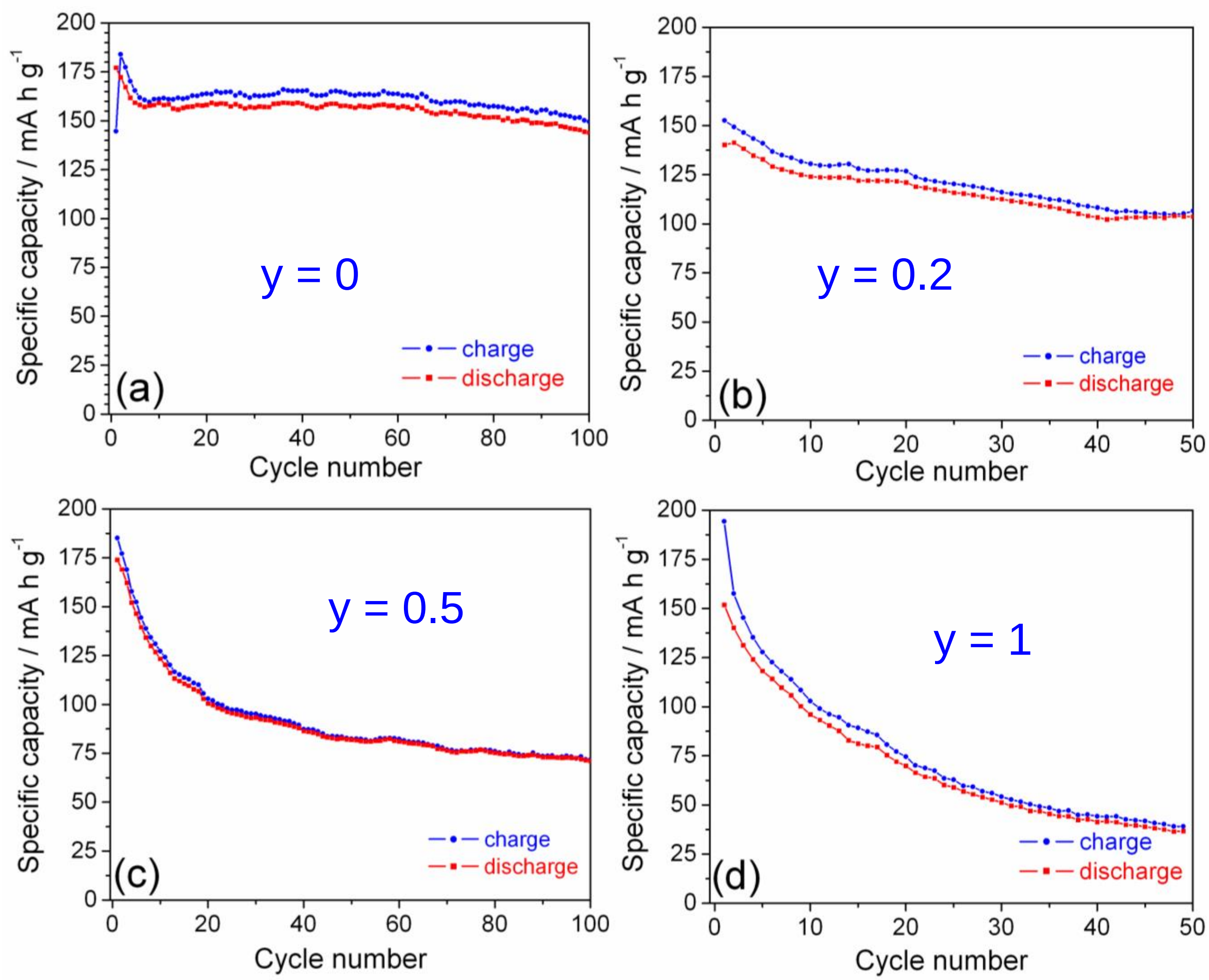
$Li_2Fe_{1-y}Mn_ySiO_4$ / C

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



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

$Li_2Fe_{1-y}Mn_ySiO_4$ / C

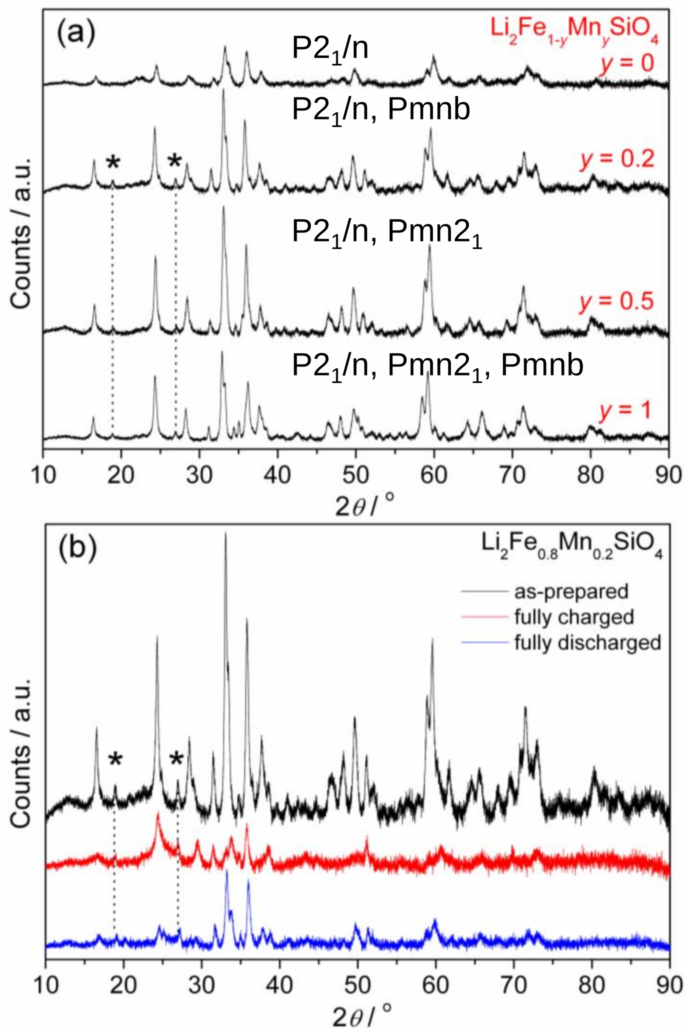


R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

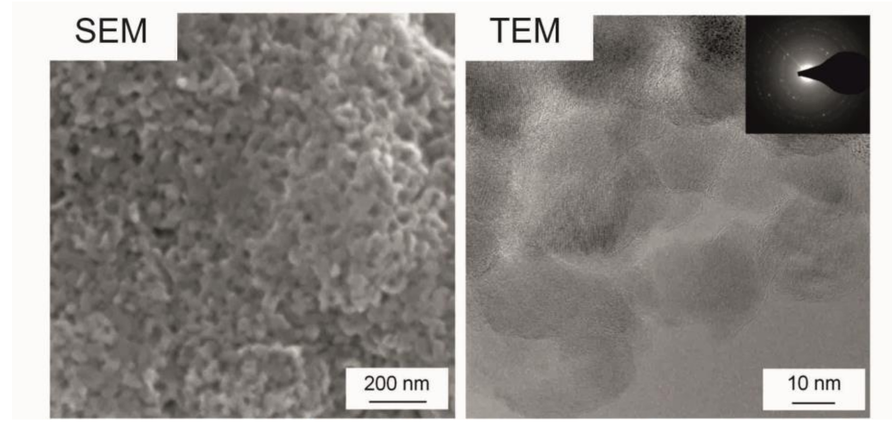
$Li_2Fe_{1-y}Mn_ySiO_4$ / C

y = 0.2

XRD

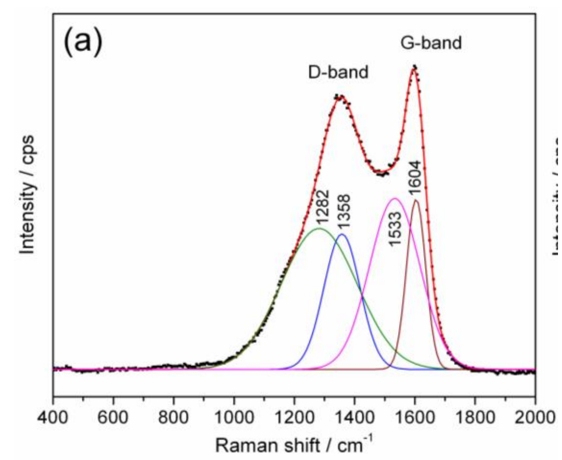


y = 0.2



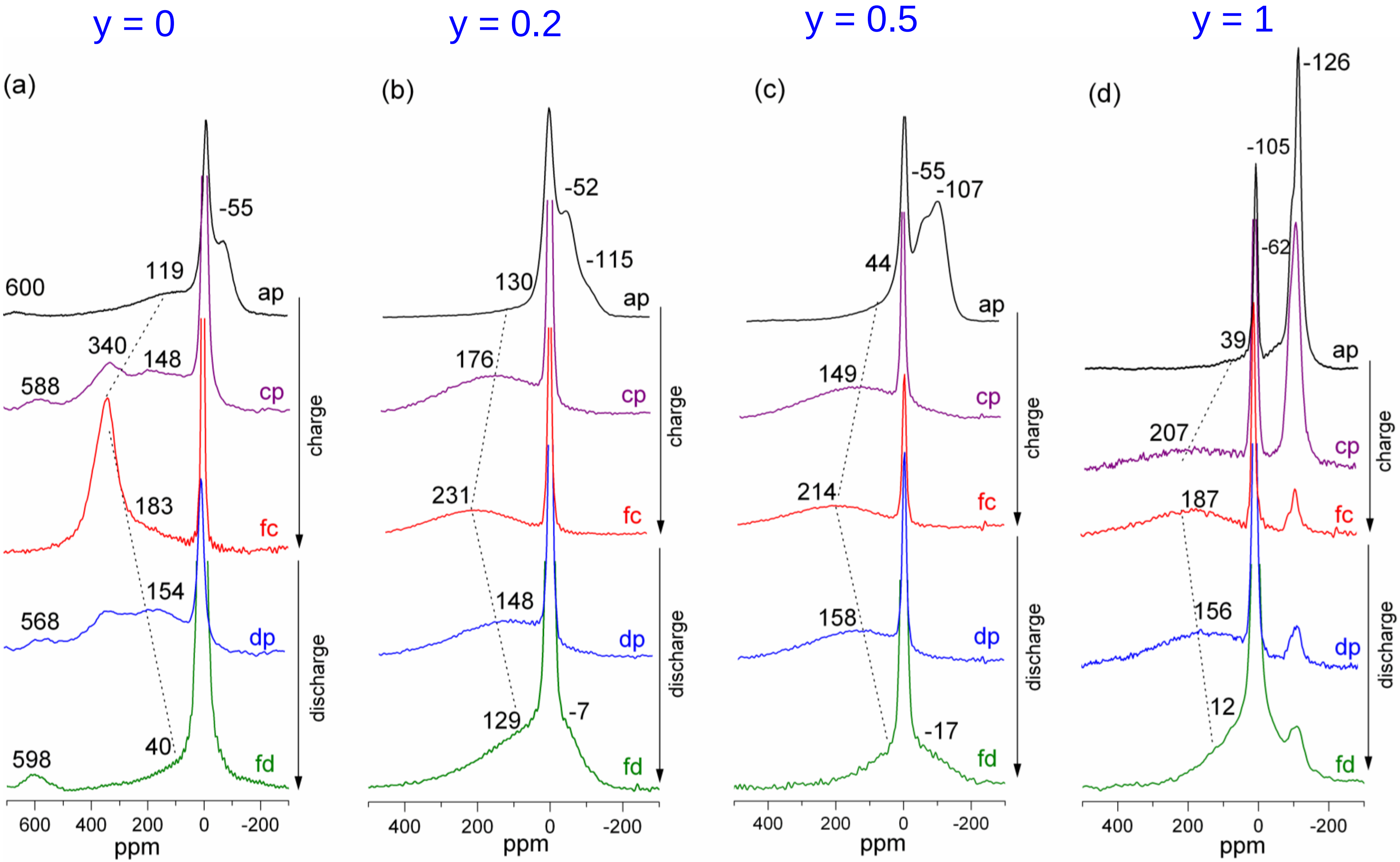
y = 0

Raman



