Particle Size Effects in Lithium ion batteries

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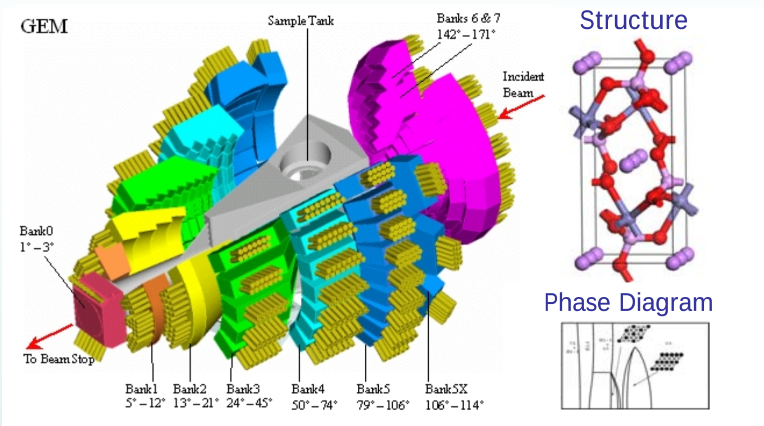
Fundamental aspects of Materials and Energy (FAME)
Radiation, Radionuclides and Reactors (R^3)
Faculty of Applied Sciences
Delft University of Technology, The Netherlands

TUD, TNW, R3, FAME

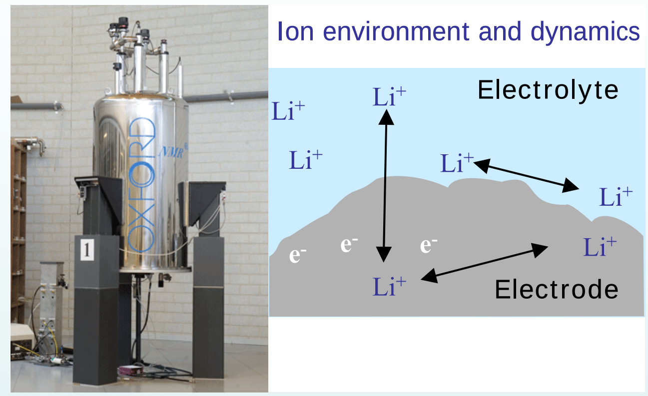
prof. Ekkes H. Brück:	Magnetocaloric materials
prof. Fokko M. Mulder:	H-Storage, Fuel-cell, Li-ion and Solar Cell materials
Niels H. van Dijk	Structural and Magnetic materials
Stephan W.H. Eijt:	H-Storage, Solar cell materials
Marnix Wagemaker	Li-ion, H-storage materials

Techniques

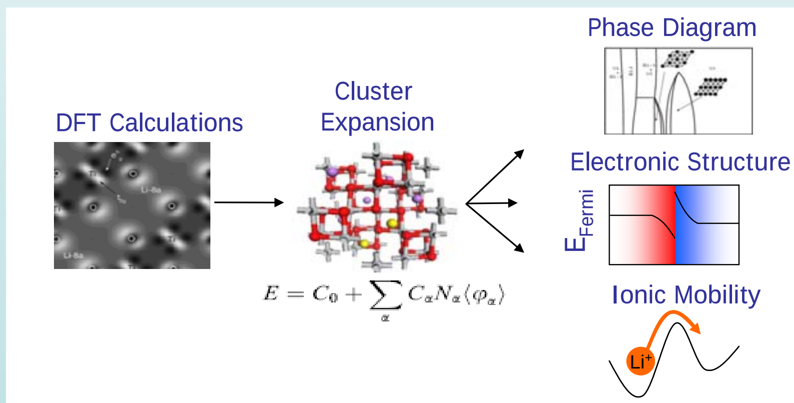
Neutron Scattering



Nuclear Magnetic Resonance



Density Functional Theory



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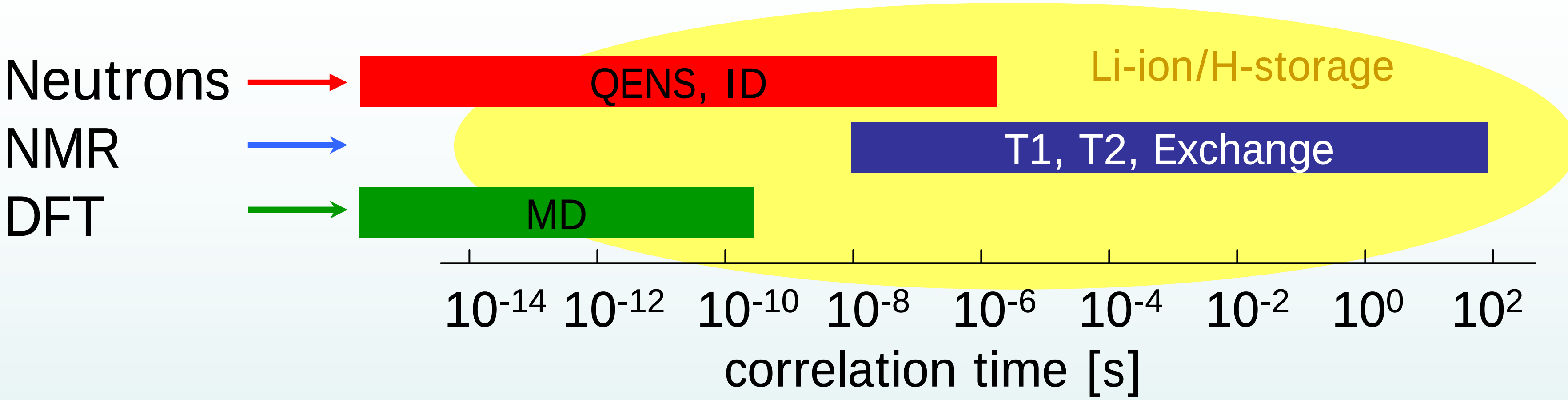
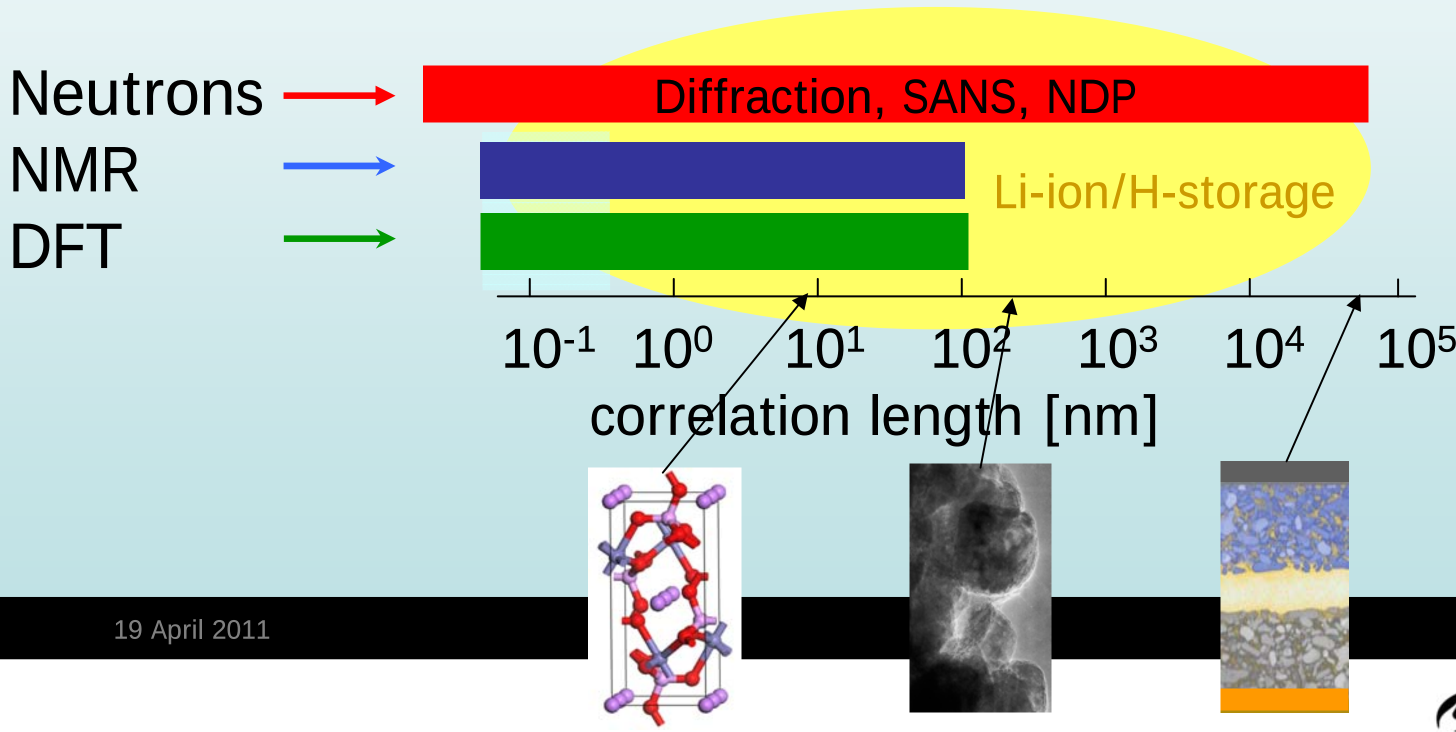
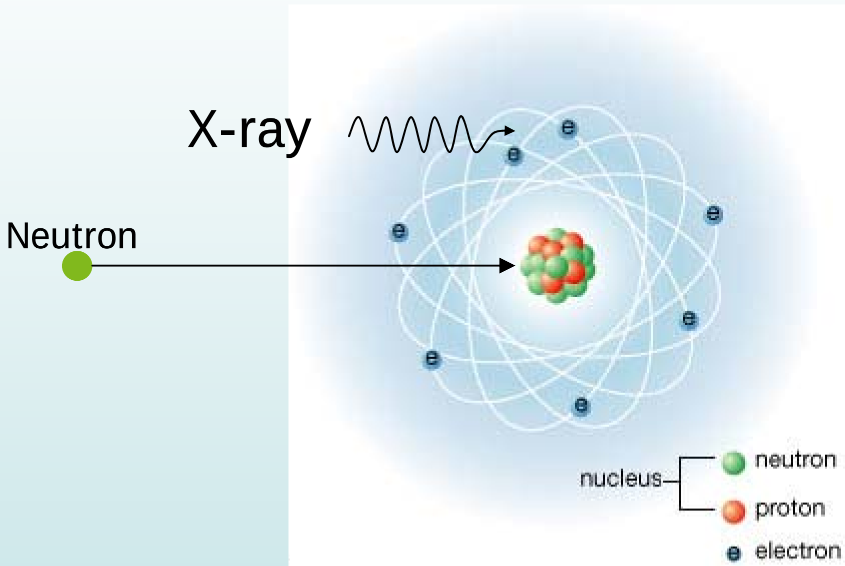
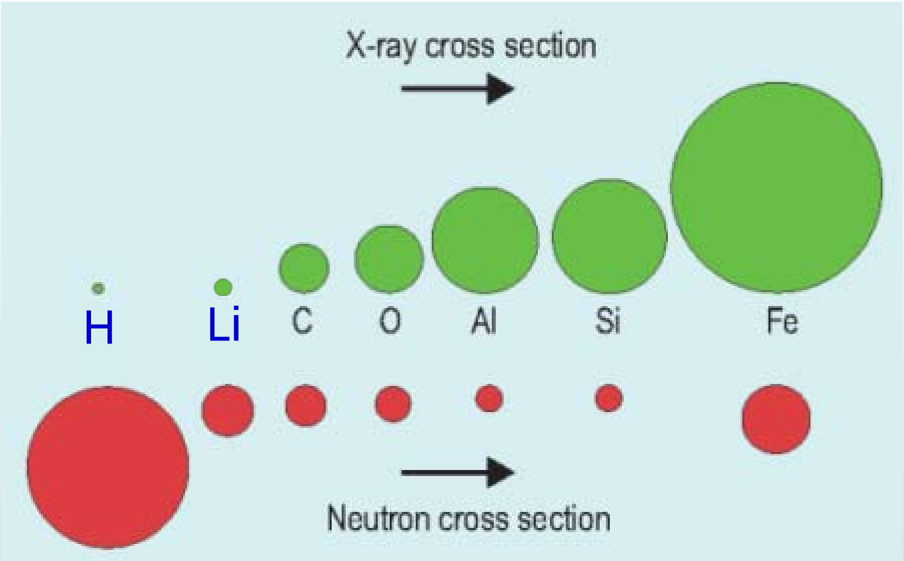
Techniques


