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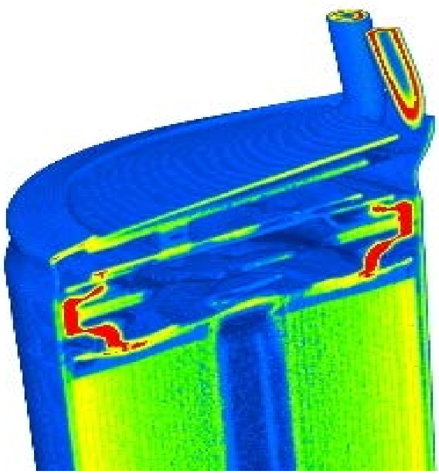
Institut für Angewandte Materialien

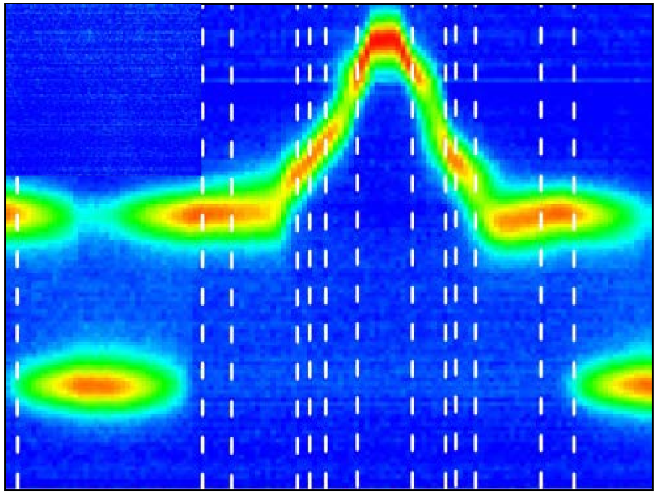
Helmholtz Institute Ulm Electrochemical Energy Storage

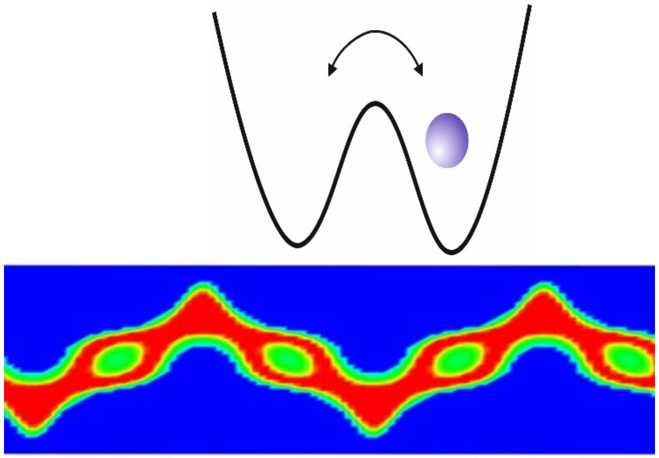
Neutron diffraction on solid-state battery materials

<u>Helmut Ehrenberg</u>, Anatoliy Senyshyn, Mykhailo Monchak, Sylvio Indris, Joachim Binder

INSTITUTE for APPLIED MATERIALS – ENERGY STORAGE SYSTEMS & Inorganic Chemistry







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- Introduction and challenges
- Pecularities and capabilites of neutron diffraction
- Selected examples addressing
  - mechanical stress due to anisotropic strain in layered oxides
  - new fluoride-based positive electrode materials
  - Li-ion conductivity in solid electrolytes

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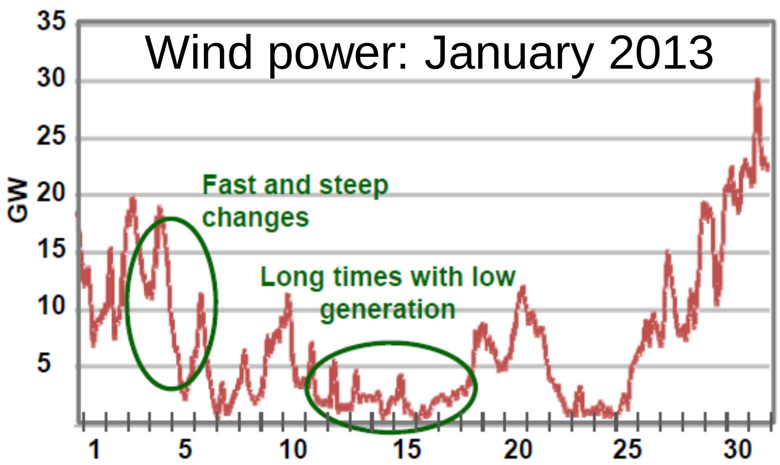
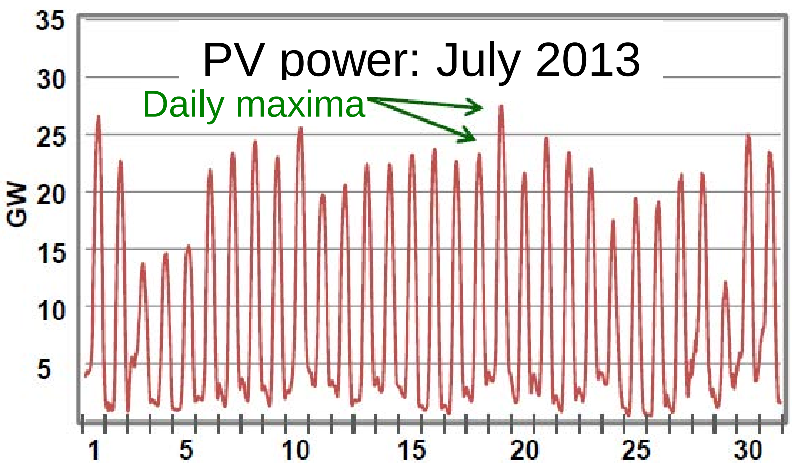
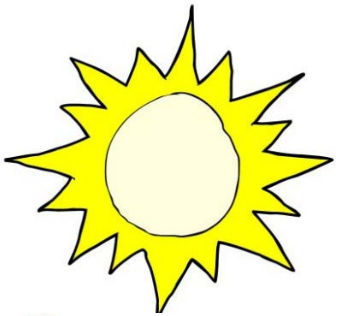
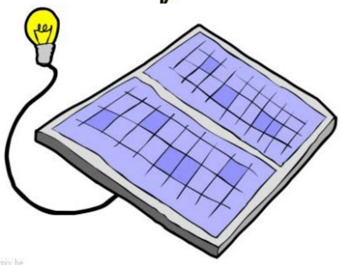
Energy storage is the key to…