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

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



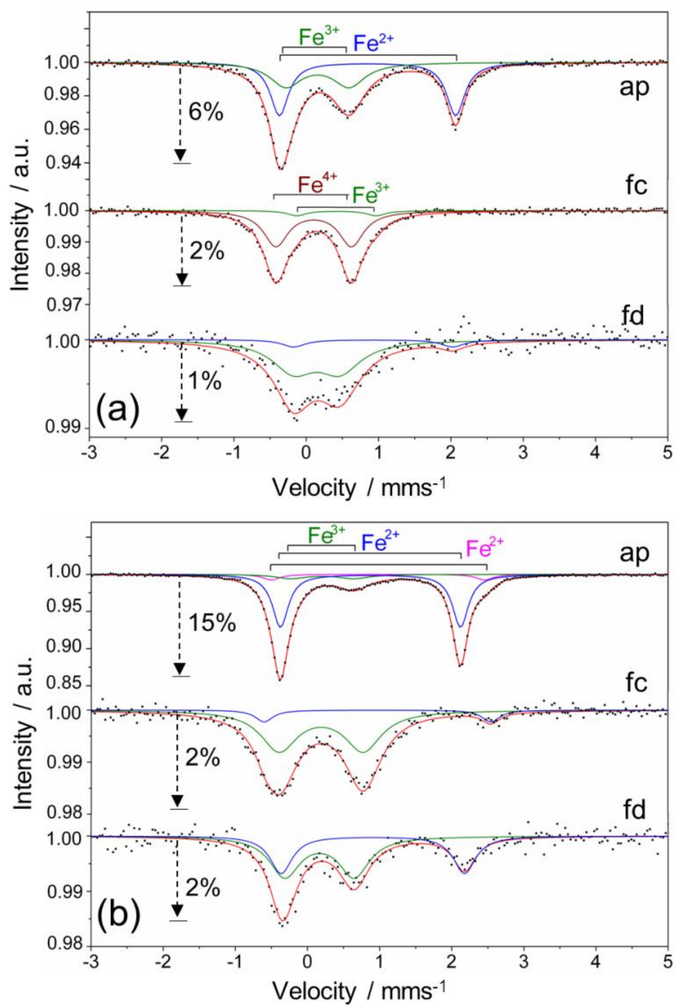
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

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

$y = 0$

$y = 0.2$

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



charge

discharge

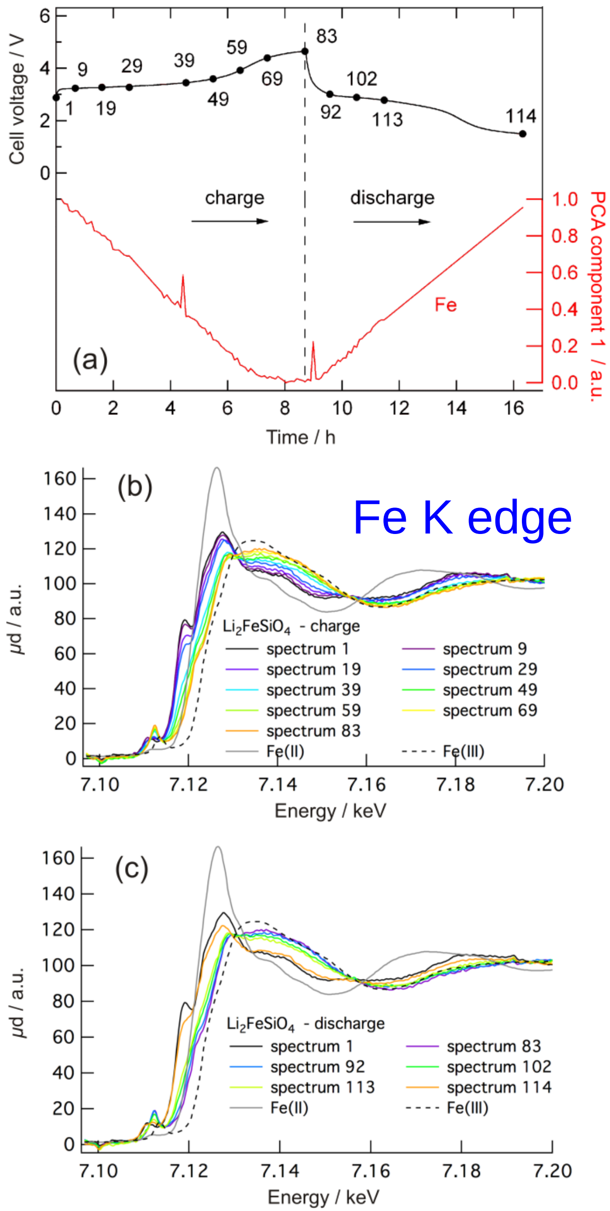
charge

discharge

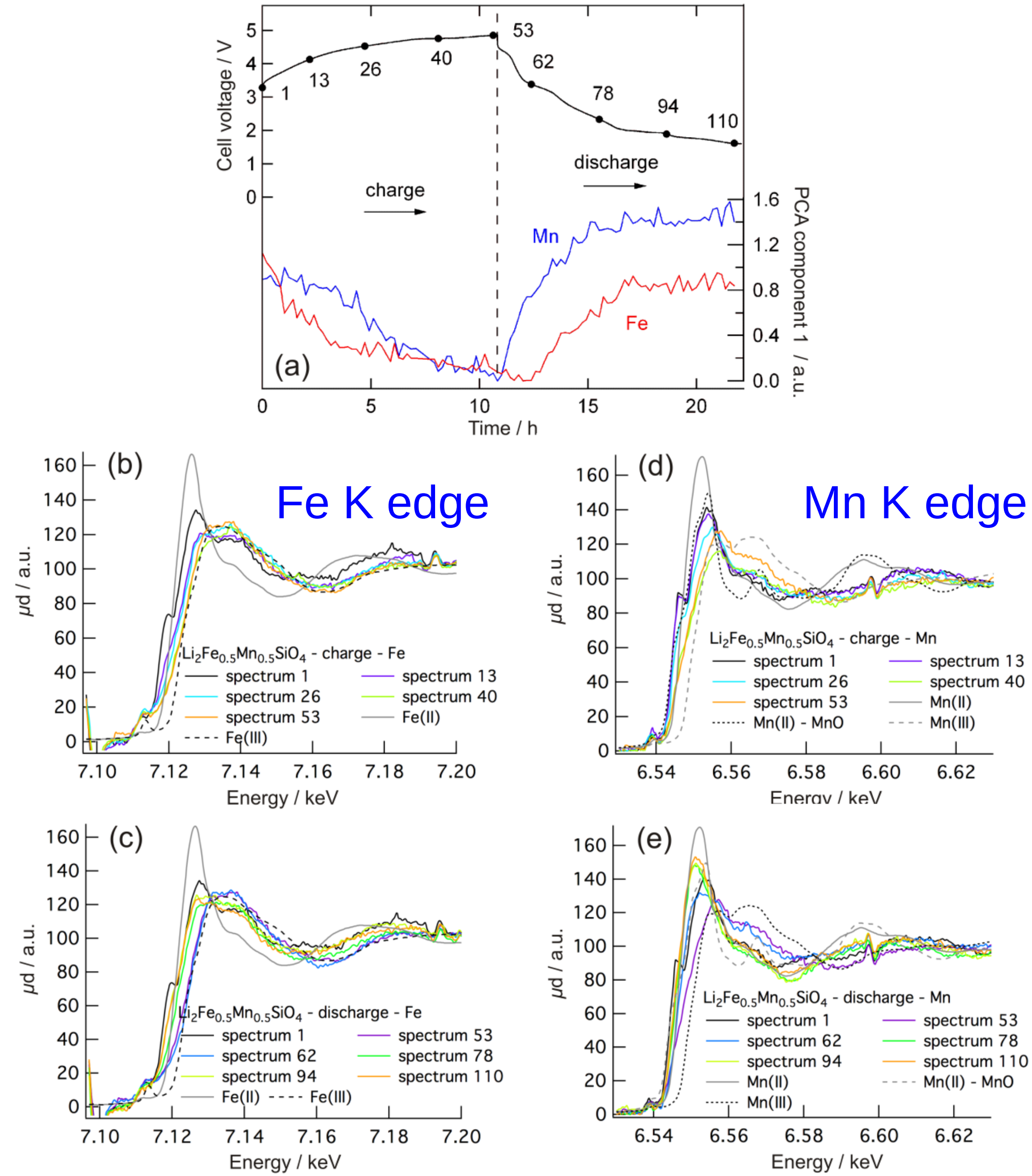
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