Neutrons
NMR
DFT
QENS, ID
T1, T2, Exchange
MD
Li-ion/H-storage
10-14 10-12 10-10 10-8 10-6 10-4 10-2 100 102
correlation time [s]


Neutrons
NMR
DFT
Diffraction, SANS, NDP
Li-ion/H-storage
10-1 100 101 102 103 104 105
correlation length [nm]

Neutronen versus X-rays





Outline

Introduction Energy Storage Li-ion batteries
Why Nano electrode materials
Why not only Nano (impact porosity in electrodes)

Impact Interfaces in $LiFePO_4$

Impact Surfaces in $Li_4Ti_5O_{12}$

Conclusions

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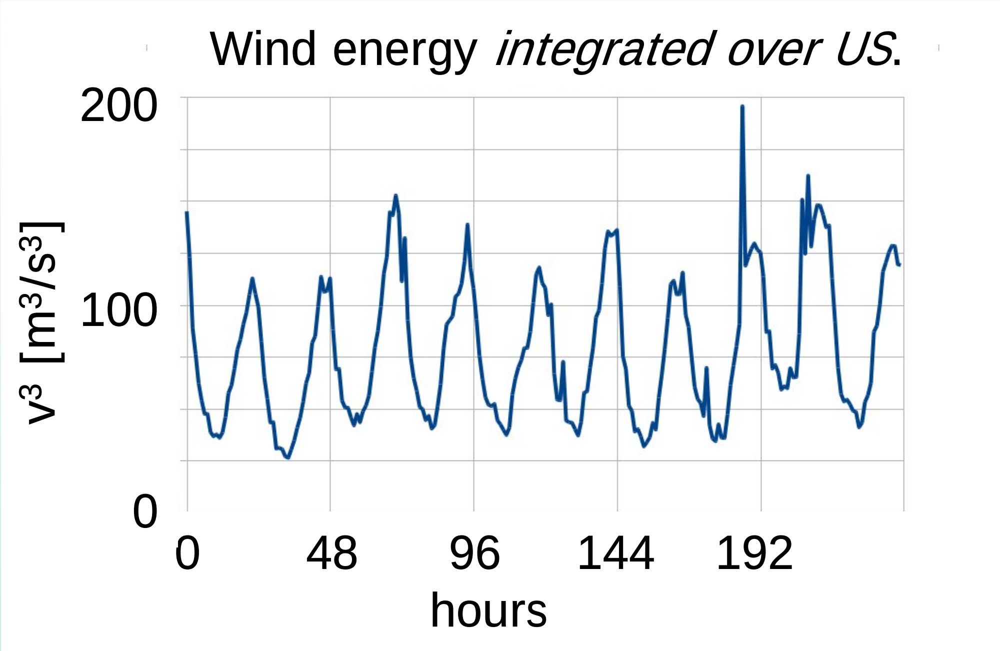
Need for Efficient Electricity Storage

Enabling renewables



Cheap efficient electricity storage
~ 3 x *less installed power!*

Efficient mobility

Range ~ 150 km
100% Charge ~ 8 hour
Li-ion battery weight ~ 250 kg

Required: 10 x energy density (comparable to gasoline)

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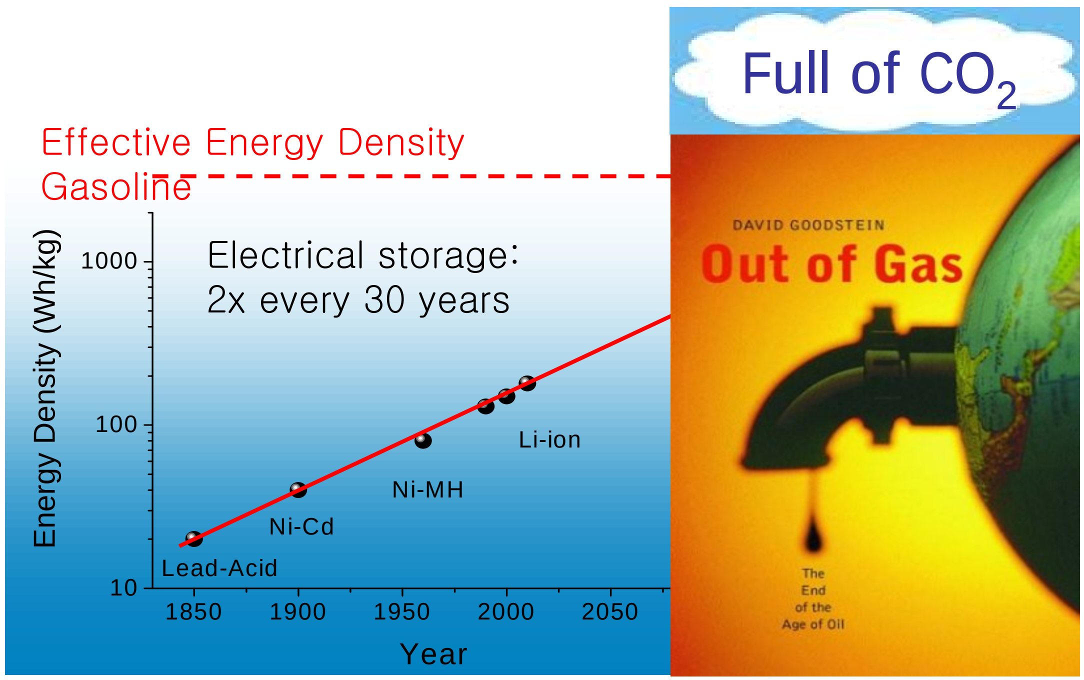
Energy storage for mobility

Energy density = Capacity density x Potential
Power density = Current density x Potential