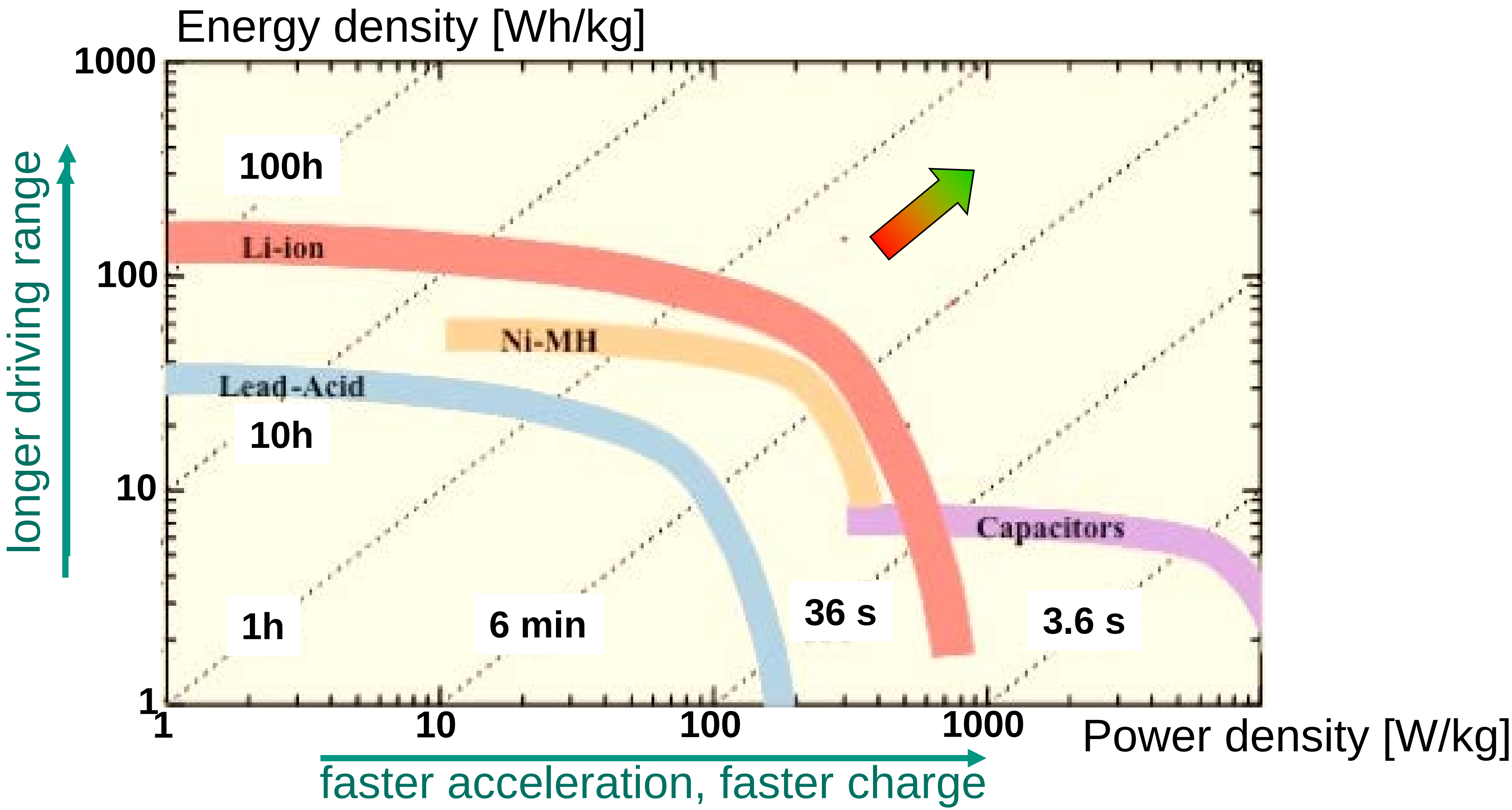


- … security of energy supplies
- … provide energy on demand
- … electromobility

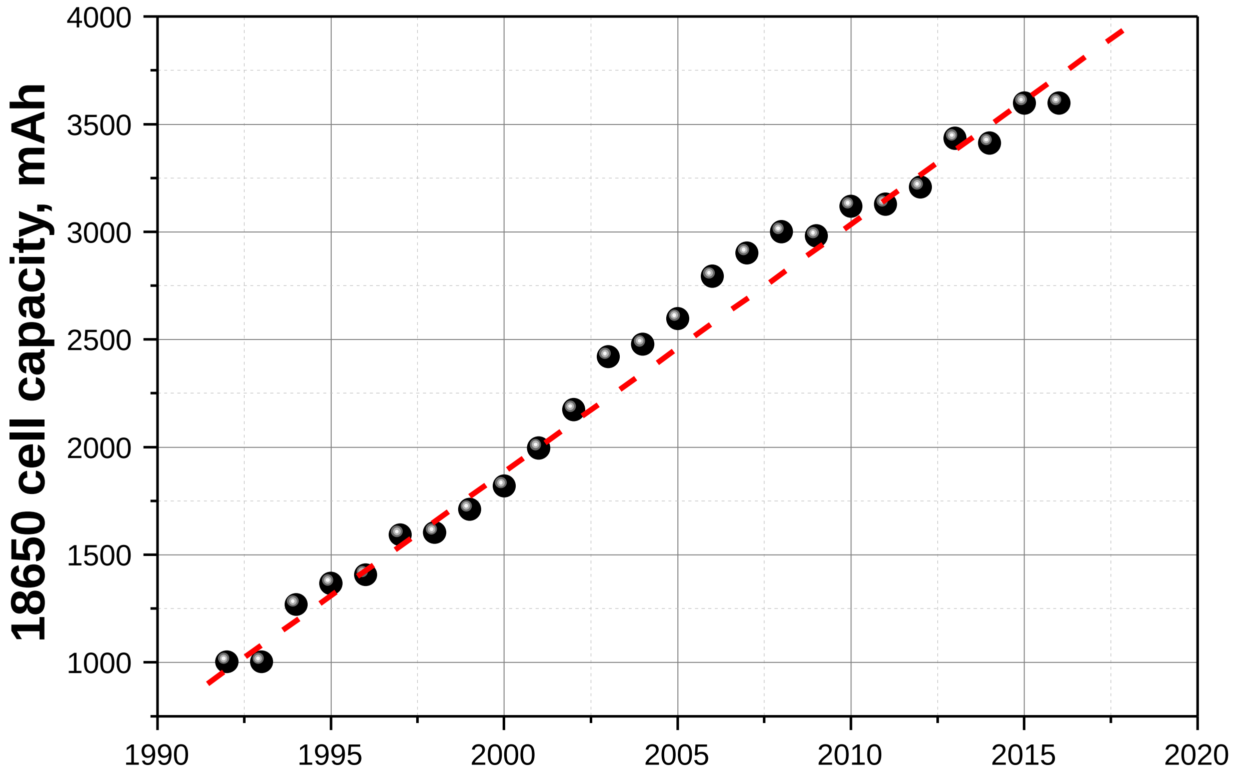




Ragone plot: Comparison of electrochemical energy storage systems

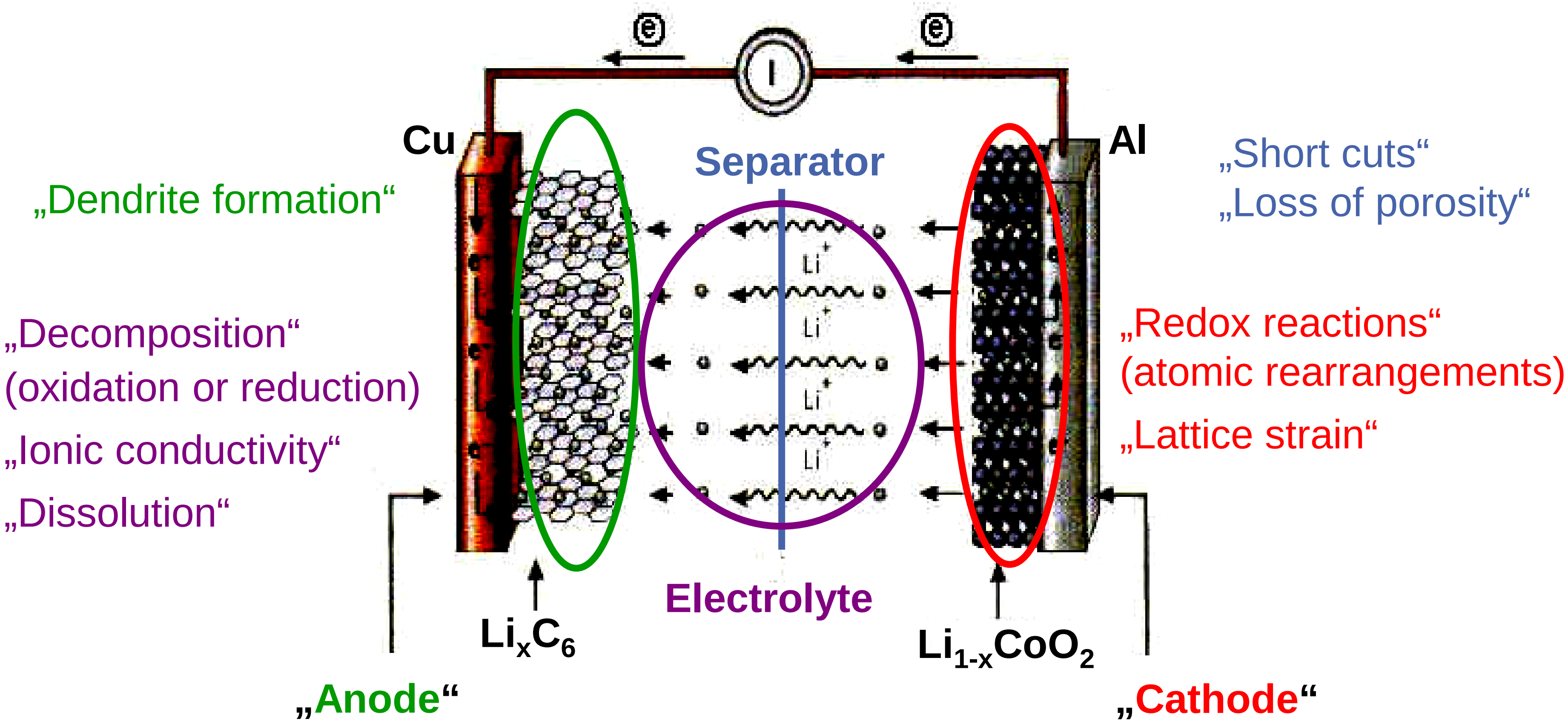


Capacity evolution of 18650-type cells



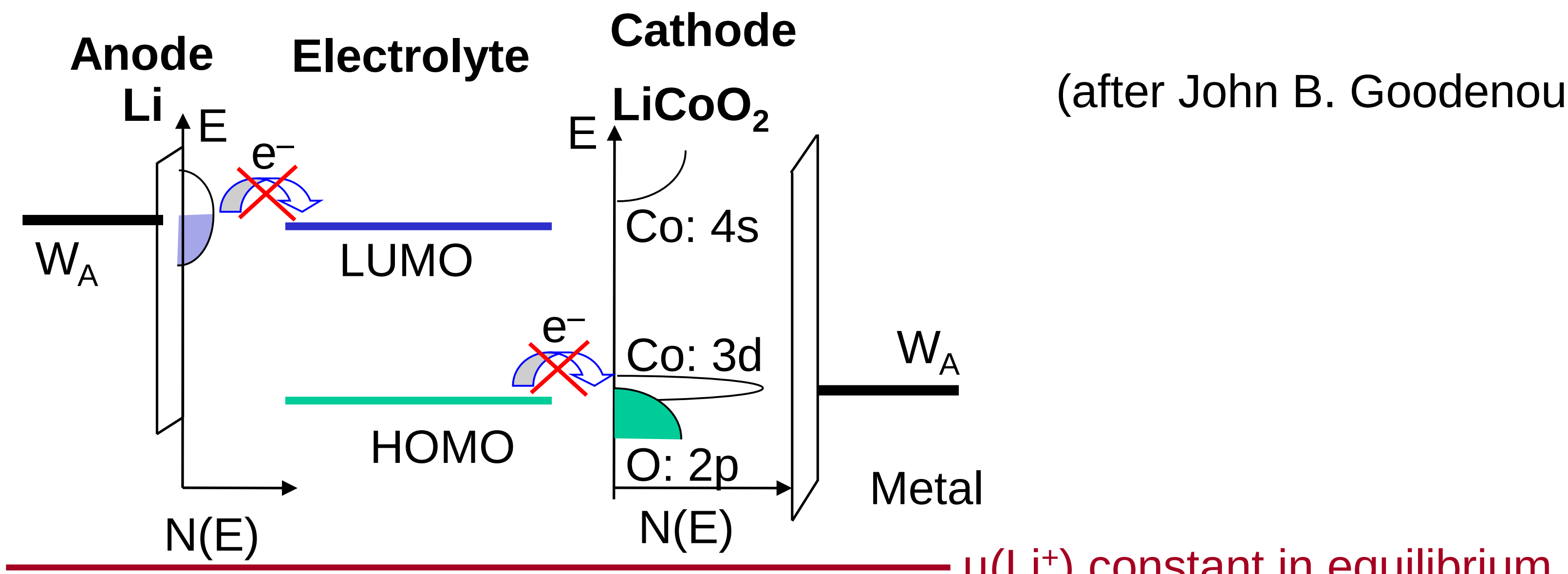
- 120 mAh/year average increase rate over almost 25 years
- Since 2012 the capacity increase is achieved by voltage increase and introduction of Si to graphite anodes

Working principle & materials challenges



- All components suffer from „Ageing“ & „Fatigue“
- Materials interactions: „Solid Electrolyte Interface/Interphase“, SEI
  „Metal dissolution“, „Loss of adhesion“

Necessary interface properties



(after John B. Goodenough)

- Electrolyte LUMO level must have a higher energy than W_A(Anode)
- Electrolyte HOMO level must be below W_A(Cathode)

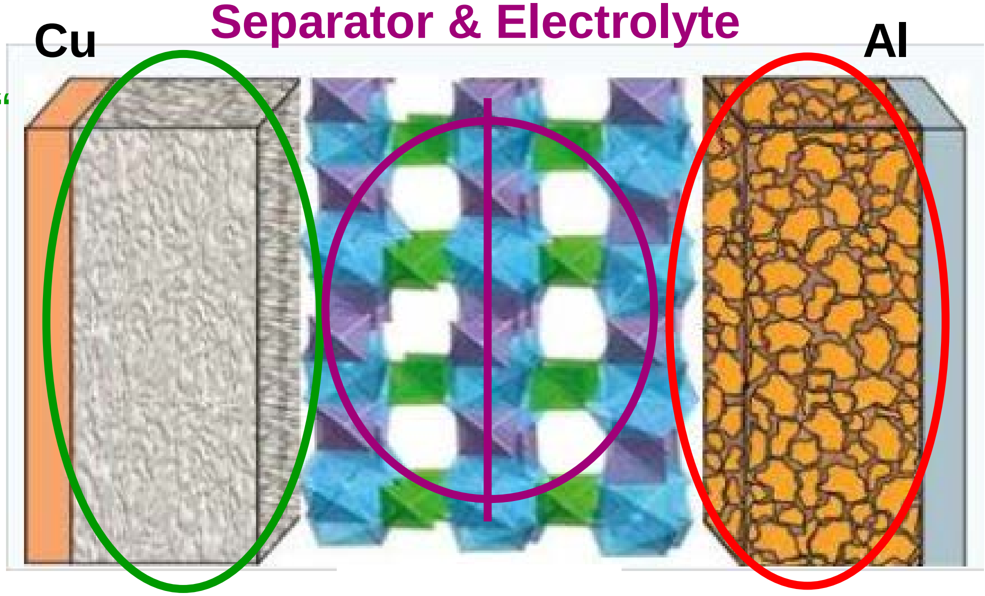
→ Requires dedicated interface properties („coating“ or „SEI“)
→ Reveal the underlying processes and mechanisms
→ Huge potential for ALL-solid state batteries

Challenges in solid state Li-ion batteries

„Redox reactions“

(„Ionic conductivity“ > 10^{-3} S/cm)

„Densification“



„Dendrite formation“

„Mechanical stress“

„Mechanical stress“

„Densification“

„Transport„

„Chemical instability“

„Anode“

Li metal
Graphite
LTO

LLZO
LLT
LATP, LAGP

$Li_{1-x}CoO_2$
NCM
New HV compounds

„Cathode“

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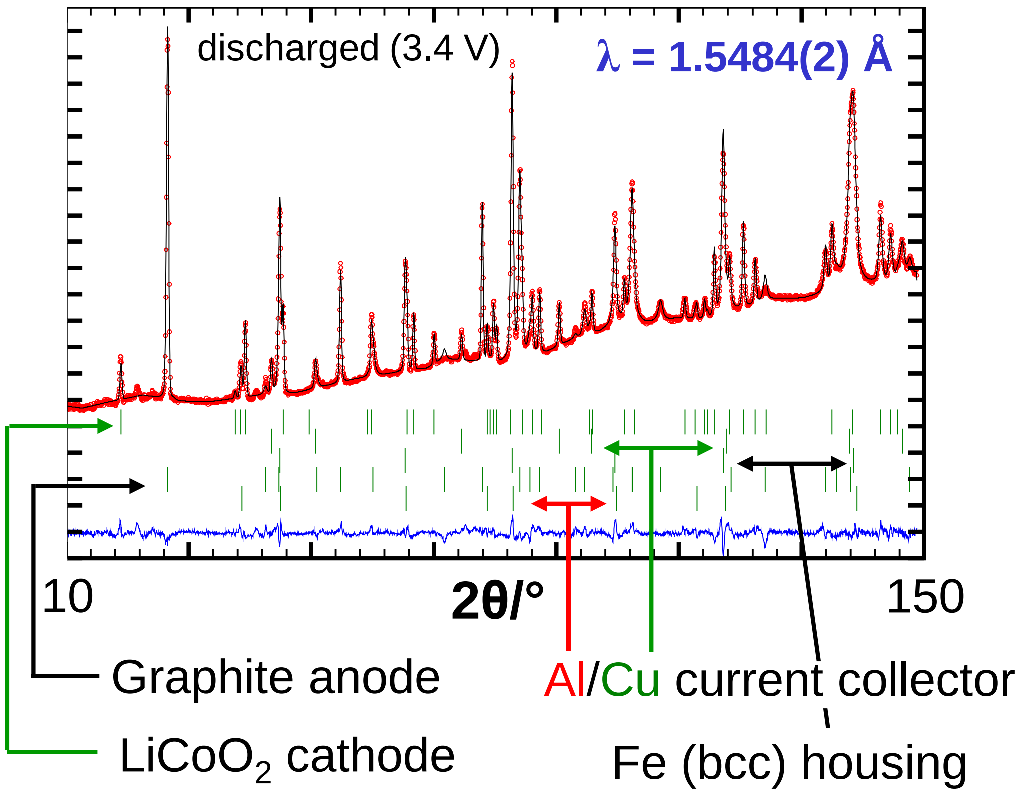
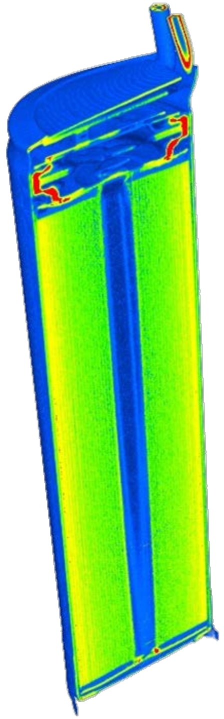
Peculiar properties of neutrons: a unique tool for battery research

- Energy of thermal neutrons is in the range of a few meV
  → weak interactions, non-destructive
- Good penetration capability
  → large objects can be studied, even in dedicated sample environments
  → local and isotope dependent absorption cross section, e.g. ^{1}H und ^{6}Li
- No charge and interaction with the nuclei and magnetic moments
  → elements with similar electron number Z can be distinguished
  → different isotopes can be used as specific markers
  → good detection and localization of light elements (H, Li, C, O, …)
  → form factor nearly constant
- Wave lenght is in the range of interatomic distances
  → exact information on crystal structures, complemenary to X-rays

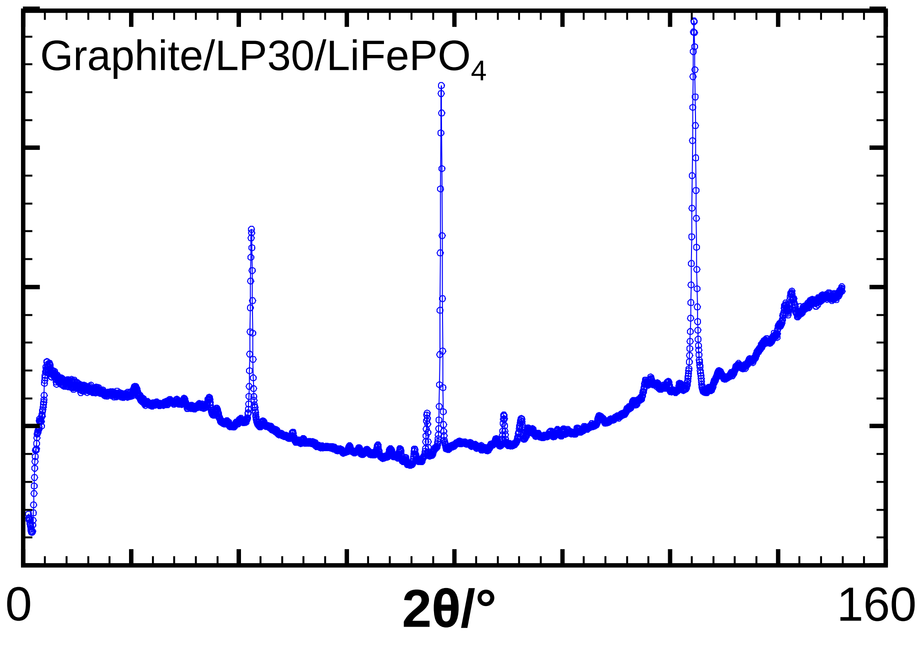
A zoom into the battery during operation

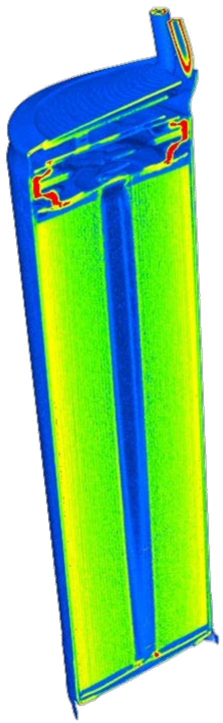




O. Dolotko et al., *J. Electrochem. Soc.* **159** (2012) A2082
A. Senyshyn et al., *J. Power Sources* 203 (2012) 126
O. Dolotko et al., *J. Power Sources* 255 (2014) 197
A. Senyshyn et al., *Scientific Reports* 5 (2015) 18380

Solid-state batteries are neutron friendly:





- Main contributions from housing & current collector
- Background from incoherent H-nuclear spin scattering
- *in operando* cells with deuterated liquid electrolyte
- All-solid state cells in progress…

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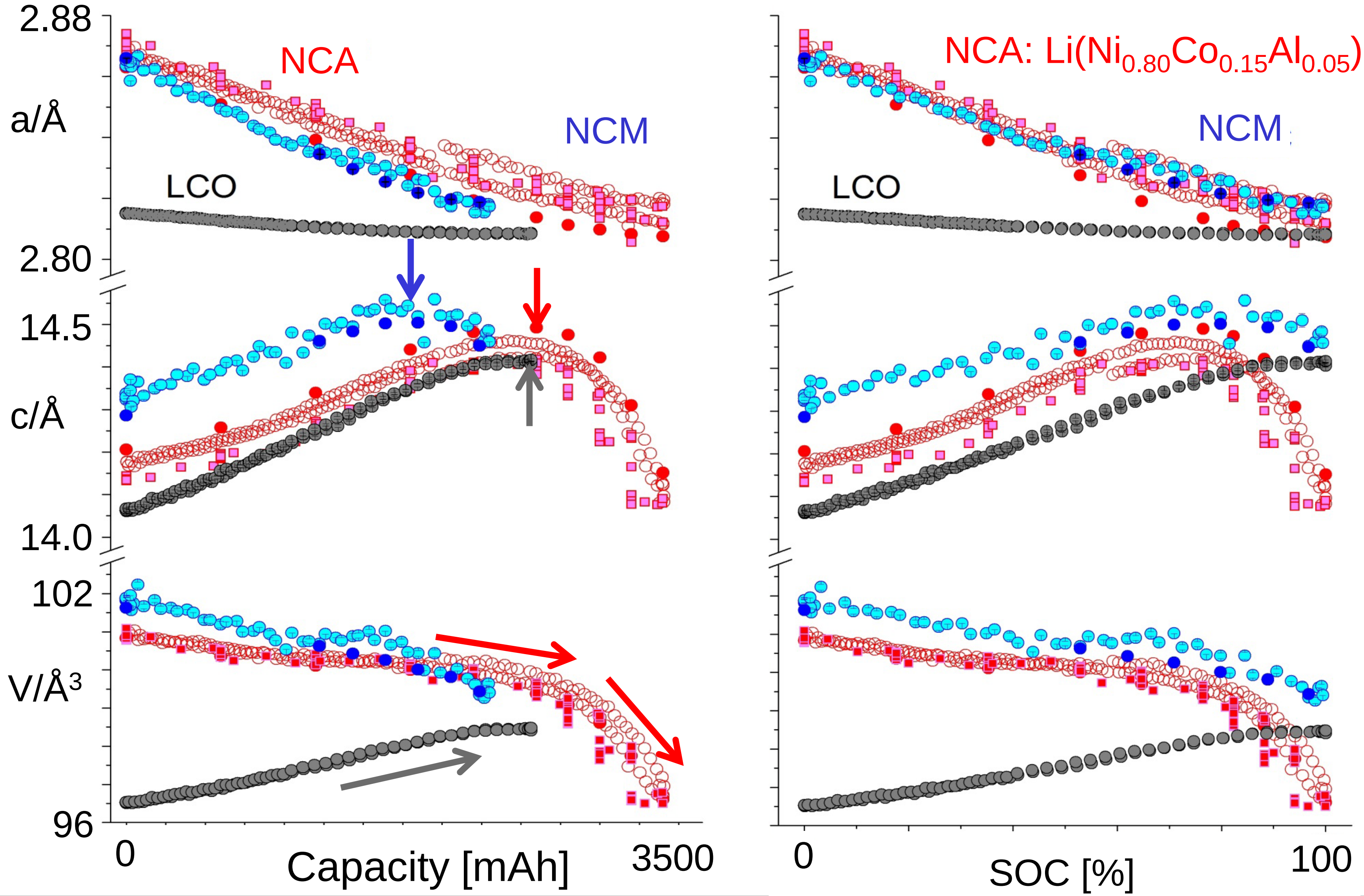
Electrochemically induced lattice strain $LiCoO_2$ (LCO), $Li(Ni,Co,Mn)O_2$ and NCA