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

y = 0



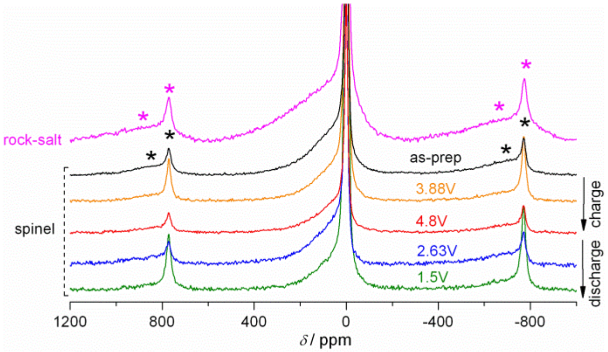
y = 0.5

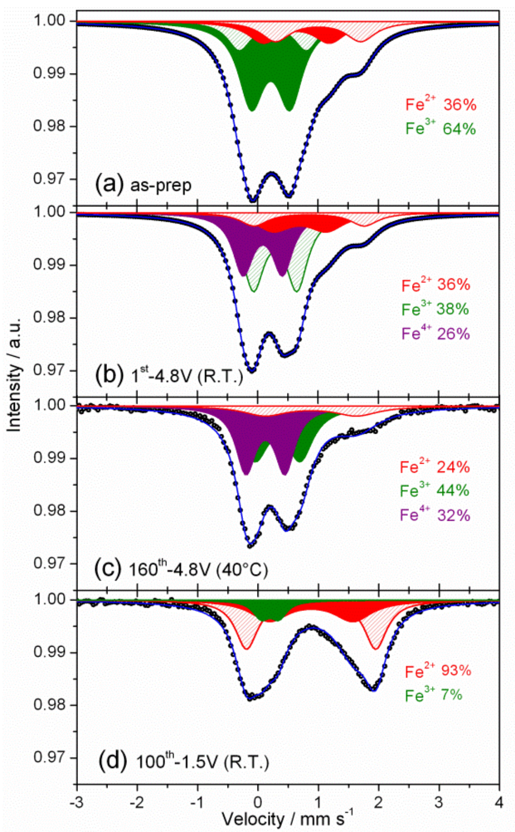


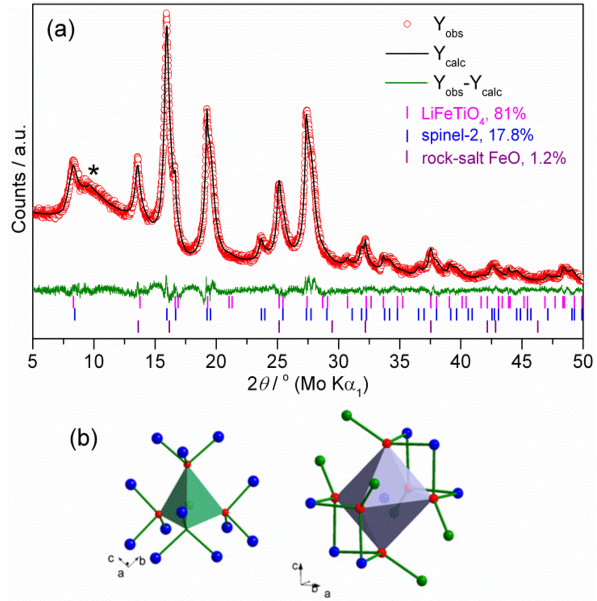
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

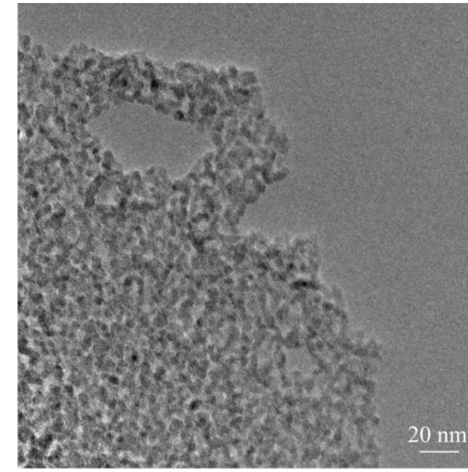
$LiFeTiO_4$

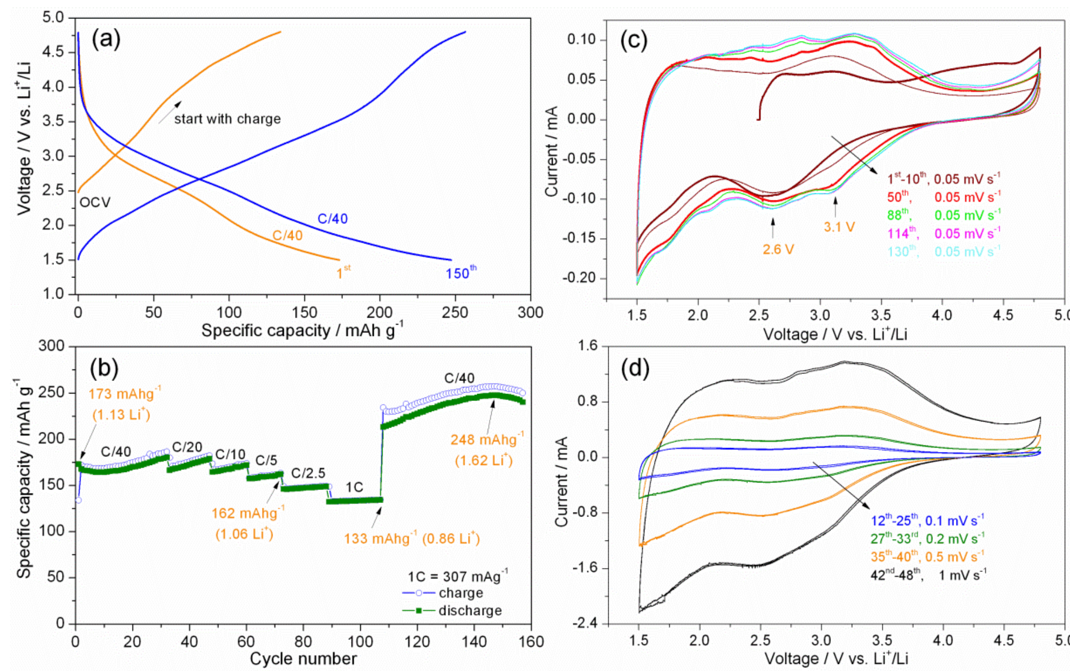
(together with M. Knapp, M. Yavuz)







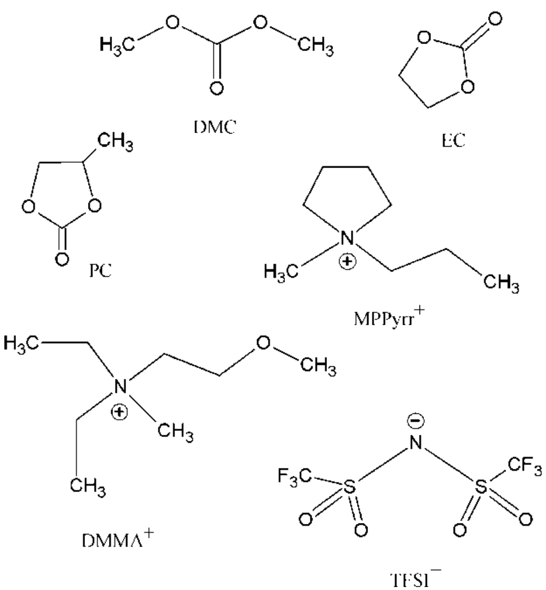


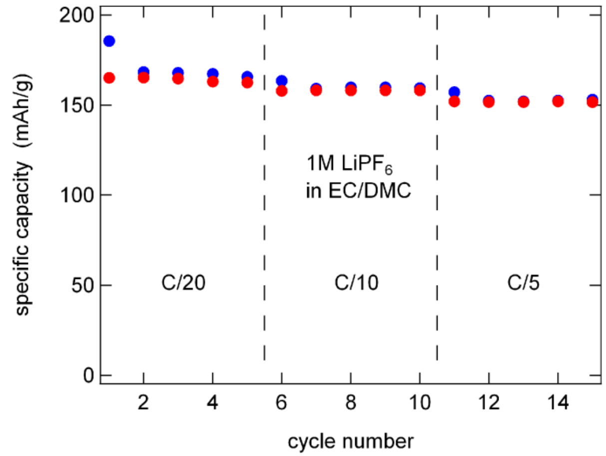


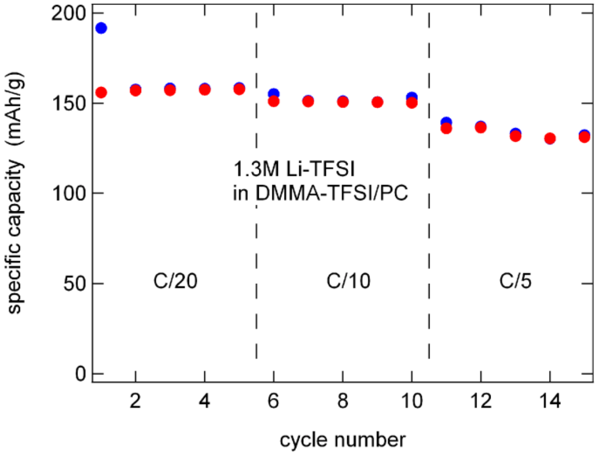
R. Chen, S. Indris, *EP* 13401030, 2013.