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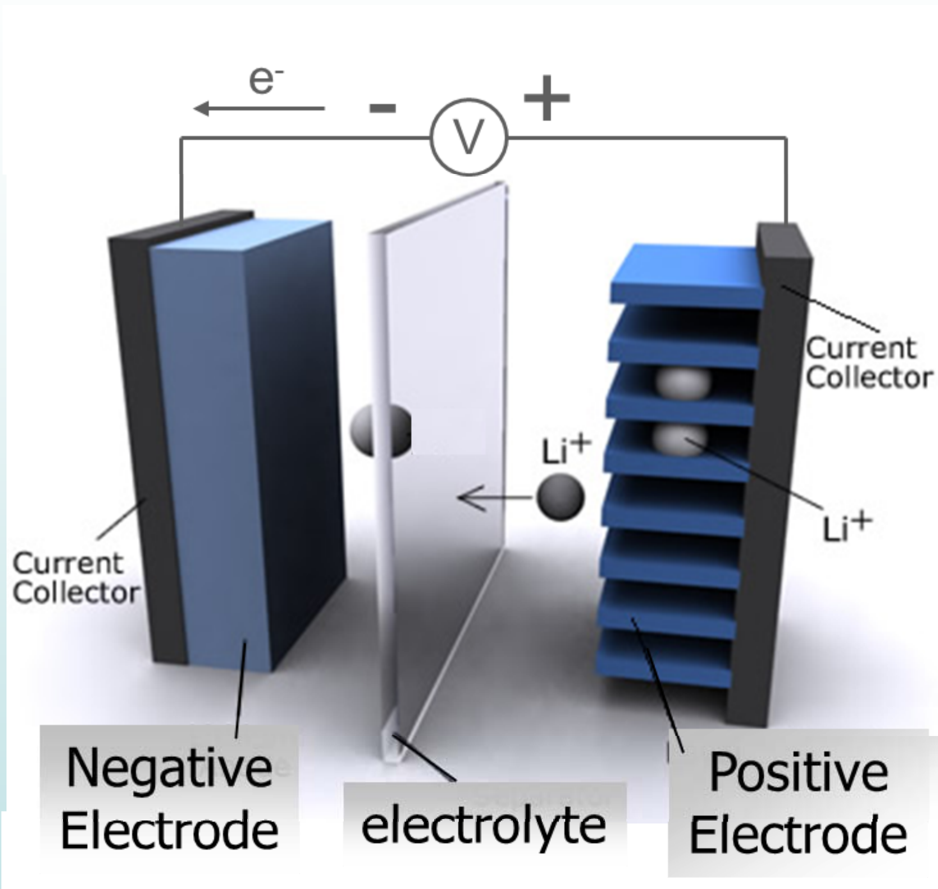
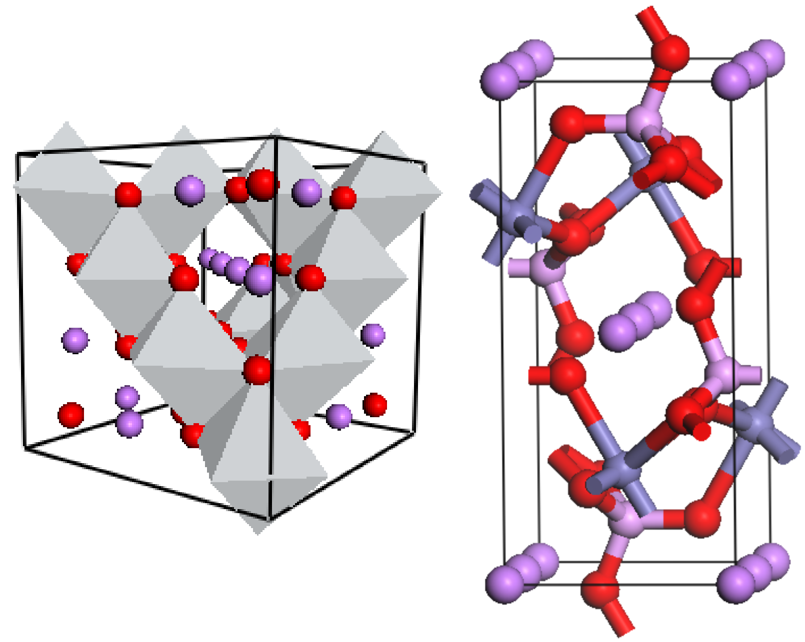
Li-ion batteries



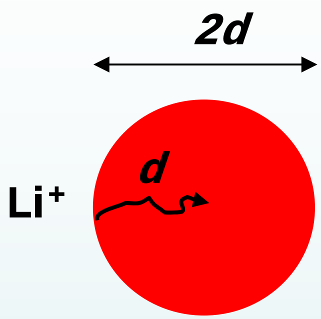
Electrode Materials

$Li_4Ti_5O_{12}$
1.6 V

$LiFePO_4$
3.6 V



Why Nano?

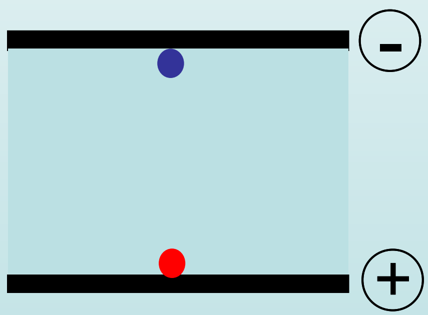


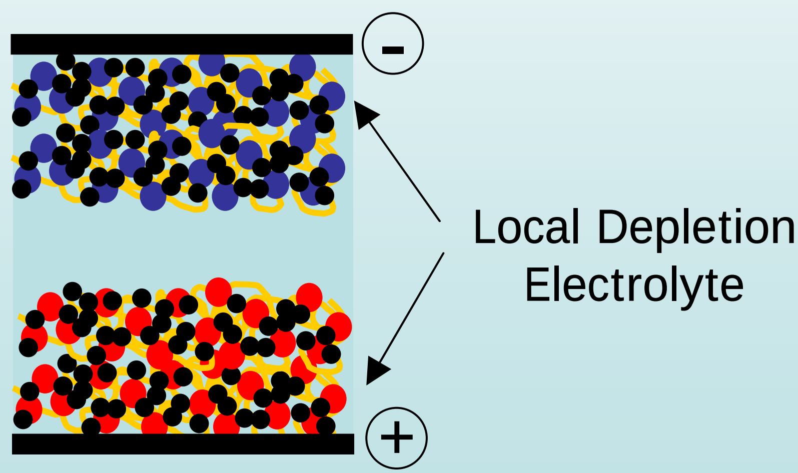
Diffusion time: $t \approx \dfrac{d^2}{\pi D}$

d = 1 μm
D = 10^{-12} cm^2/s ⇒ ***t = 53 min***

d = 43 nm
D = 10^{-12} cm^2/s ⇒ ***t = 6 s***

Charge battery in Seconds!





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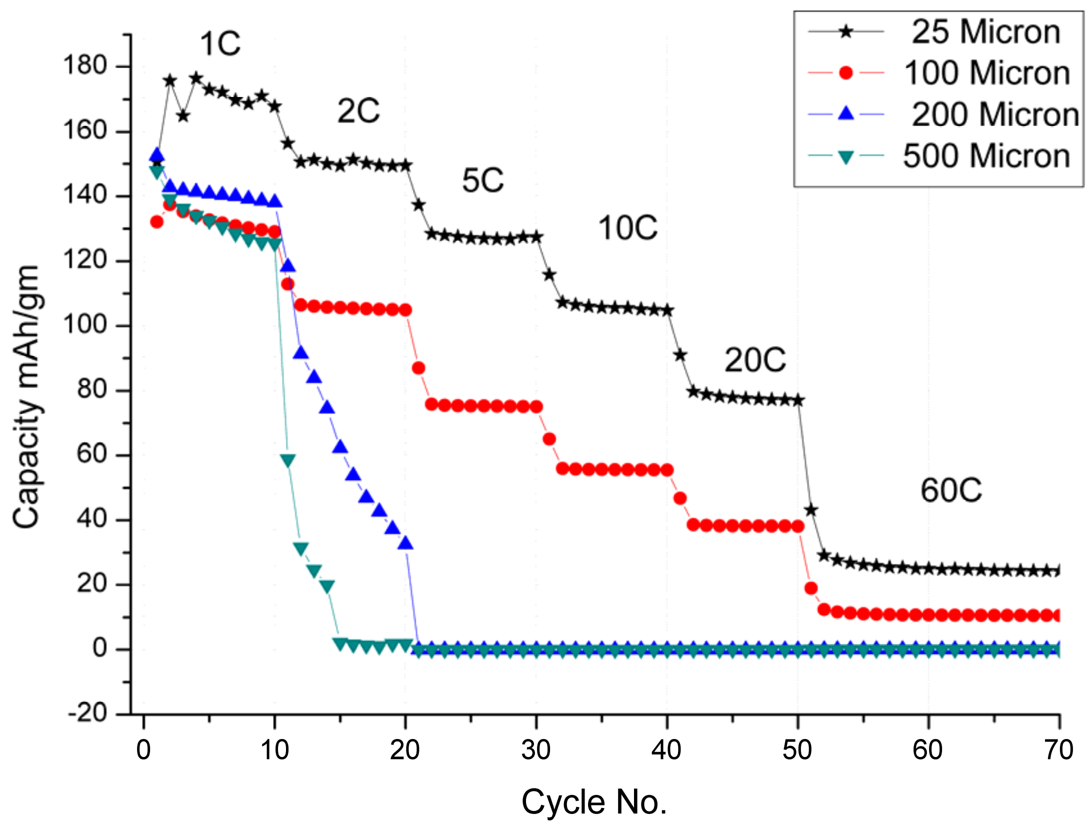
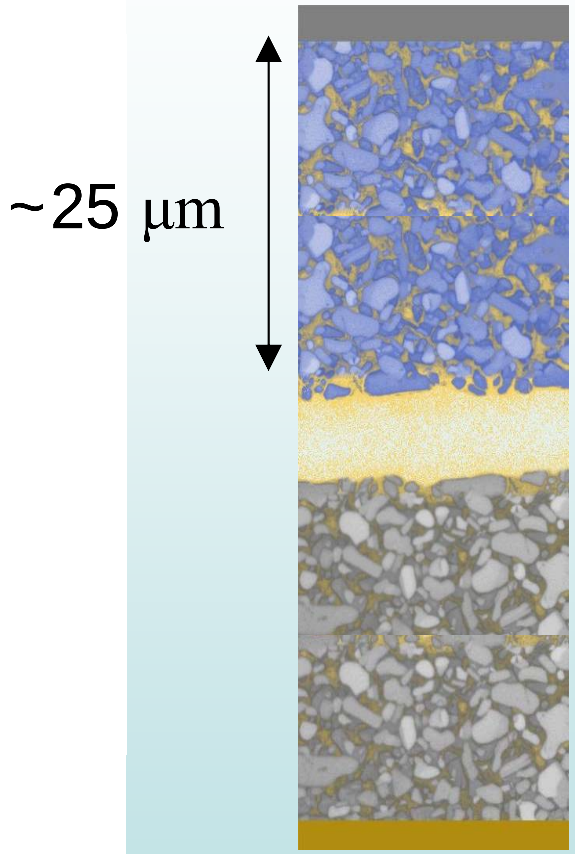
Vary electrode film thickness





