Li-Ionen-Dynamik in Kondensierter Materie: Vom Einkristall bis zu Li-Ionen-Batterien

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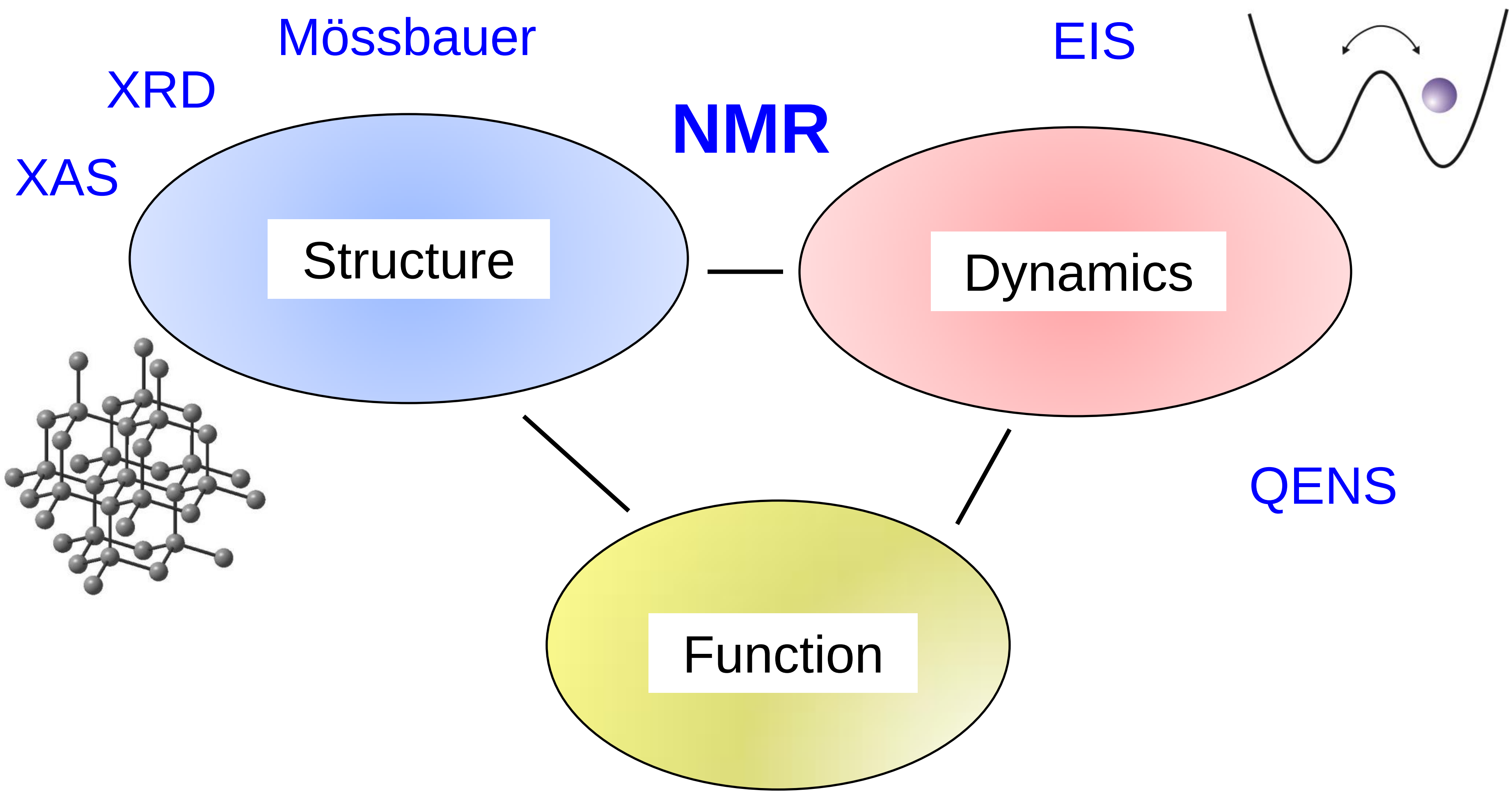
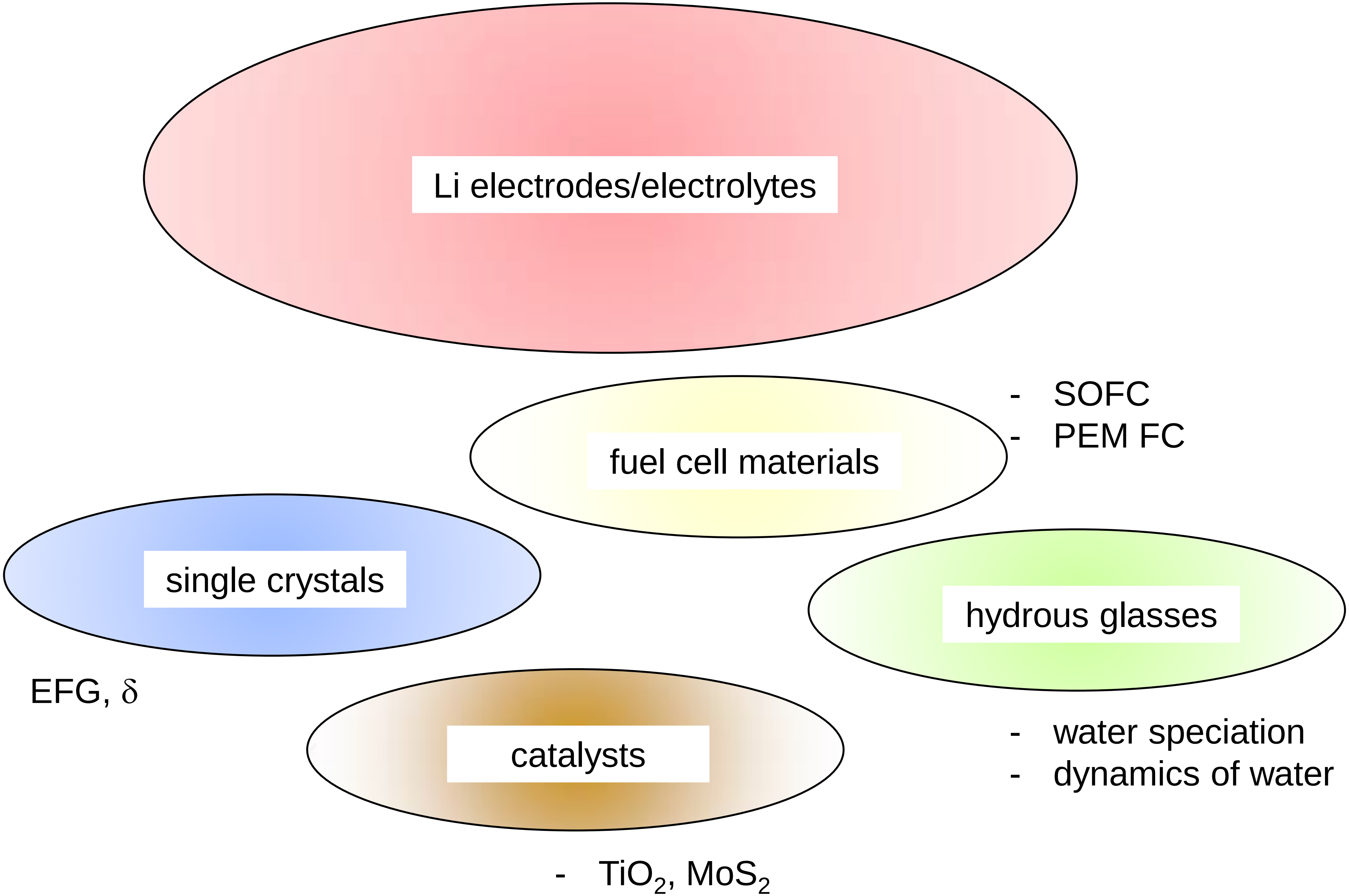
Experimental Techniques:



Materials Science, Energy Storage/Conversion, Geoscience
(Li-Ion Batteries, SOFC, Catalysis, …)

Research Topics



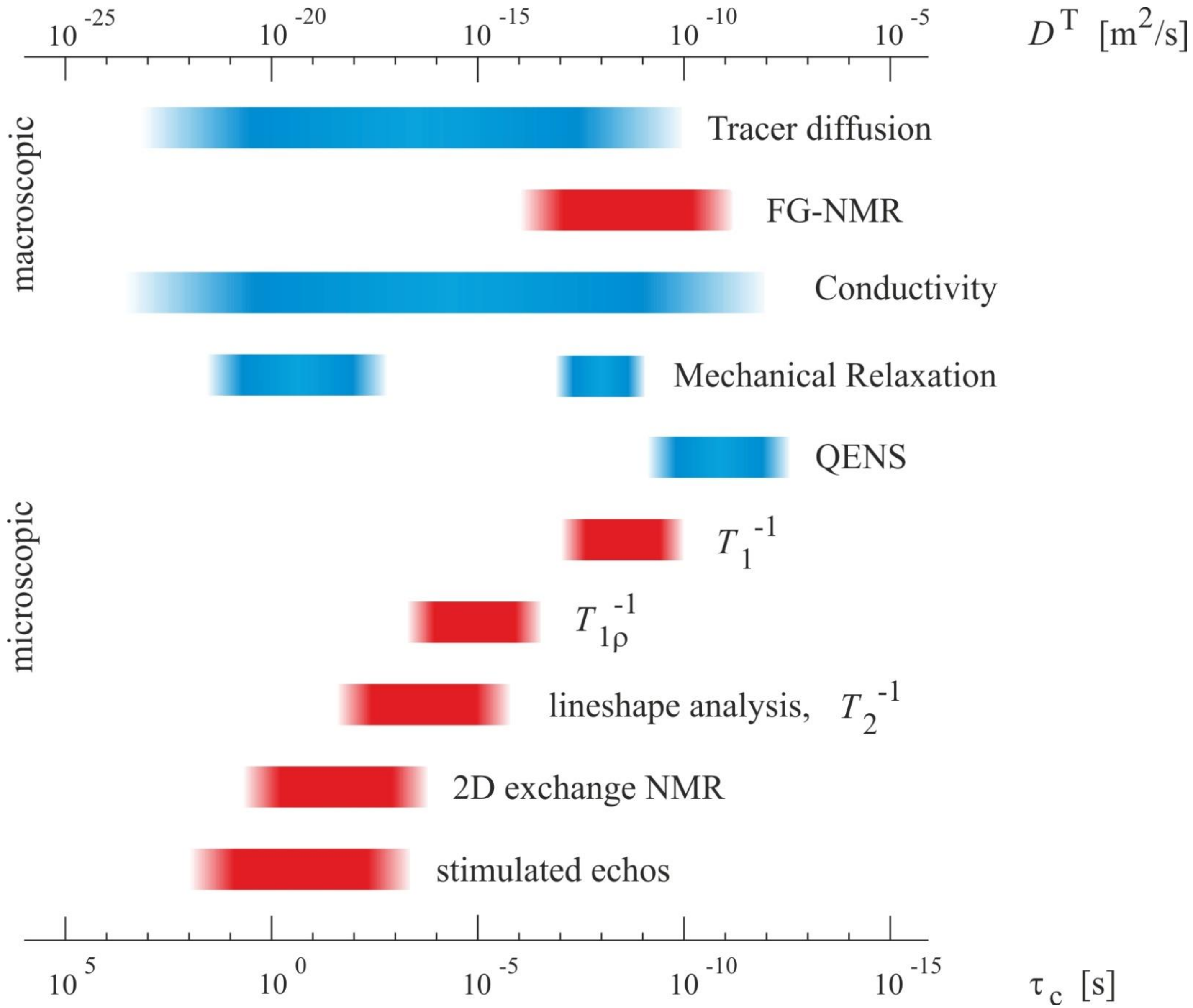
NMR techniques

- MAS NMR   (^{7}Li, ^{6}Li, ^{1}H, ^{2}H, ^{27}Al, ^{29}Si, ^{119}Sn, …)
- Single crystals
- VT-NMR, lineshape analysis
- 2D exchange NMR
- Field-gradient NMR (SFG/PFG)
- *In situ* NMR on complete battery cells
- Relaxometry
- β-NMR

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

- 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, ...)

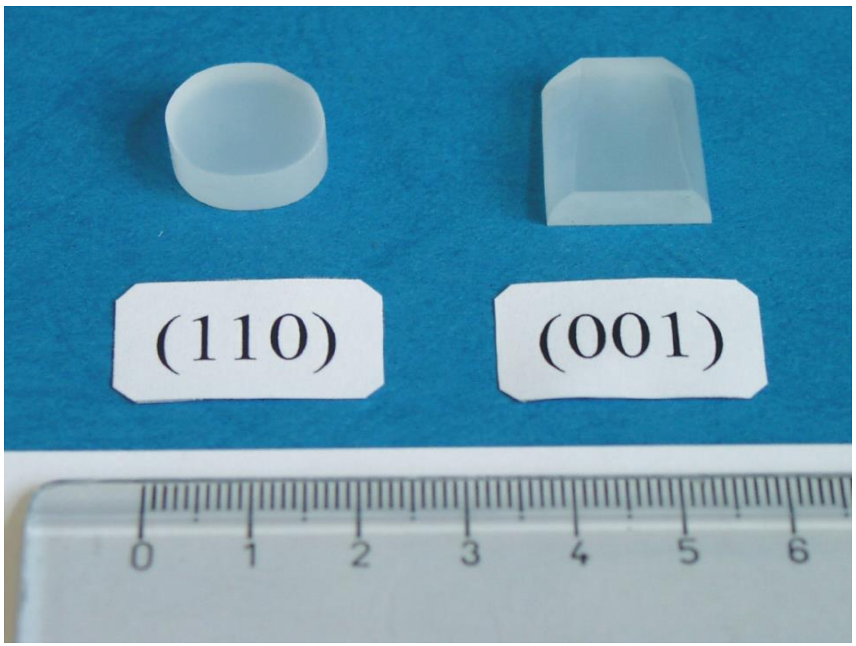
Ion Dynamics in Condensed Matter



$LiAlO_2$ Single Crystal

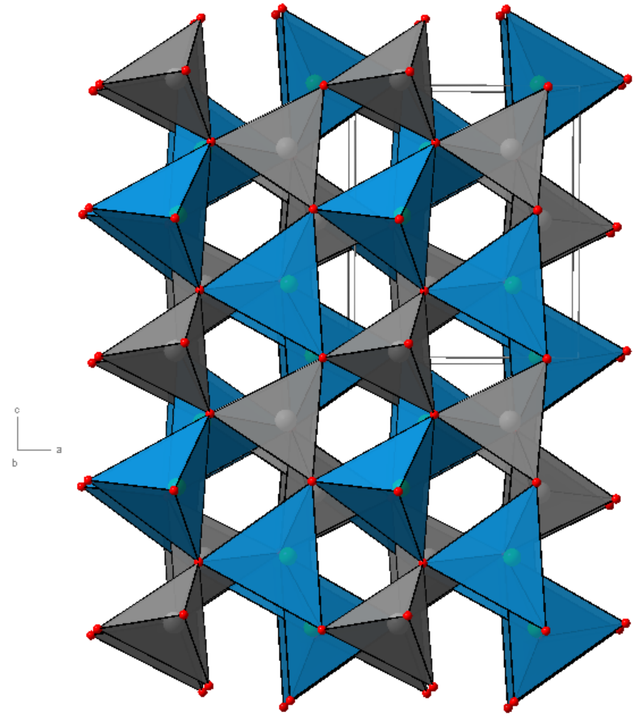
Reinhard Uecker, IKZ Berlin

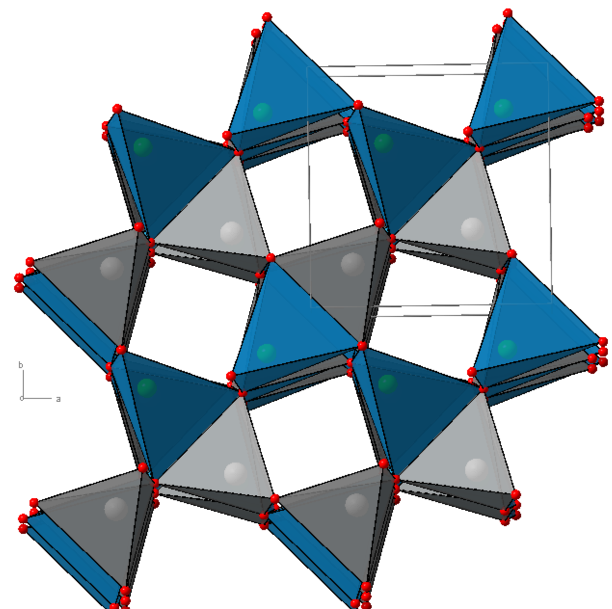
(isotopically pure ^{7}Li)



space group $P4_12_12$

a = 5.189 Å, c = 6.268 Å



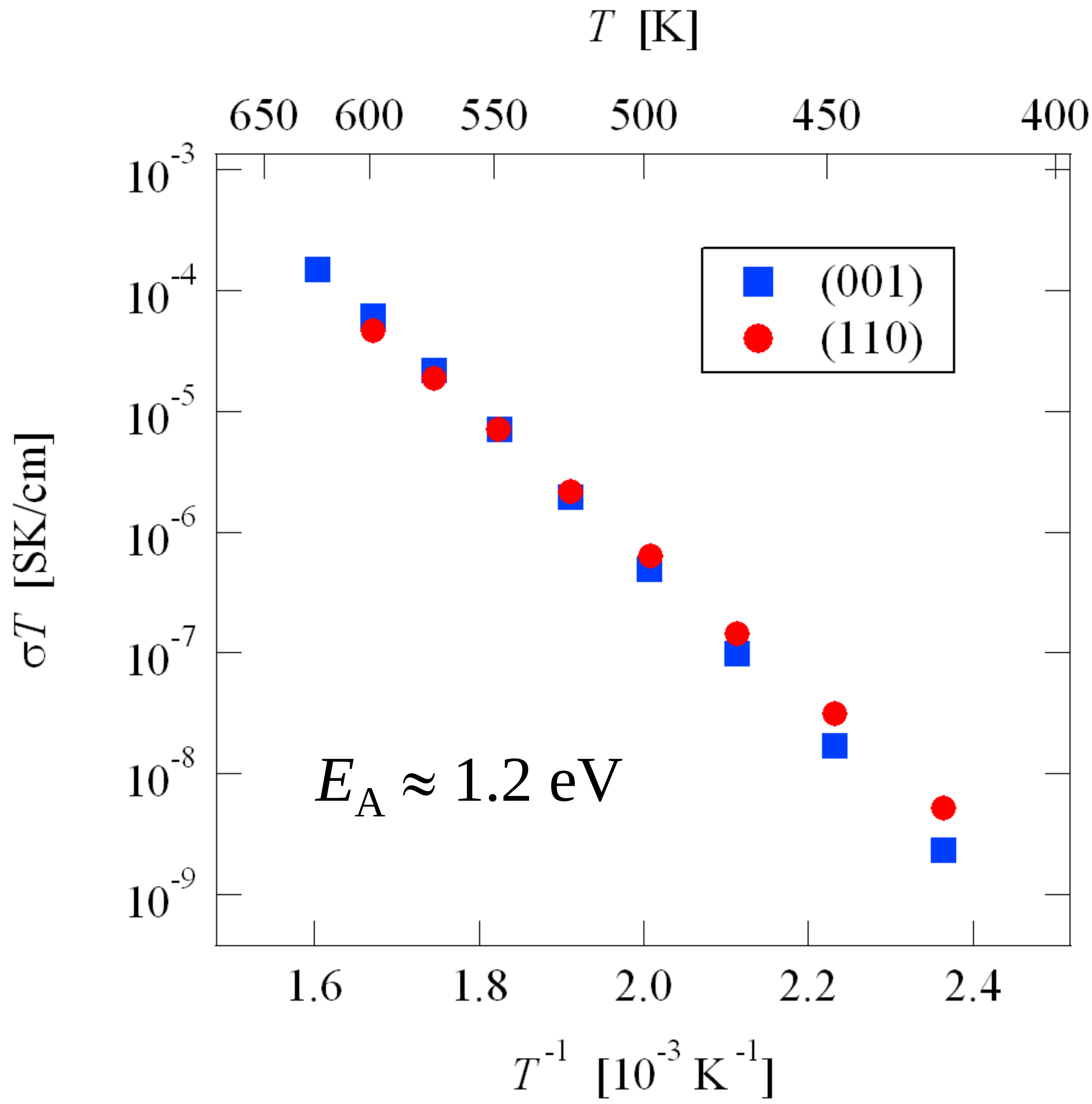


$LiAlO_2$ Applications

- Substrate for epitactic growth of III-V-type Semiconductors (e.g. GaN)
- Fusion and Tritium Breeder Reactors
- Coating in Electrodes for Li-Ion Batteries
- Additive in Composite Polymer Electrolytes