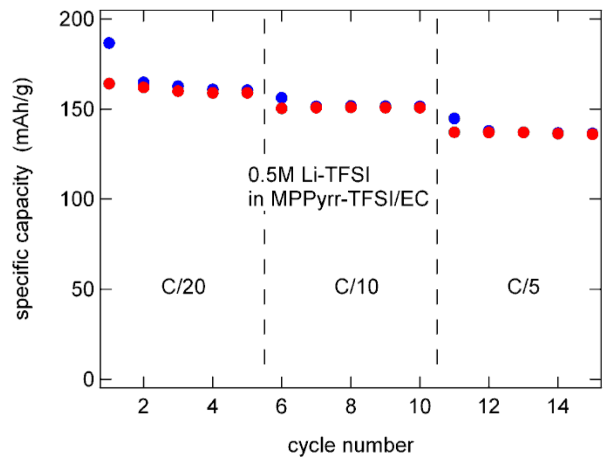
Ionic liquids as electrolytes   cycling with NMC + Li

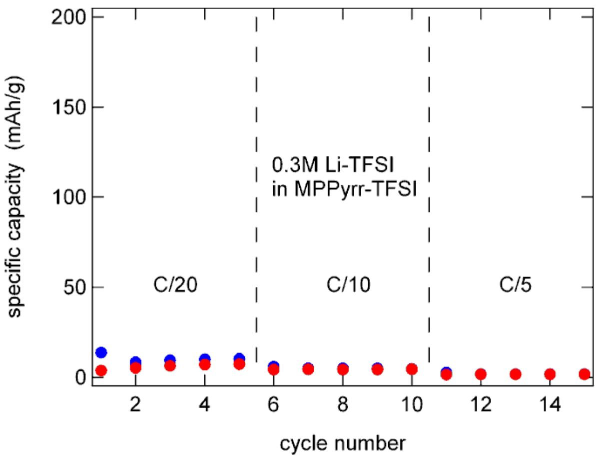
(together with M. Schulz, KIT-IAM)









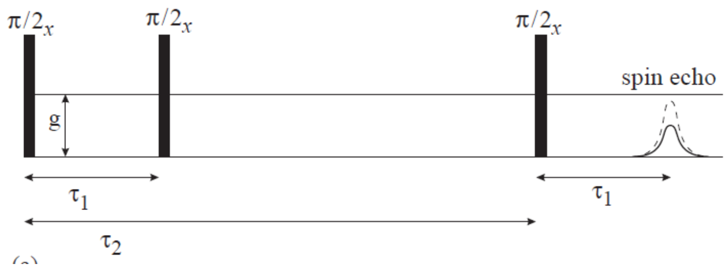


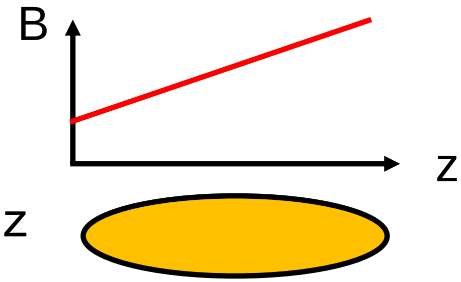
Electrolytes: transference numbers → Field Gradient NMR

(together with M. Schulz, KIT)

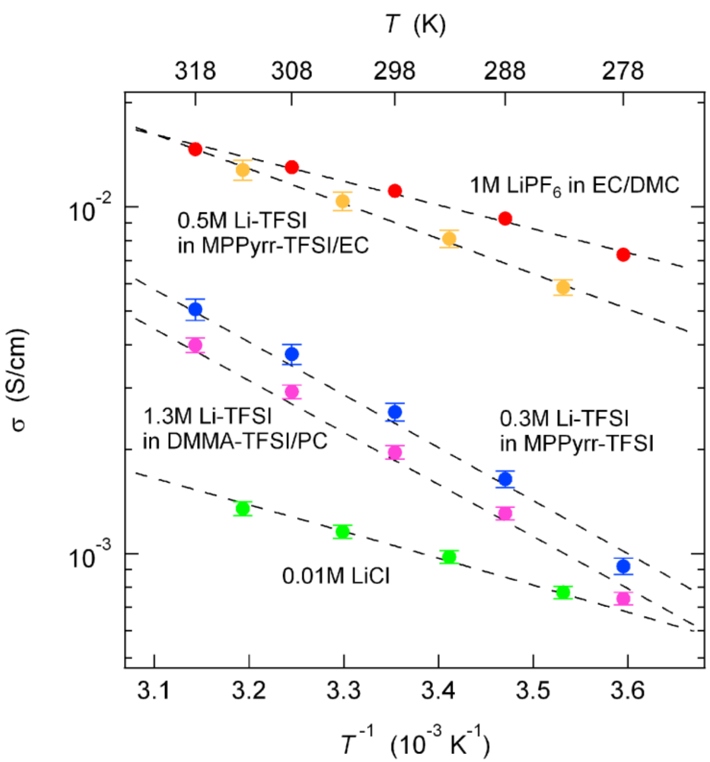
$$t_{Li} = \frac{\sigma_{Li}}{\sigma_{ges}}$$

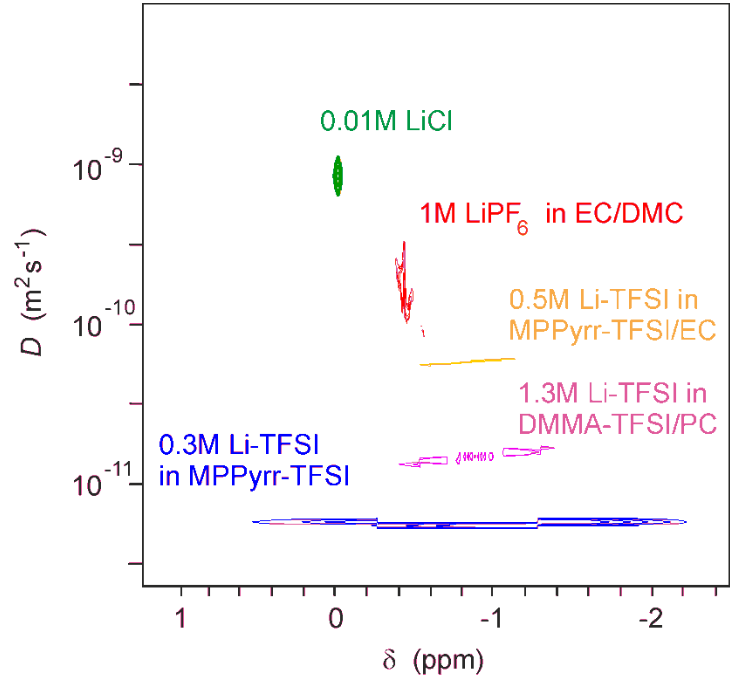
$$\omega = \gamma \cdot B$$





$$B = B_0 + \Delta B \cdot z$$





$1M\ LiPF_6$ in EC/DMC : $t_{Li} = 0.76$

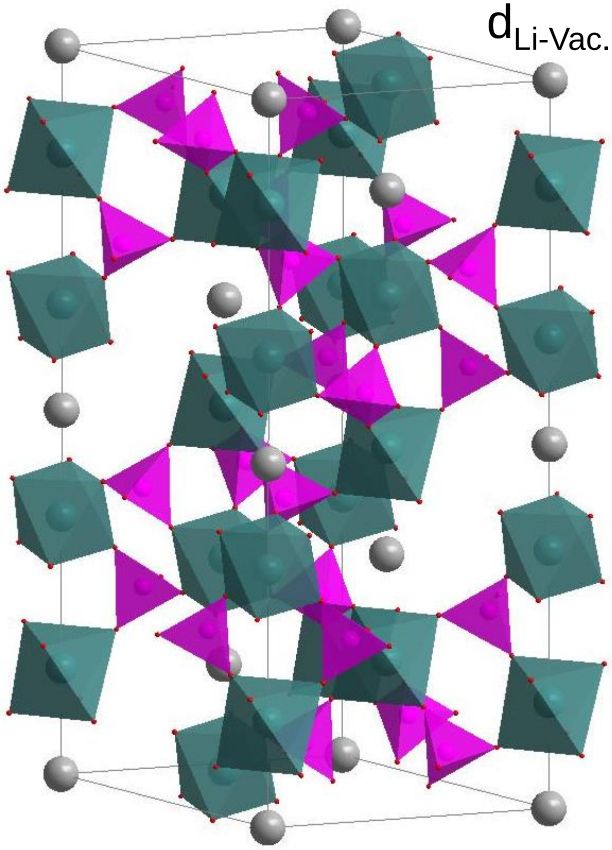
$0.3M\ LiNTf_2$ in MPPyrr-TFSI: $t_{Li} = 0.025$

$Li_{1.6}Al_{0.6}Ti_{1.4}(PO_4)_3$ and $Li_{1.6}Al_{0.6}Ge_{1.4}(PO_4)_3$

(together with M. Rohde, IAM-AWP)