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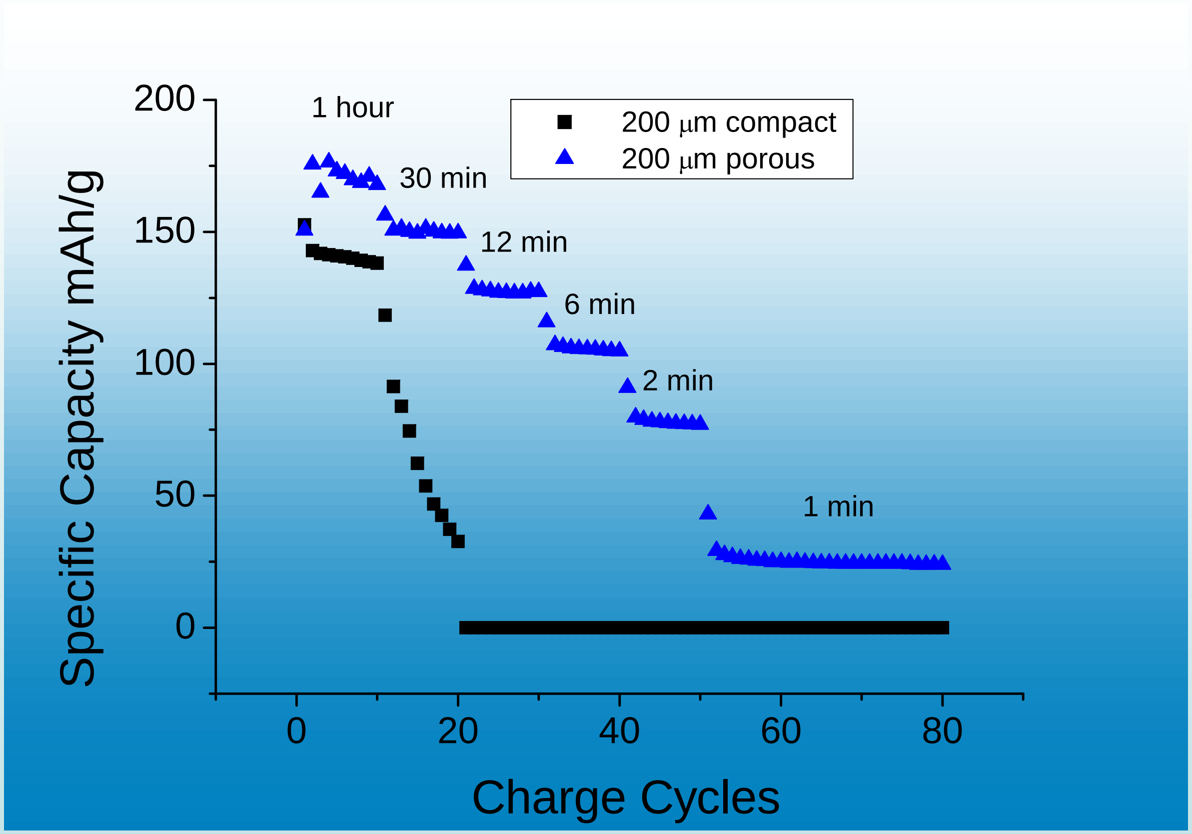
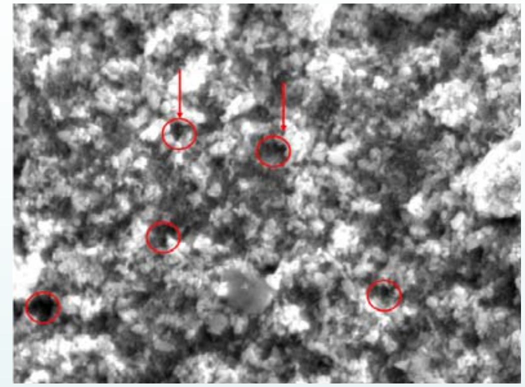
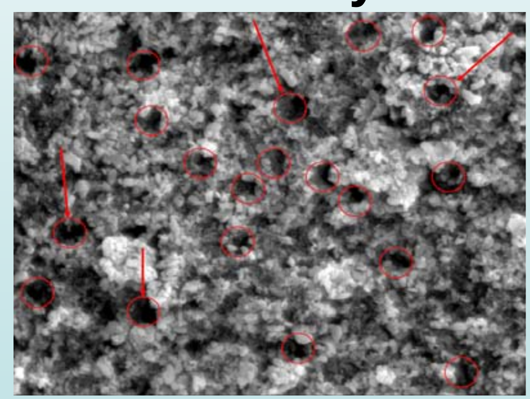
Impact of porosity



Compact



Add ~ 5% (volume) Porosity



1 μm

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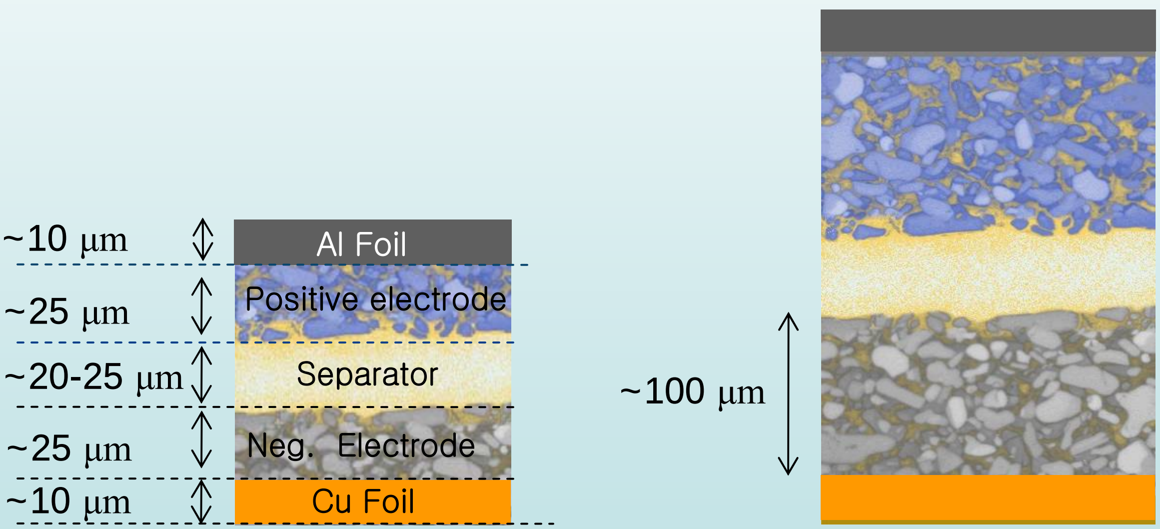
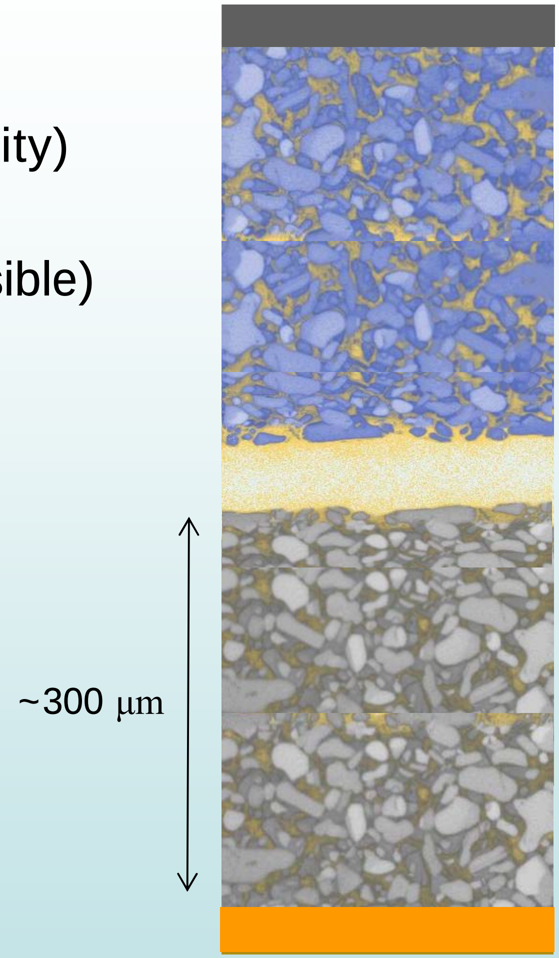
Impact of porosity

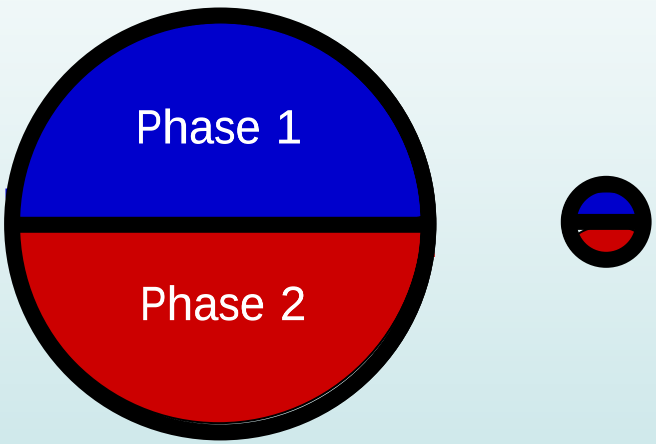
Porosity ⇨ Improve (dis)charge rate (power density)

Improve energy density (factor 2 possible)





Impact Particle size on Li-ion electrode properties



$LiFePO_4$: Impact Interface

$Li_4Ti_5O_{12}$: Impact Surface

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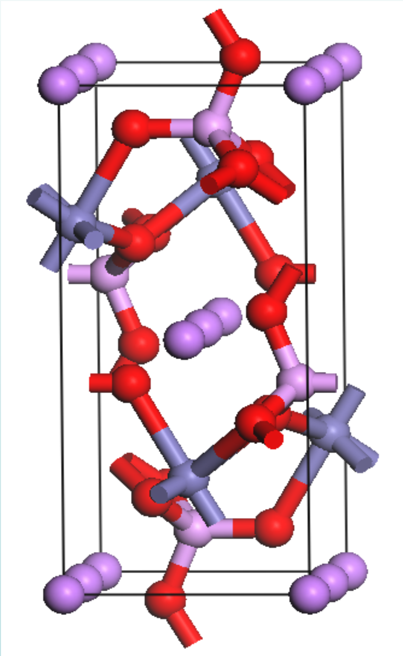
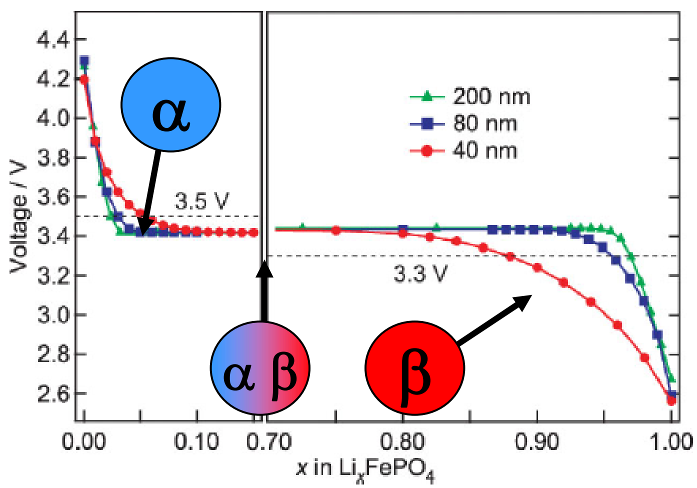
Nano effects $LiFePO_4$