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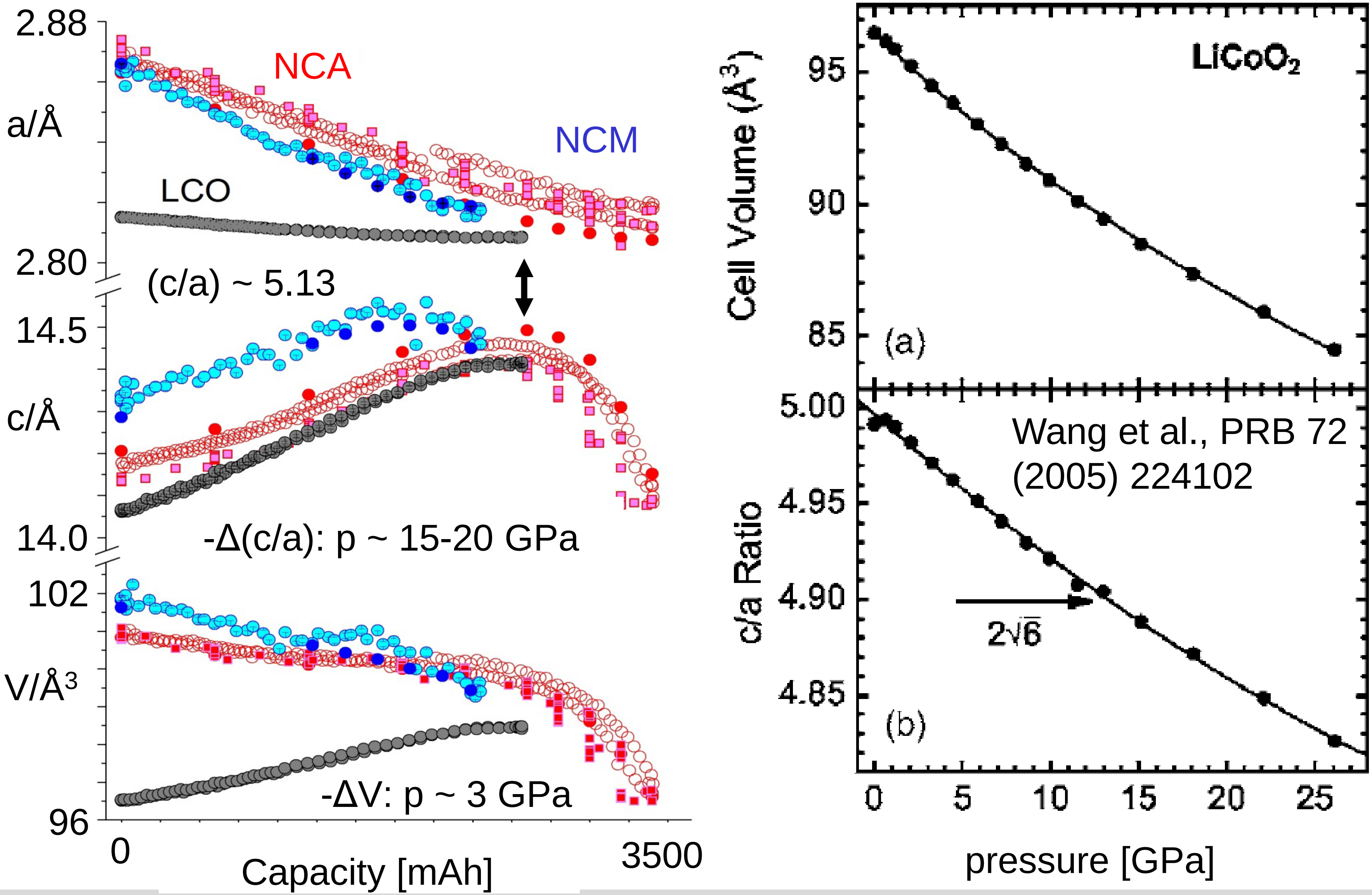
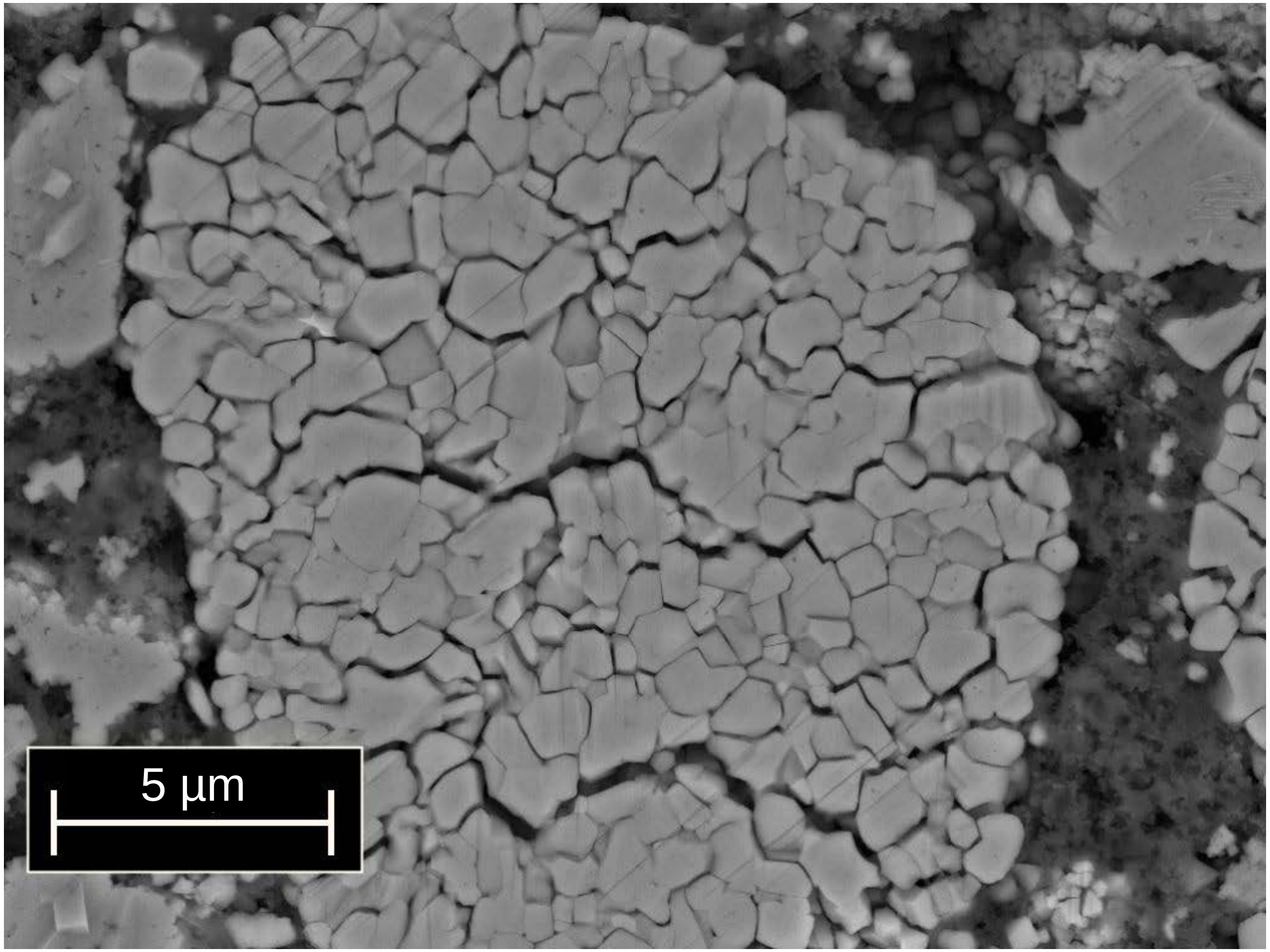


Lattice strain and microstructure: NCM



- Fatige due to cracks only relevant at very high C-rates (fast charge/discharge)
- Tesla S: 640 kg battery, BMW i3: 233 kg of battery

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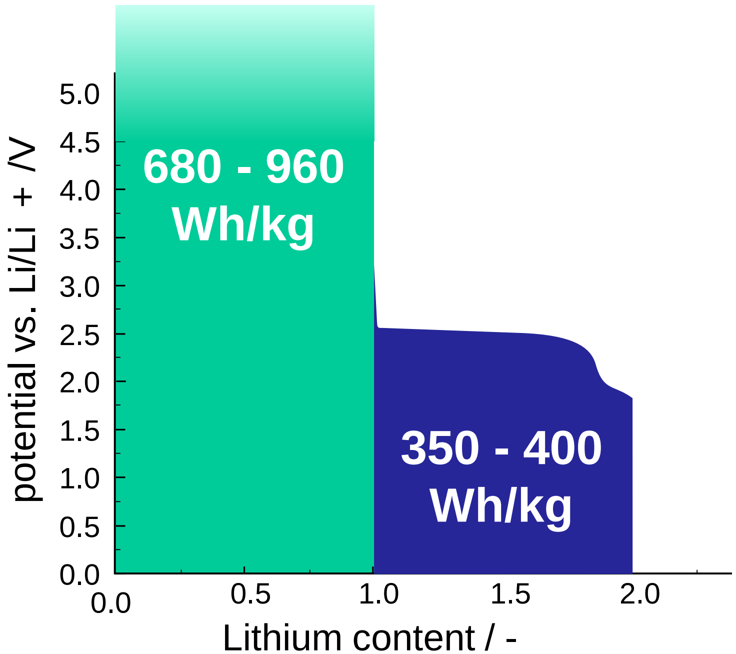
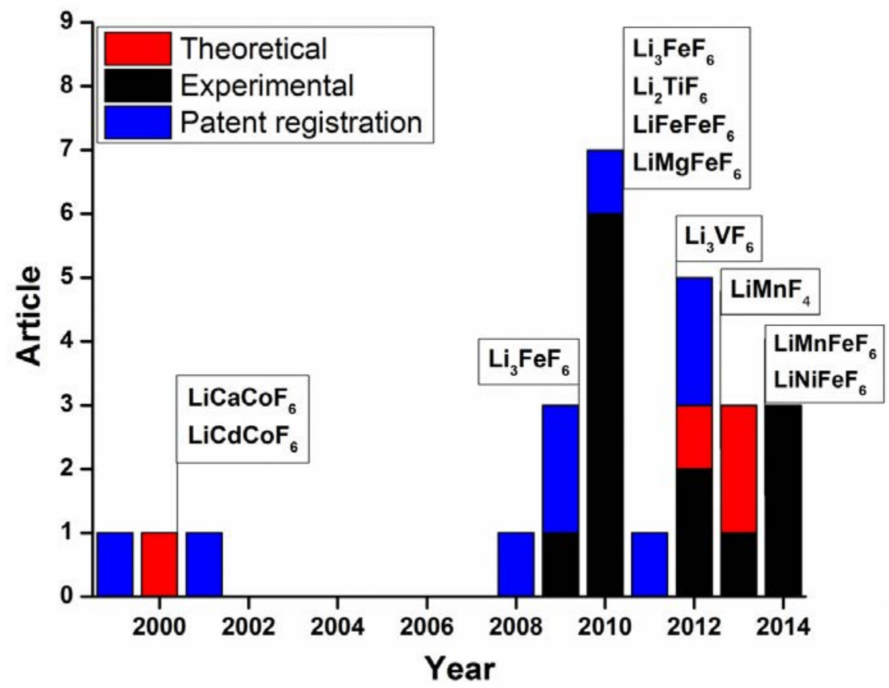
Li-3d-metal fluorides as positive electrodes

High-voltage area

- High voltages (4.7 - 6.7 V *) were theoretical predicted for lithium metal fluorides
- Up to now, no experimental proof could be provided





Low-voltage area

- Only lithiation of lithium metal fluorides was shown so far.

* Y. Koyama et al., *J. Electrochem. Soc.*, **147** (2000) 3633

J. Kohl et al., *J. Mater. Chem.*, **22** (2012) 15819

Li-3d-metal fluorides as positive electrodes

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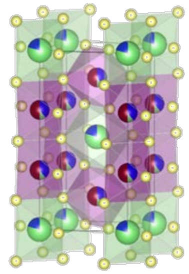
- **3 different structure types**
- **similar electro-chemistry**
- **3 different Li insertion mechanisms**

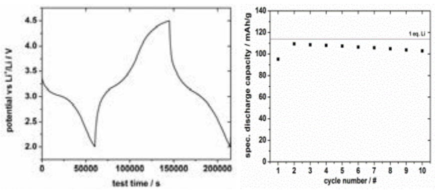
Trirutile (tetragonal)

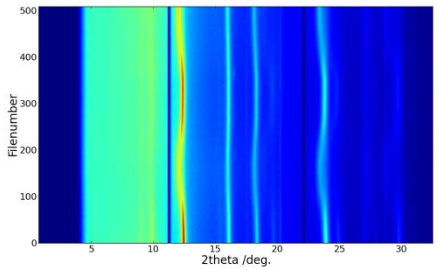
$LiNiFeF_6$

$P4_2/mnm$



Lieser et al., JES 161 (2014) A1071

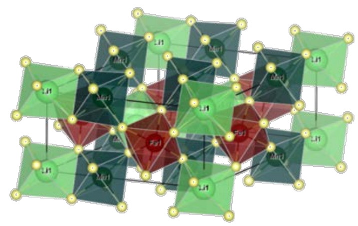




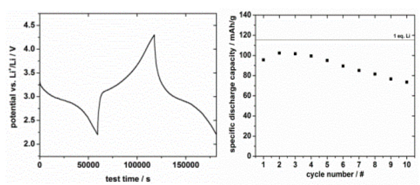
Na_2SiF_6 (trigonal)

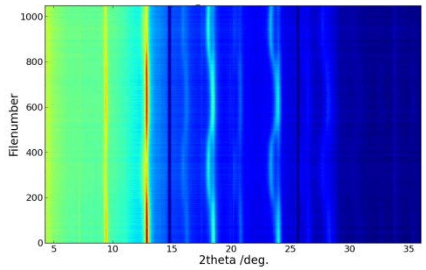
$LiMnFeF_6$

P321



Lieser et al., JES 161 (2014) A1869

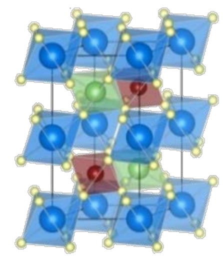




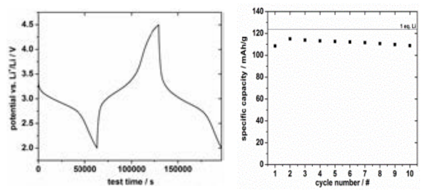
Colquiriite (trigonal)

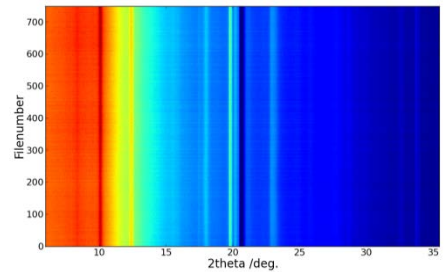
$LiCaFeF_6$

$P\bar{3}1c$



de Biasi et al., J. Power Sources (2017)





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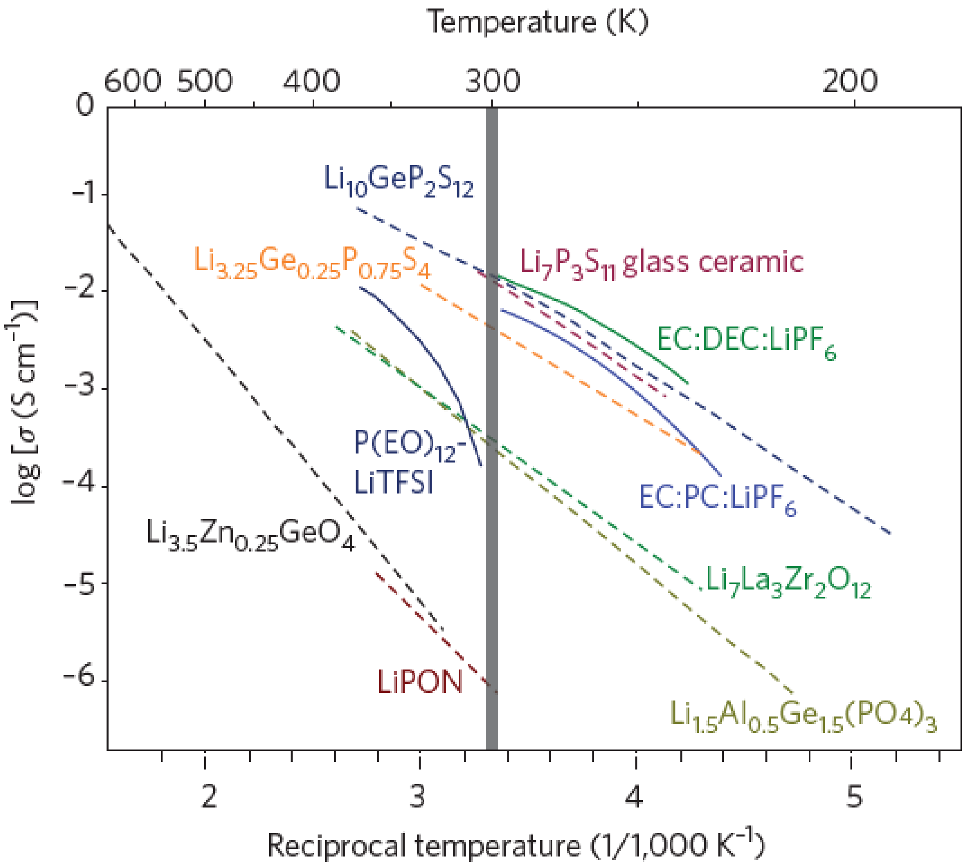
    - **Li-ion conductivity in solid electrolytes**

Ionic conductivity of solid electrolytes…

- … is a challenge, but not the most serious concern.
- … determined by vacancies and activation energies.