$LiAlO_2$:

B. Roling



Microscopic and Macroscopic Diffusion Quantities

Einstein-Smoluchowski

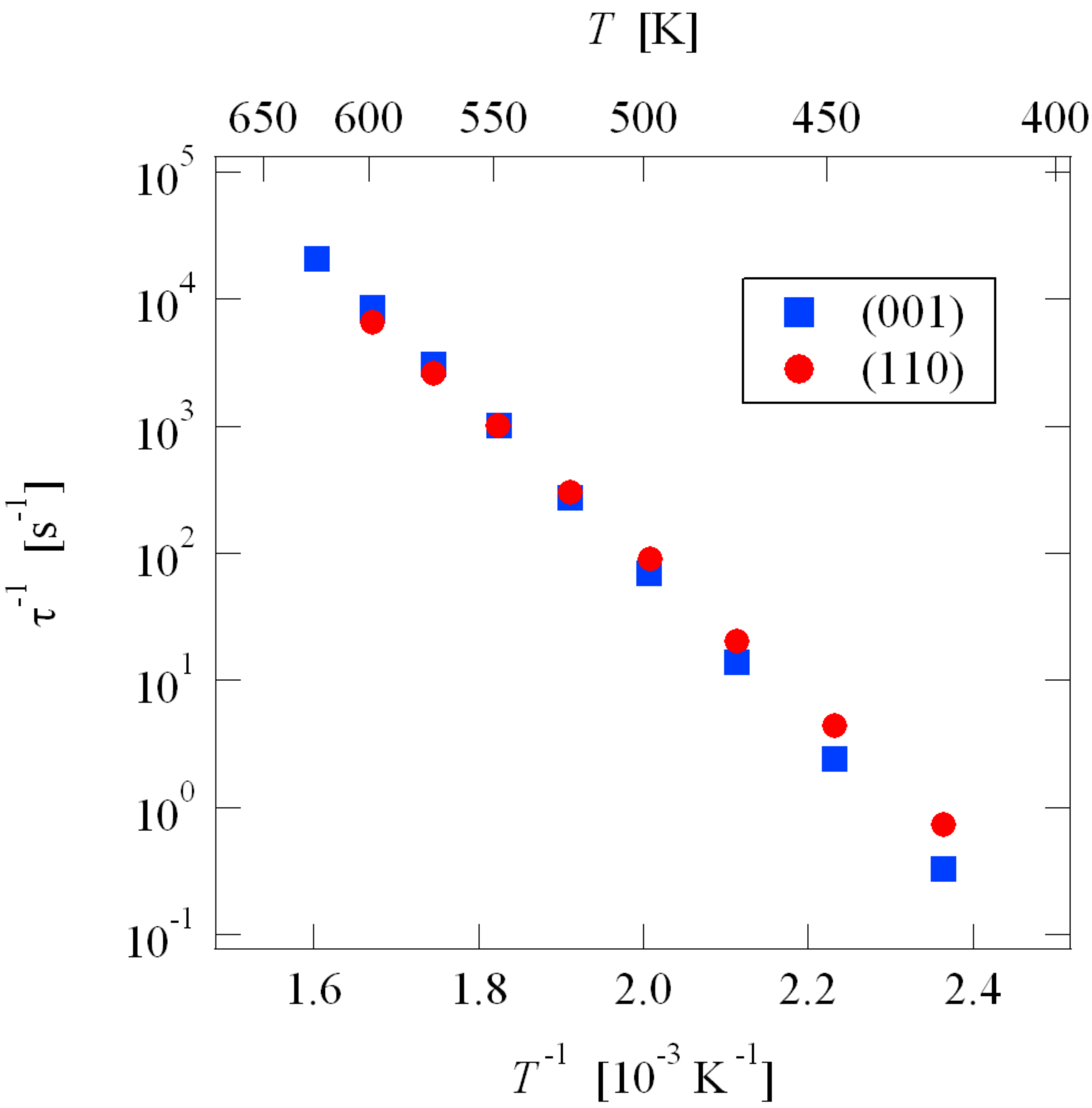
Jump rate $$\tau^{-1} \cdot \frac{\ell^2}{6} \cdot f = D^{\mathrm{T}}$$ *Tracer diffusivity*

Nernst-Einstein

Conductivity $$\sigma \cdot \frac{k_{\mathrm{B}} T}{N q^2} \cdot H_{\mathrm{R}} = D^{\mathrm{T}}$$

Temperature dep. $\Rightarrow$ E_{A} (depends on time window)

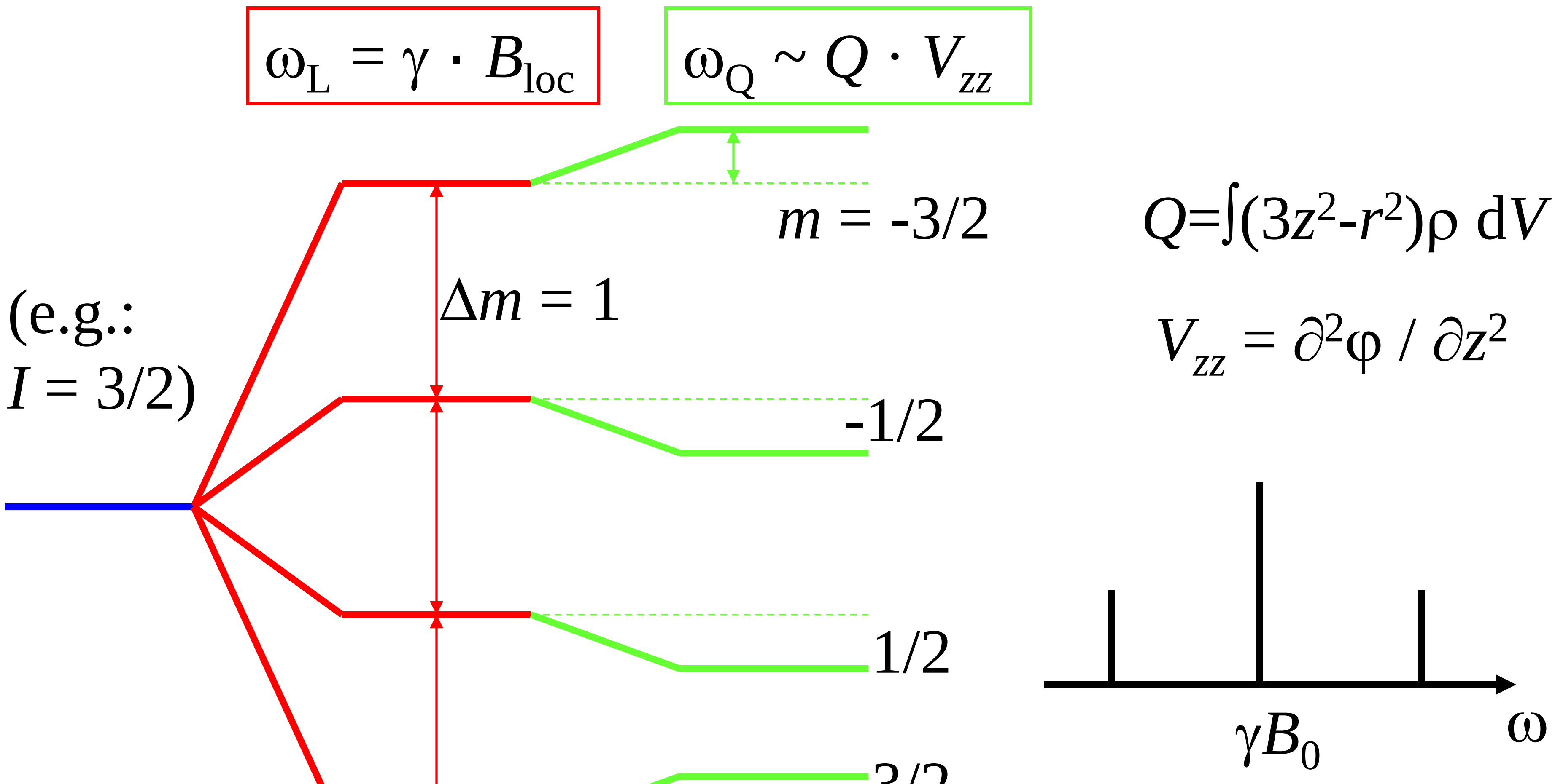
LiAlO$_2$:



T [K]
650
600
550
500
450
400
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
τ^-1 [s^-1]
(001)
(110)
1.6
1.8
2.0
2.2
2.4
T^-1 [10^-3 K^-1]

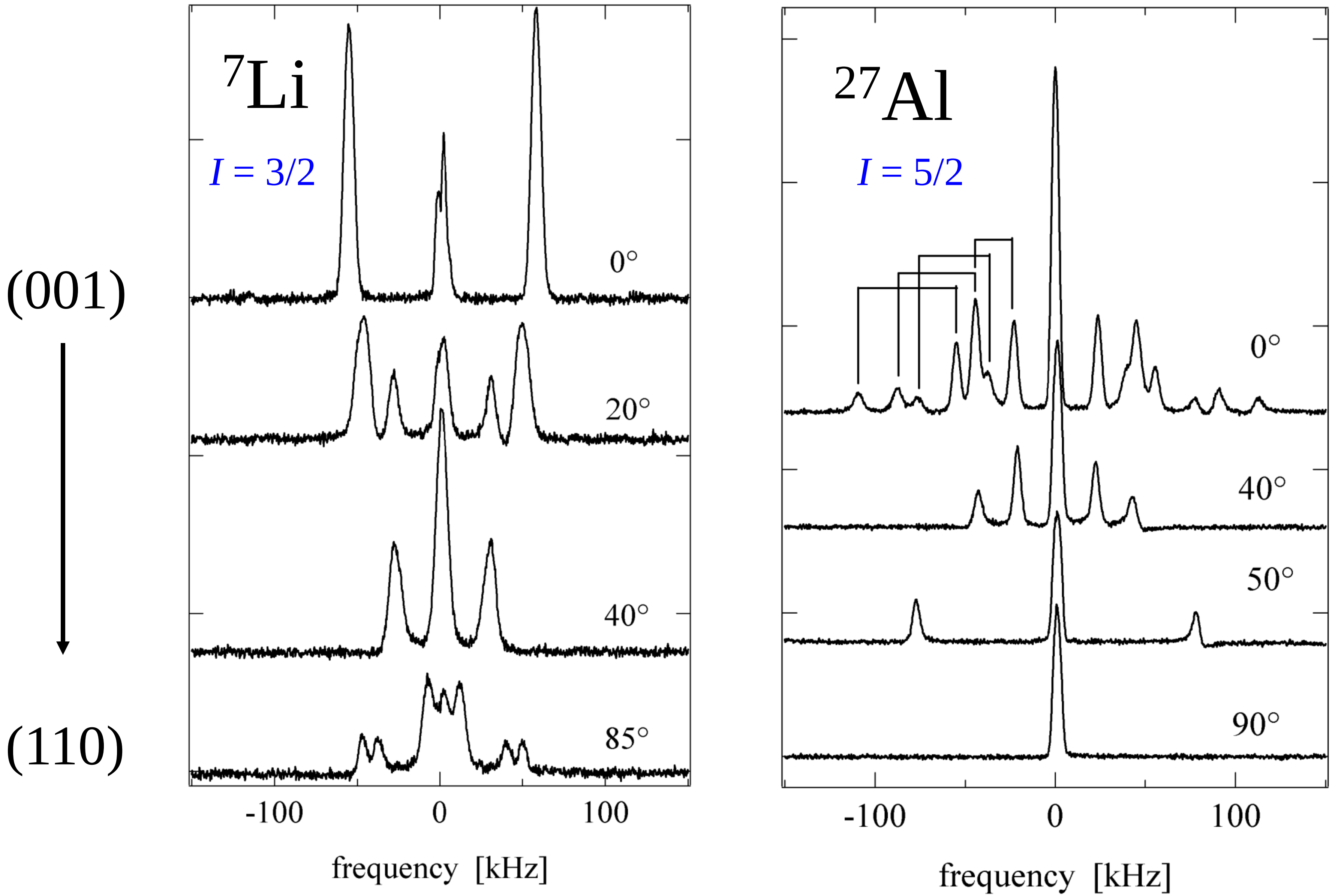
Zeeman Splitting + Quadrupolar Shifts

^{7}Li NMR

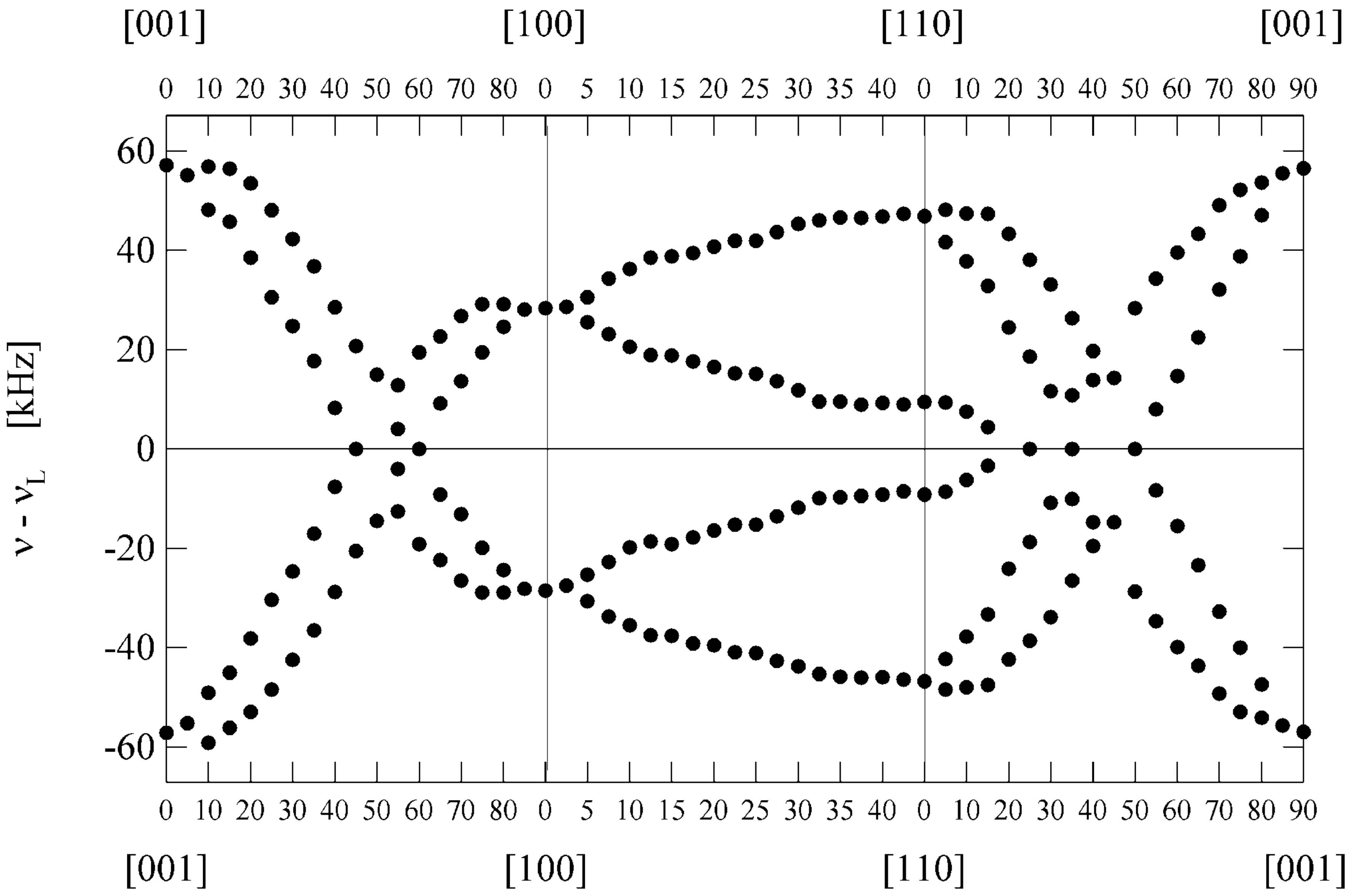


Zeeman splitting quadrupolar shifts

^7Li and ^{27}Al NMR on $LiAlO_2$ Single Crystal



^{7}Li NMR on $LiAlO_2$ Single Crystal



Electric field gradient tensor

$$V_{ij} = d^2\varphi \,/\, dx_i\, dx_j$$

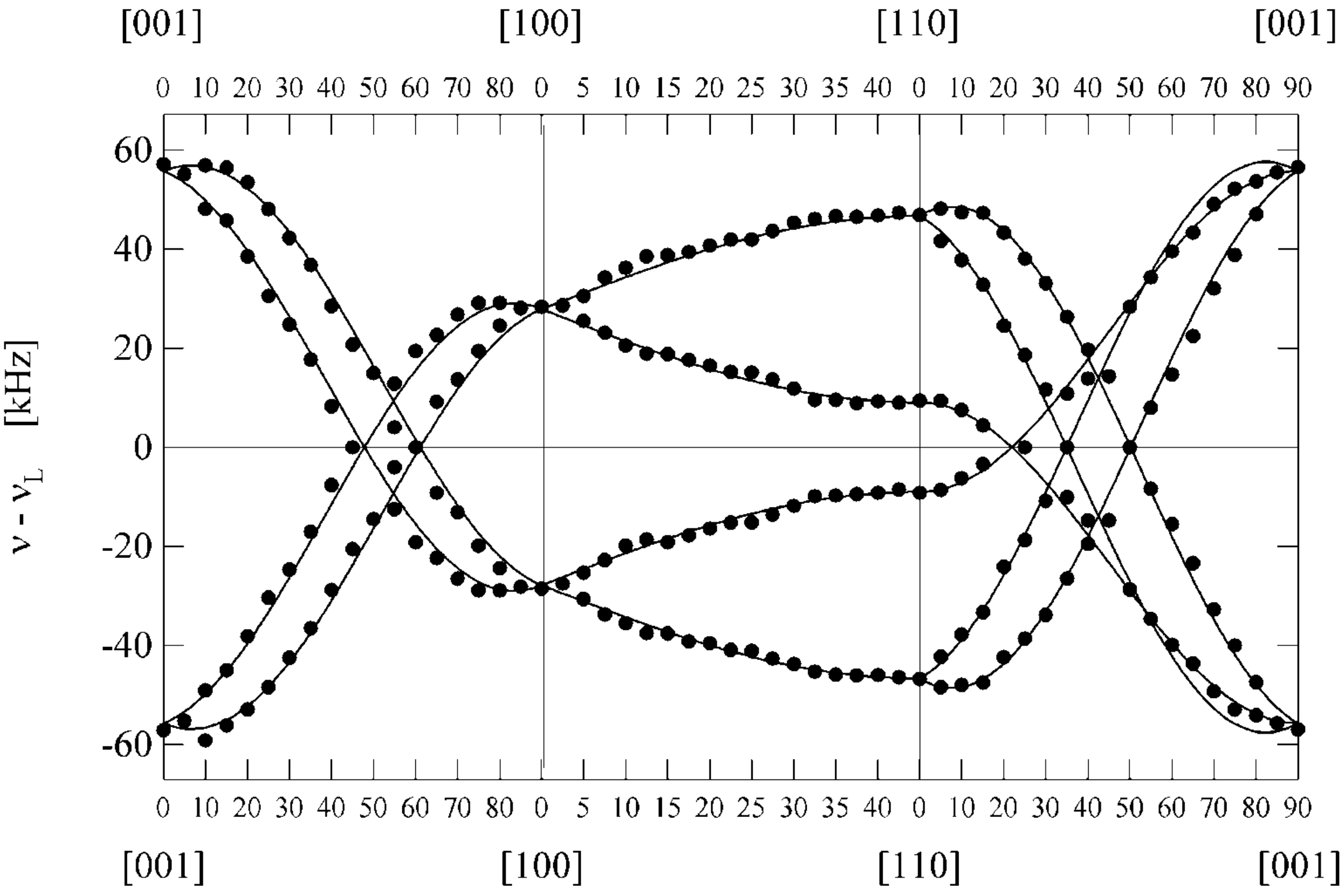
Eigenvalues? Eigenvektors?