$LiFePO_4$

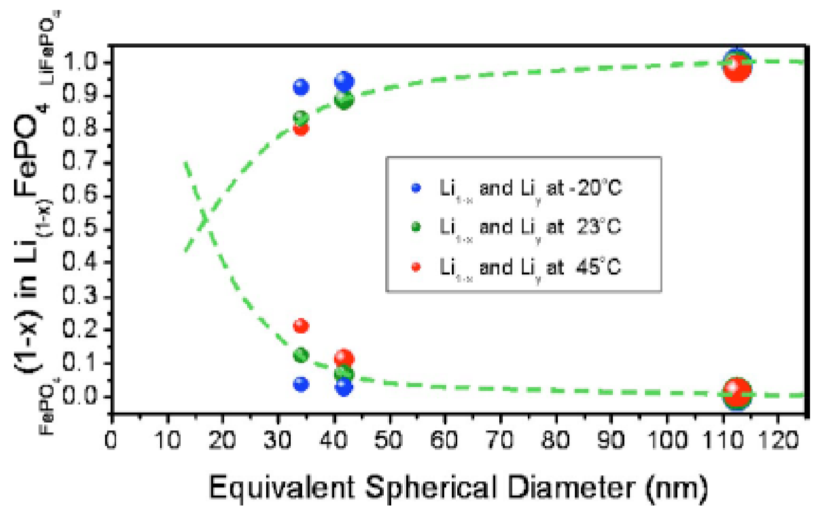


Impact nano size on material properties $LiFePO_4$

Shrinking miscibility gap with decreasing particle size



Source: Kobayashi et al, Adv. Funct. Mat. 2009, 19, 395



Source: Meethong et al, Electrochem Sol. State L. 2007, 10, A134

α FePO4

β LiFePO4

Shrinking miscibility gap?

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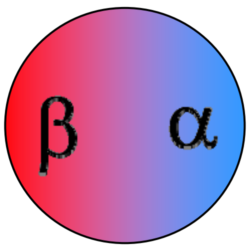
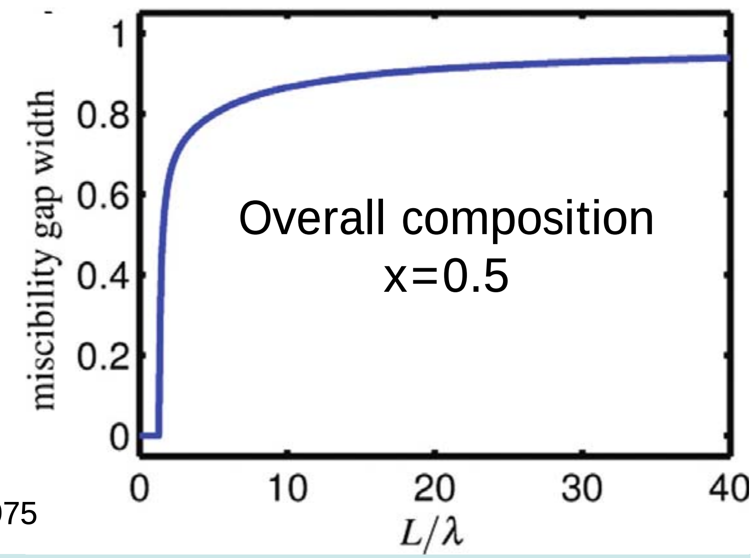
Impact nano size on material properties $LiFePO_4$

Diffuse Interface



$$G_{mix} = \int_V \left(g_{\text{hom}}(c) + \frac{1}{2}(\nabla c) \bullet K(\nabla c) \right) \rho dV$$

Cahn & Hilliard 1958

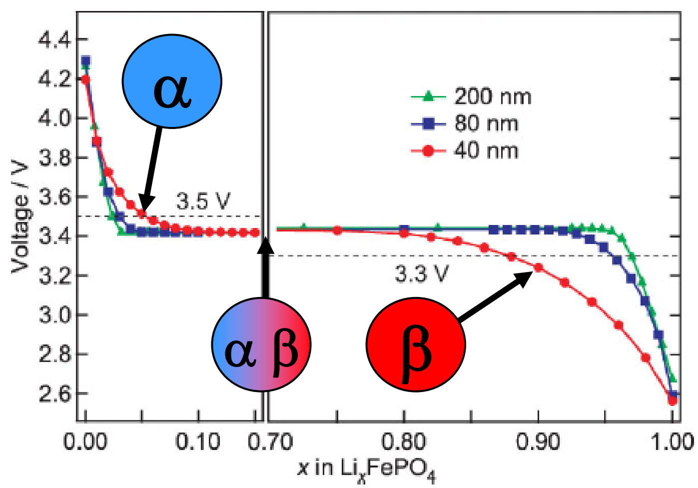


Source: Burch et al, Nano Let. 2009, 9, 3975

Calculations predict shrinking miscibility gap

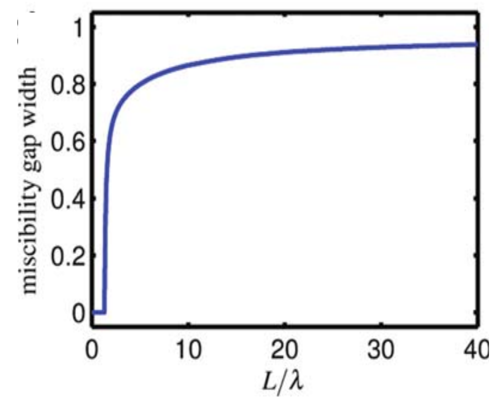
Question and Goal

Shrinking miscibility gap with decreasing particle size



Source: Kobayashi et al, Adv. Funct. Mat. 2009, 19, 395

Diffuse interface model predicts also shrinking miscibility gap due to the interface



Source: Burch et al, Nano Let. 2009, 9, 3975

Question

Can we directly observe the shrinking miscibility gap?

Goal

(1) Impact size and overall composition on the solubility limits

(2) Compare results with prediction diffuse interface model

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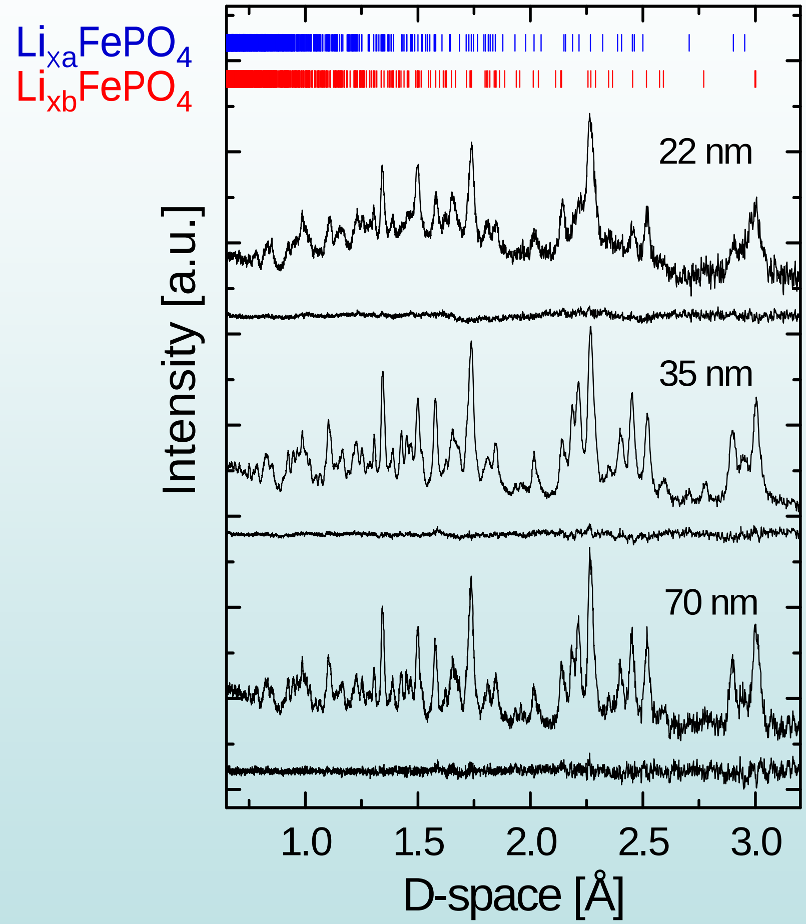
Accurate Li-occupancies: Neutron diffraction nano $LiFePO_4$



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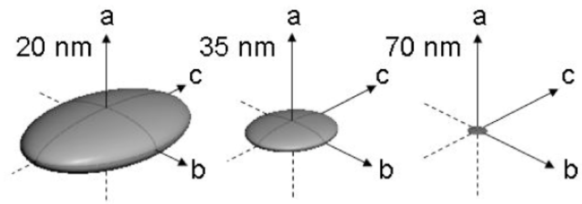
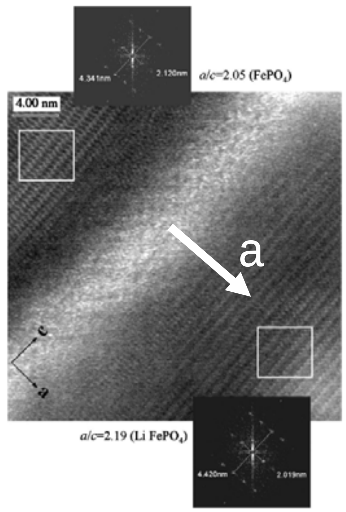
Anisotropic strain