LAGP

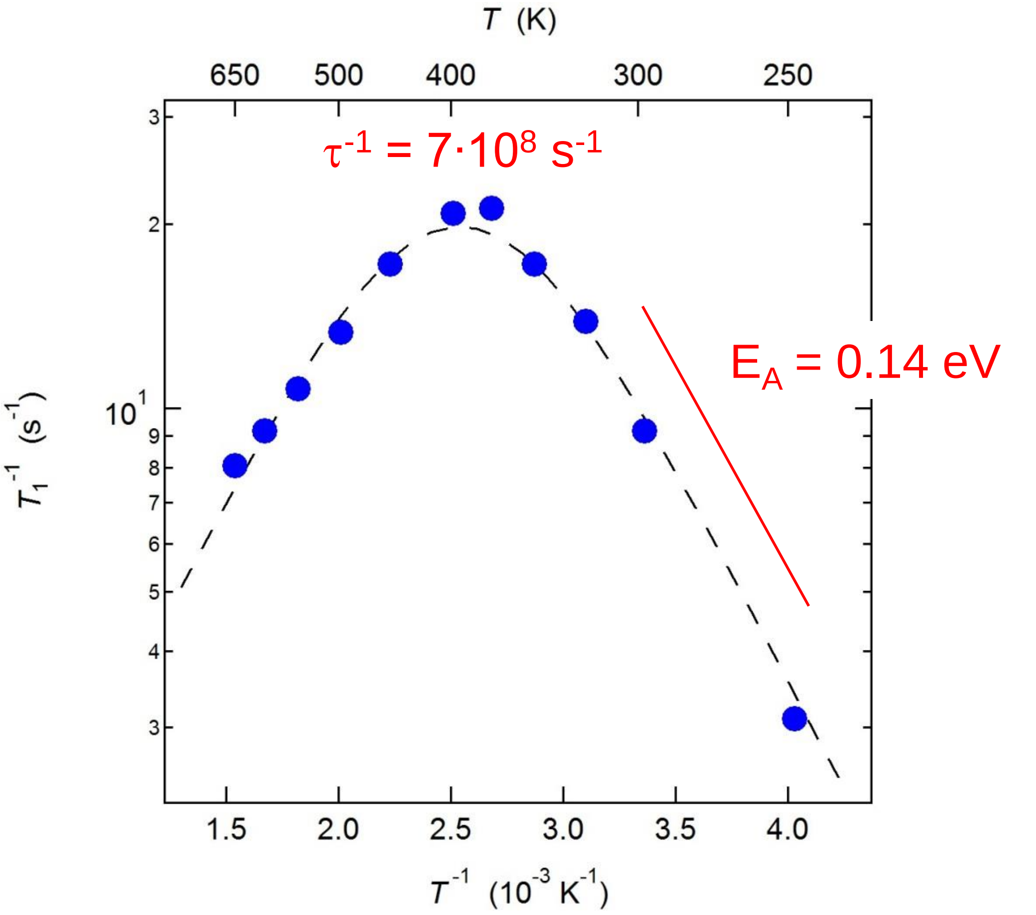
$d_{Li\text{-}Vac.} = 3Å$



$D = \ell^2 / 6\tau = 10^{-11}\ m^2/s$ (at 400 K)

$\sigma_{Li} = 3.6\ mS/cm$

^7Li NMR relaxometry

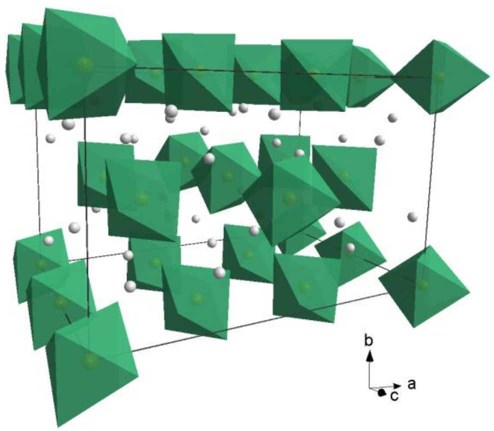


α-Li_3FeF_6

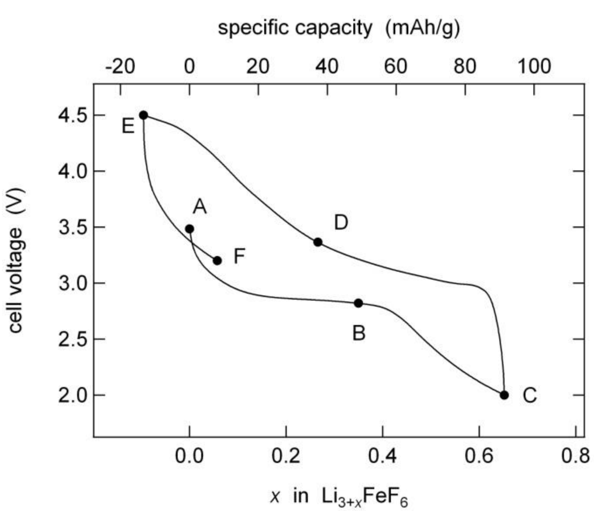
(together with J. Binder, KIT-IAM)

$Fe^{(3+)}$: $3d^5$

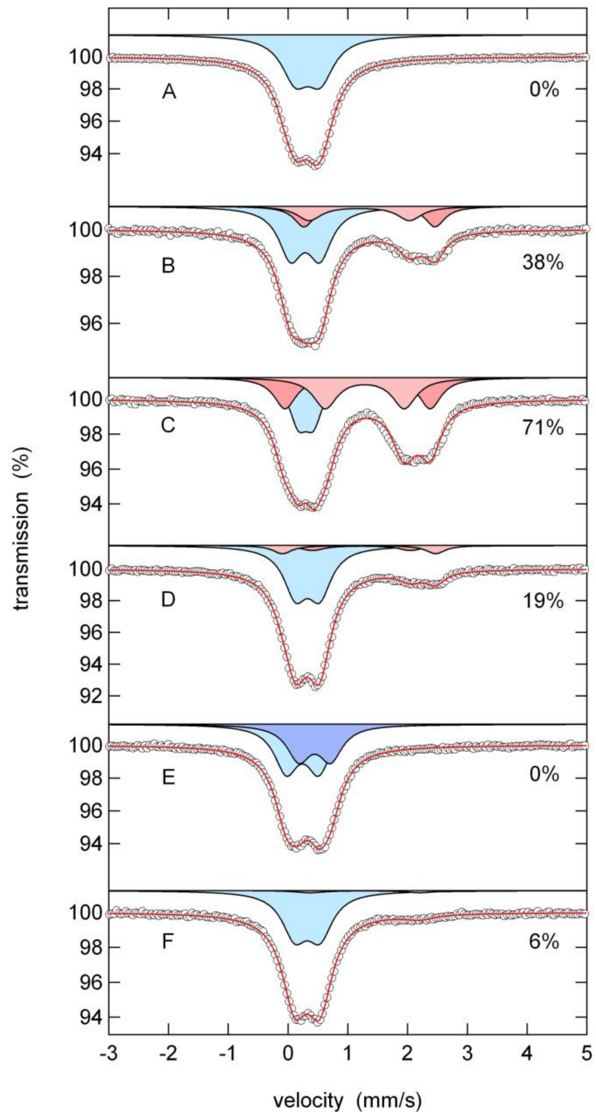
$Fe^{(2+)}$: $3d^6$



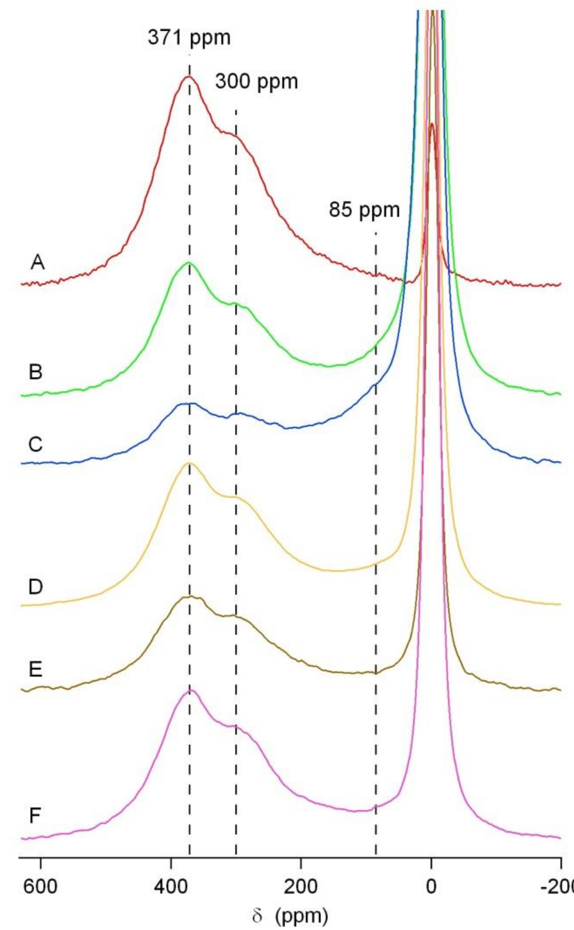
$$Li_3Fe^{(3+)}F_6 + Li \leftrightarrow Li_4Fe^{(2+)}F_6$$



^{57}Fe Mössbauer

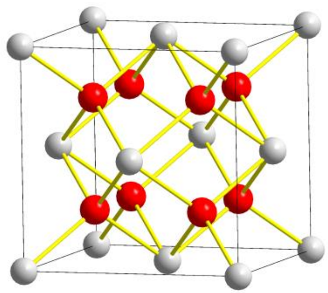


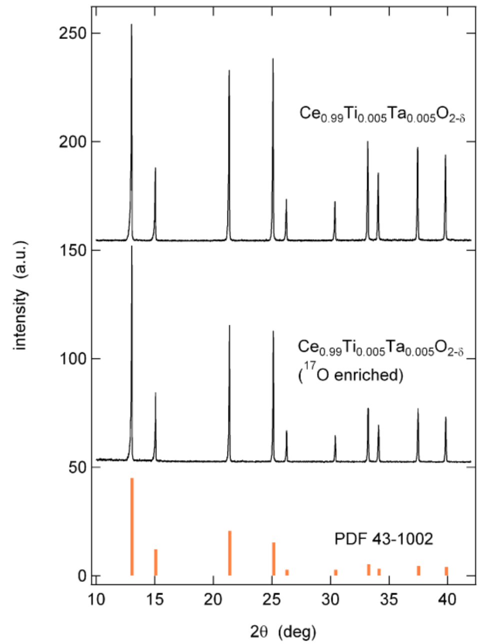
^{7}Li MAS NMR



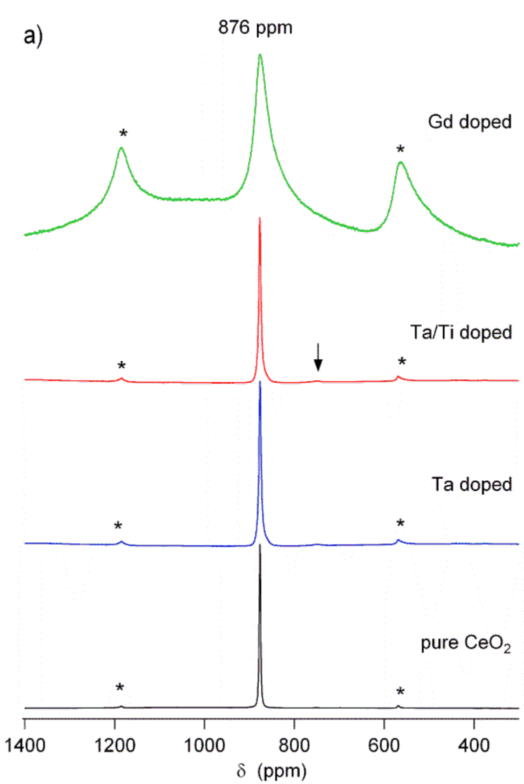
CeO_2 doped with Ta and Ti/Ta

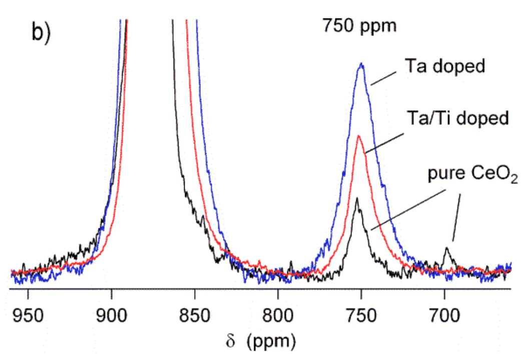
(together with J. Janek, Uni Giessen)