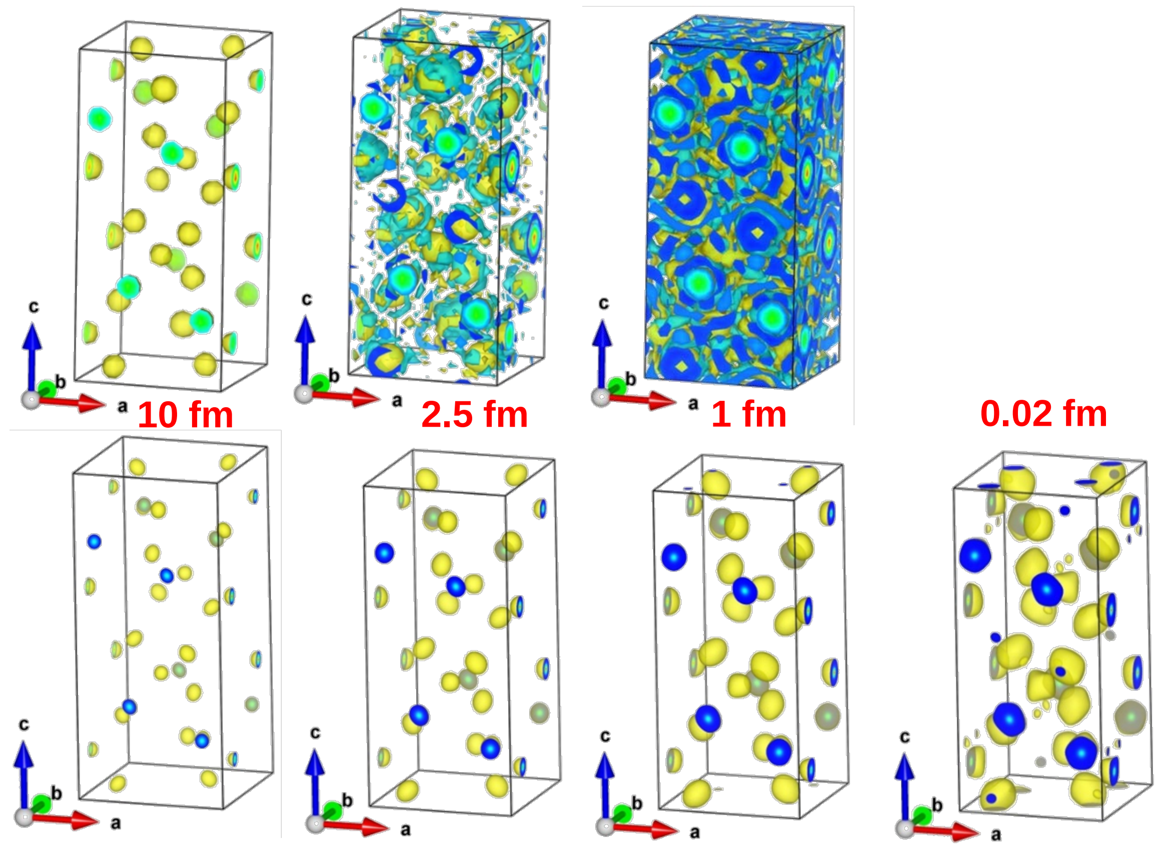


J. Janek, W. G. Zeier, Nature Energy (2016) 16141

Challenges in the analysis of Fourier difference maps

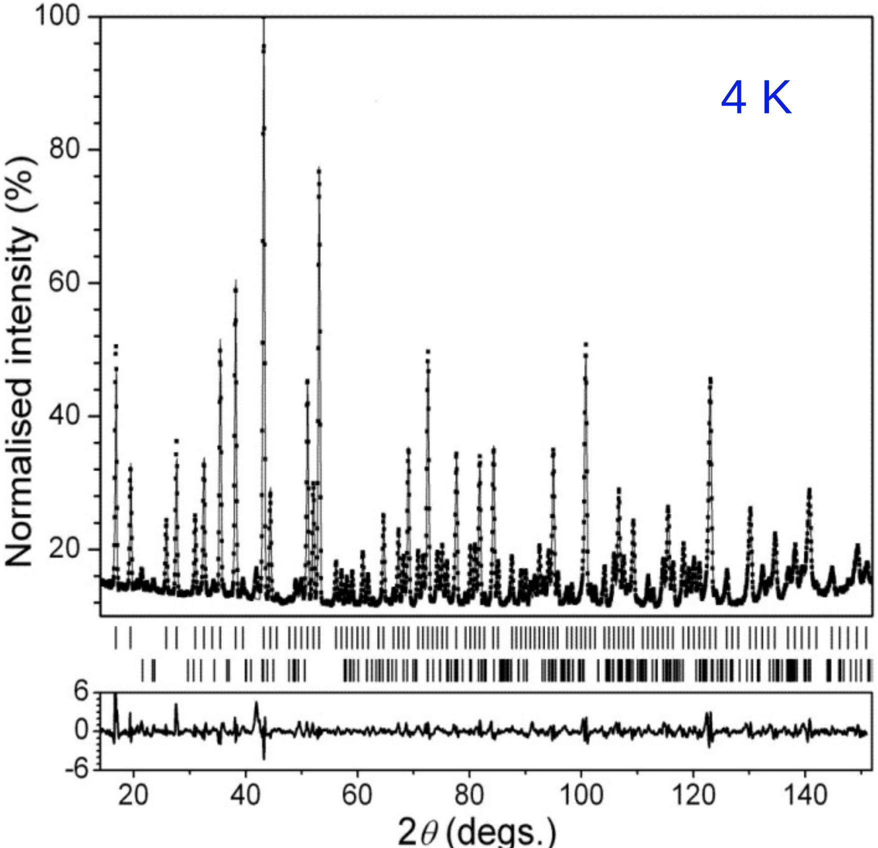
- High-quality diffraction data with very good counting statistics
- Appropriate material with almost no impurity and well known structure & disorder
- Need for low-temperature and elevated-temperature data sets
- Filtering method based on Bayesian statistics: Maximum Entropy Method (MEM)

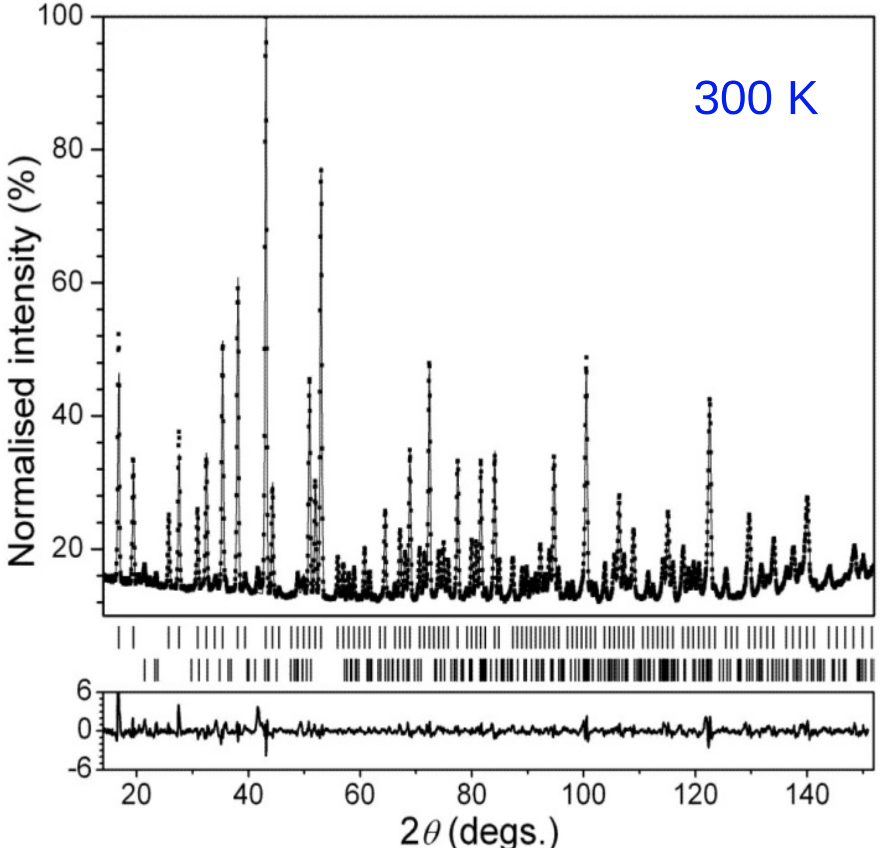
- Experimental nuclear density maps (“F_{obs}”):
- MEM reconstructed nuclear density maps:



Lithium diffusion pathways in $Li_7La_3Zr_2O_{12}$

- High-resolution neutron diffraction at SPODI, FRM II/MLZ



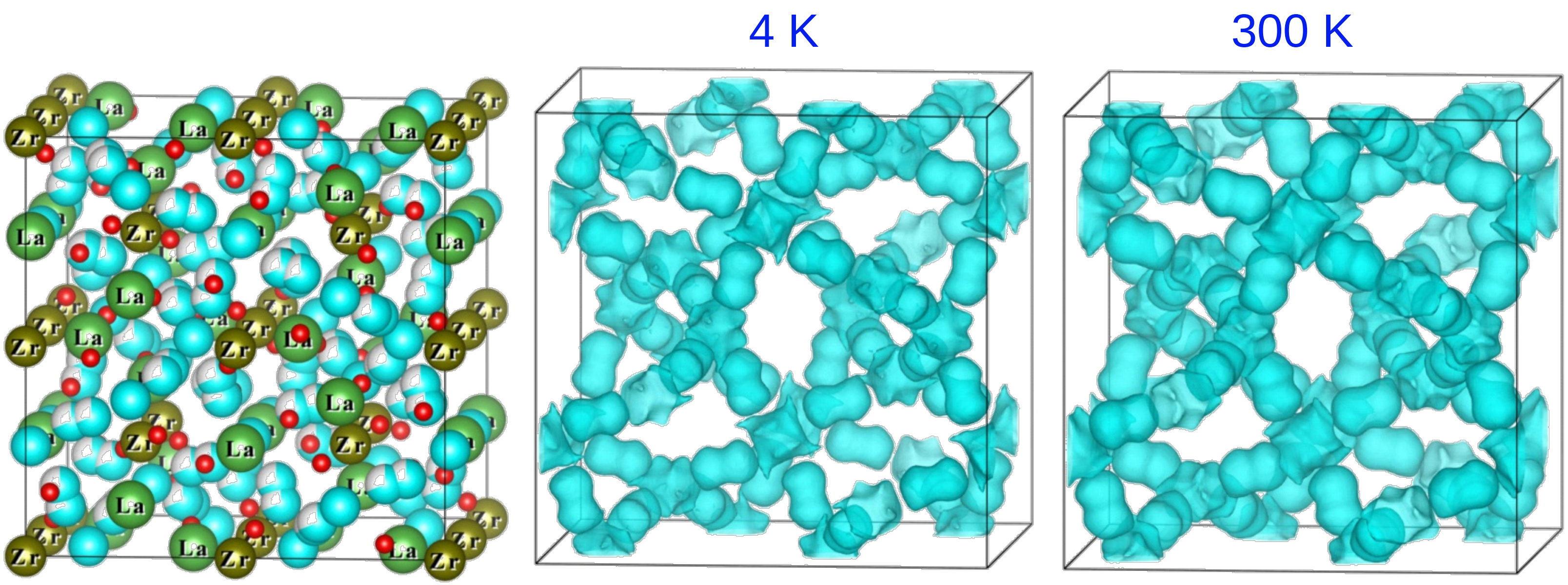


< 2% Li_2CO_3 impurity

Buschmann et al., Phys. Chem. Chem. Phys., 2011, **13**, 19378 (with J. Janek)

Lithium diffusion pathways in $Li_7La_3Zr_2O_{12}$

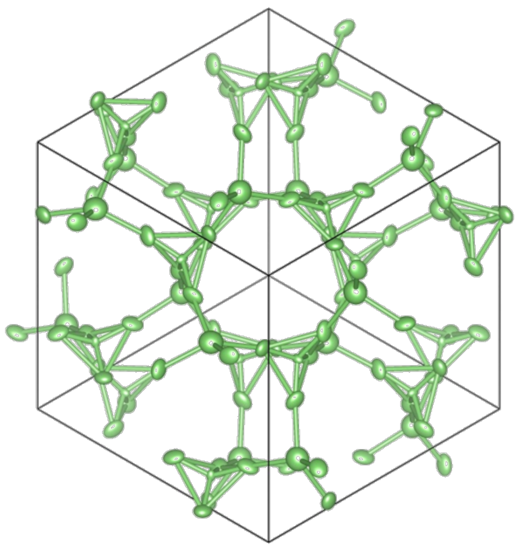
- Structural model and MEM reconstruction of negative scattering densities
- Detailed investigation of Li-disorder (on 24d- and 96h-sites in Ia-3d)
- Combination with NMR spectroscopy (^{7}Li NMR relaxometry) and calculations give a complete picture on Li-diffusion in solid electrolytes.



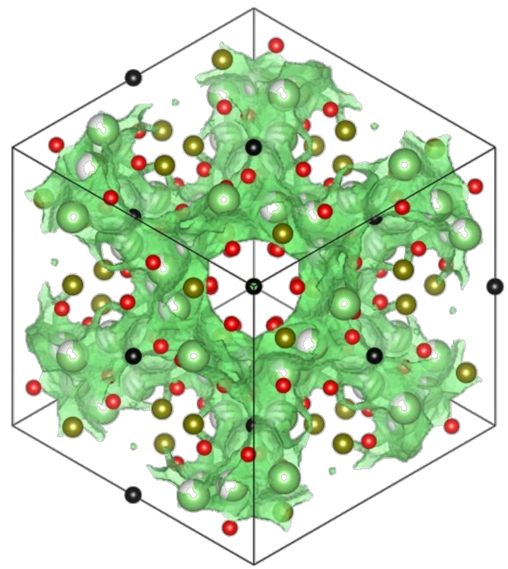
Buschmann et al., Phys. Chem. Chem. Phys., 2011, **13**, 19378 (with M. Wilkening & J. Janek)

Lithium diffusion pathways in $Li_7La_3Zr_2O_{12}$

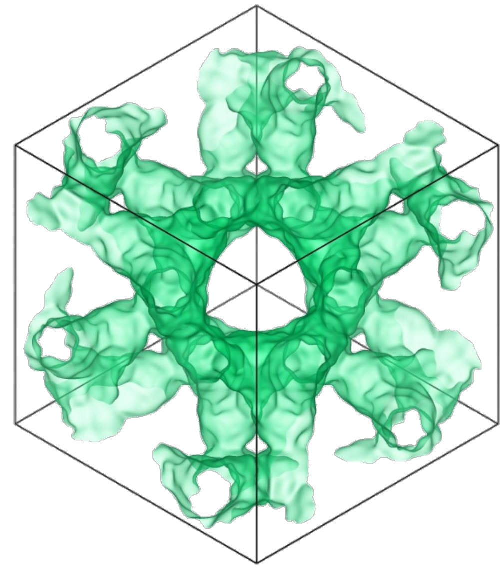
Lithium framework
(from Rietveld refinement)



Bond-valence mismatch*



MEM analysis**



* La, Zr and O atomic positions (no lithium) were used for prediction;
** Negative nuclear densities (from structure factors analysed using maximum entropy method).