Anisotropic strain parameters



$Li_{xa}FePO_4$



$Li_{xb}FePO_4$

Source: Chen et al, ESSL 2008, 9, A295

Coexisting $Li_{xa}FePO_4$ with $Li_{xb}FePO_4$

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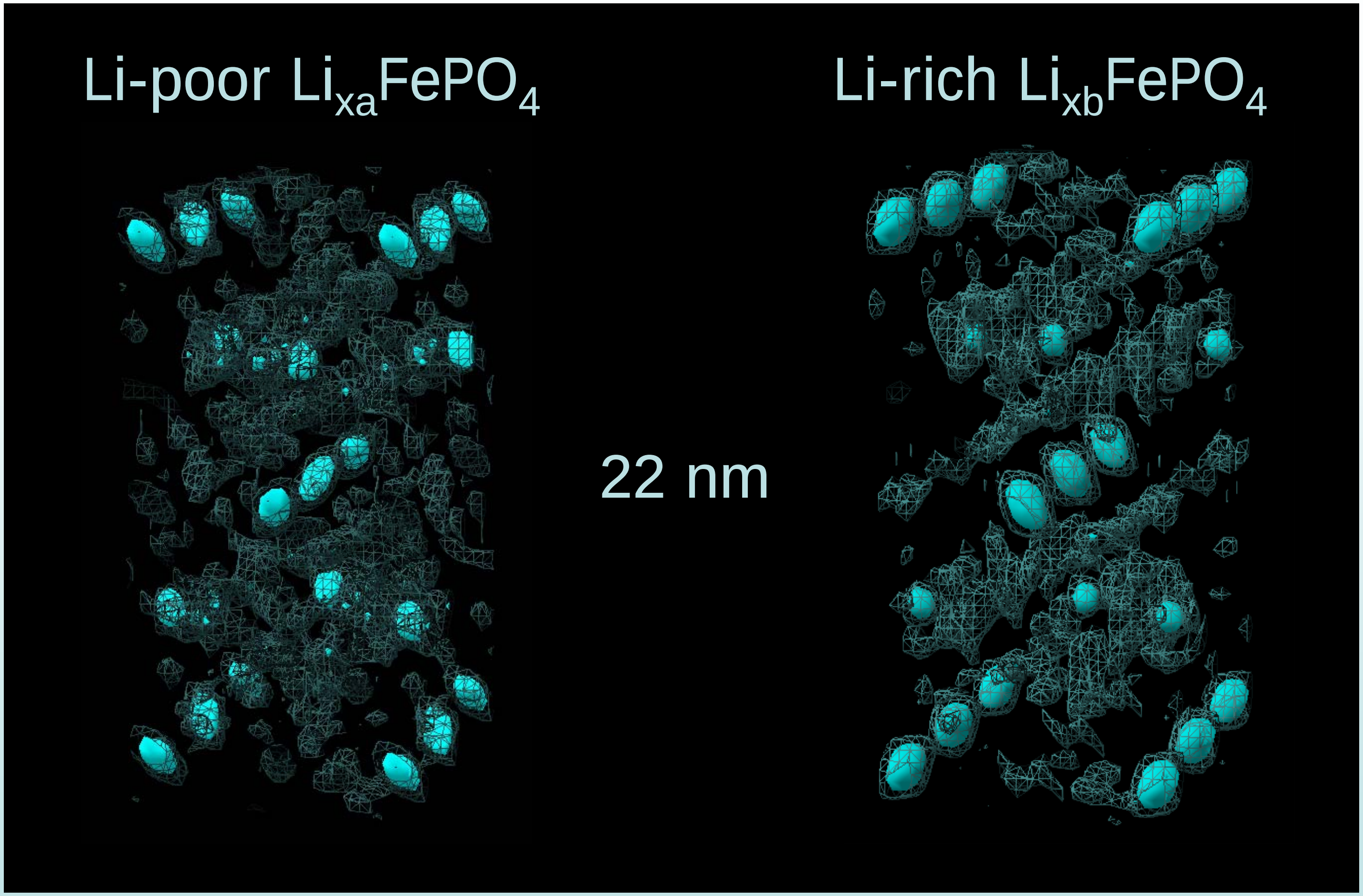
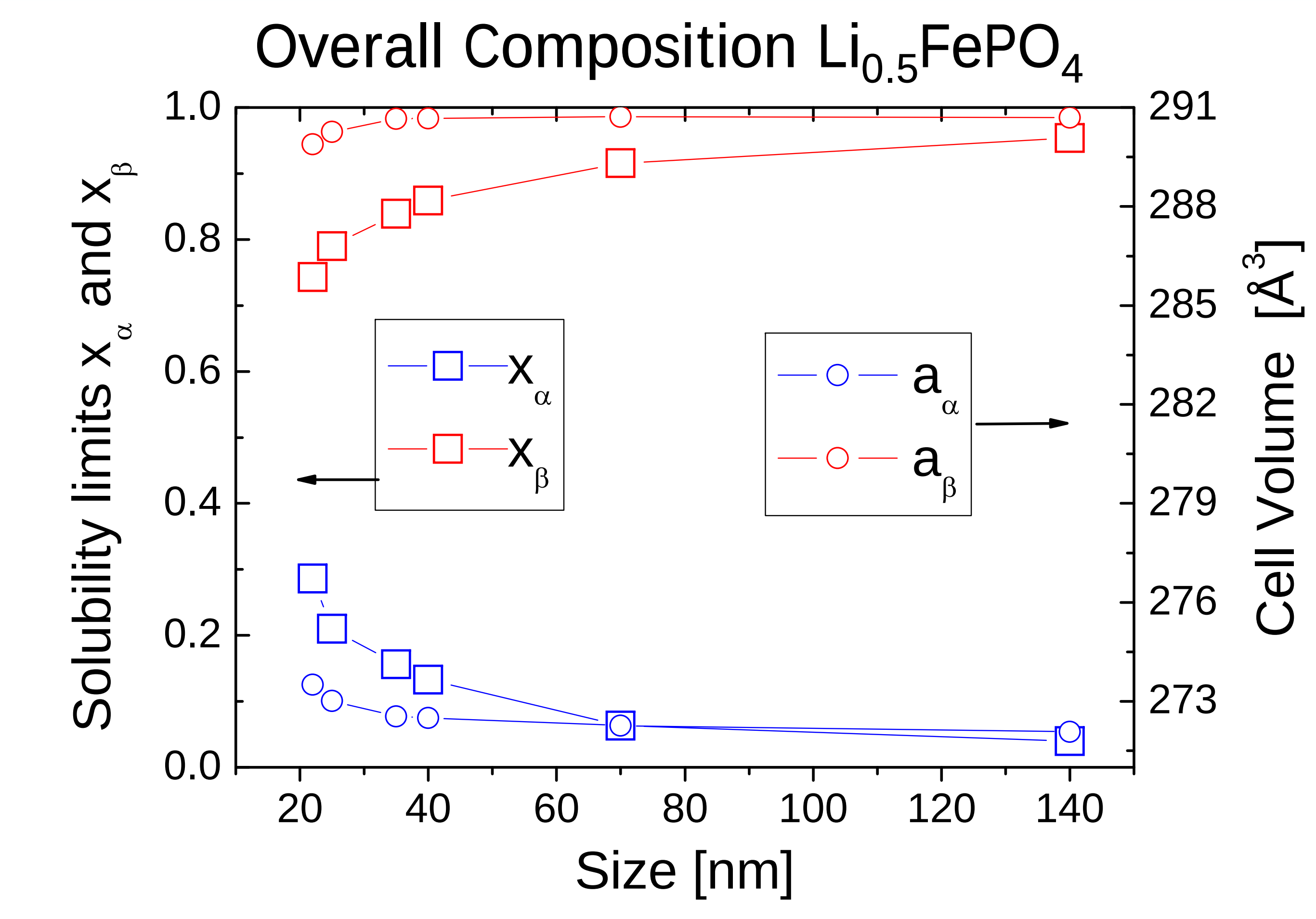
Fourier Density Difference Maps



Results Fixed Overall Composition



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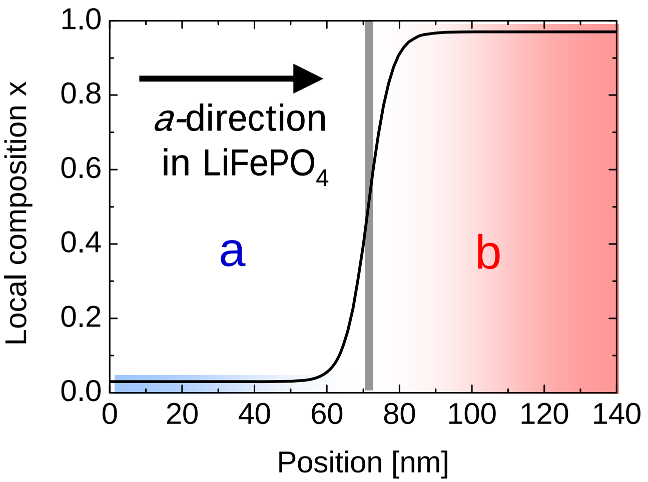
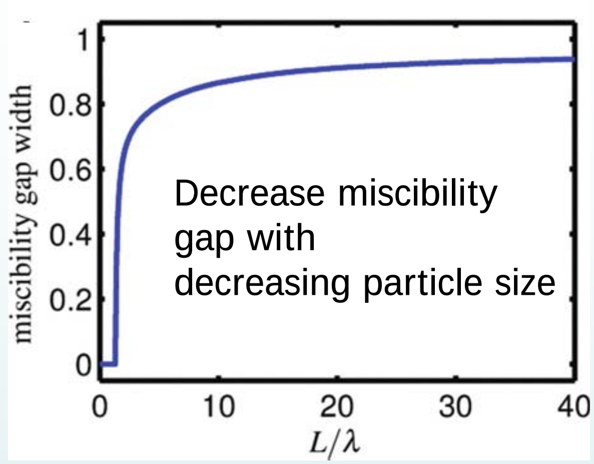
Calculation Diffuse Interface