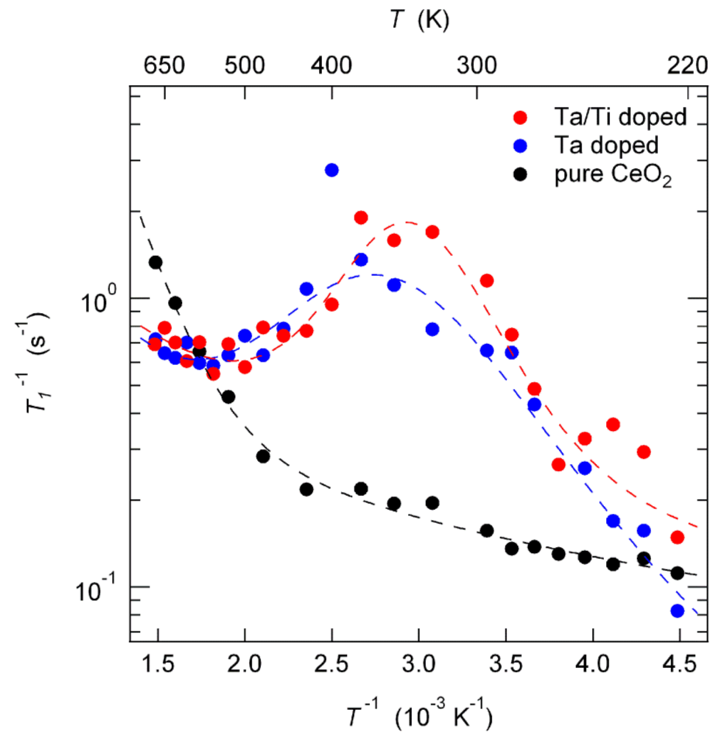


^{17}O MAS NMR





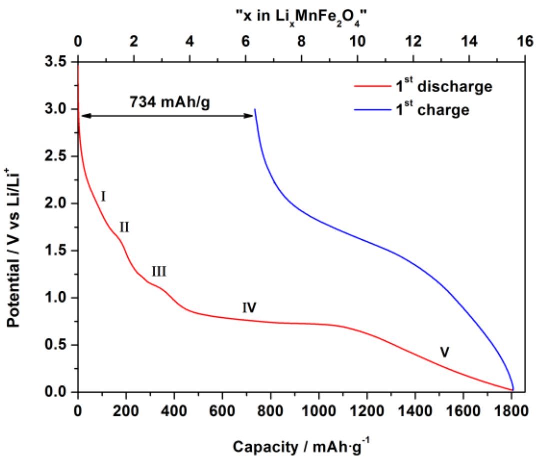
^{17}O NMR relaxometry

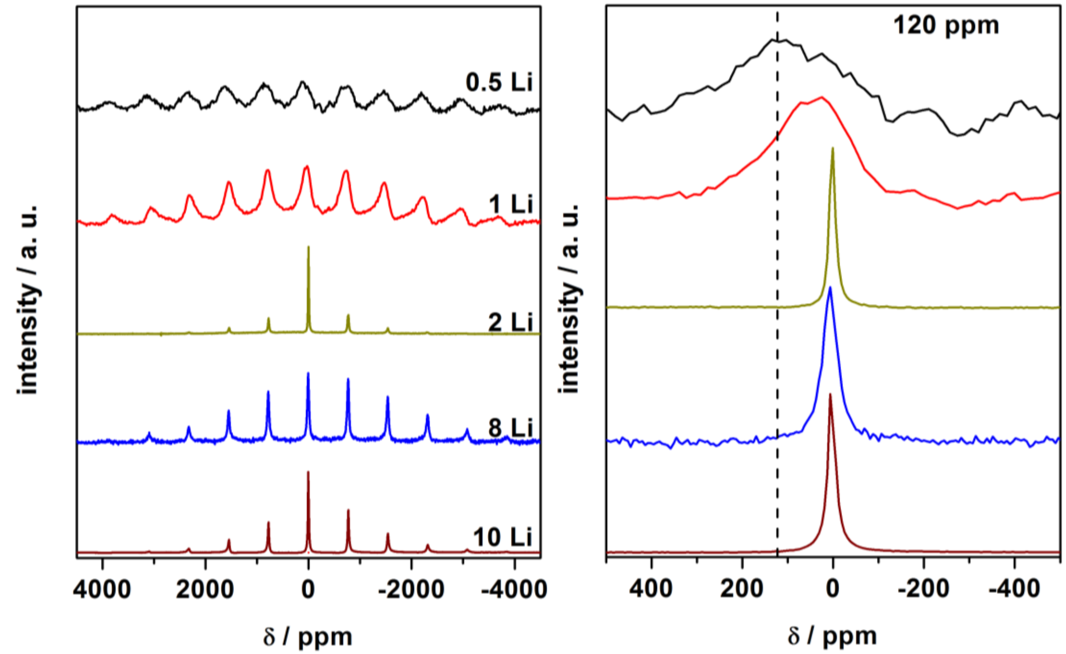


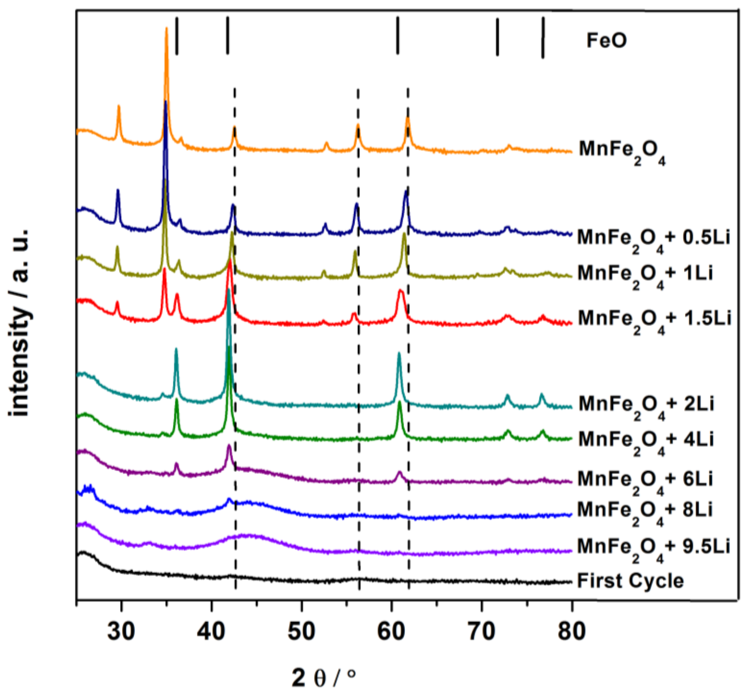
$\tau^{-1} = 2.5 \cdot 10^{8}\ s^{-1}$ at 350 K

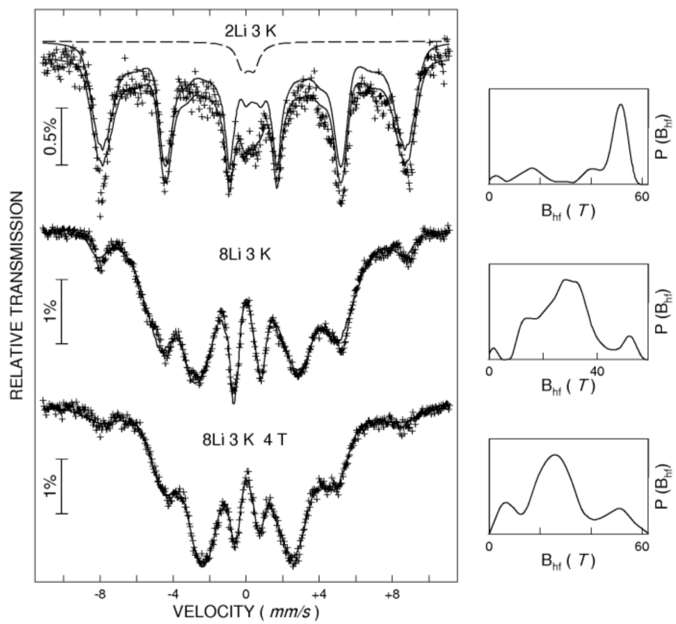
$E_A = 0.3$ eV

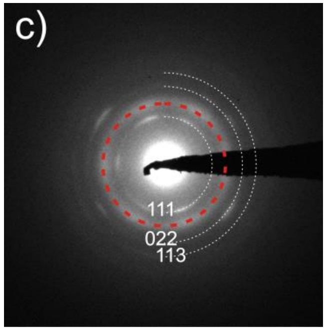
Nanocrystalline $MnFe_2O_4$











Conclusions

- observation of reaction mechanisms
  at components and interfaces during Li insertion/removal
- understanding function and degradation of materials/cells

$LiCoPO_4$:

- reversible phase transformation with intermediate phase
  $LiCoPO_4 \leftrightarrow Li_{0.7}CoPO_4 \leftrightarrow CoPO_4$
- two-step mechanism, both steps: two-phase reaction
- highly reversible oxidation/reduction $Co^{2+} \leftrightarrow Co^{3+}$
- intermediate $Li_{2/3}CoPO_4$
- degradation of electrolyte?