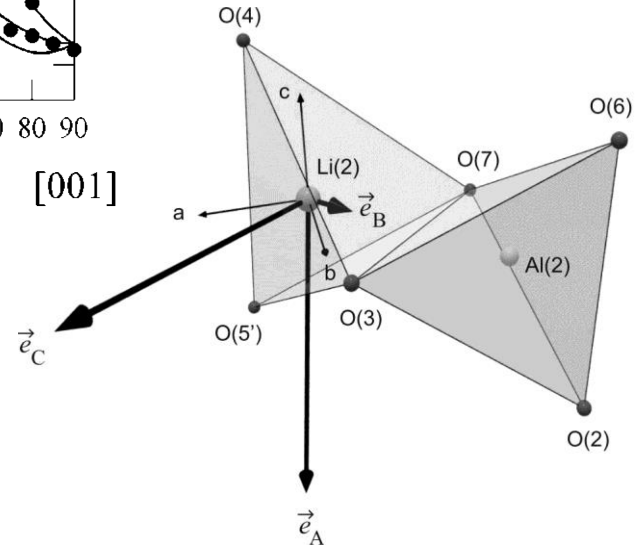
$$\begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}$$

$$V_{ij} = V_{ji} \qquad \Sigma\, V_{ii} = 0$$

$$\begin{pmatrix} A & B & C \\ B & A & -C \\ C & -C & -2A \end{pmatrix}$$

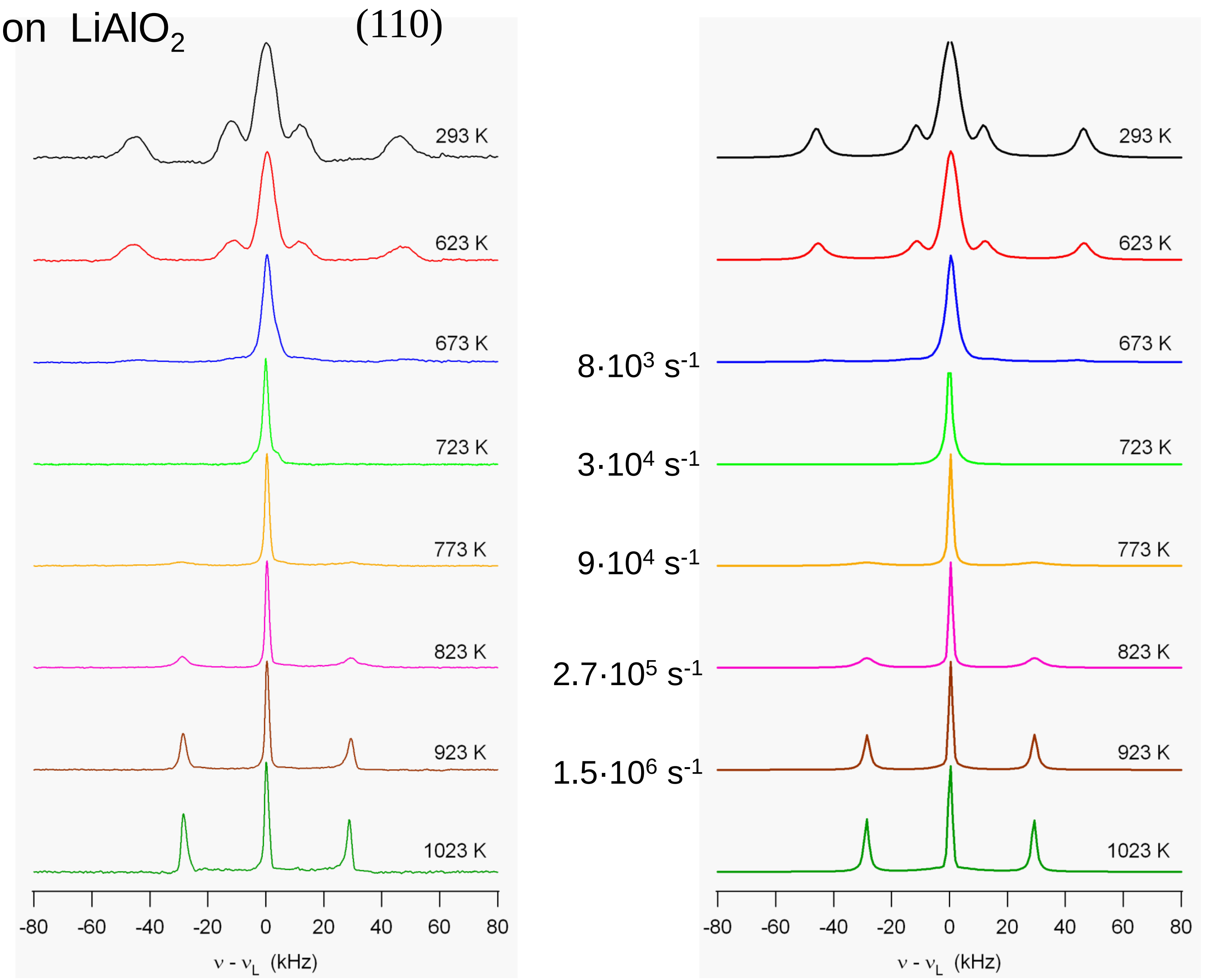
3-parameter fit of EFG tensor





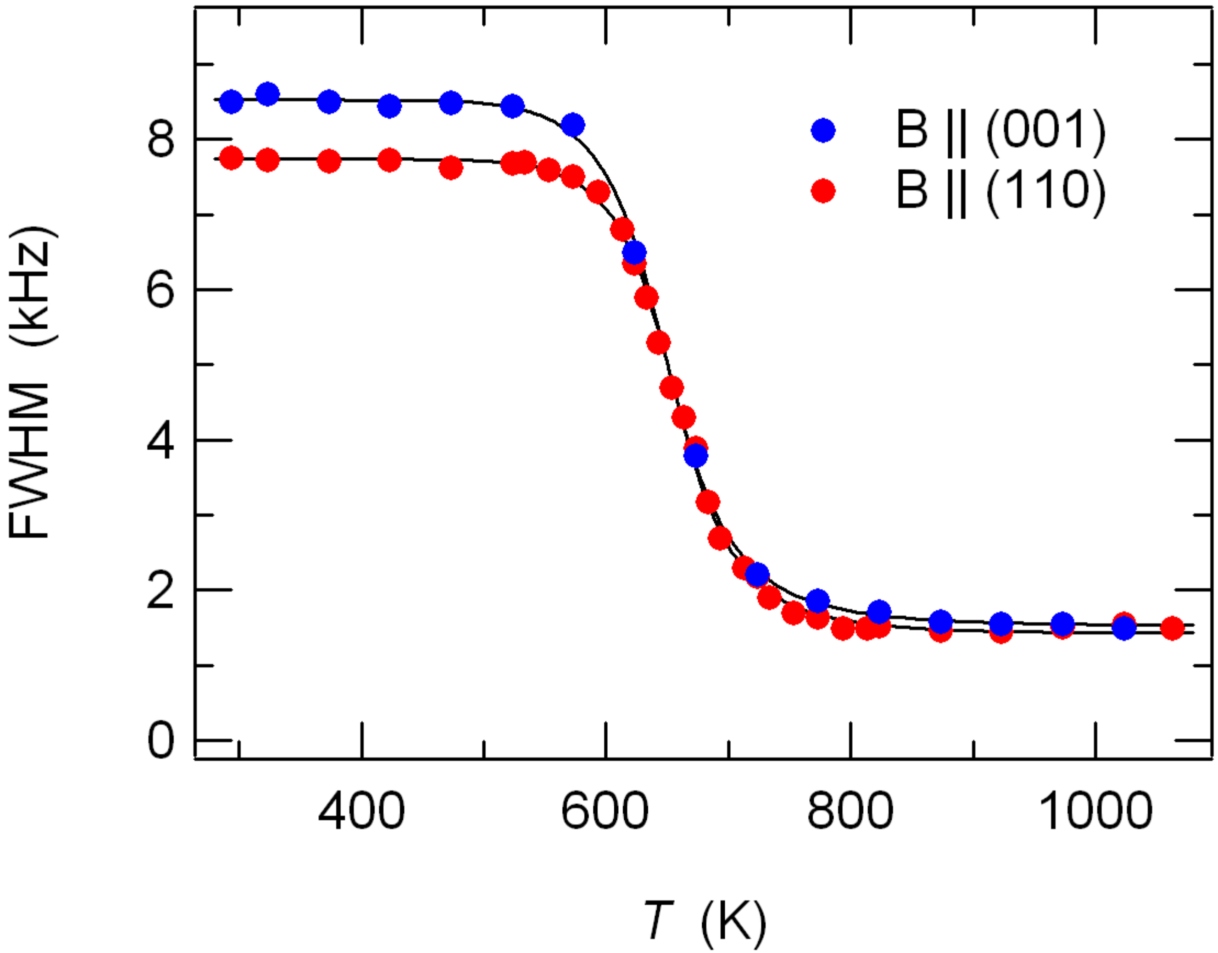
Indris et al., *Phys. Rev. B* **74** (2006), 245120.

^{7}Li NMR on $LiAlO_2$



Indris et al., *J. Phys. Chem. C* **116** (2013), 14243.

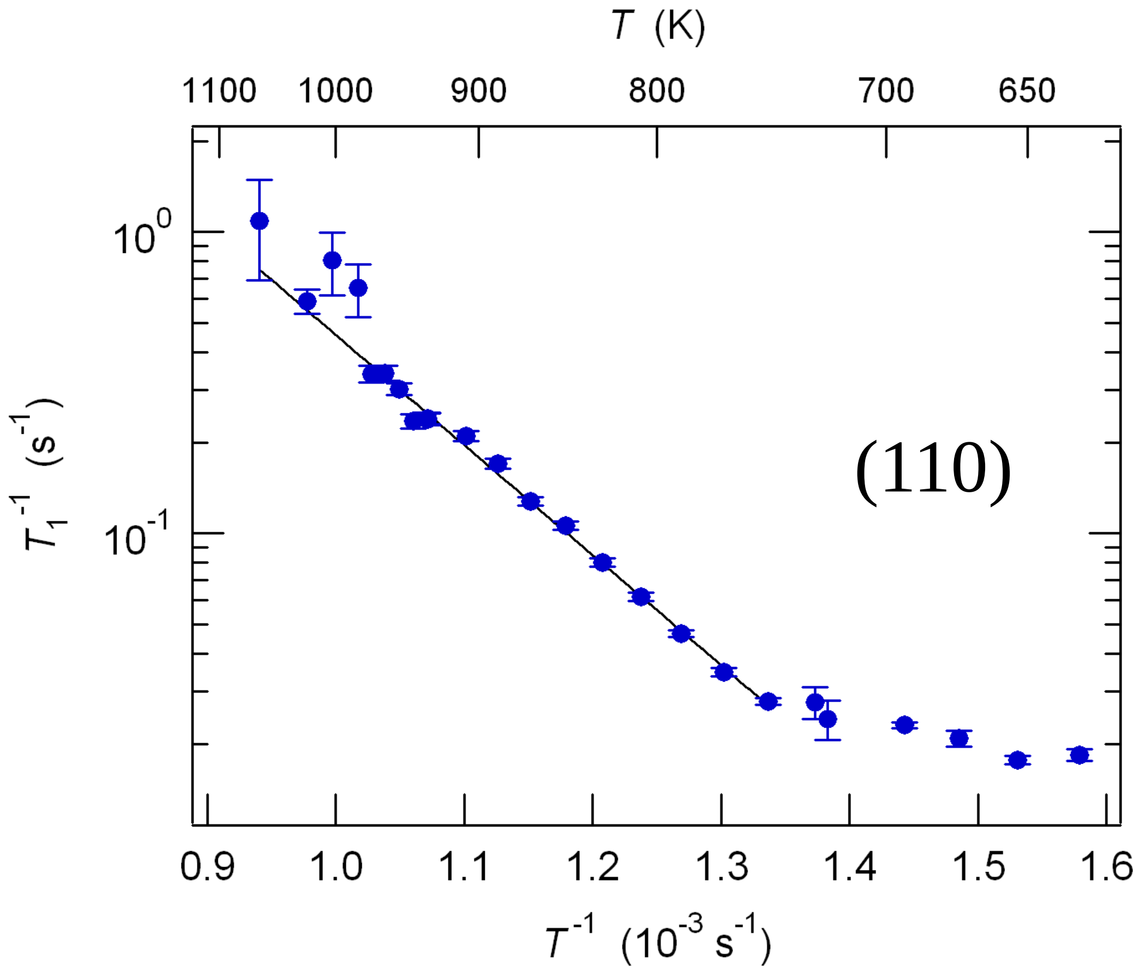
^{7}Li and NMR on $LiAlO_2$: Motional narrowing



Hopping rate of 8 kHz at about 650K, $E_A \approx 1.0$ eV

Indris et al., *J. Phys. Chem. C* **116** (2013), 14243.

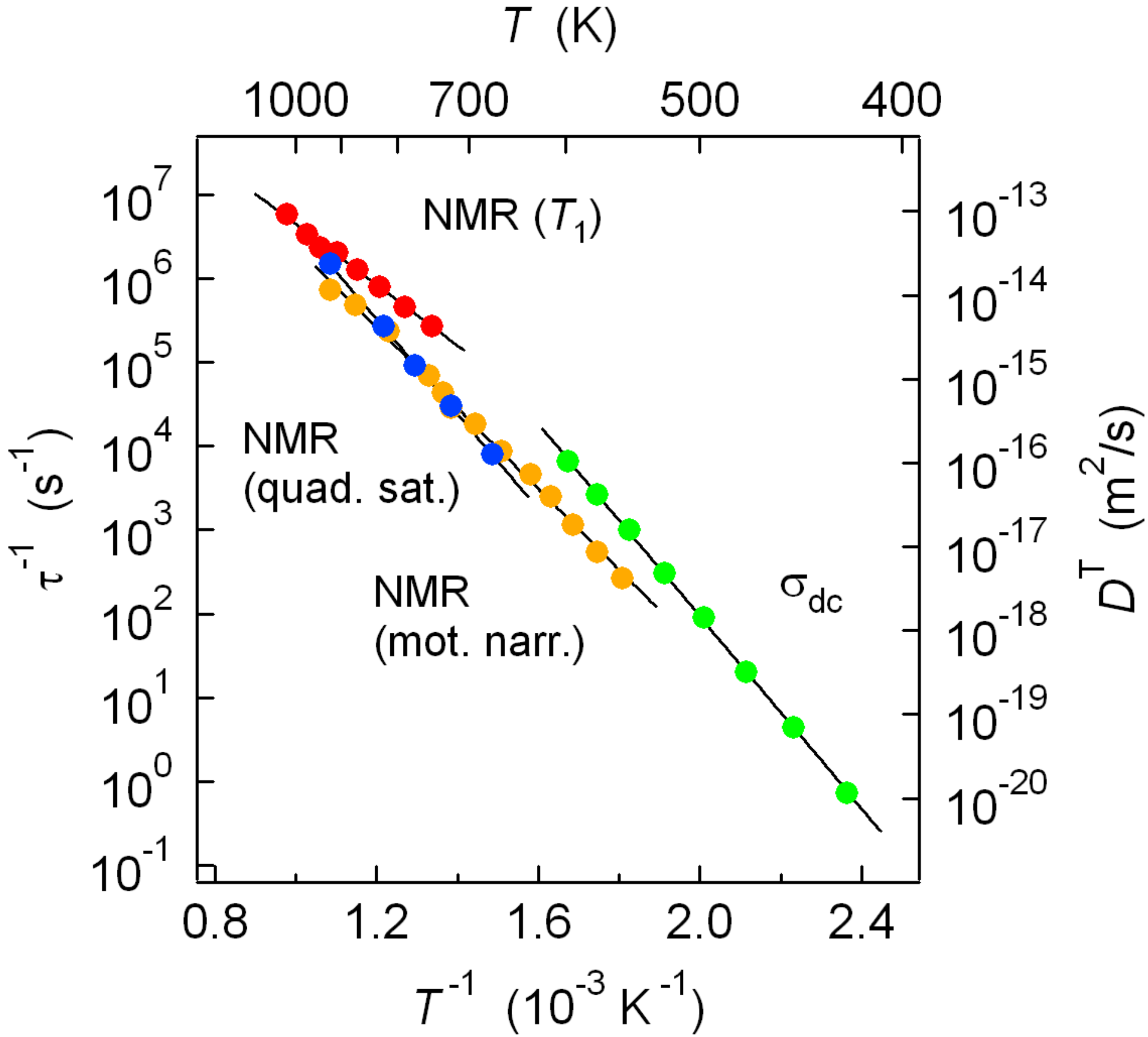
^7Li and NMR on $LiAlO_2$: T_1 relaxation time



$E_A \approx 0.7$ eV (from σ : 1.2 eV $\rightarrow$ correlated motion)

Indris et al., *J. Phys. Chem. C* **116** (2013), 14243.