Energy Penalty Diffuse Interface:

$$G_{mix} = \int_V \left(g_{\text{hom}}(c) + \frac{1}{2}(\nabla c) \bullet K(\nabla c) \right) \rho dV$$

Cahn & Hilliard 1958



Source: Burch et al, Nano Let. 2009, 9, 3975

This work:

(1) Repeat calculations Burch et al. ⇨ Direct comparison ND results

(2) Expand calculations ⇨ Impact overall composition Li_xFePO_4 and compare with ND results

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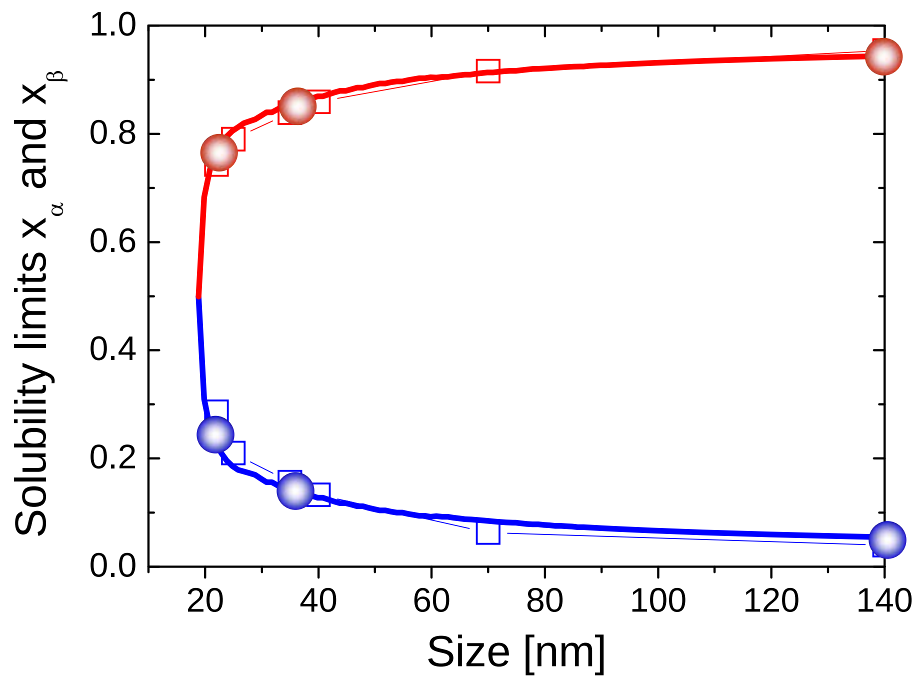
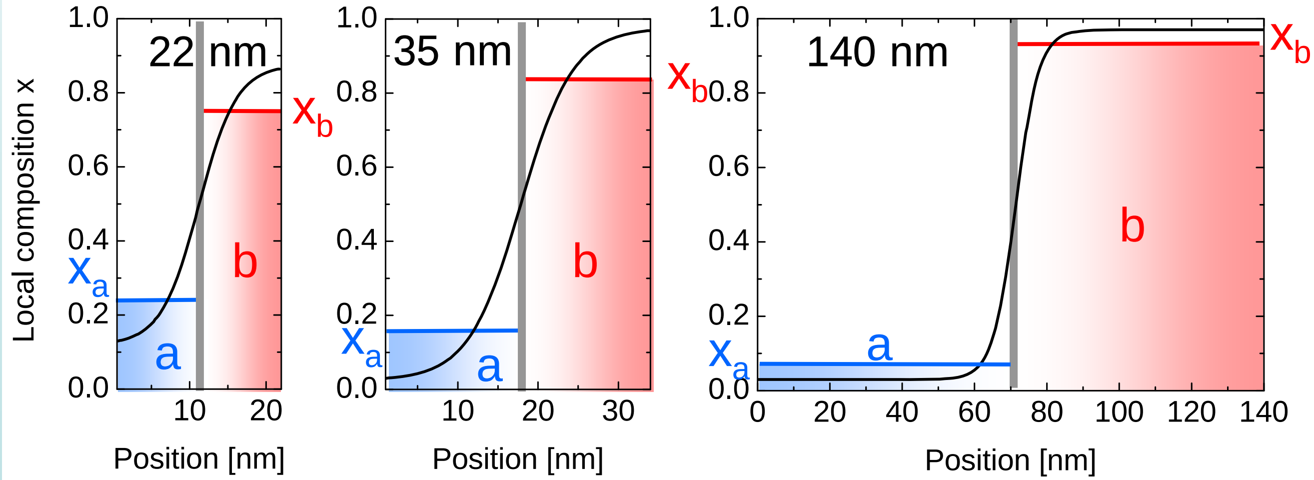
Vary particle size

Overall Composition $Li_{0.5}FePO_4$





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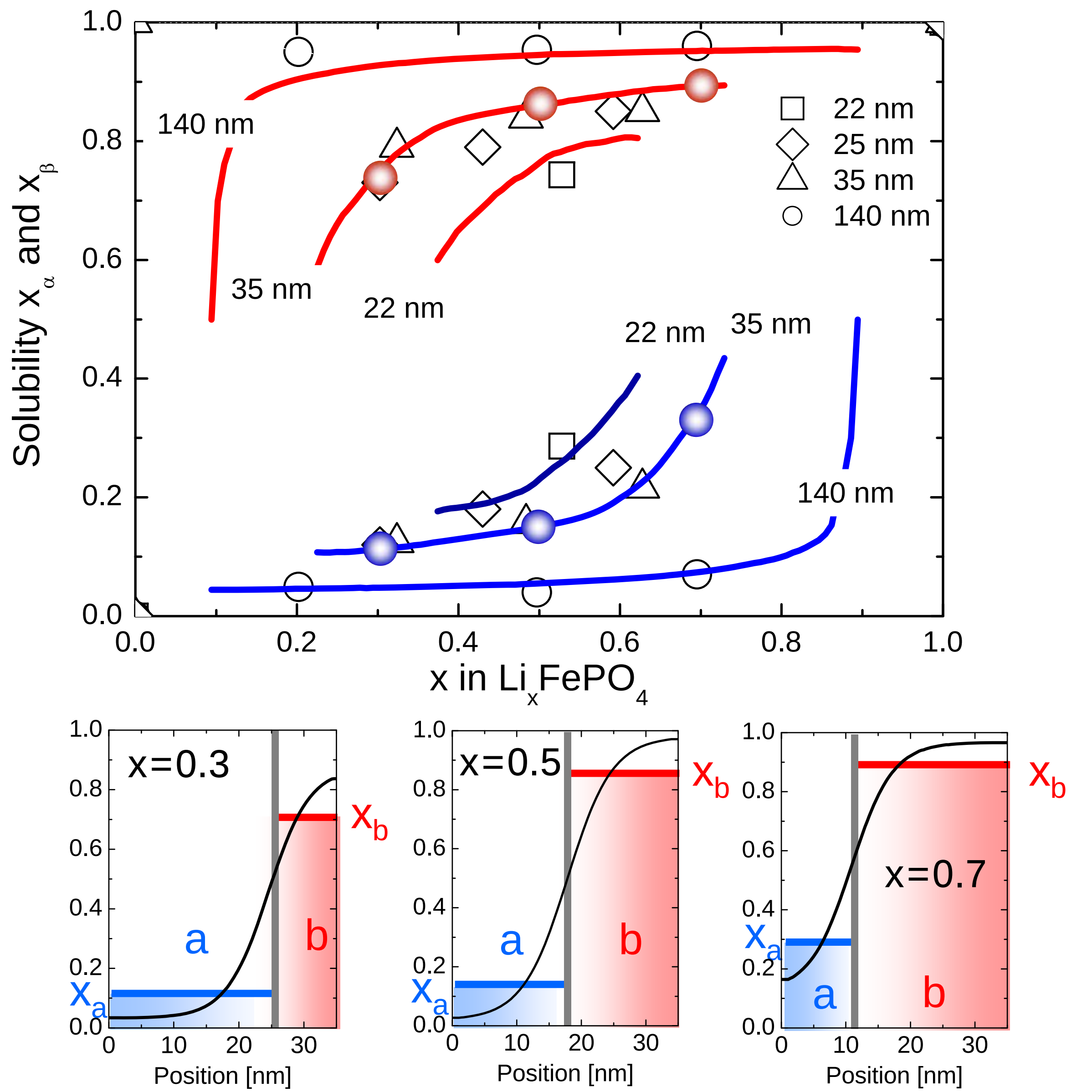
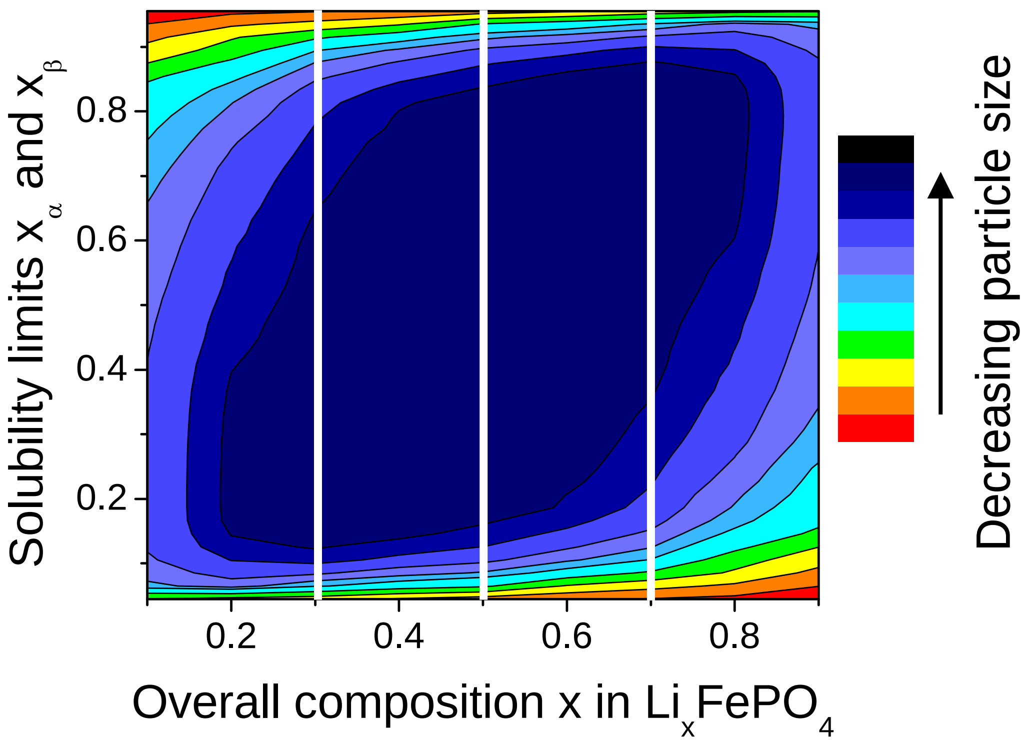
Vary overall composition