Lithium diffusion pathways in $Li_7La_3Zr_2O_{12}$

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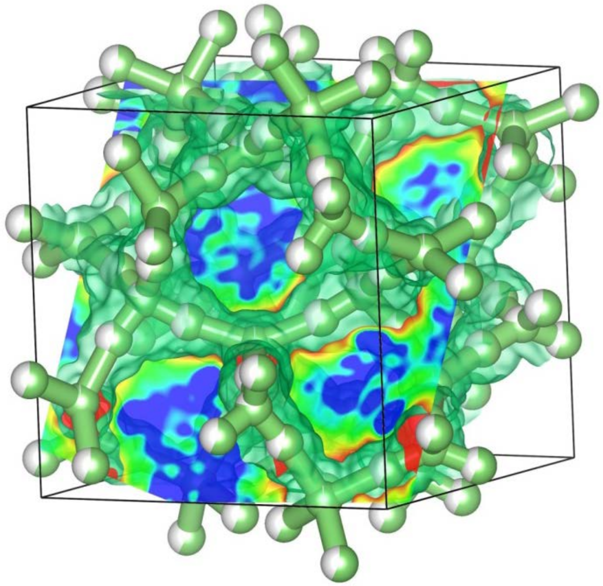
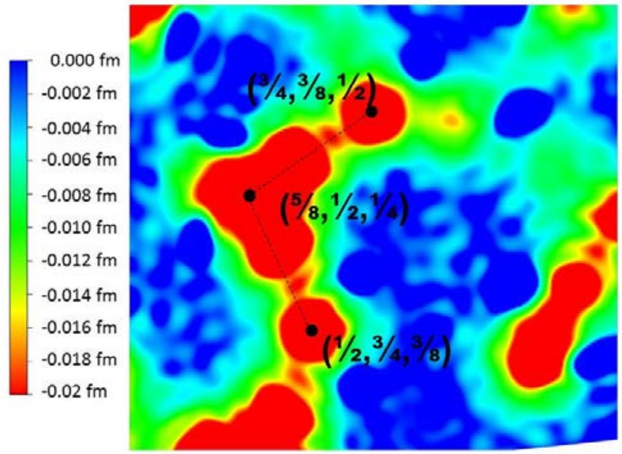
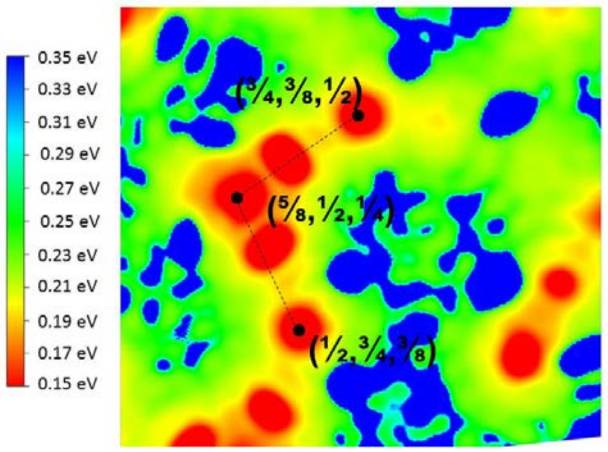
- MEM reconstruction of negative nuclear densities in LLZO



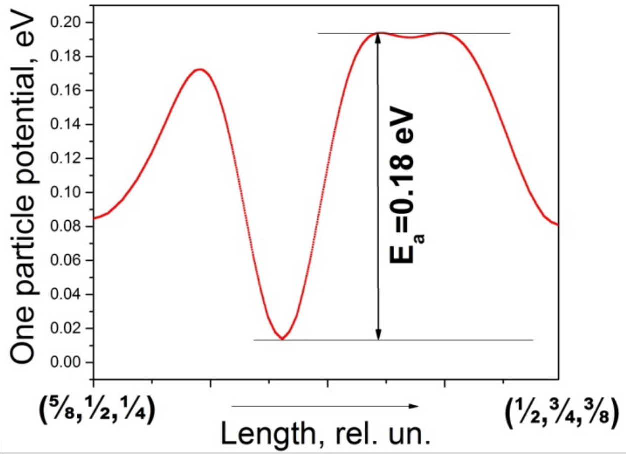
Density slice through plane [53-1]



OPP slice through plane [53-1]



Diffusion energy barrier in LLZO



Conclusions

- Structure-property relationships in solid electrolytes are at present a primary topic for the combination of neutron diffraction, NMR spectroscopy and DFT calculations.
- Many examples of solid electrolytes are studied in this way, e.g.

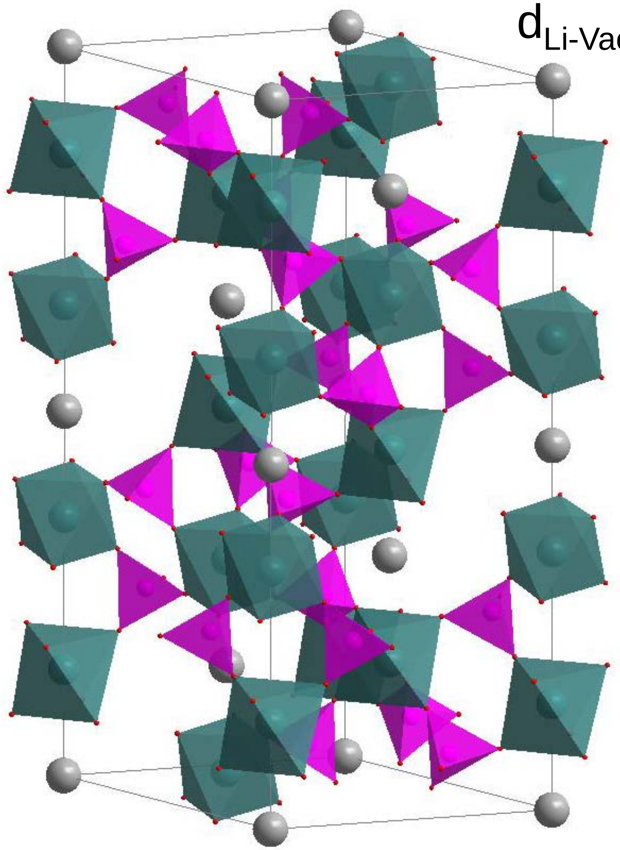
  NASICON-type structures $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ and $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$, $Li_{10}SnP_2S_{12}$, Li_4PS_4I, …

Institute for Applied Materials - Energy Storage Systems (IAM-ESS)

Lithium diffusion in $Li_{1.6}Al_{0.6}Ge_{1.4}(PO_4)_3$

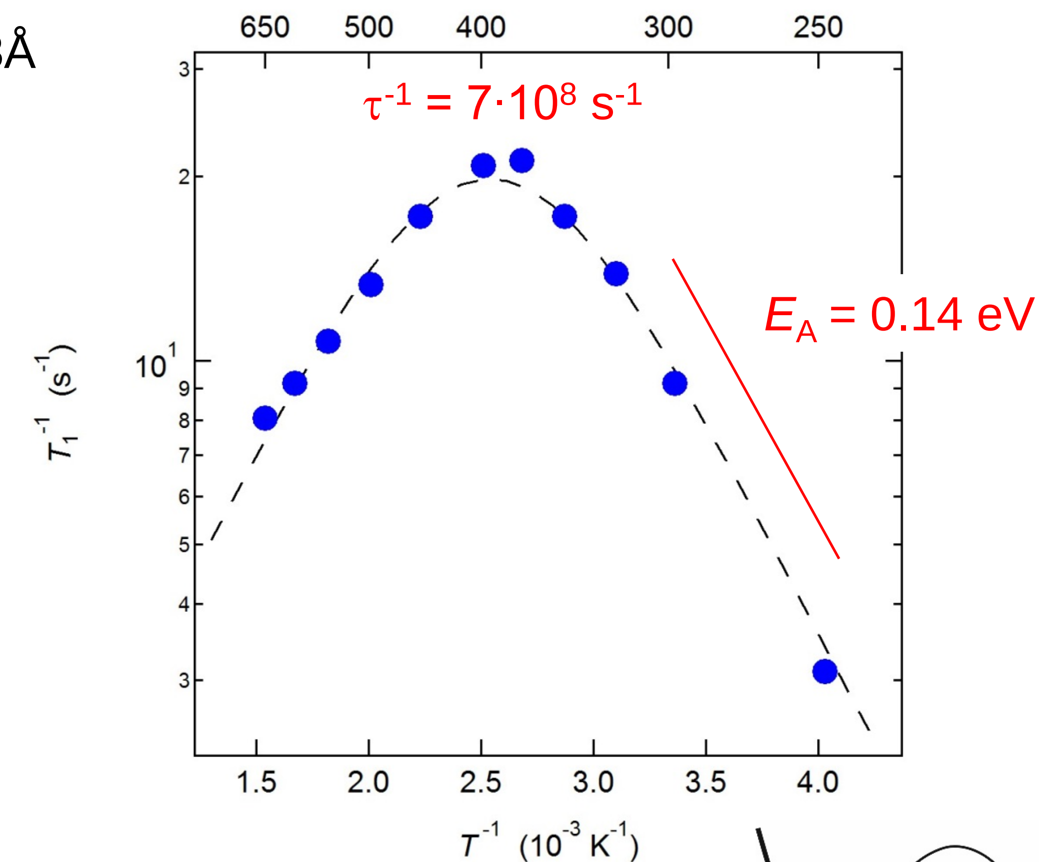
LAGP

$d_{Li\text{-}Vac.} = 3Å$

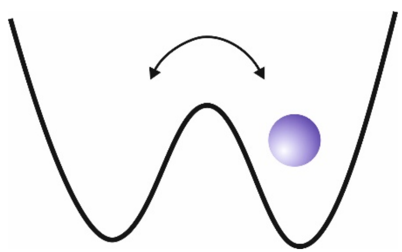


$\sigma_{Li} = 3.6$ mS/cm

^{7}Li NMR relaxometry



$\omega_L \approx t^{-1}$



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IAM Institut für Angewandte Materialien

KIT Karlsruhe Institute of Technology

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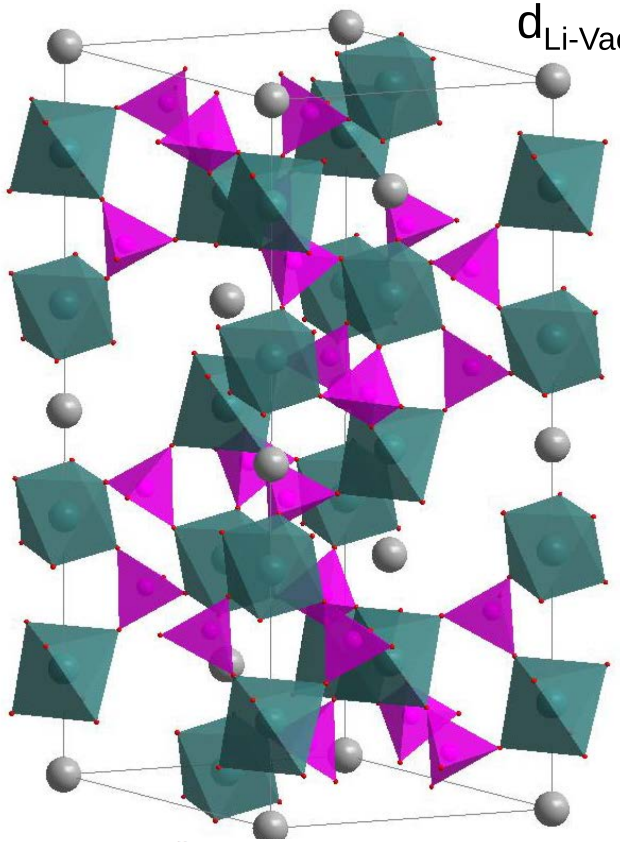
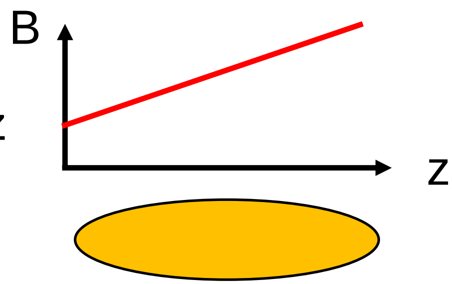
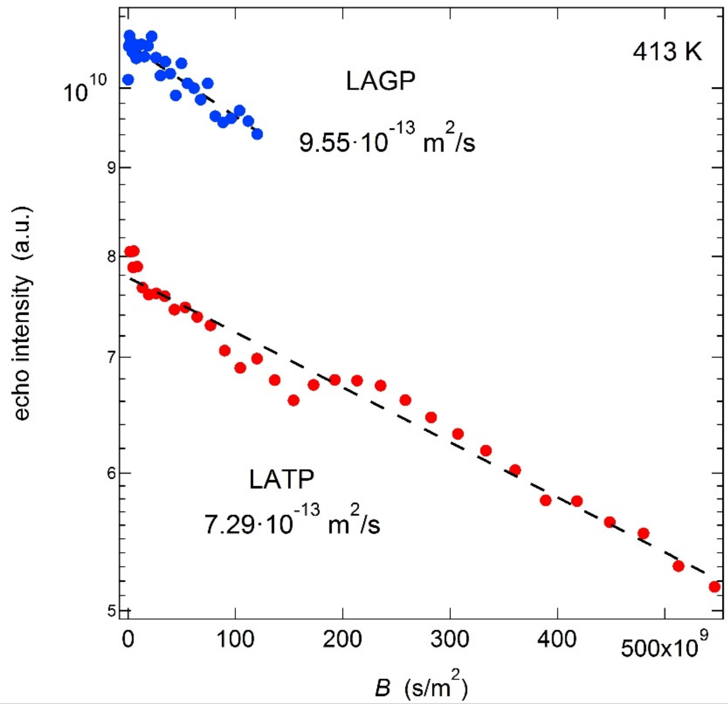