$LiAlO_2$



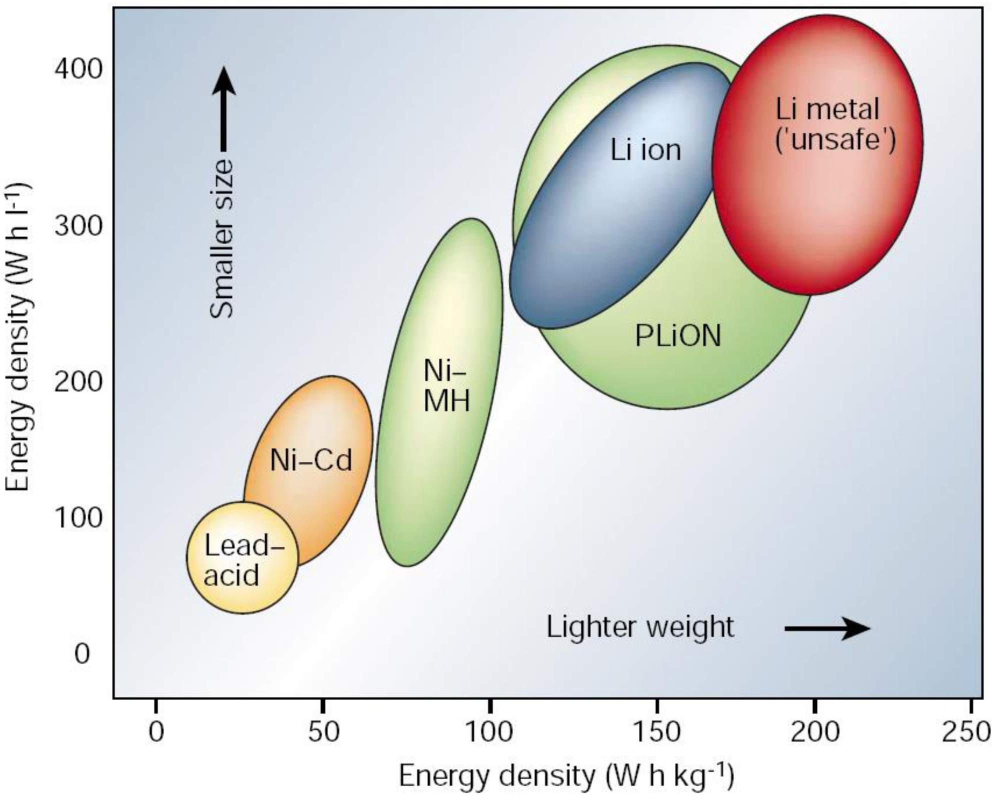
Indris et al., *J. Phys. Chem. C* **116** (2013), 14243.

Conclusion / Outlook:

- different NMR techniques have been applied to study Li diffusion in $LiAlO_2$ over about 7 decades for D, τ^{-1}

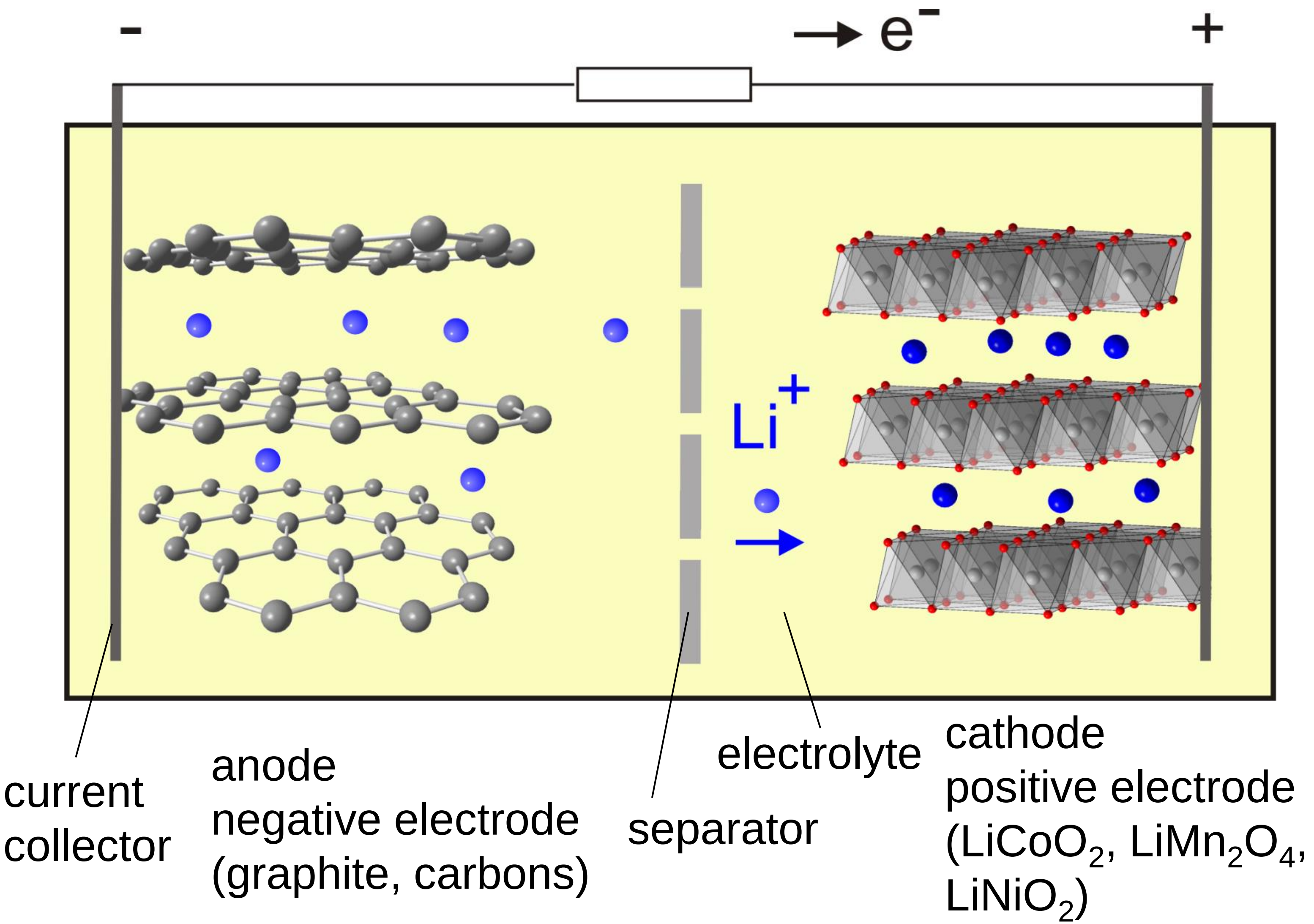
- good agreement with σ_{dc}

Li ion batteries: high energy density → smaller devices



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

Li ion batteries: principle (here: discharging)



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

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

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

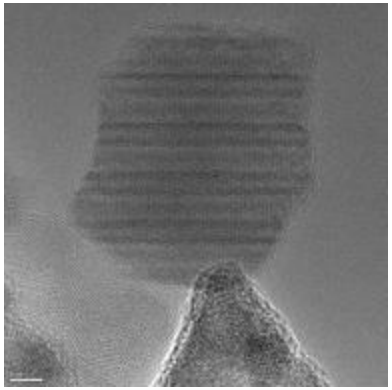
$\Delta_R G^{\ominus} = -U_0 \cdot n \cdot F$

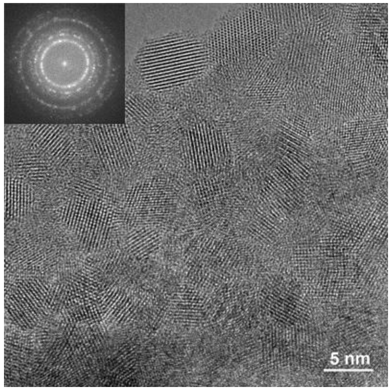
Overview: Electrode materials

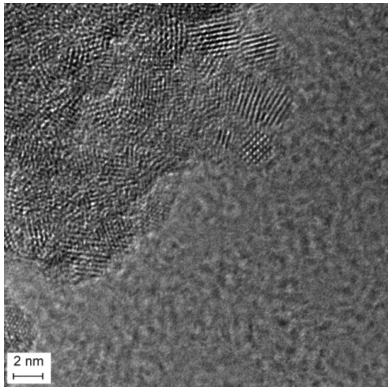
- anodes
  - $Li_4Ti_5O_{12}$
  - TiO_2
  - SnO_2, $(Ti/Sn)O_2$, $(Al/Sn)O_2$, $(Mg/Al/Sn)O_2$ …
  - ZnO
  - $MnFe_2O_4$, $MgFe_2O_4$, …
  - $Y_2Ti_2O_5S_2$, …

- cathodes

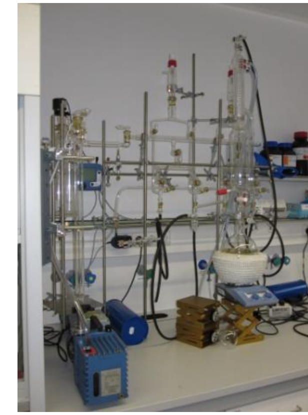
$Li(Co/Ni/Mn/Al)O_2$	0.5 Li per TM	140 mAh/g
$Li(Ni/Mn)_2O_4$	0.5 Li per TM	150 mAh/g
$Li(Fe/Mn/Co)PO_4$	1 Li per TM	170 mAh/g
$Li_2(Fe/Mn)SiO_4$	2 Li per TM ?	330 mAh/g ?
$Li_2(Fe/Mn)TiO_4$, …	2 Li per TM ?	290 mAh/g ?







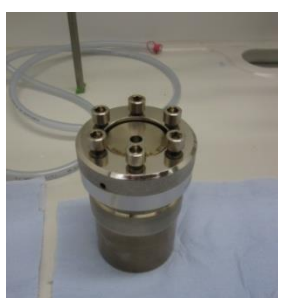
Synthesis

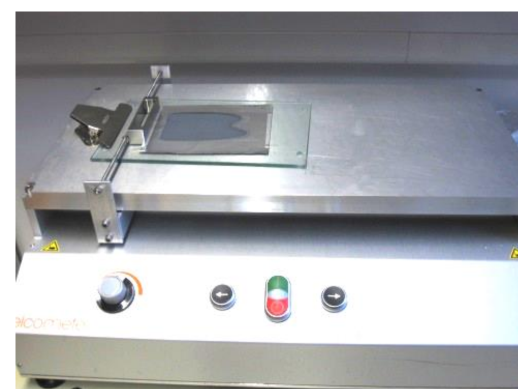


Synthesis of Nanoparticles, Nanostructures and Nanocomposites:

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

→ electrode film preparation





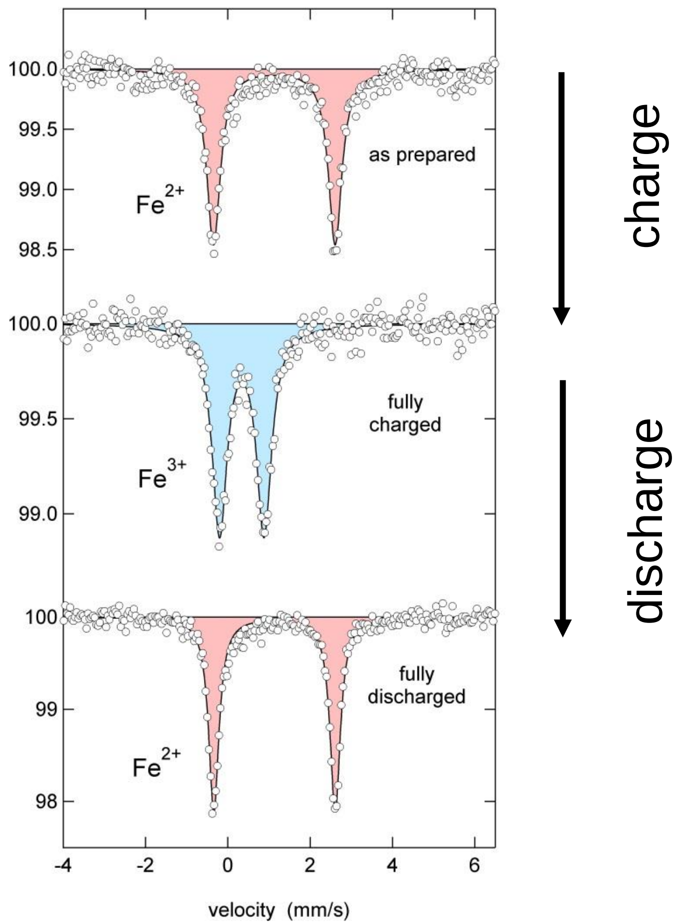
Overview: Experimental Methods

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

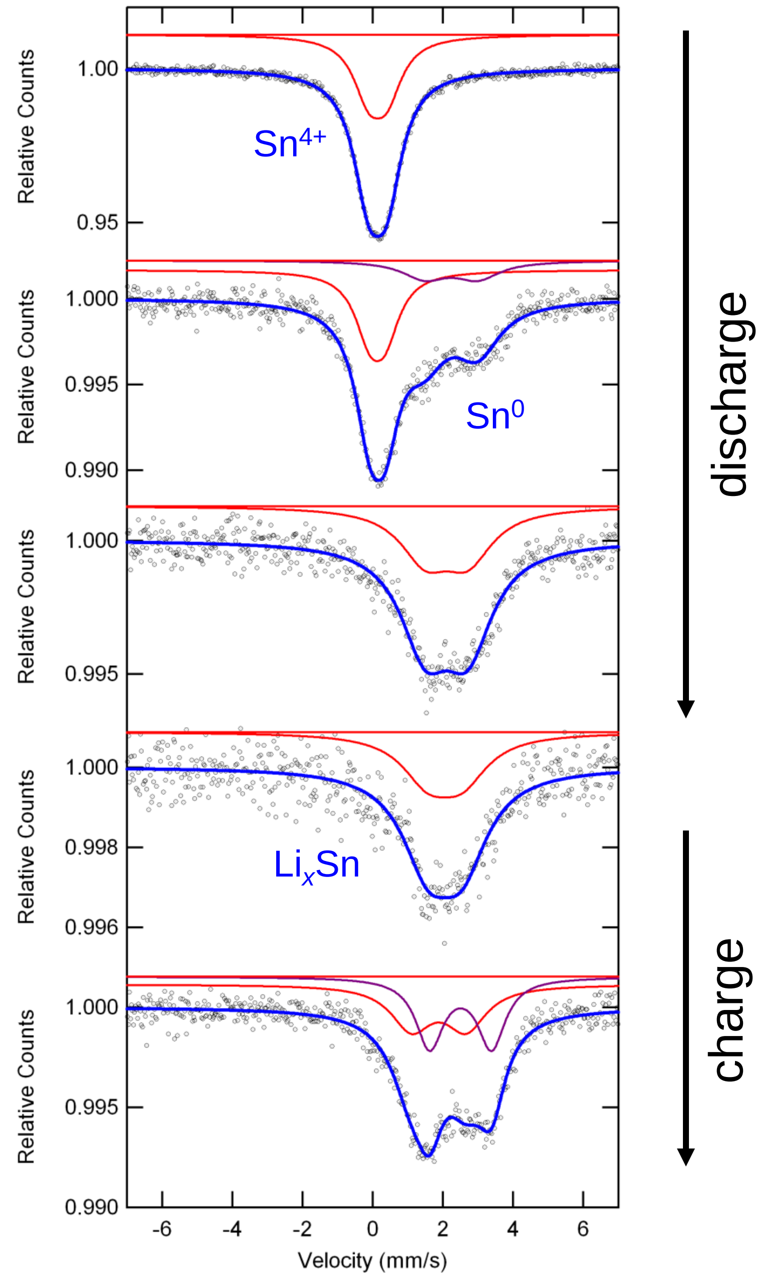
Mössbauer spectroscopy

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

$LiFe_{0.4}Mn_{0.6}PO_4$



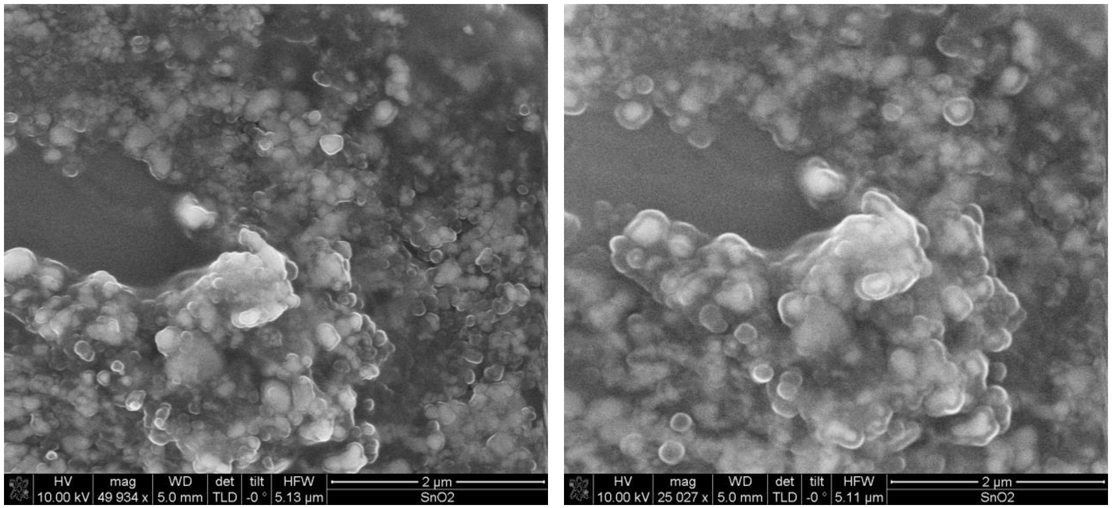
Zn_2SnO_4



In situ SEM

(together with R. Mönig, KIT-IAM)

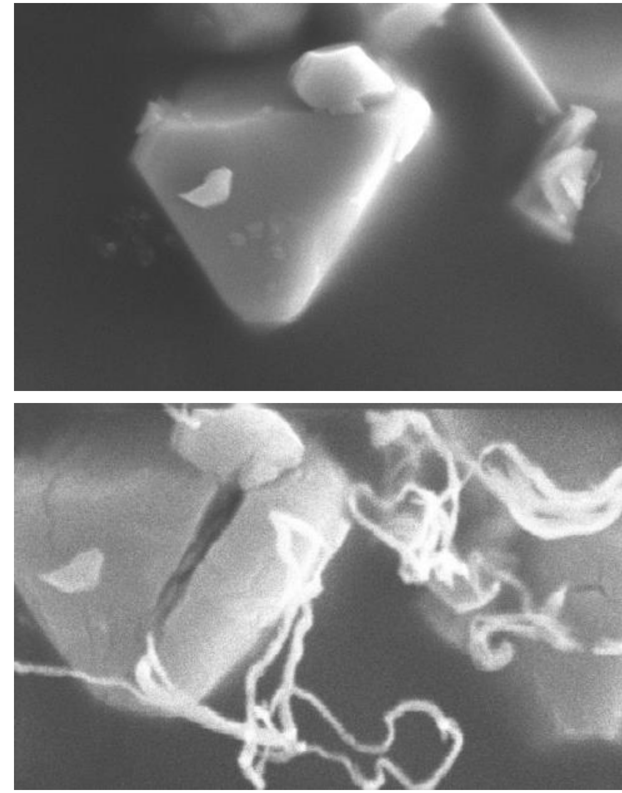
SnO_2



- 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.