$Li_2(Fe/Mn)SiO_4$:

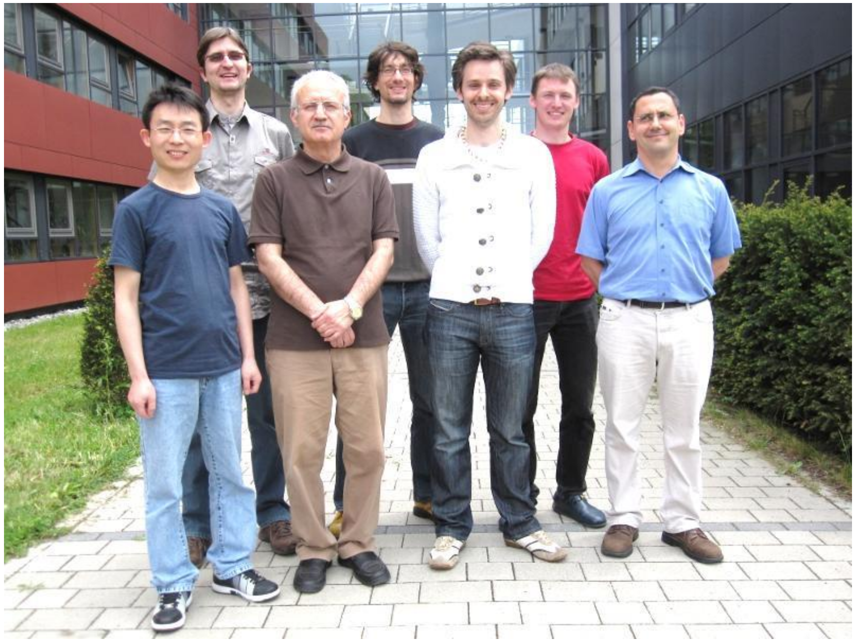
- preparation of nanocrystalline materials with C-coating
- Fe: single polymorph, Fe/Mn: mixture of polymorphs
- highly reversible oxidation/reduction $Fe^{2+} \leftrightarrow Fe^{3+}$
  $Mn^{2+} \leftrightarrow Mn^{3+}$
- high degree of structural disorder after cycling

Ionic liquid electrolytes: (σ_{dc}) PFG-NMR $\rightarrow$ Li diffusion

Thanks

Marco Scheuermann
Ruiyong Chen
Maximilian Kaus
Krystyna Bachtin
Christof Dräger
Nilüfer Kiziltaz Yavuz

Ralf Heinzmann
Ibrahim Issac
Holger Hain
Nina Schweikert
Sebastian Becker
Linda Wünsche



GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

ptJ
Projektträger Jülich
Forschungszentrum Jülich

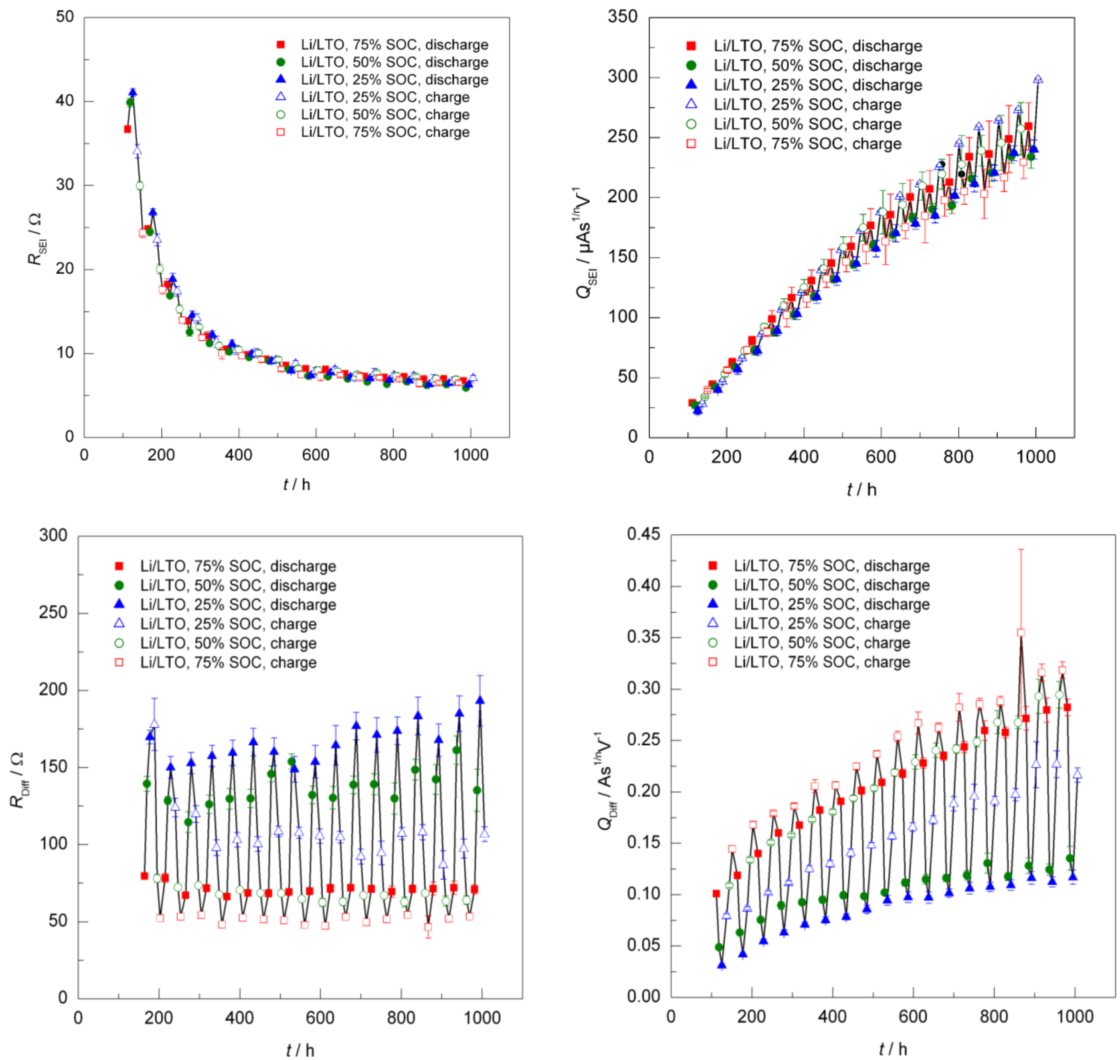
CFN

Deutsche Forschungsgemeinschaft
DFG

YIN

Impedance Spectroscopy: Internal Interfaces → degradation

Li/LTO

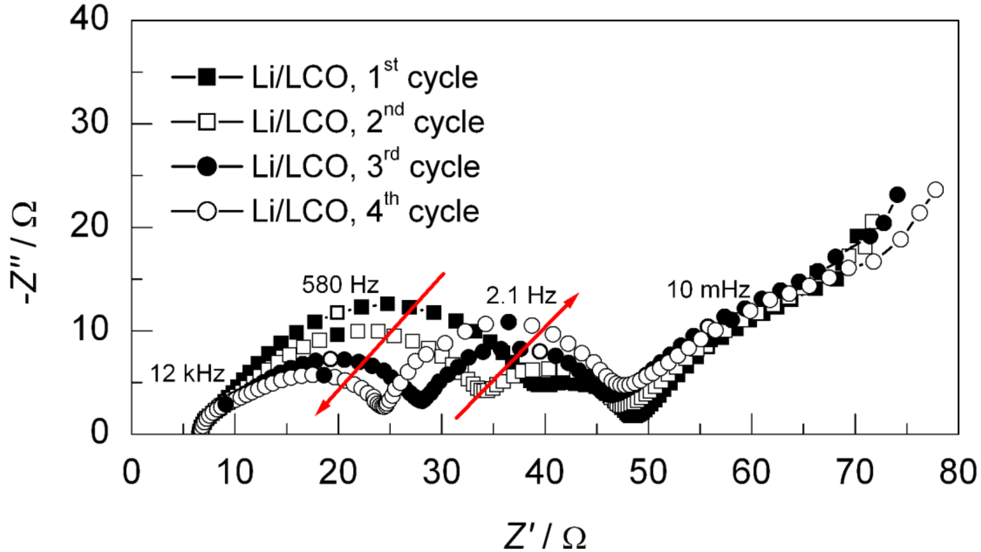


Determination

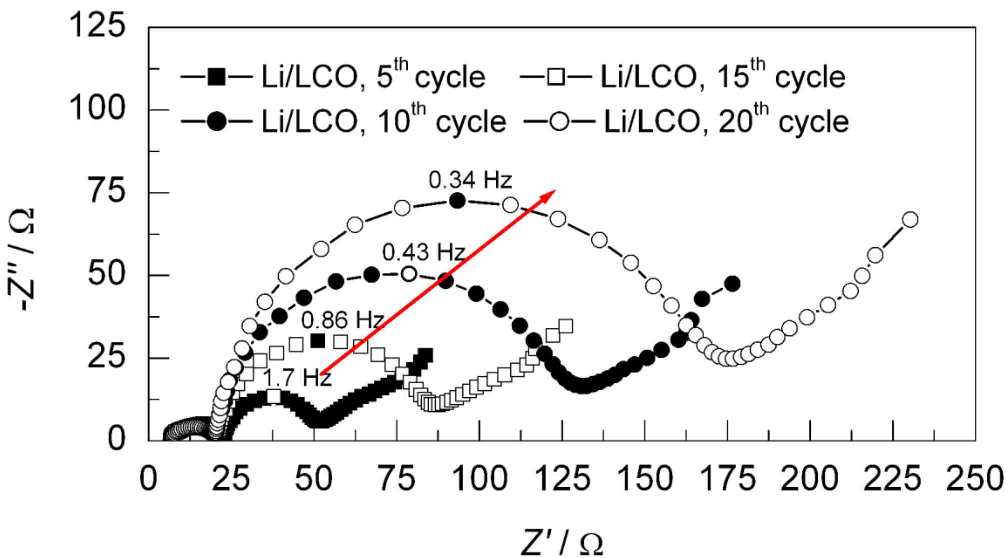
- SOC
- SOH

N. Schweikert et al., *Solid State Ionics* **226** (2012), 15.

Impedance Spectroscopy: Internal Interfaces → degradation



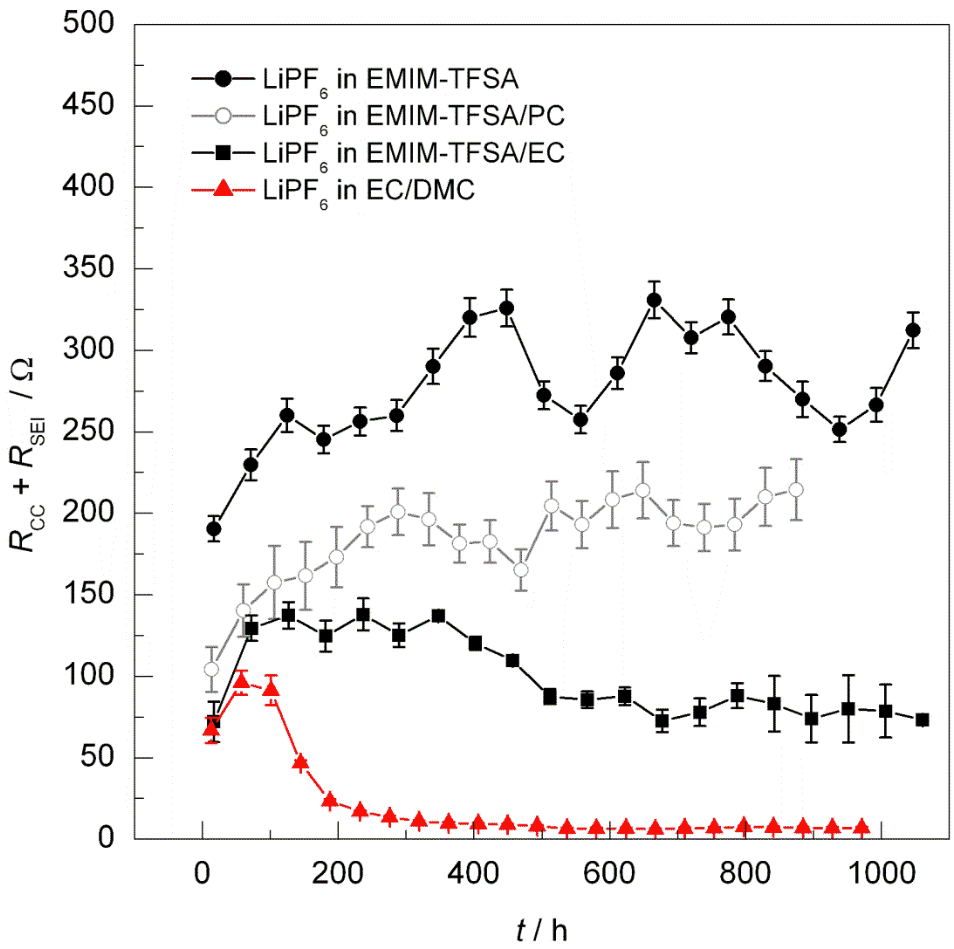
Li/LCO



Galvanostatic cycling:
No changes

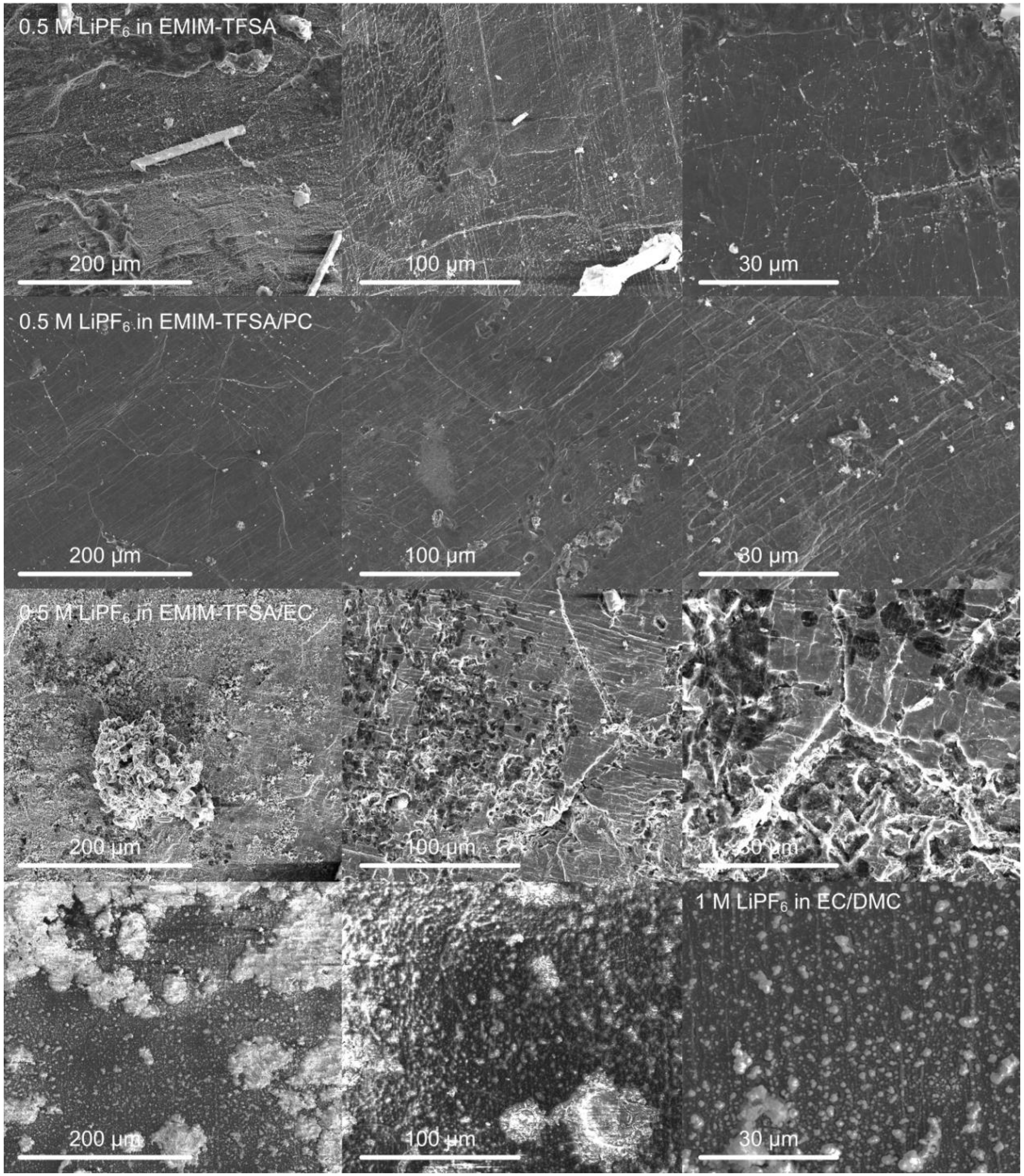
N. Schweikert et al., *Solid State Ionics* **226** (2012), 15.

Impedance Spectroscopy: Li dendrite growth



N. Schweikert et al., *J. Power Sources* **2269** (2013), 149.

Impedance Spectroscopy: Li dendrite growth



0.5 M $LiPF_6$ in EMIM-TFSI

0.5 M $LiPF_6$ in EMIM-TFSI/PC

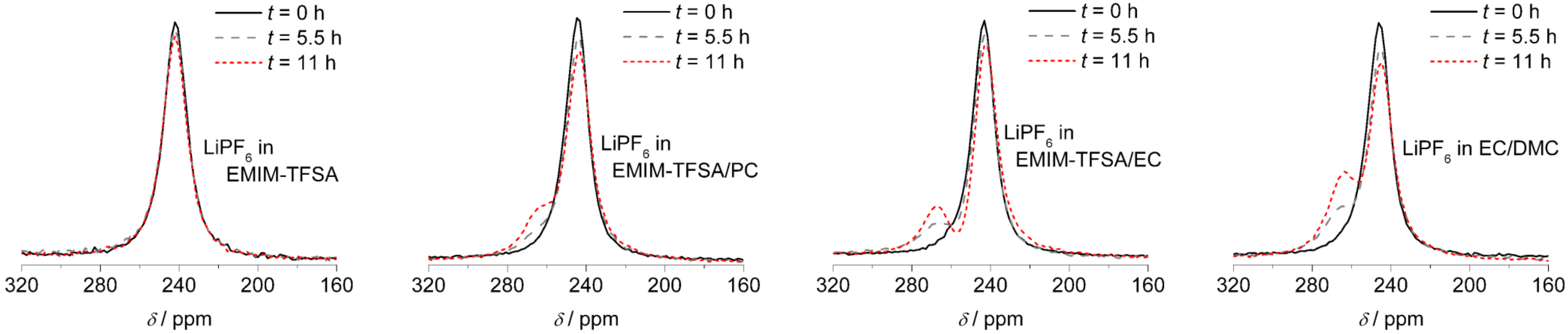
0.5 M $LiPF_6$ in EMIM-TFSI/EC

1 M $LiPF_6$ in EC/DMC

N. Schweikert et al., *J. Power Sources* **2269** (2013), 149.

^{7}Li *In situ* NMR: Li dendrite growth

symmetric Li-Li cells



suppressed dendrite growth for $LiPF_6$ in EMIM-TFSA

good agreement with impedance data, SEM, and *in situ* NMR

N. Schweikert et al., *J. Power Sources* **2269** (2013), 149.