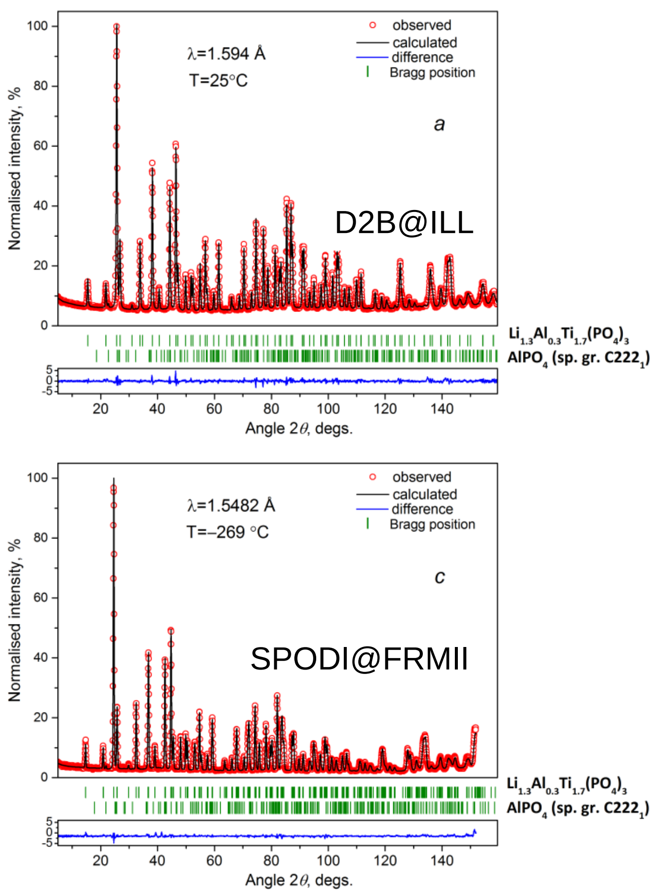
$$B = B_0 + \Delta B \cdot z$$

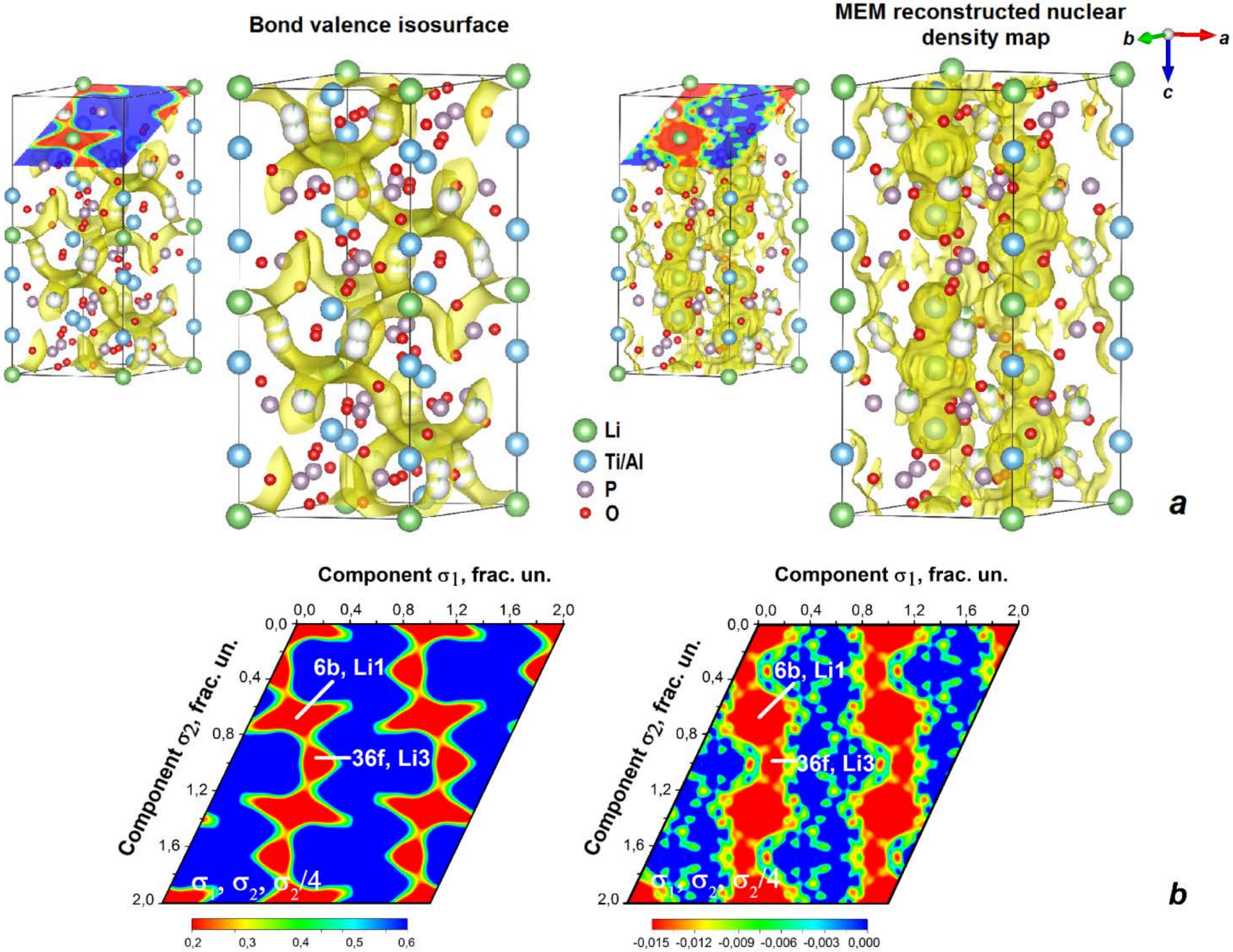


^{7}Li field gradient NMR



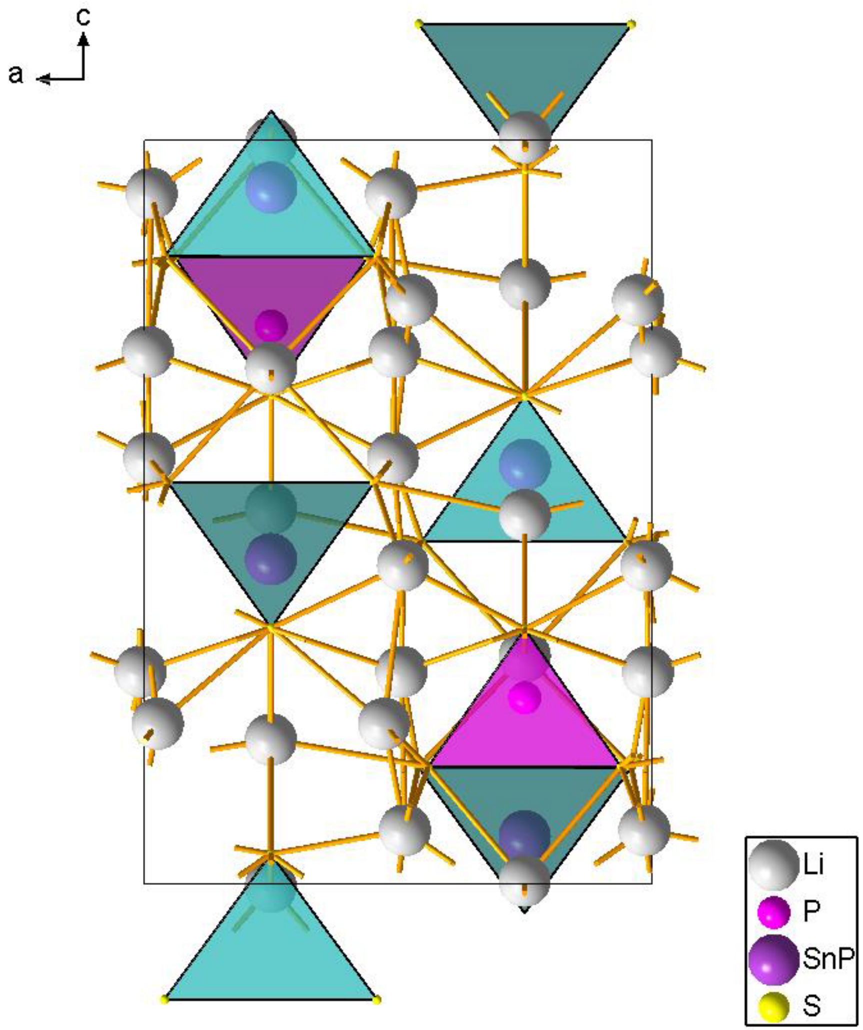
Lithium diffusion in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$



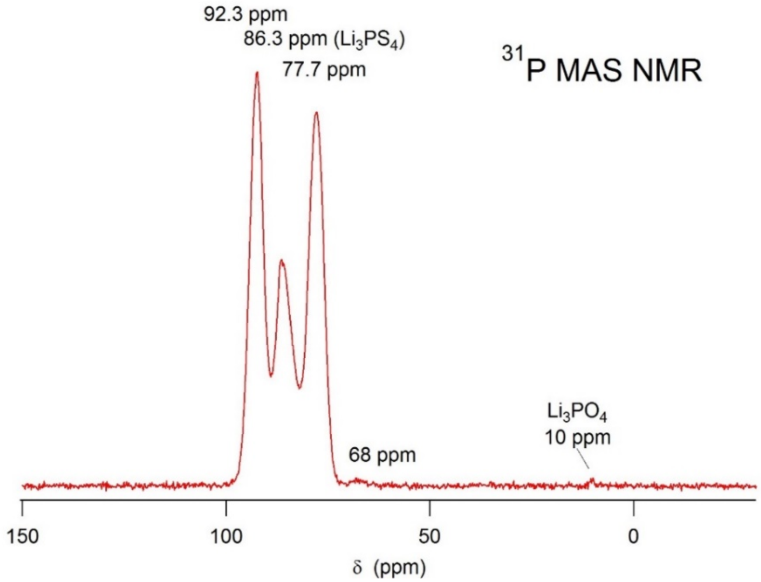


M. Monchak et al., Inorg. Chem. 55 (6) (2016) 2941-2945

Lithium diffusion in $Li_{10}SnP_2S_{12}$



^{31}P MAS NMR   (I = ½,

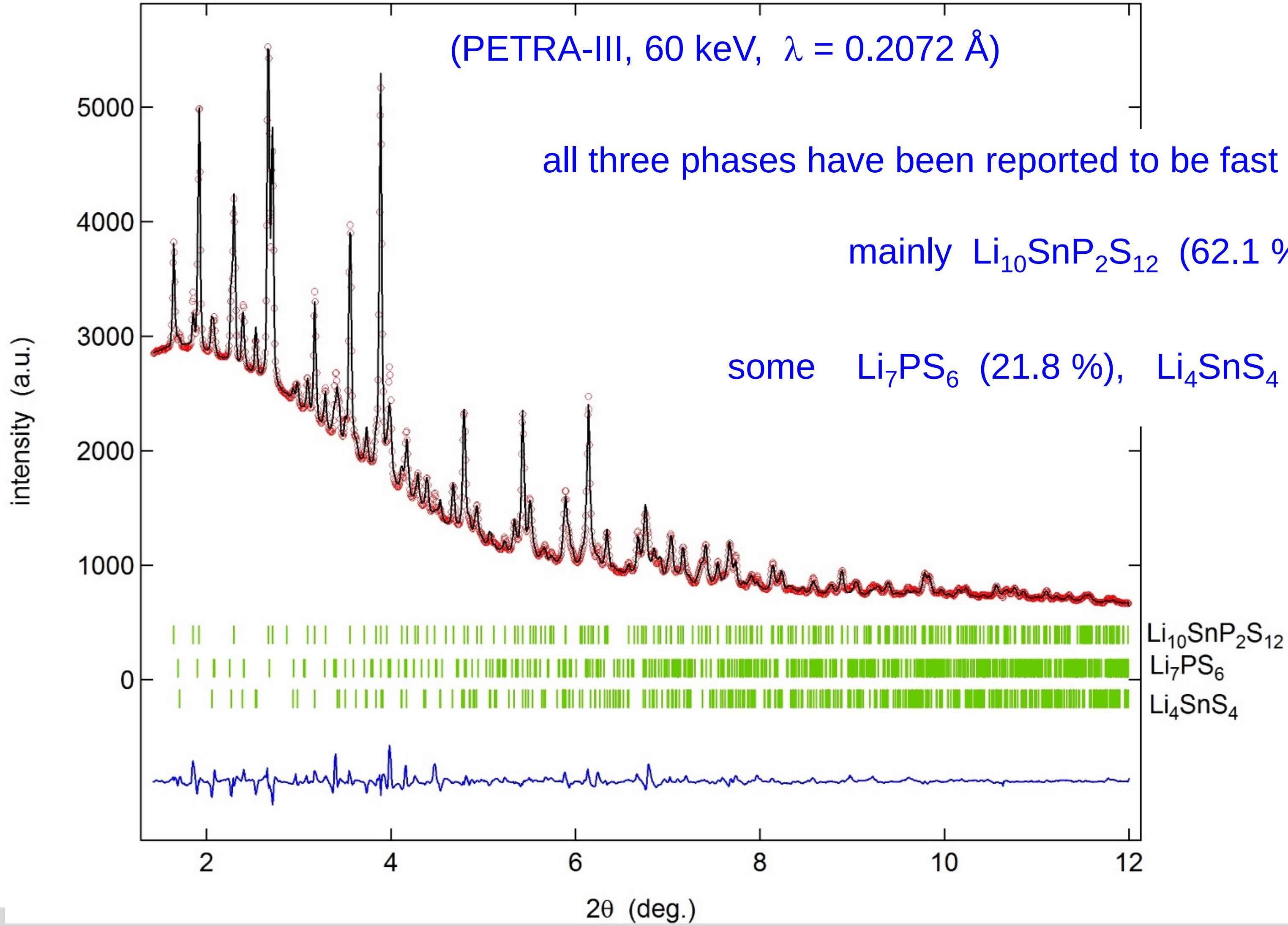


sulfidic environments

oxidic environments

P. Bron et al., *JACS* **135** (2013) 15694

Lithium diffusion in $Li_{10}SnP_2S_{12}$



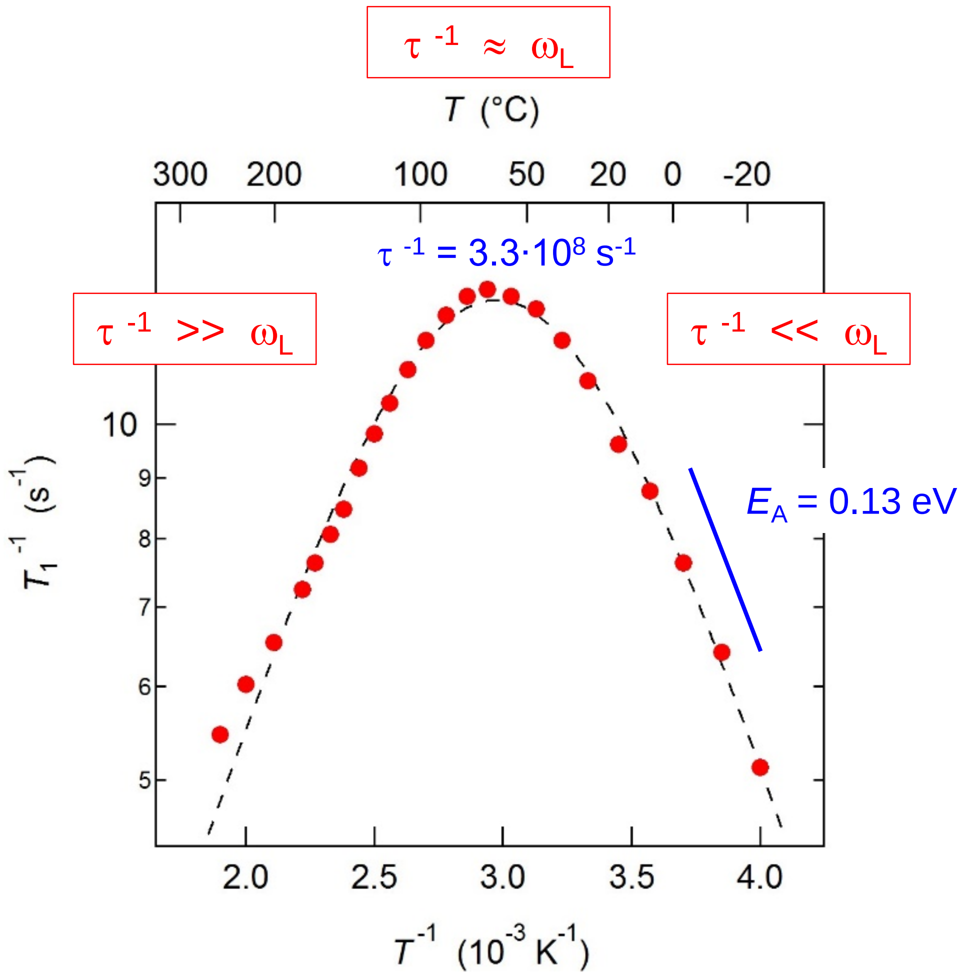
all three phases have been reported to be fast Li ion conductors

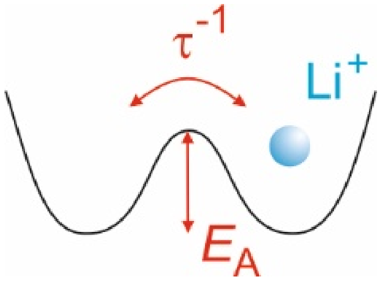
mainly $Li_{10}SnP_2S_{12}$ (62.1 %)

some Li_7PS_6 (21.8 %), Li_4SnS_4 (16.1 %)

Lithium diffusion in $Li_{10}SnP_2S_{12}$

^{7}Li NMR relaxation times T_1





$d_{Li\text{-}Li} \approx 2Å$

$D_{Li} = 3.3 \cdot 10^{-12}$ m²/s (at 336 K)

$\sigma_{Li} = 3.8$ mS/cm (at 336 K)

Conclusions

Karlsruhe Institute of Technology

- Structure-property relationships in solid electrolytes are at present a primary topic for the combination of neutron diffraction, NMR spectroscopy and DFT calculations.
- Electronic and ionic transport have to be considered in composite electrodes.
- Different behaviour of solid electrolytes needed in the separator layer and a composite electrode.
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- „Coatings“ versus „contacts“ challenge → coating on electrode level.
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Acknowledgement

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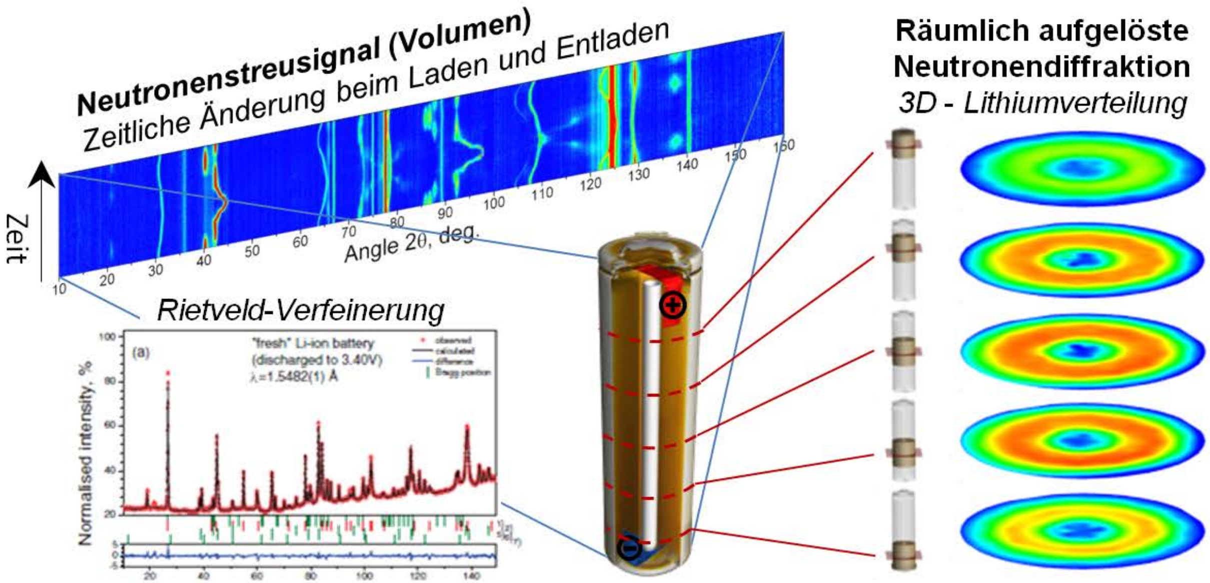
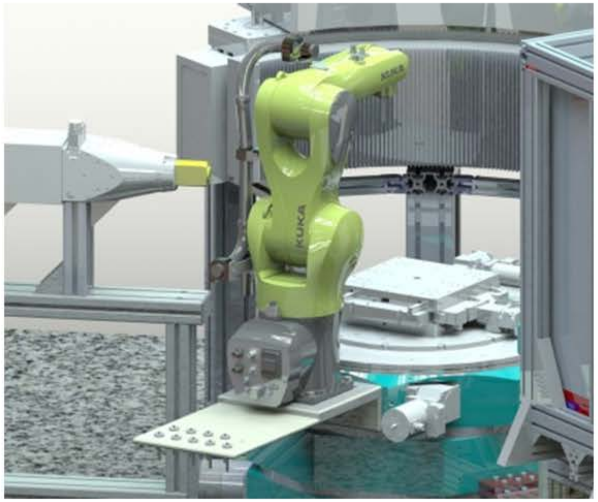
ERWIN: **E**nergy **R**esearch **Wi**th **N**eutrons (at FRM II in Garching)



ERWIN CAD Simulation



Thanks!