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

$CuCr_2Se_4$



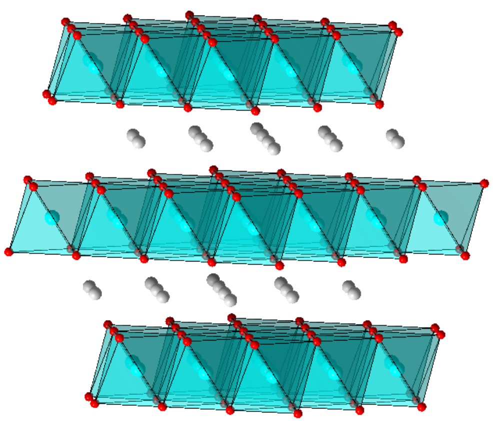
- Particles grow and break apart
- formation of Cu metal whiskers

$\rightarrow$ Cu-Li exchange mechanism

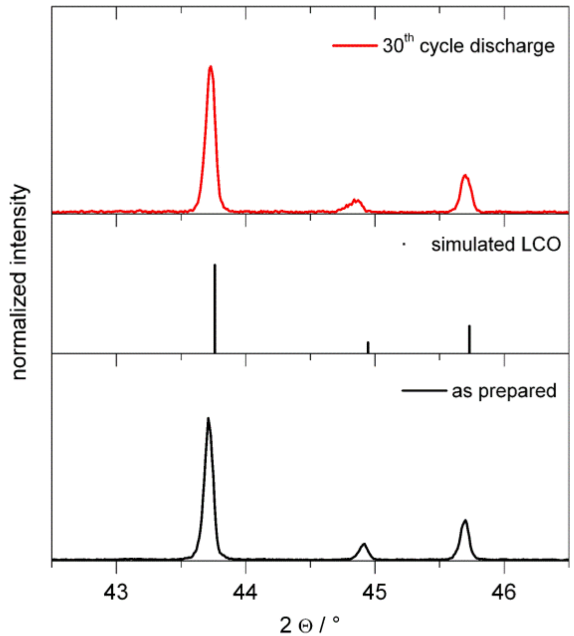
W. Bensch et al., *Phys. Chem. Chem. Phys.* **14**, 7509 (2012).

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

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

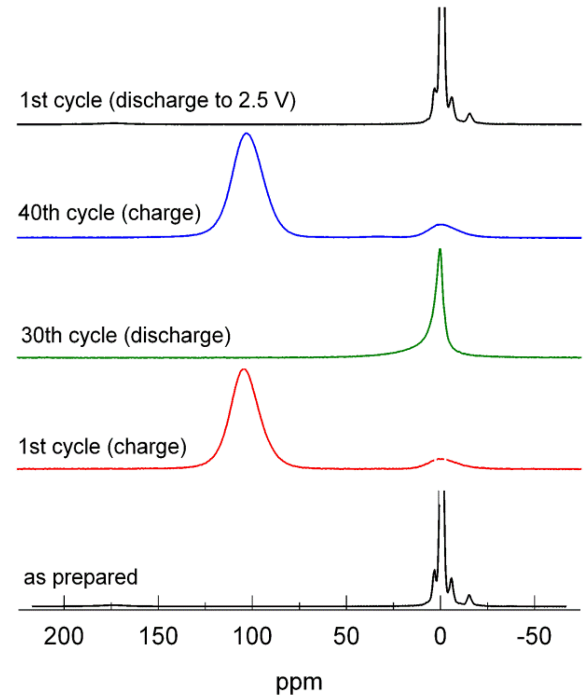


XRD



long-range structure

^{7}Li MAS NMR



local structure

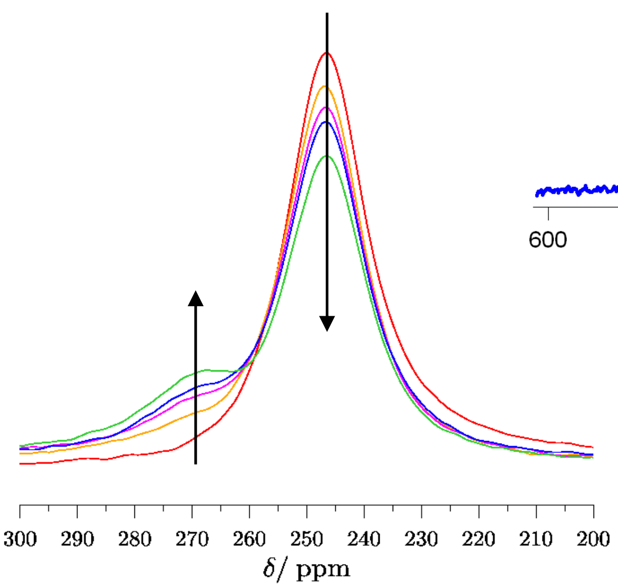
$Co^{(3+)}$: $3d^6$

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

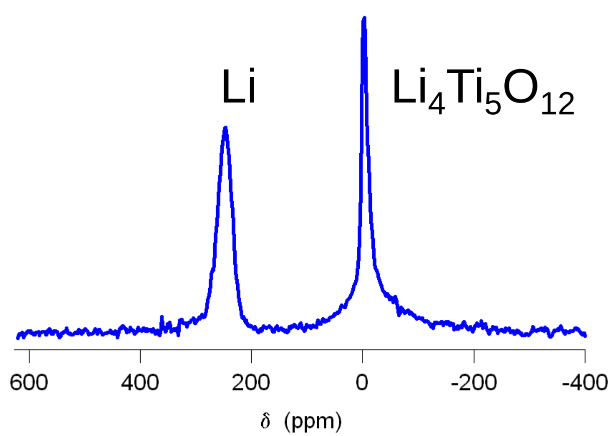
N. Schweikert et al., *Solid State Ionics* **226** (2012), 15.

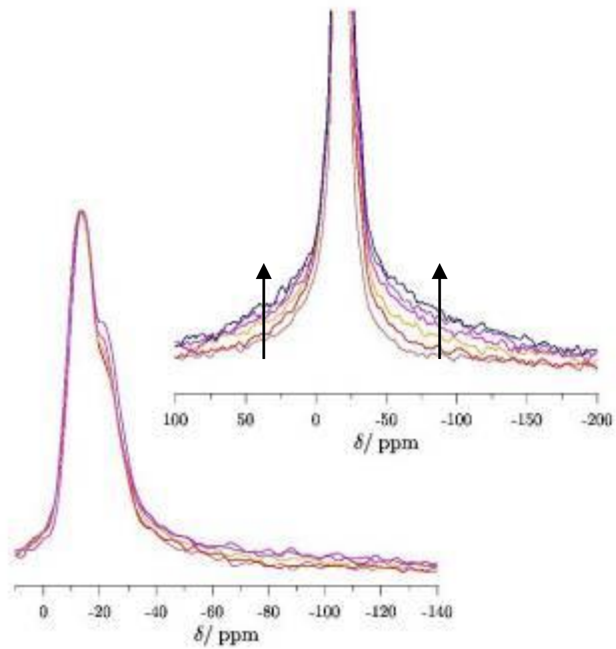
In situ NMR Spectroscopy

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



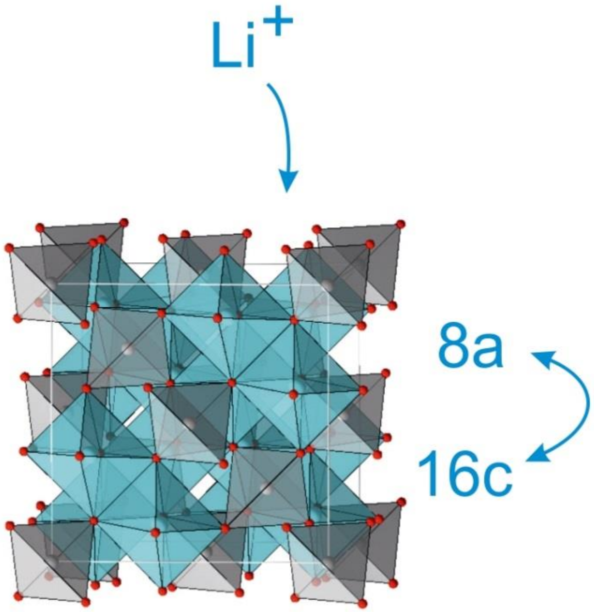
^{7}Li NMR spectrum of complete Li battery

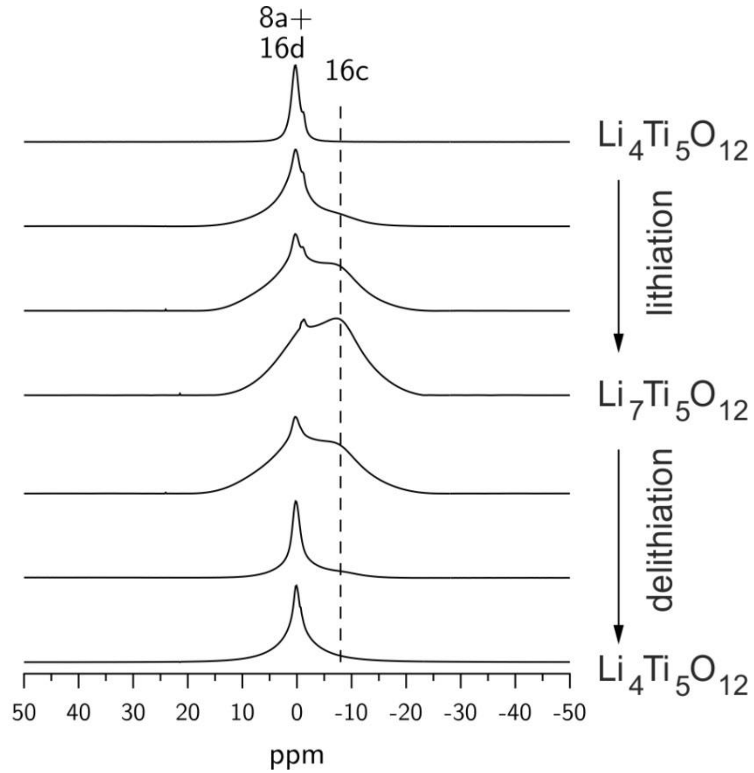




N. Schweikert et al., *J. Power Sources* **228** (2013), 237.

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





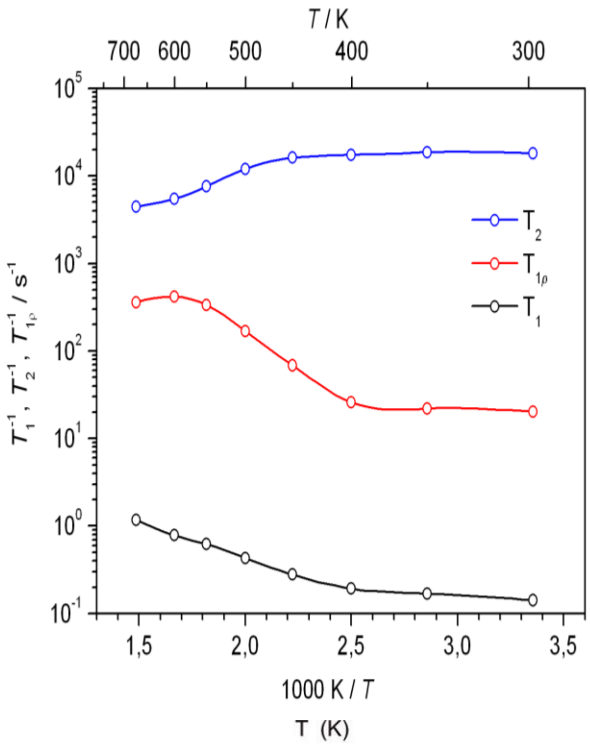
Rearrangement of Li ions:

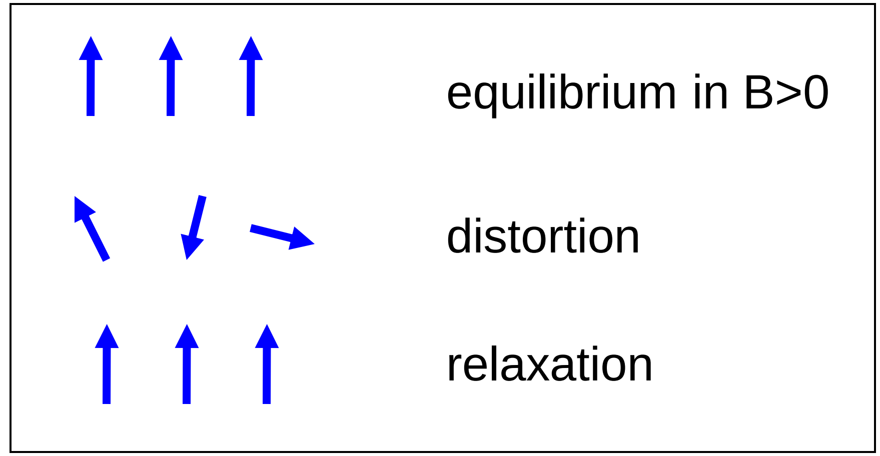
$Li^+ \rightarrow$ Li(16c)

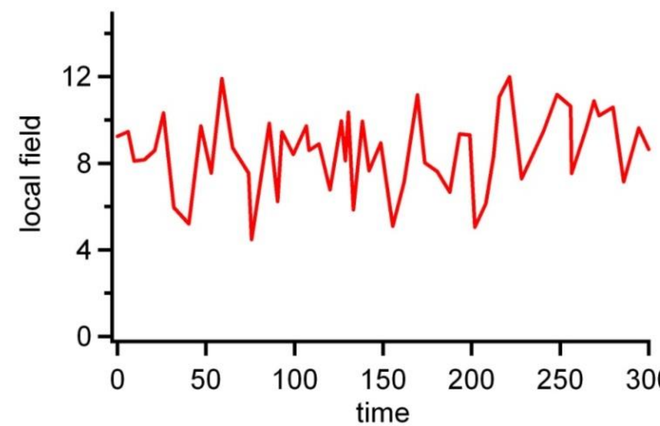
Li(8a) $\rightarrow$ Li(16c)

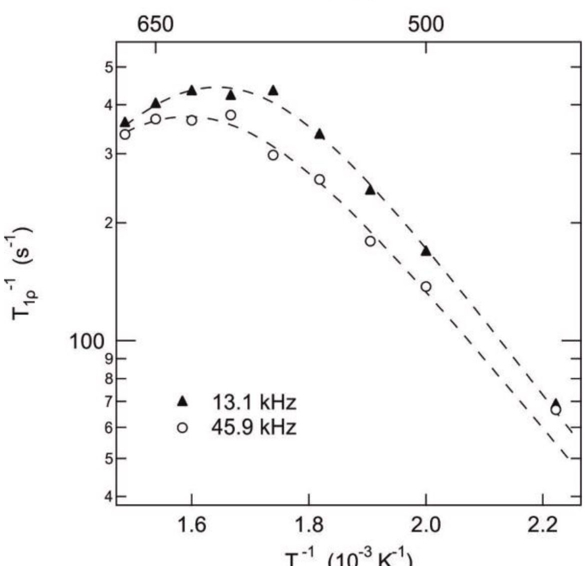
H. Hain et al., *Solid-State Nucl. Magn. Reson.* **42** (2012), 9.

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





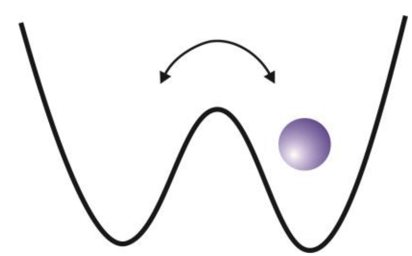




maximum:
$\omega_L \approx \tau^{-1}$

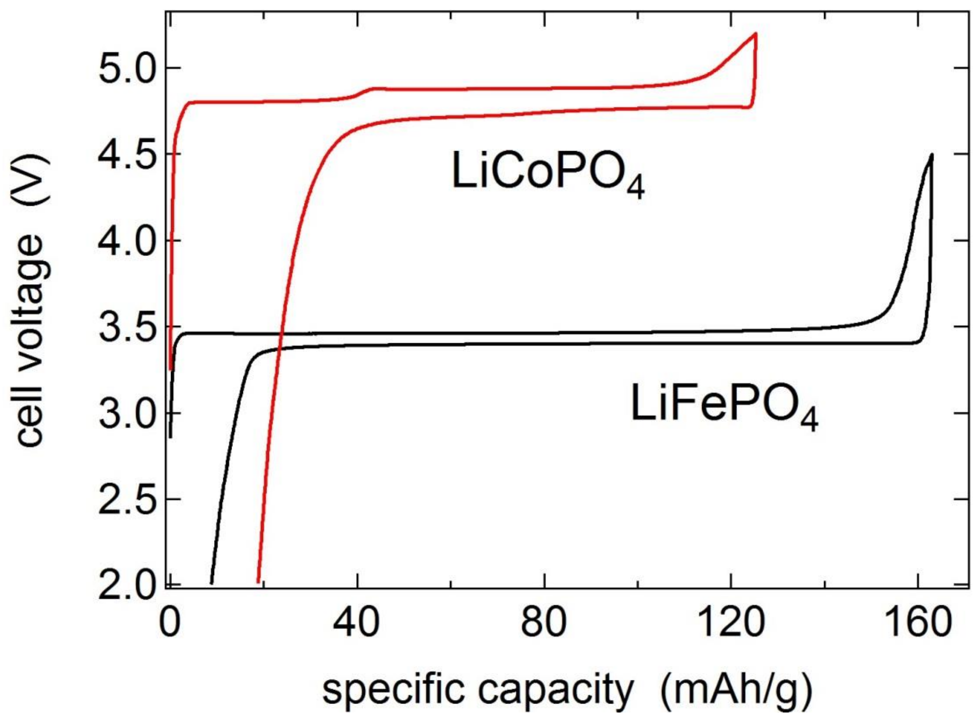
spin dynamics → Li ion dynamics

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

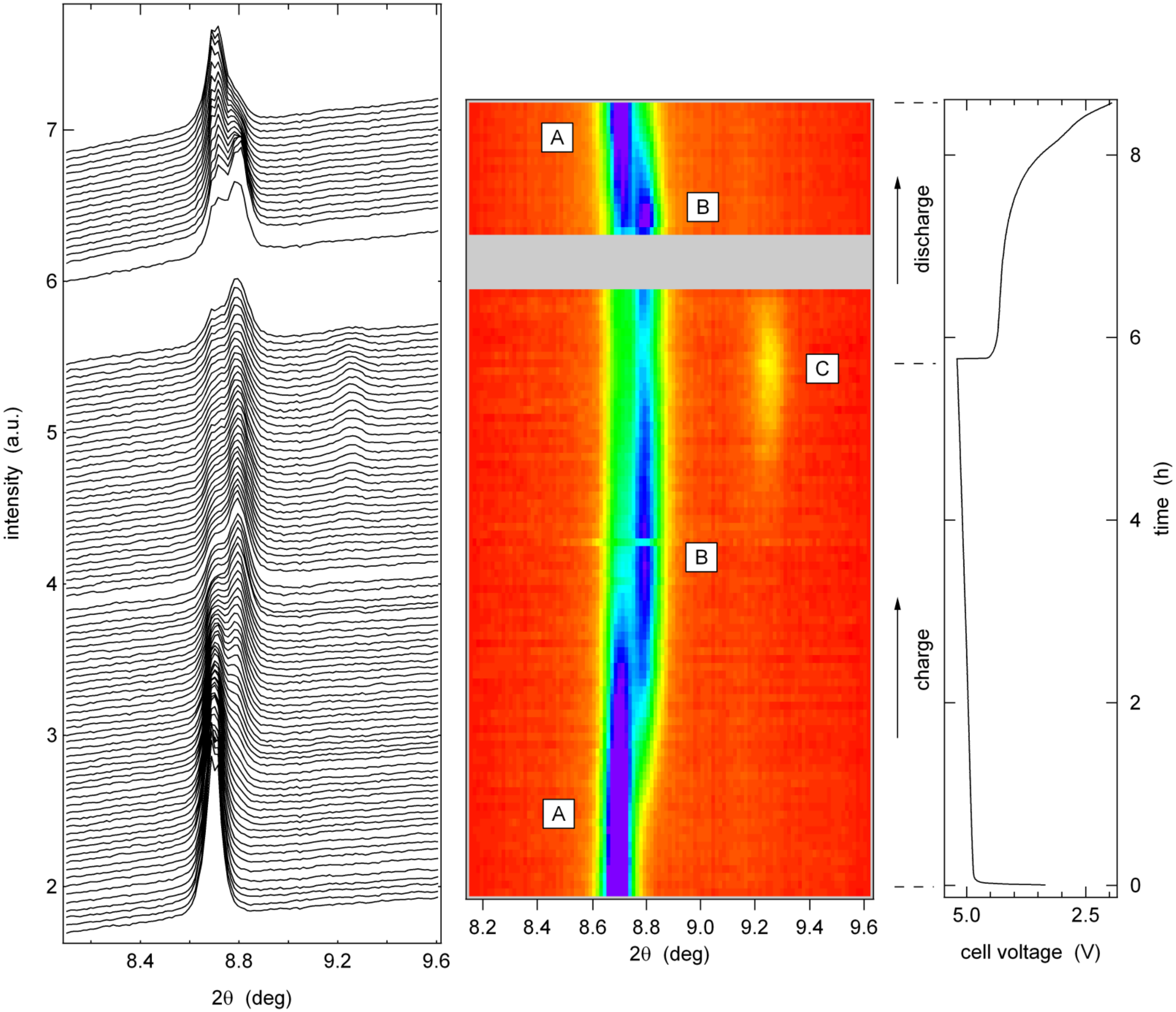


H. Hain et al., *Solid-State Nucl. Magn.* Reson. **42** (2012), 9.

$LiFePO_4 \leftrightarrow LiCoPO_4$:



LiCoPO$_4$: *in situ* XRD



LiCoPO$_4$

Li$_{0.7}$CoPO$_4$

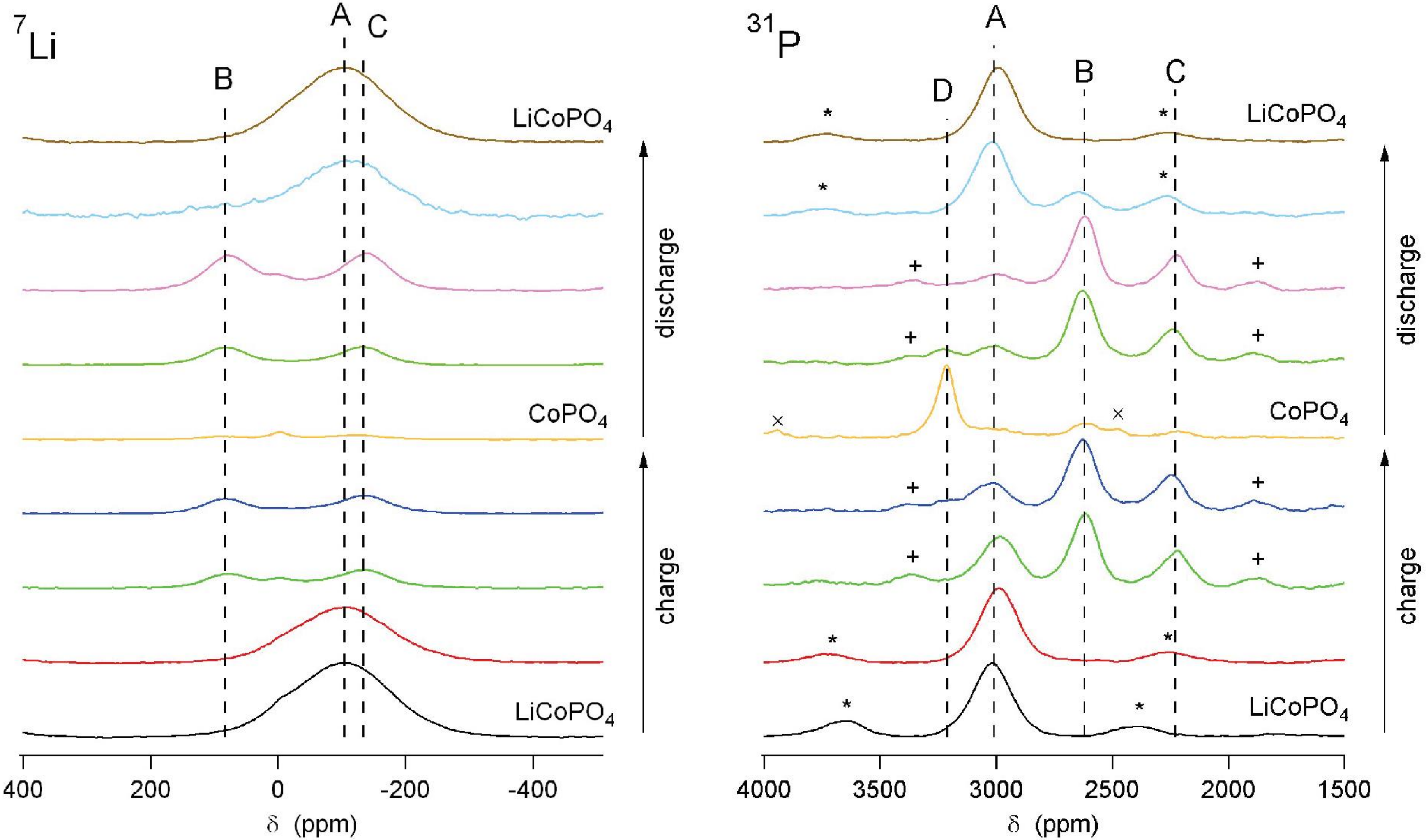
CoPO$_4$

Li$_{0.7}$CoPO$_4$

LiCoPO$_4$

2-step mechanism + intermediate phase (≠ Fe)

$LiCoPO_4$:



2 step reaction

intermediate phase: $Li_{0.7}CoPO_4$

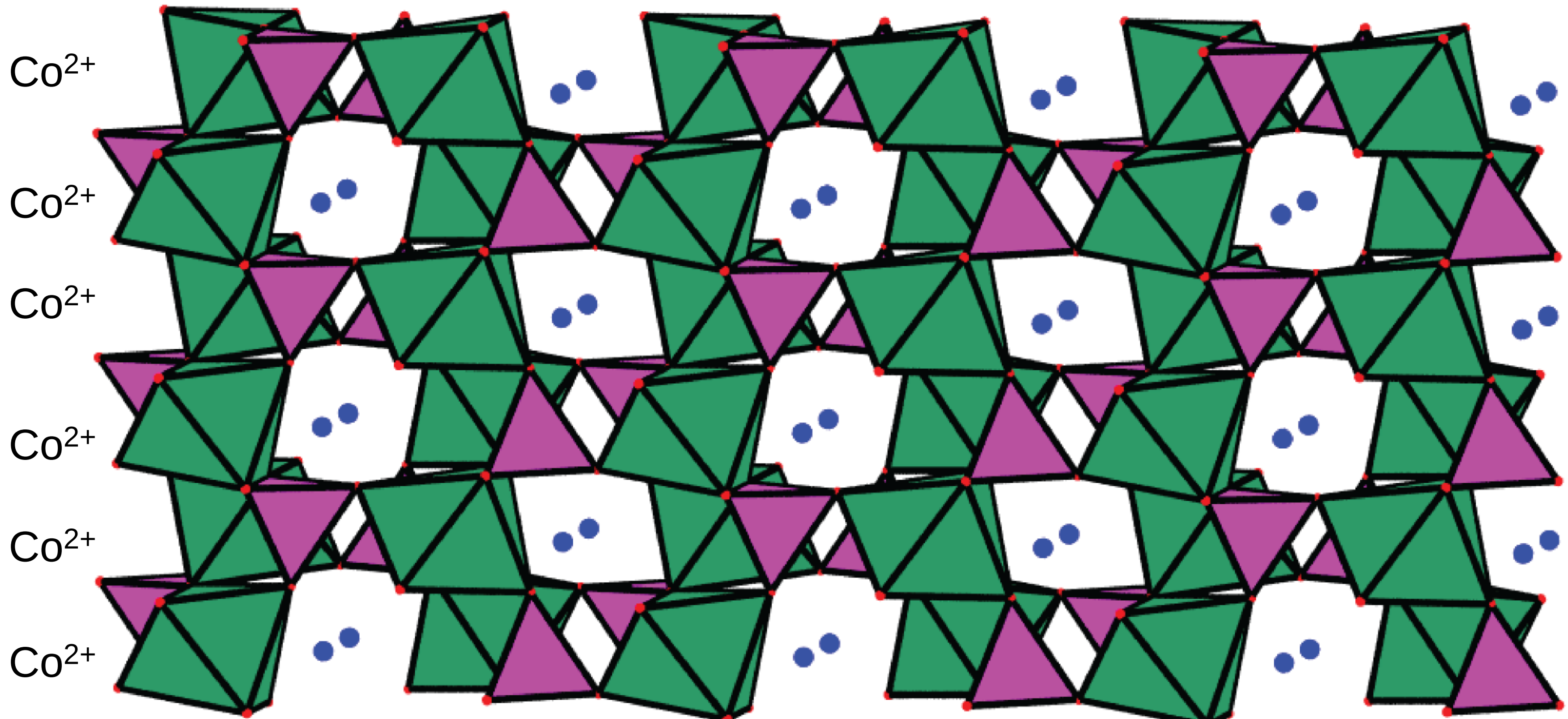
2/3 3/4

2 Li environments (1:1)

2 P environments (2:1)

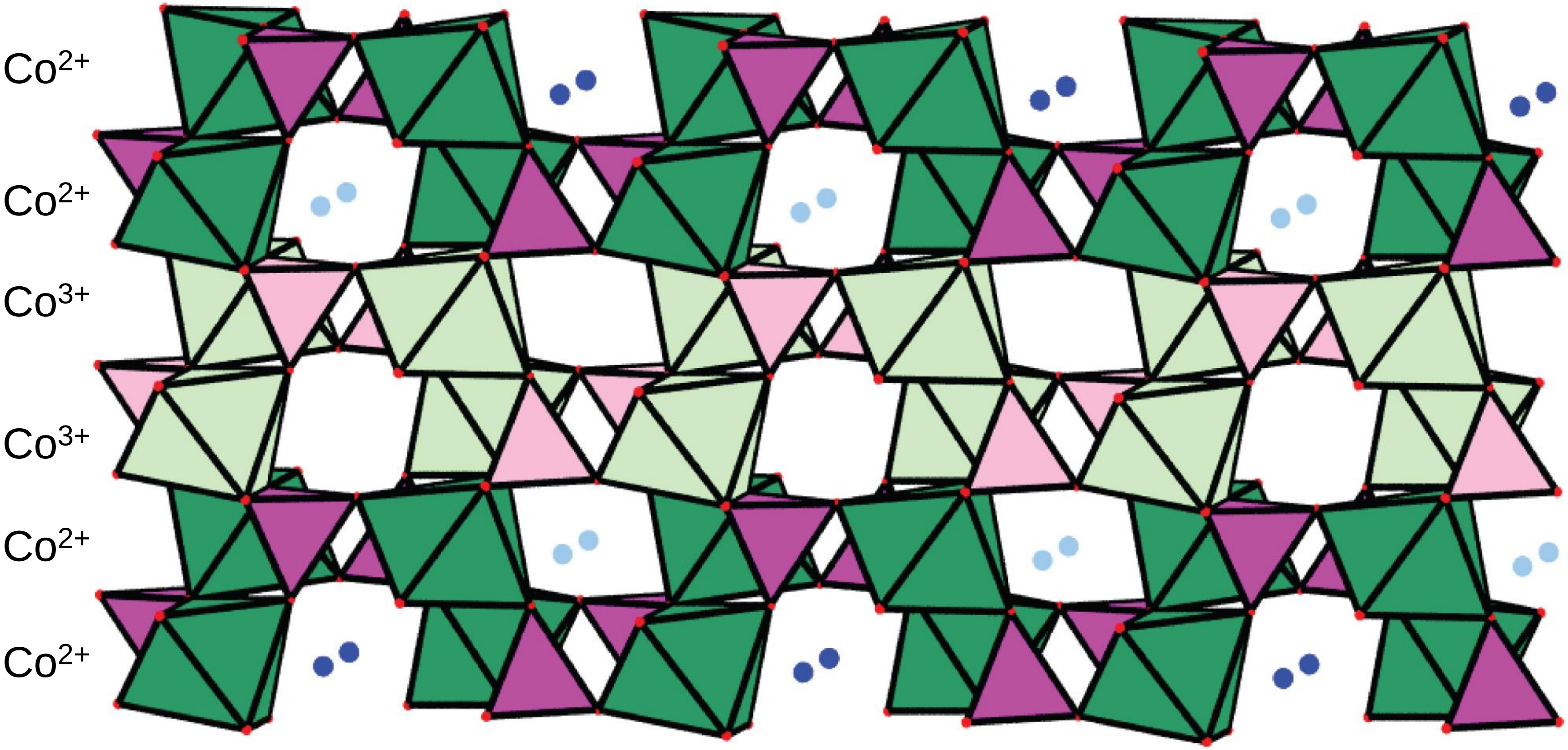
$LiCoPO_4$

view along c axis



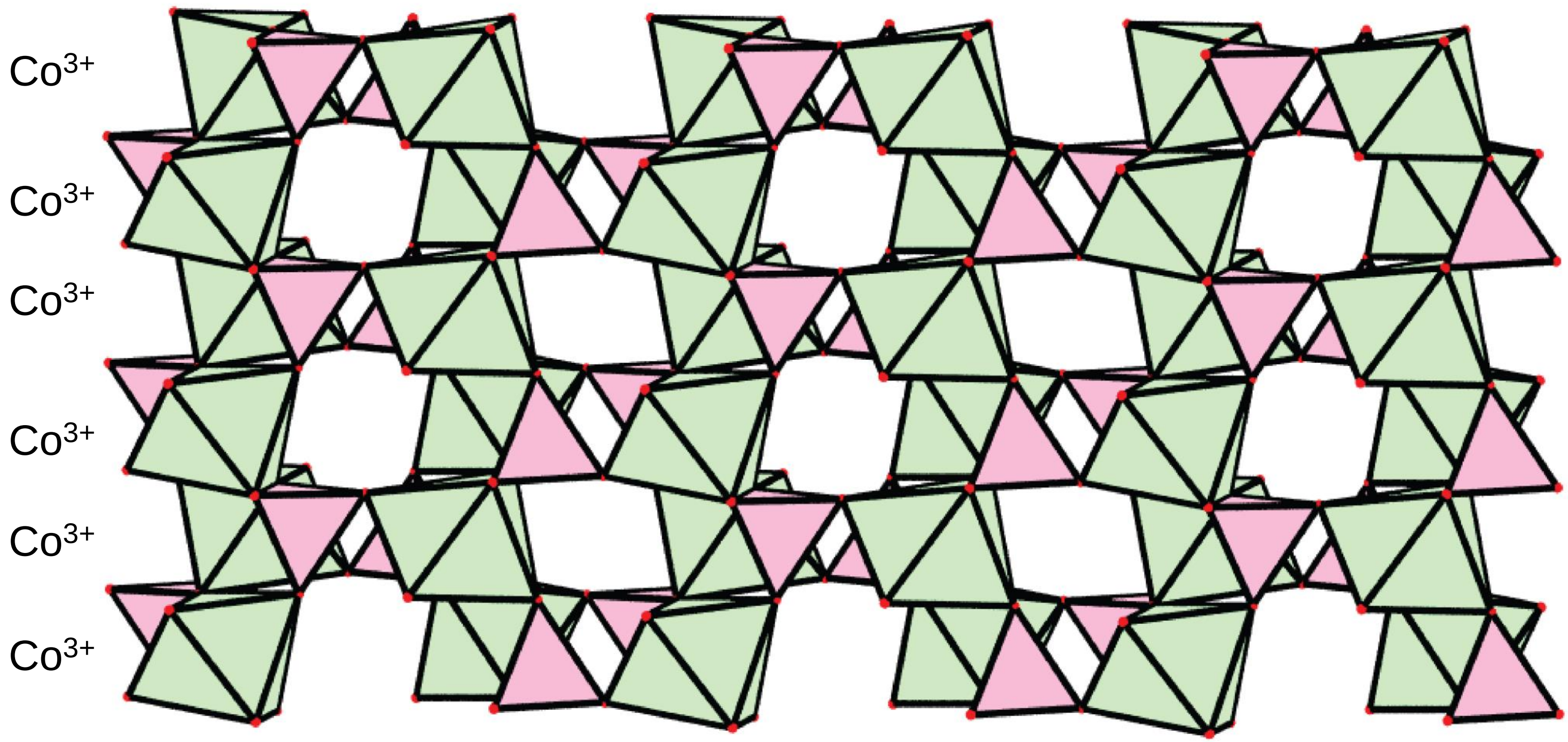
$Li_{2/3}CoPO_4$

view along c axis

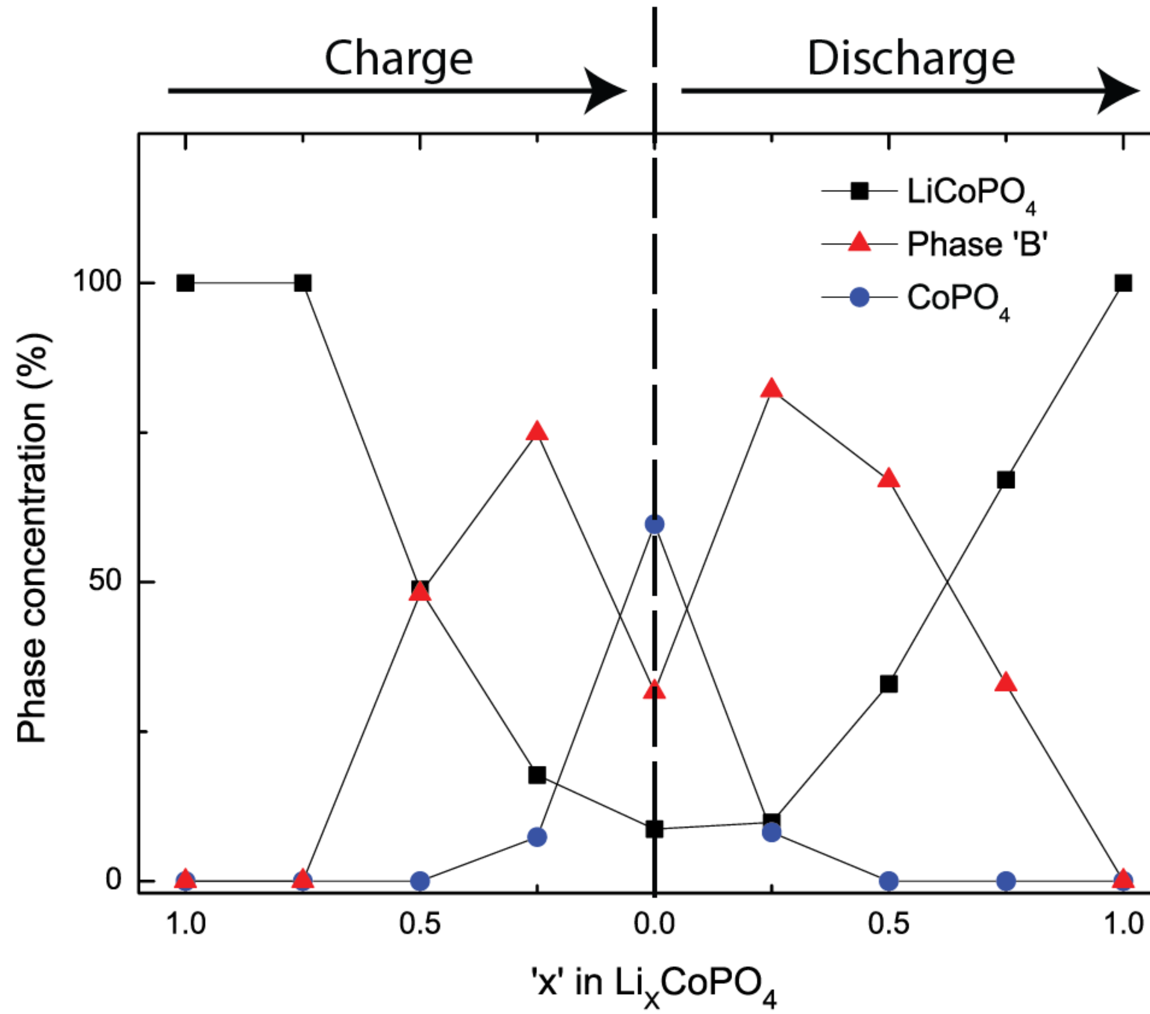


$CoPO_4$

view along c axis

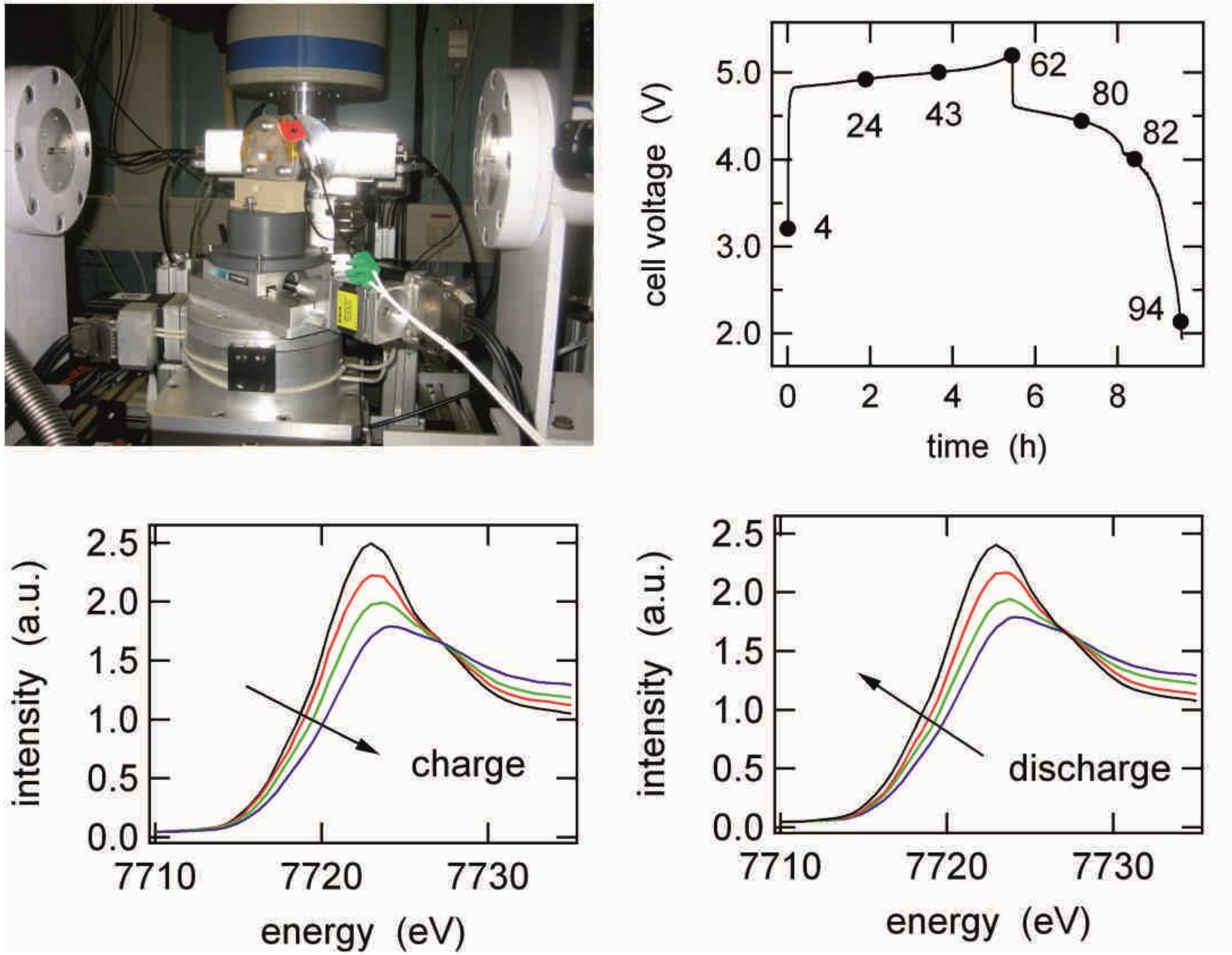


$LiCoPO_4$:



Charge
Discharge
LiCoPO4
Phase 'B'
CoPO4
100
50
0
Phase concentration (%)
1.0
0.5
0.0
0.5
1.0
'x' in LixCoPO4

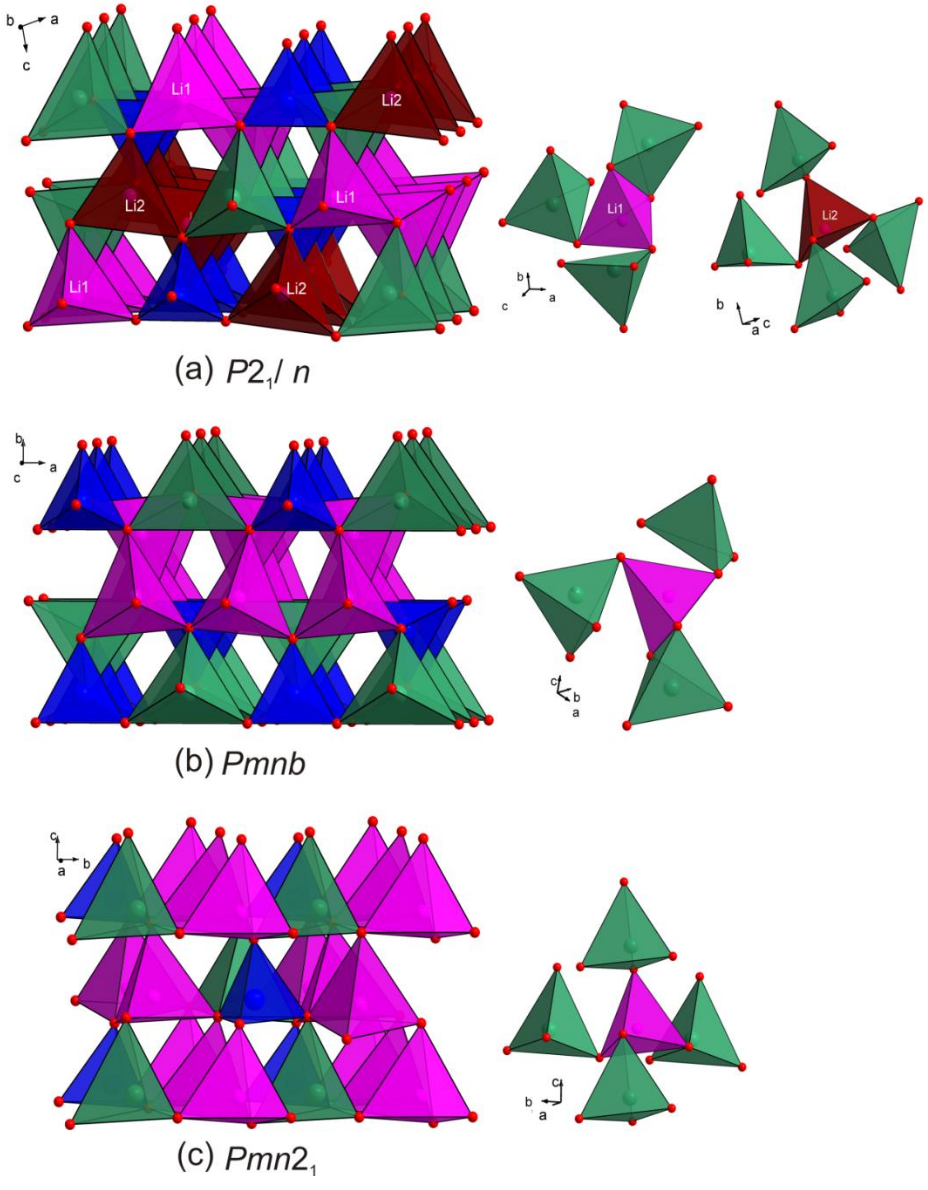
$LiCoPO_4$: *in situ* XAS on Co K edge



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

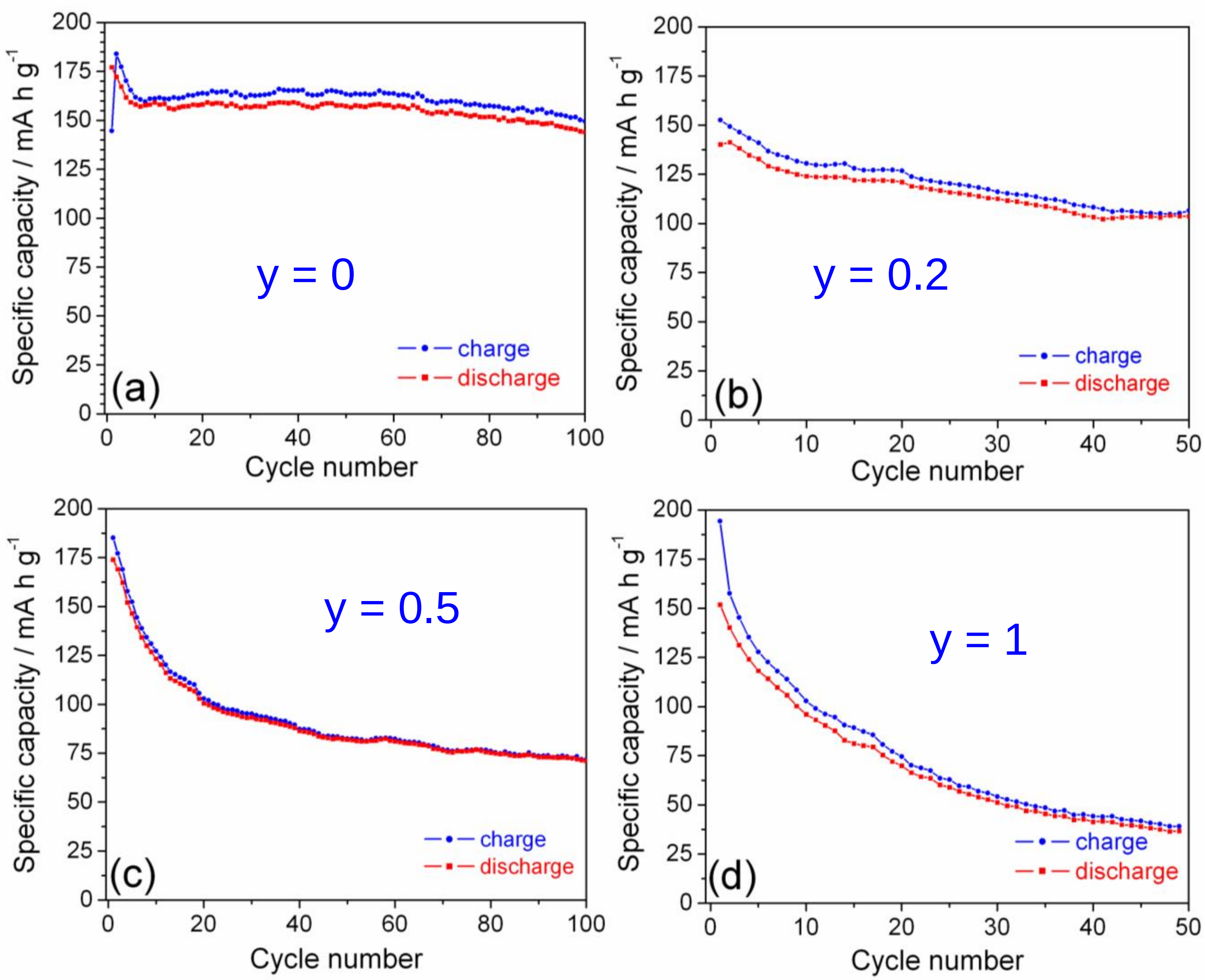
$Li_2Fe_{1-y}Mn_ySiO_4$ / C

- 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.