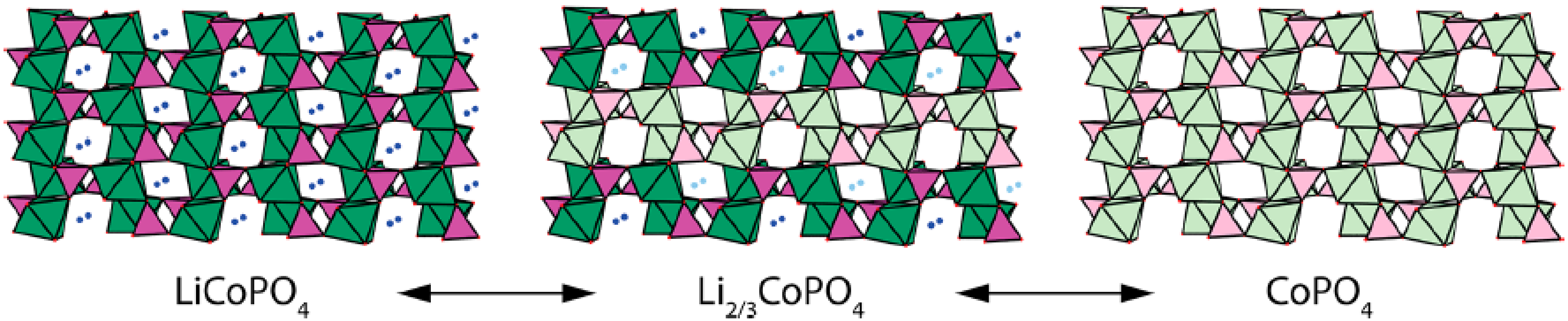
Neutron diffraction on solid-state battery materials

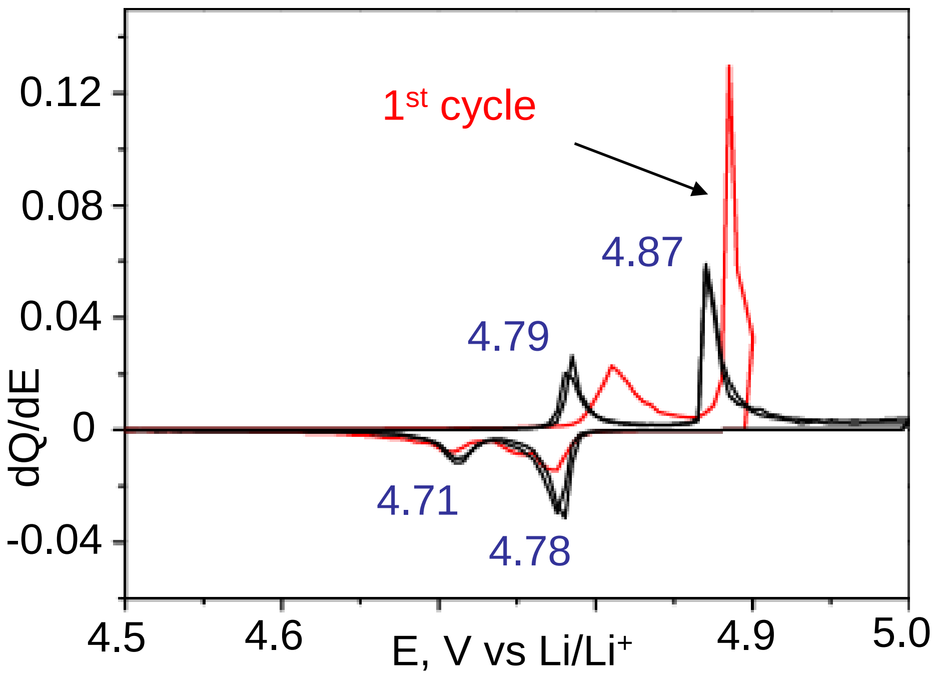
Helmut Ehrenberg, Anatoliy Senyshyn, Mykhailo Monchak,
Sylvio Indris, Joachim Binder

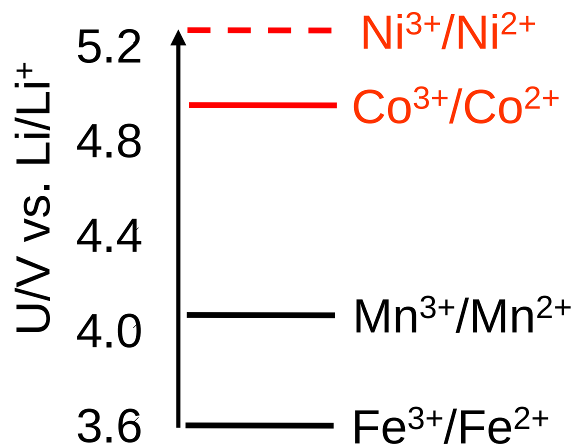
INSTITUTE for APPLIED MATERIALS – ENERGY STORAGE SYSTEMS & Inorganic Chemistry

- Introduction and challenges
- Popularities and capabilities of neutron diffraction
- Selected examples addressing
  - mechanical stress due to anisotropic strain in layered oxides
  - Li-ion conductivity in solid electrolytes
  - **chemical instability of the metastable highly-oxidized state „$CoPO_4$“**

Phosphoolivine $LiCoPO_4$ as positive electrodes







Phosphoolivines as positive electrodes: $LiMPO_4$

- Apparantly different, but identical space groups:
  - Pnma: a > b > c, (a=10.201 Å, b= 5.923 Å, c = 4.700 Å)
  - Pbnm: „cab“ (permutation of axes)
  - Pmnb: „bac“
- $LiCoPO_4$: 2-step mechanism with an intermediate phase Li_zCoPO_4
  - From lattice parameters: z=0.7(1)

    Bramnik et al., Chem. Mater. 5 (2007) 357

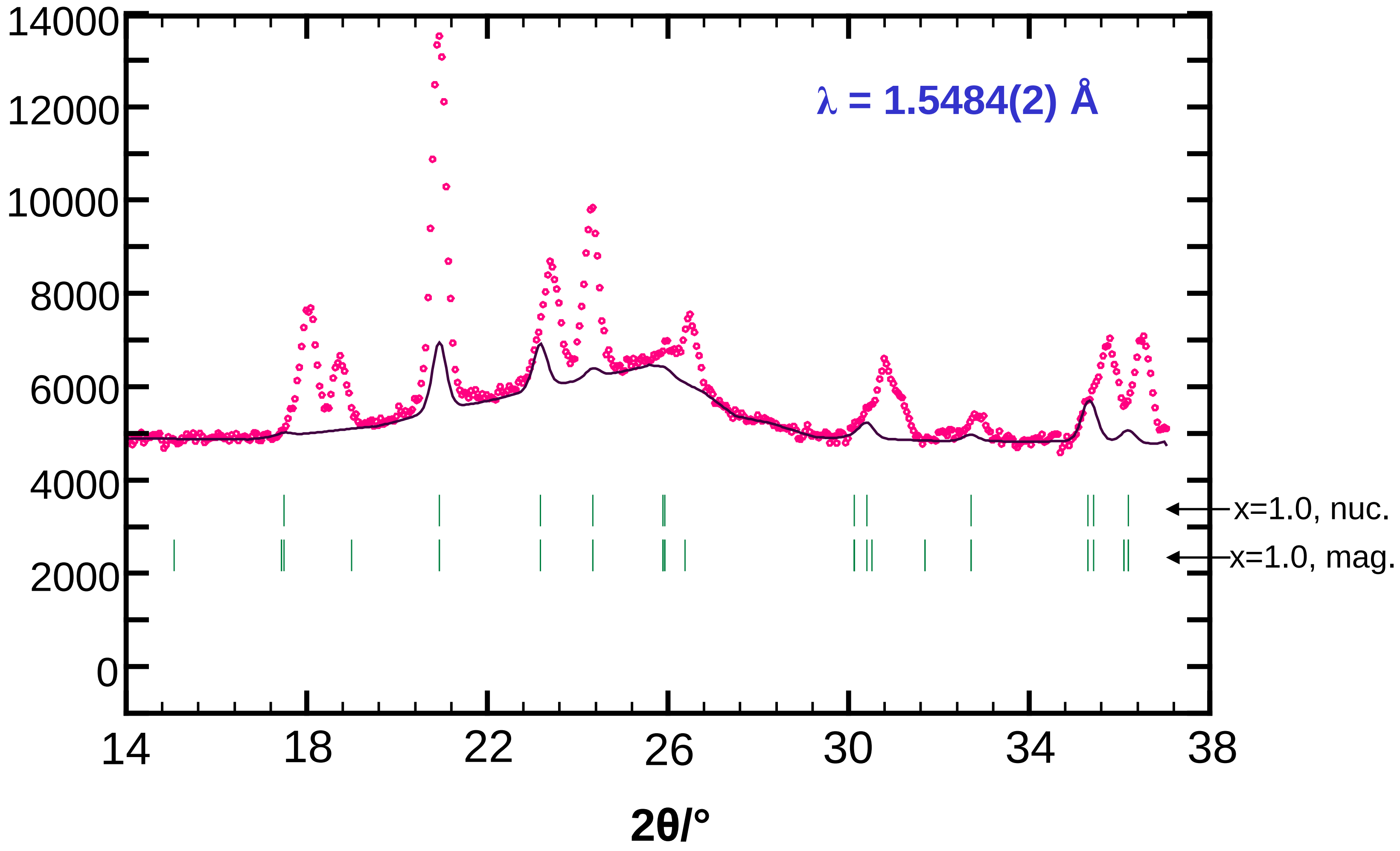
  - From Rietveld refinements, based on NPD: z=0.6(1)

    Ehrenberg et al., Solid State Sciences 11 (2009) 18

  - From ^{31}P and ^{7}Li NMR spectroscopy: z=⅔

    Kaus et al., J. Phys. Chem. C 118 (2014) 17279

Neutron diffraction on „$Li_{0.2}CoPO_4$“



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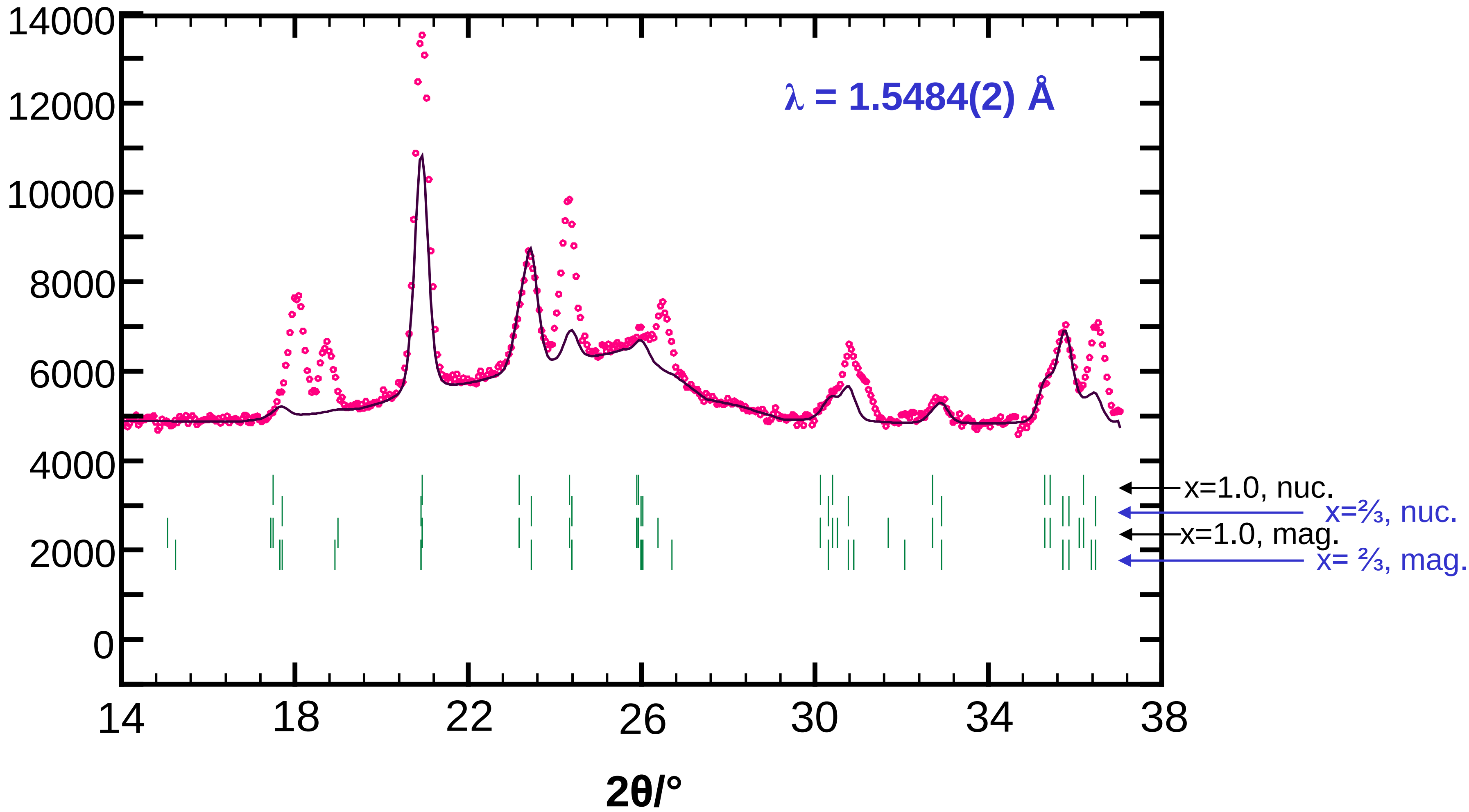