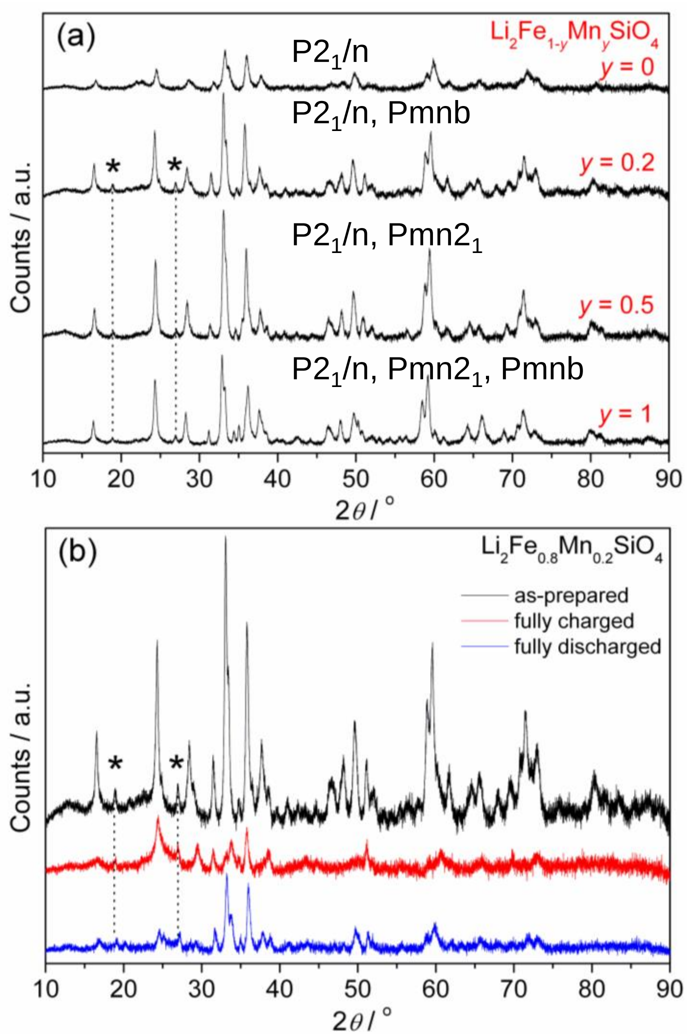
$Li_2Fe_{1-y}Mn_ySiO_4$ / C



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

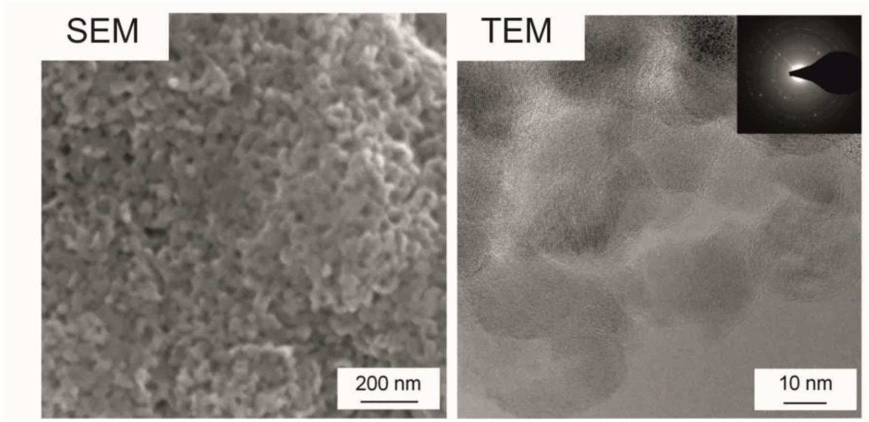
$Li_2Fe_{1-y}Mn_ySiO_4$ / C

XRD



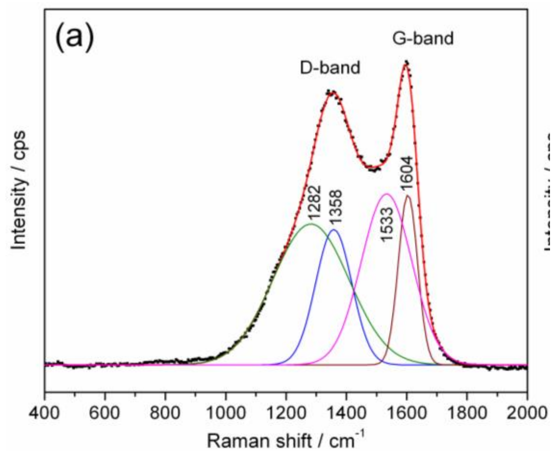
y = 0.2

y = 0.2



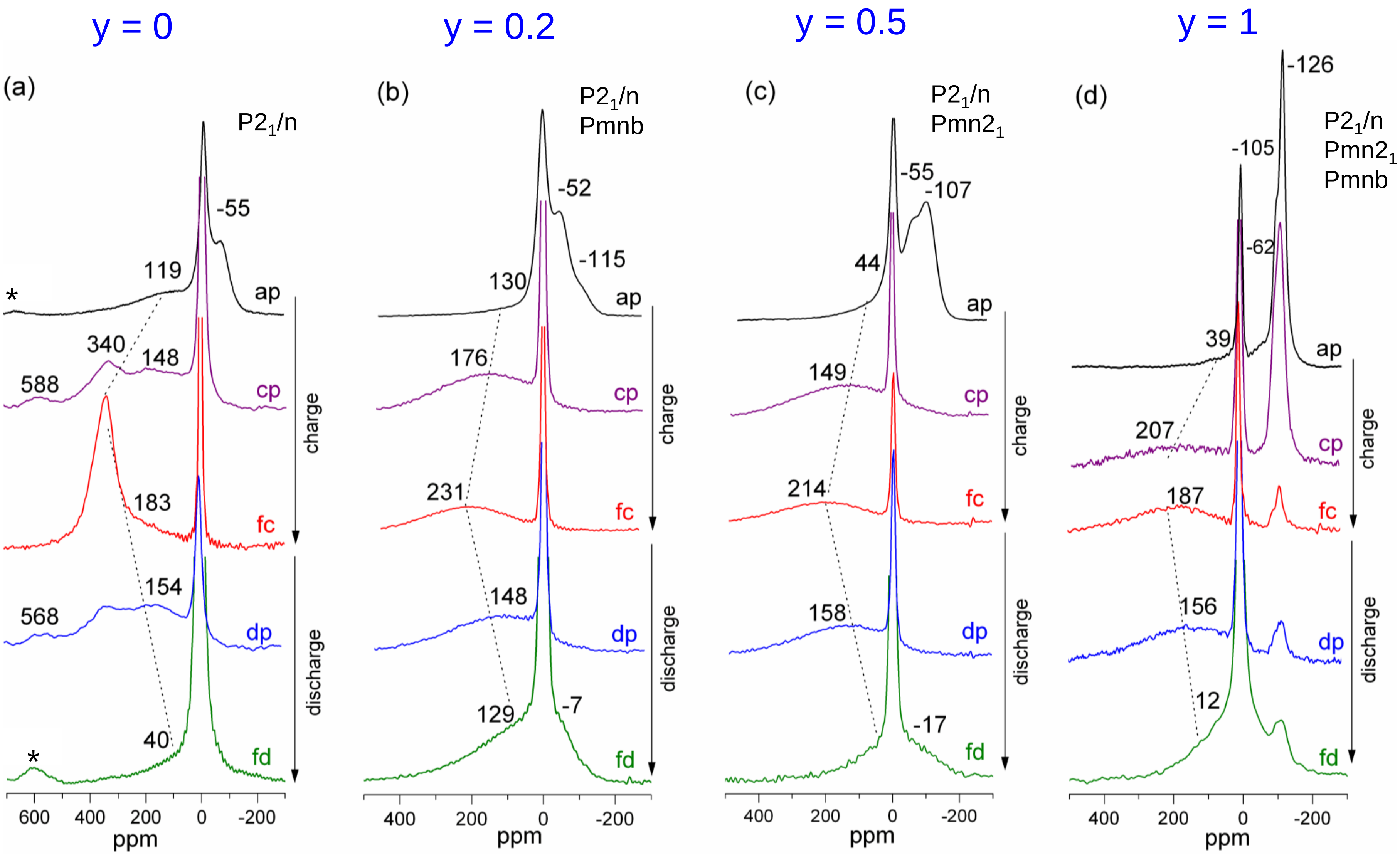
y = 0

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+} ↔ Fe^{3+} , Mn^{3+}



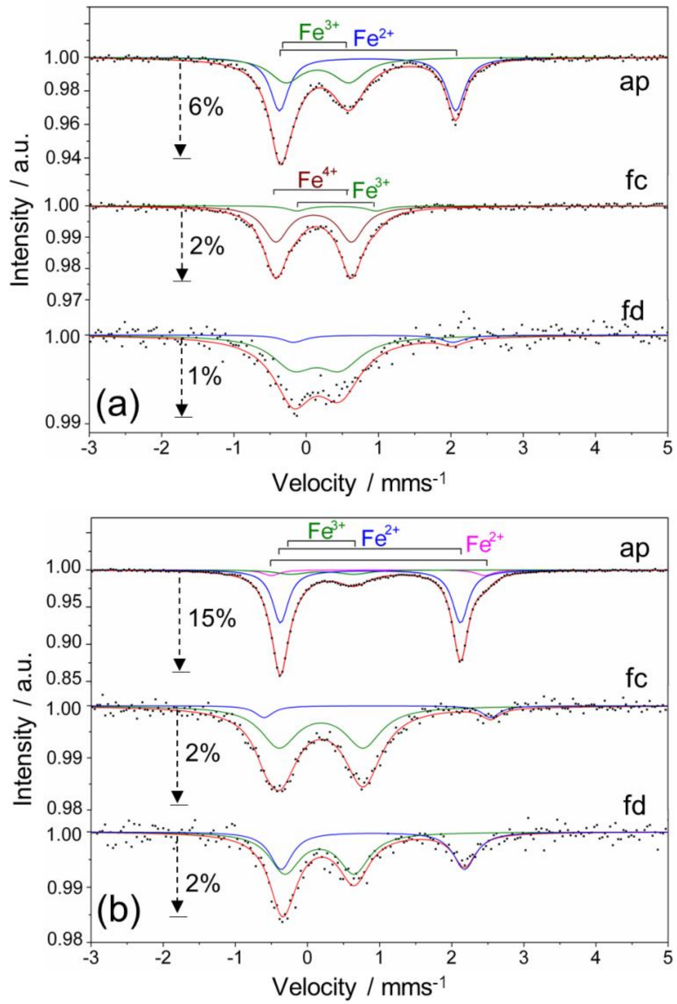
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

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

y = 0

y = 0.2

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



charge

discharge

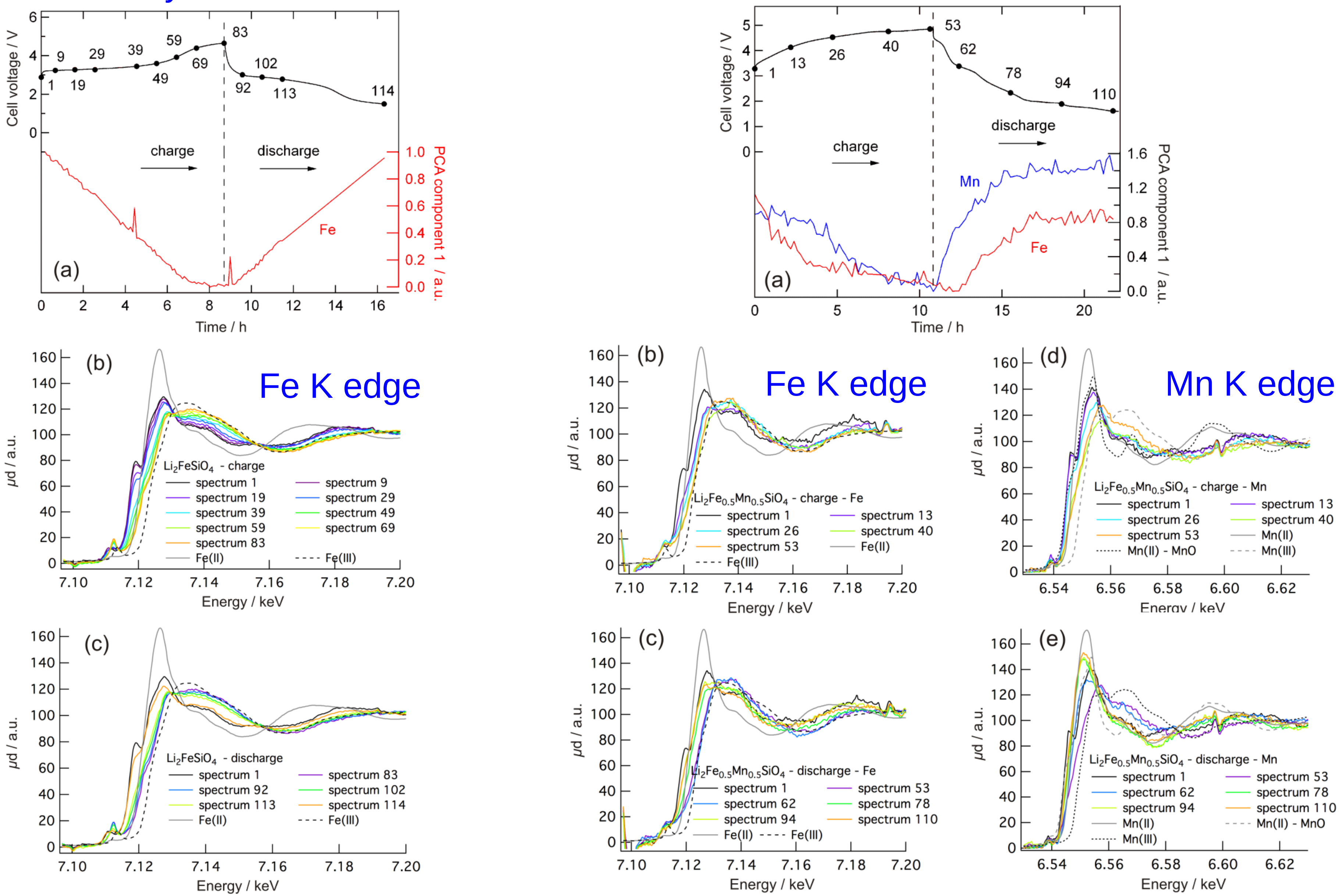
charge

discharge

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

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

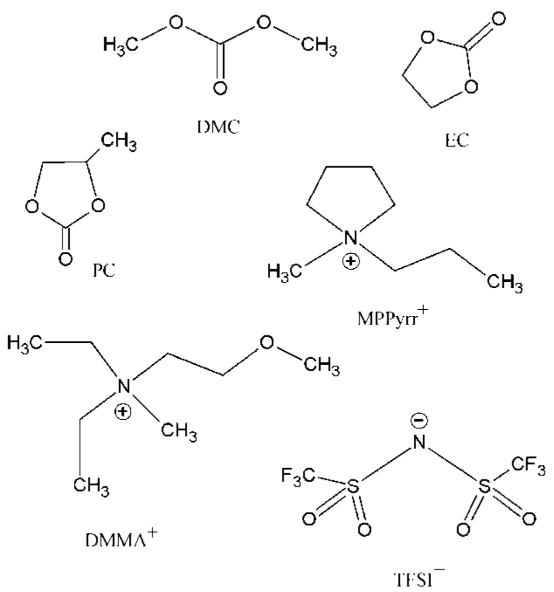
y = 0 | y = 0.5

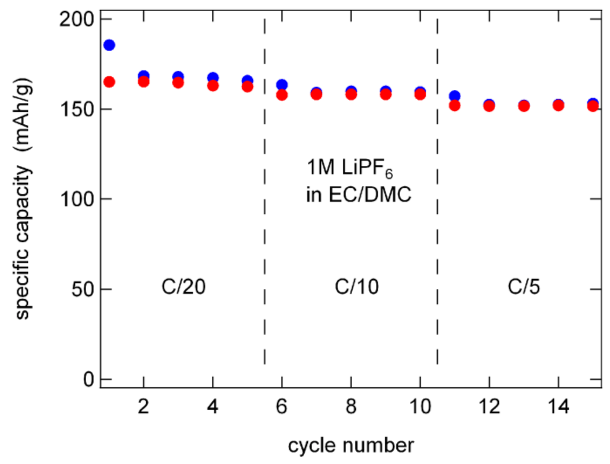


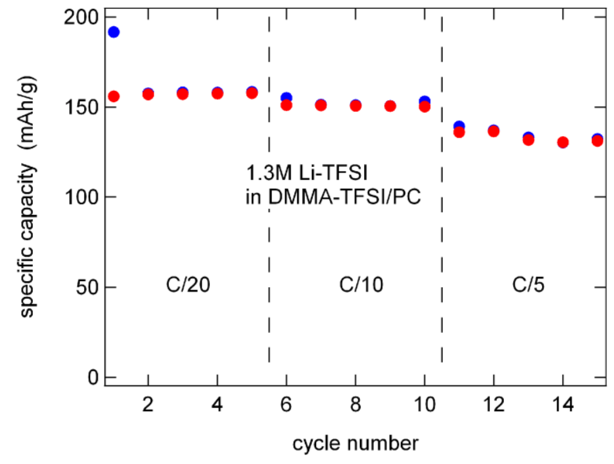
R. Chen et al., *J. Phys. Chem. C* **117** (2013), 884.

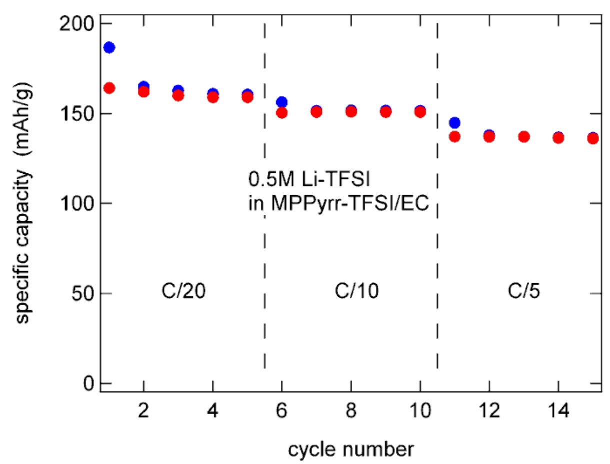
Ionic liquids as electrolytes cycling with NMC + Li

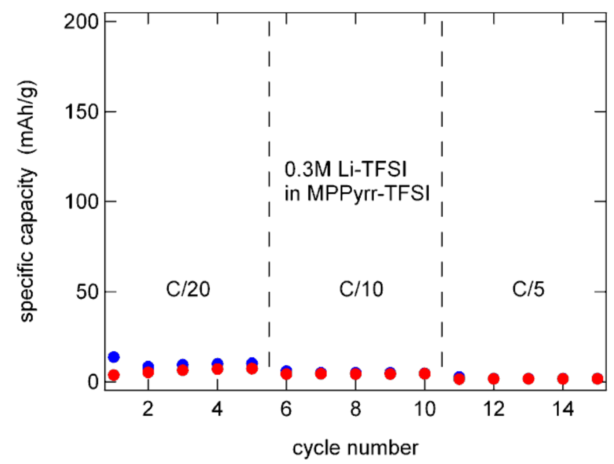
(together with M. Schulz, KIT-IAM)







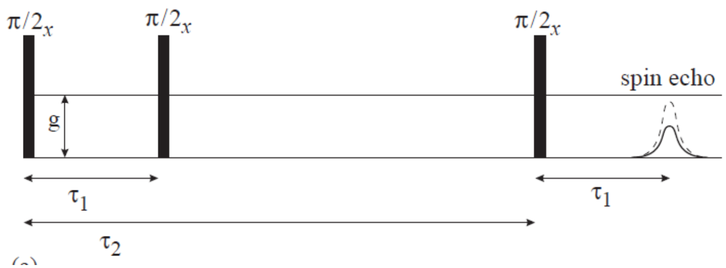




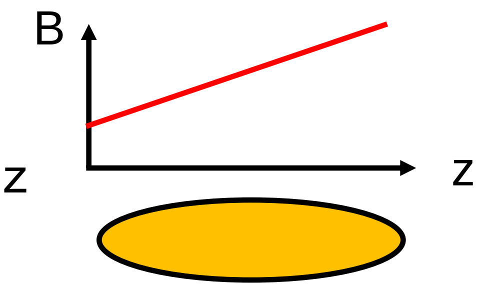
Electrolytes: Diffusion coefficients → Field Gradient NMR

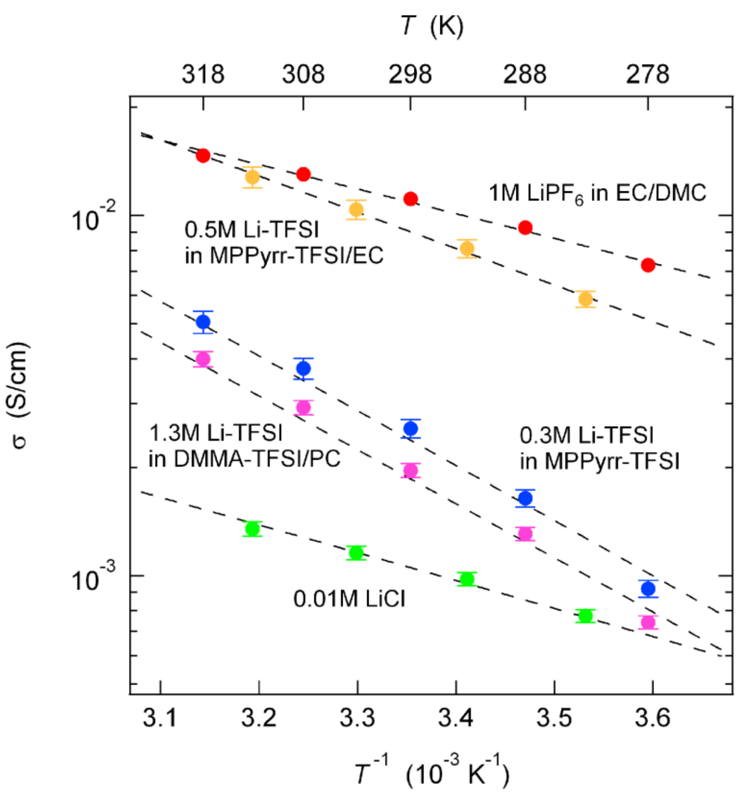
(together with M. Schulz, KIT)

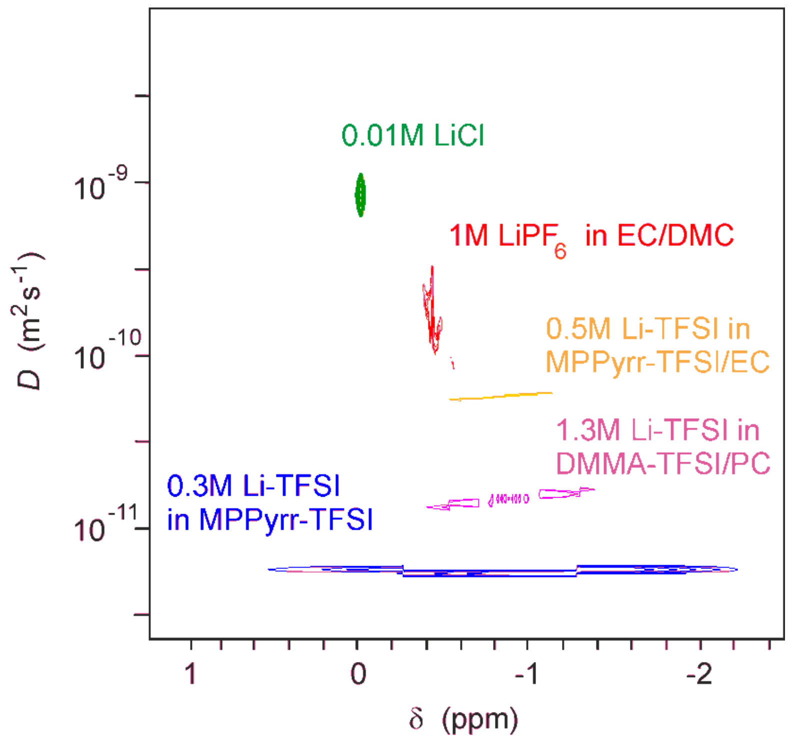
$\omega = \gamma \cdot B$



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







Conclusions

- observation of reaction mechanisms
  at components and interfaces during Li insertion/removal
- measurement of Li ion mobility: τ^{-1}, E_A, D
- understanding function and degradation of materials/cells

$LiCoPO_4$:

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

$Li_2(Fe/Mn)SiO_4$:

- 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

Outlook

- Li-Ion Batteries, SOFC, PEM, …
- Method Development: - high temperature
  - tomography
  - electrophoretic NMR

NMR center:	structure/dynamics/methods
Theory/Modelling:	Ion dynamics electronic structures spin density
MEET:	electrodes/electrolytes for Li-ion batteries

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YIN