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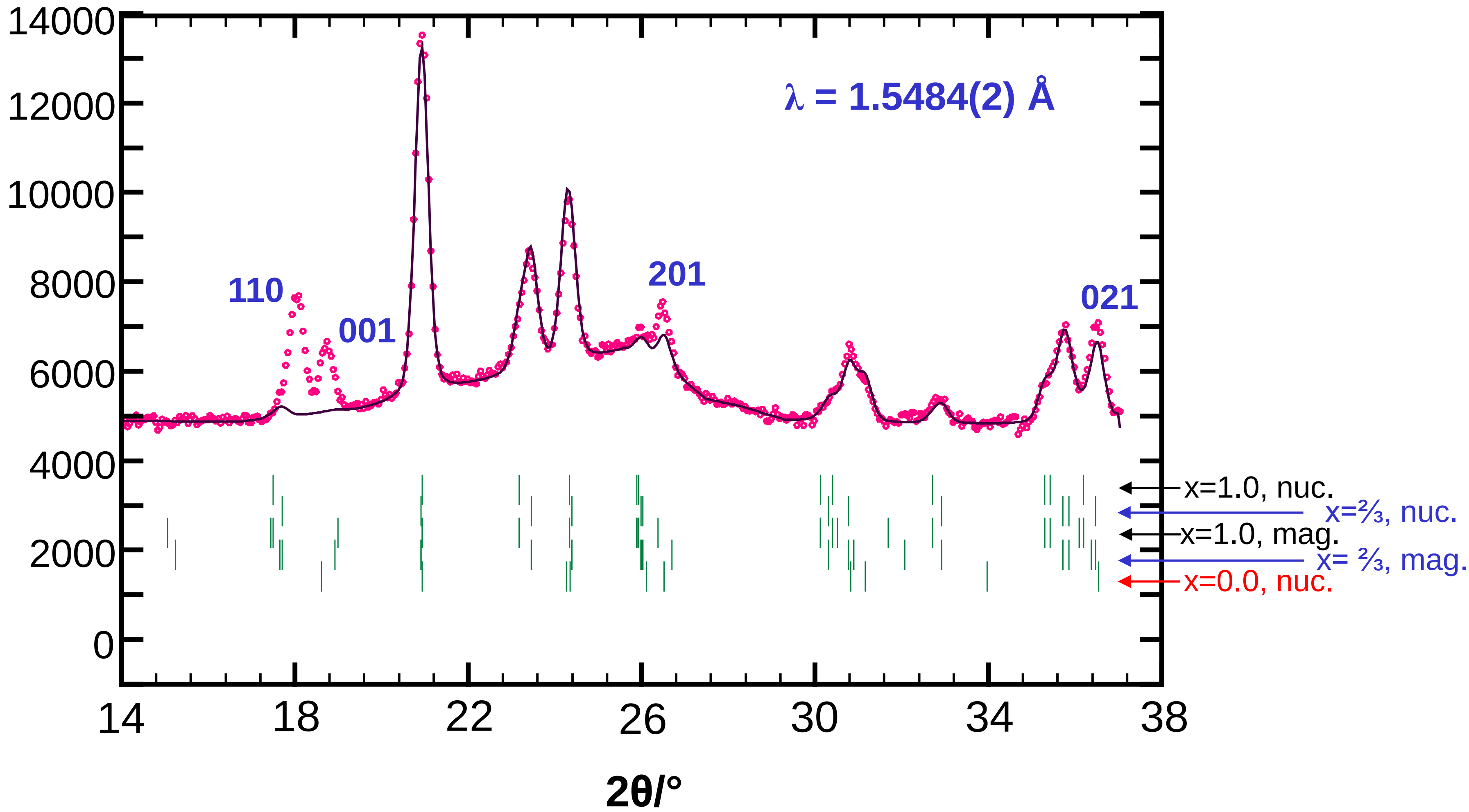

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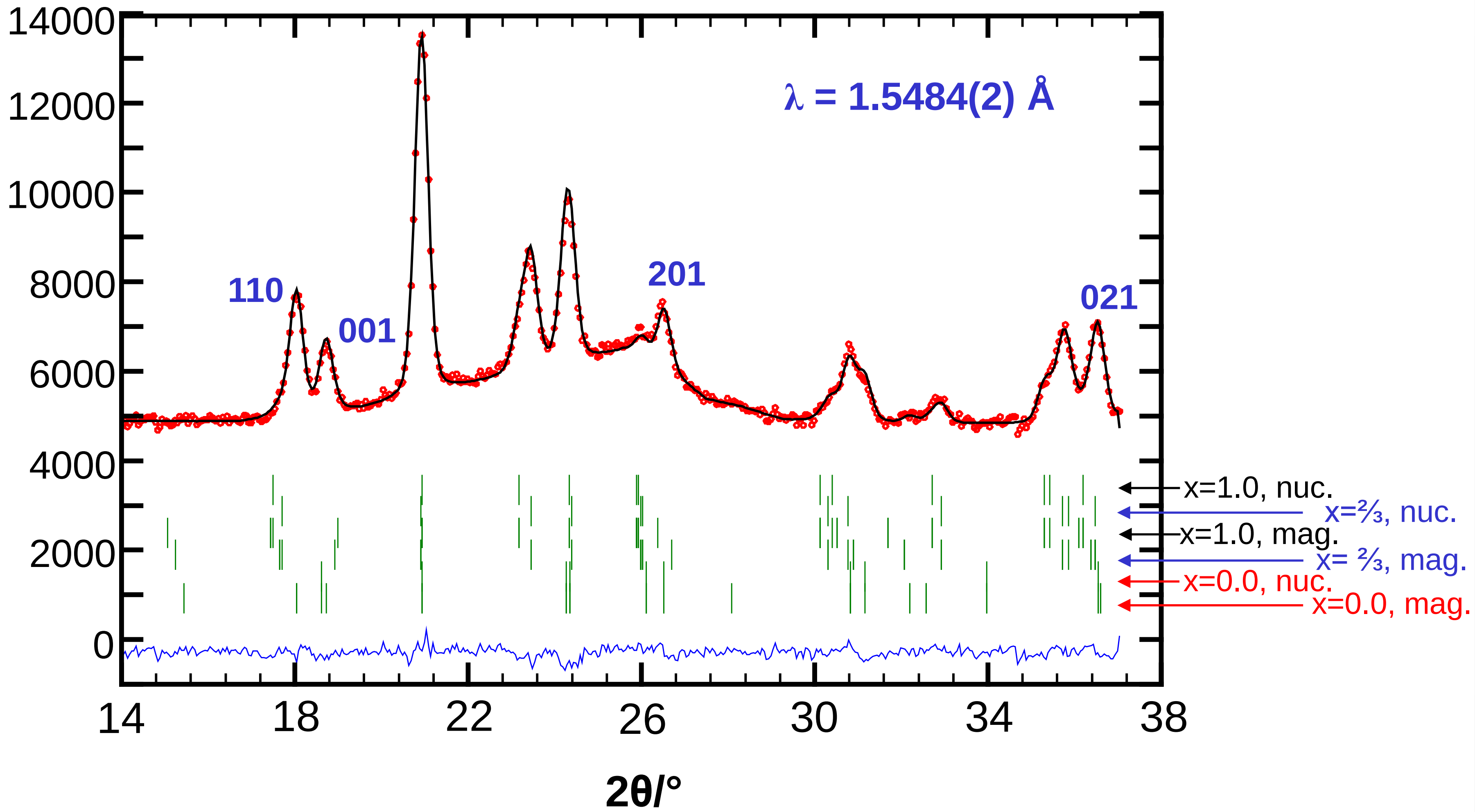

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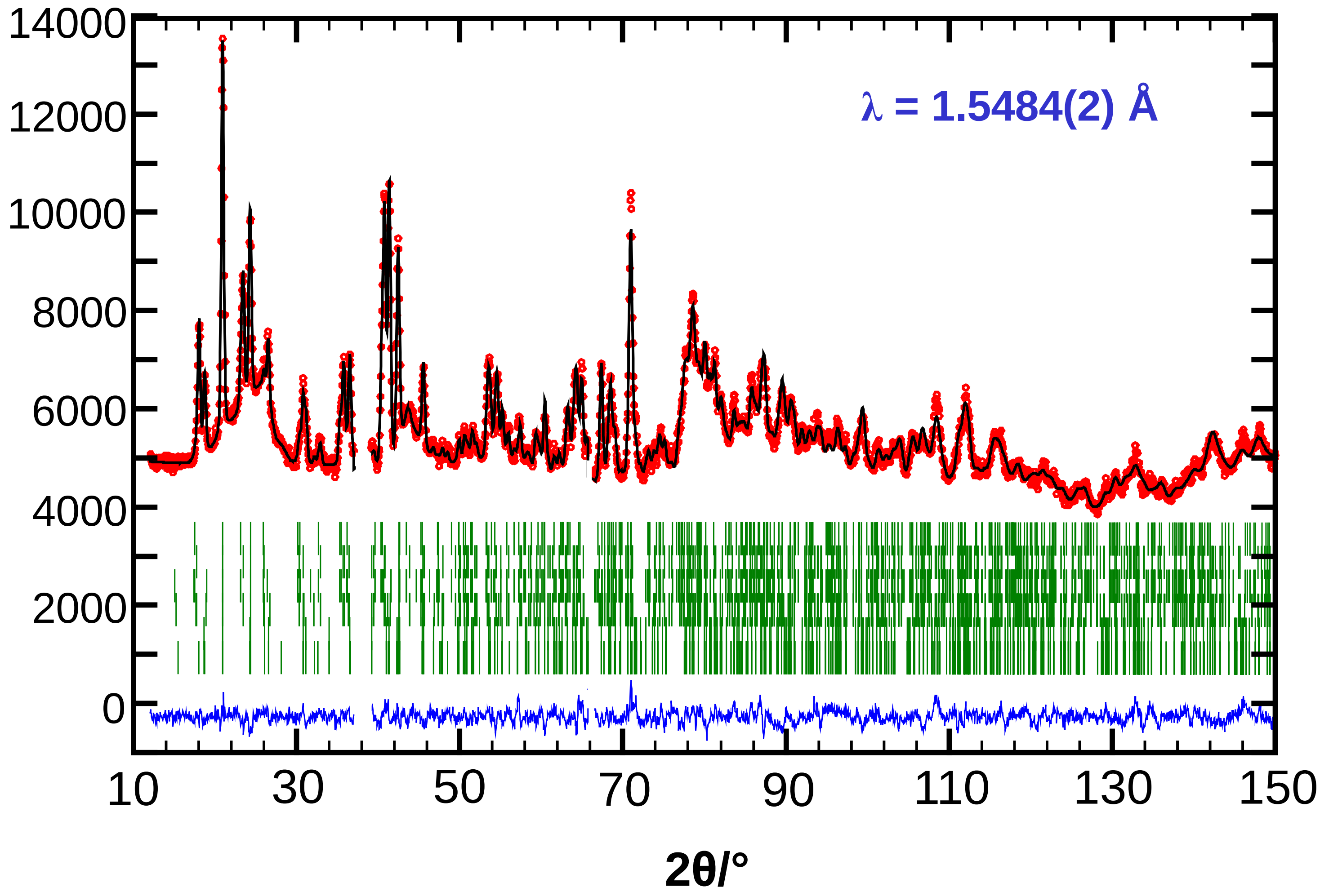
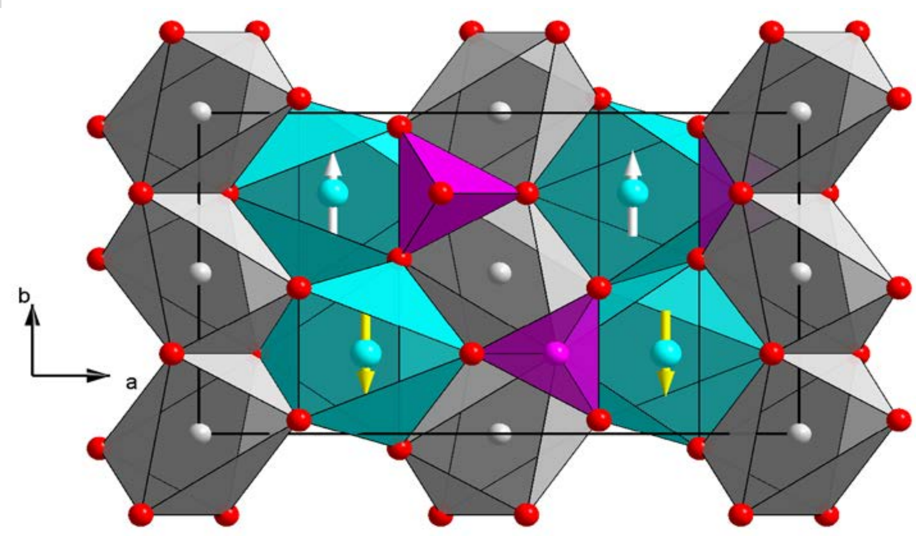
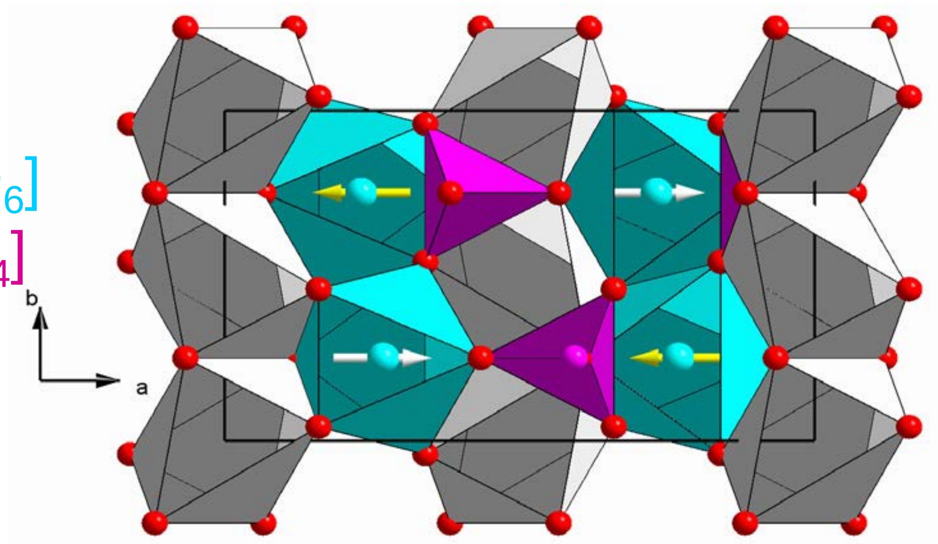


Magnetic structures of $LiCoPO_4$ and $CoPO_4$



$[CoO_6]$
$[PO_4]$



$[LiO_6]$

$LiCoPO_4$

collinear antiferromagnetic

$\mu_x=3.2(1)\mu_B$, $\mu_z=0.2(7)\mu_B$

$CoPO_4$ $[V_{Li}O_6]$

weak ferromagnetic z-component

$\mu_x=3.1(1)\mu_B$, $\mu_z=0.1(7)\mu_B$

„high-spin“ state of Co^{3+} in $CoPO_4$ → instability in the charged state

•in air •at elevated temperature •self discharge •poor cycle stability •slow kinetics

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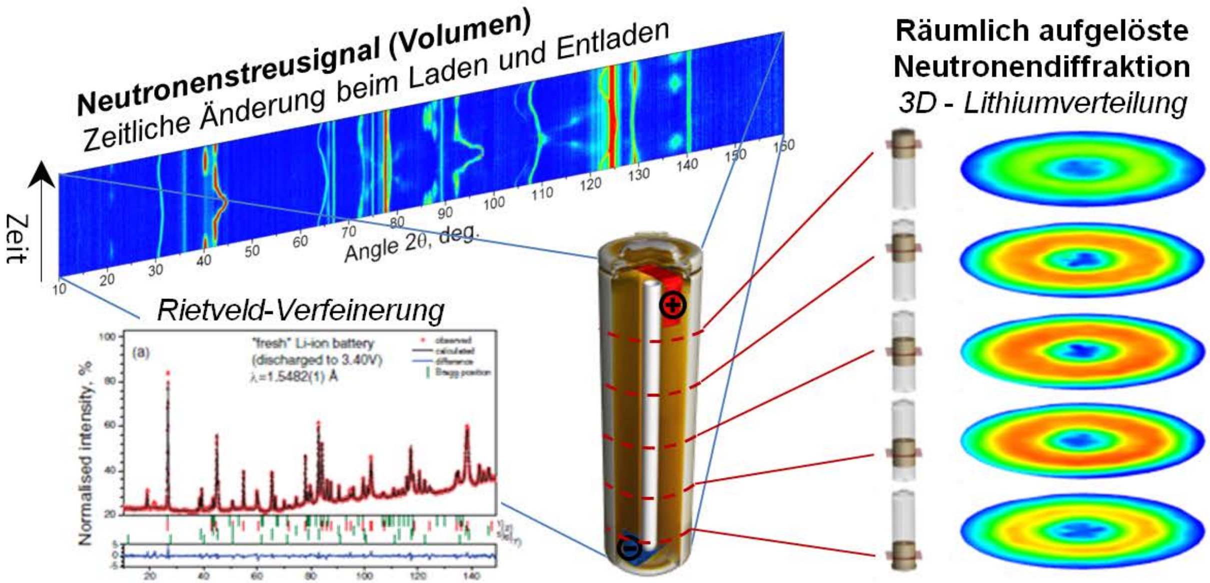

ERWIN CAD Simulation