Calculated Phase-Size Diagram



Conclusions

Decreasing miscibility gap with decreasing particle size

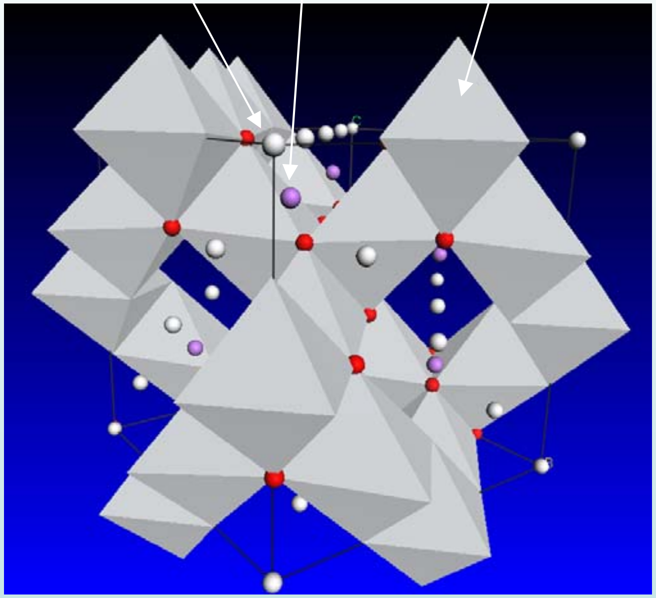
Solubility limits depend on overall composition

Diffuse interface appears to explain both phenomena

Compositions are continuously changing while charging!

Nano effects $Li_4Ti_5O_{12}$

Li-16c Li-8a $[Li_{1/6}Ti_{5/6}]O_6$



$Li_4Ti_5O_{12}$: Li 8a $Li_7Ti_5O_{12}$: Li 16c

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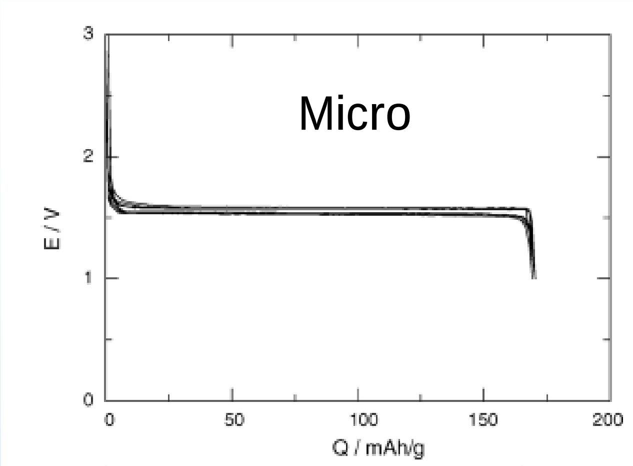
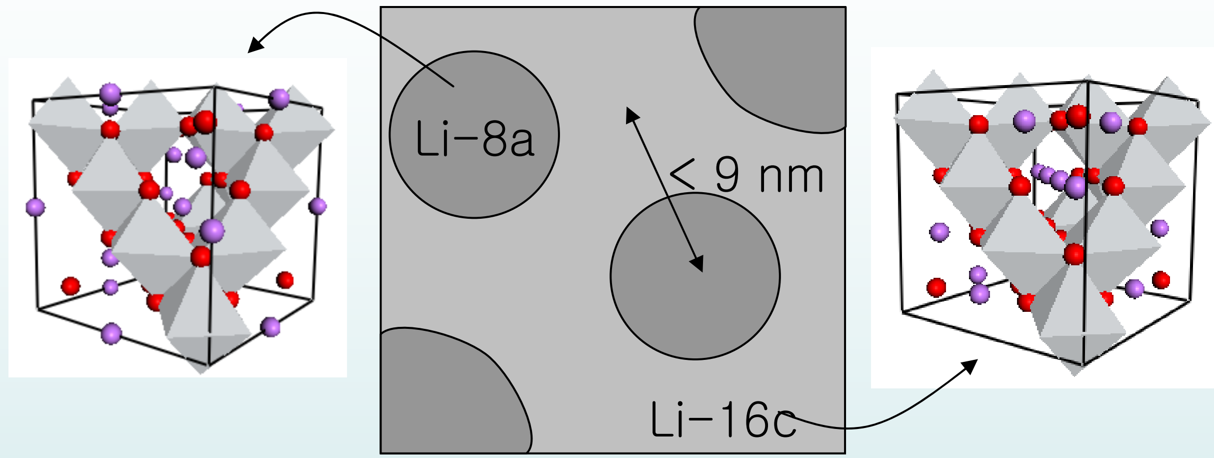
Introduction $Li_{4+x}Ti_5O_{12}$ Spinel



$Li_4Ti_5O_{12}$
Li on 8a

$Li_7Ti_5O_{12}$
Li on 16c

Spinel $Li_{4+x}Ti_5O_{12}$



M. Wagemaker et al, J. Phys. Chem. B, 113 (2009) 224 and
M. Wagemaker et al, Advanced Materials 18 (2006) 3169

- Phase transition from $Li_4Ti_5O_{12}$ (Li-8a) to $Li_7Ti_5O_{12}$ (Li-16c)
- Zero strain
- In equilibrium nano-domains -> Very low interface energy

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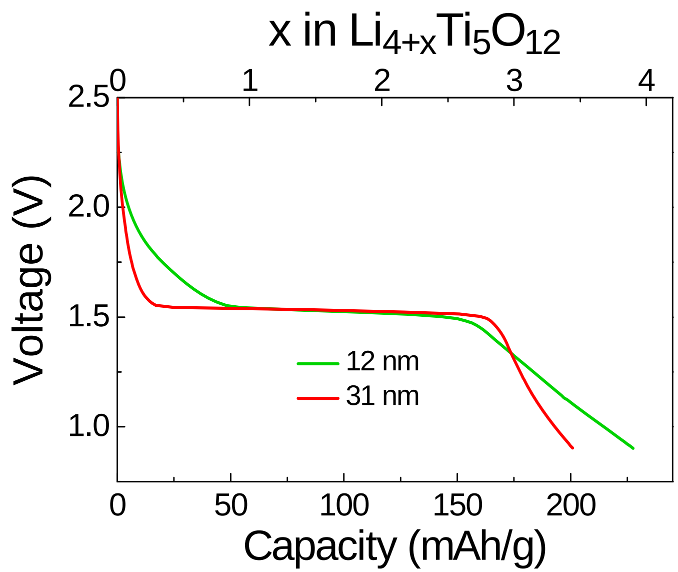
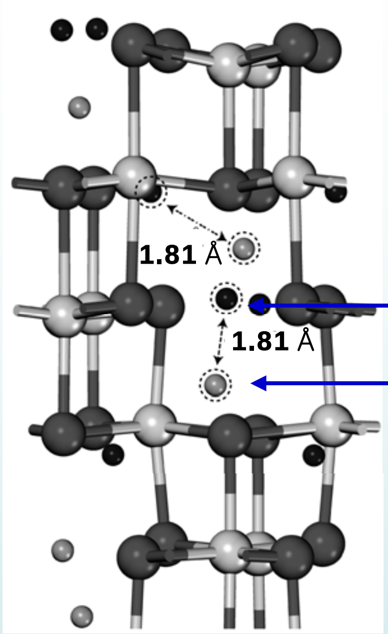
Impact nano-size Li-ion: spinel $Li_{4+x}Ti_5O_{12}$



C/10 galvanostatic (dis)charge 2.5-0.9 V

Borghols et al, J. Am. Chem. Soc. 131 (2009) 17786



Short Li^+-Li^+ distances high repulsive energy

Li_{8a}

Li_{16c}

Questions

(1) What is the origin of the extra capacity in smaller particles?

(2) How can we understand the apparent reduced miscibility gap

Goal

Use Neutrons to see where the Li goes

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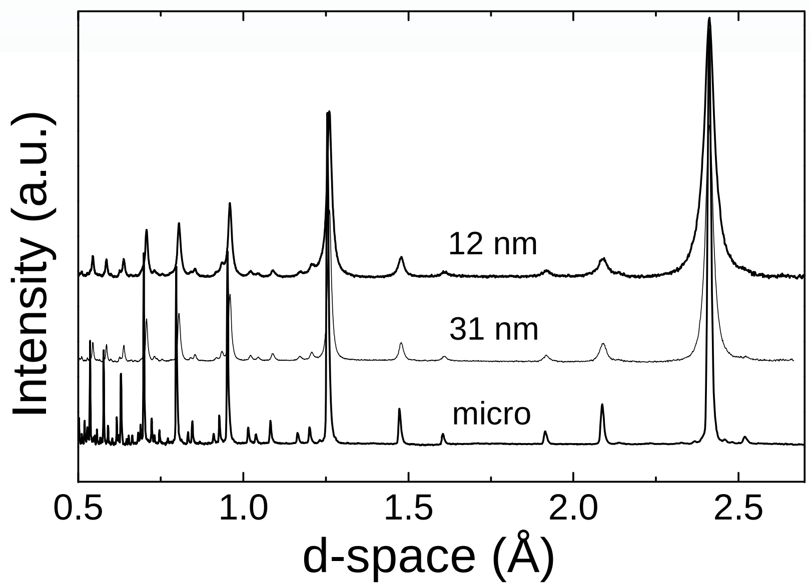
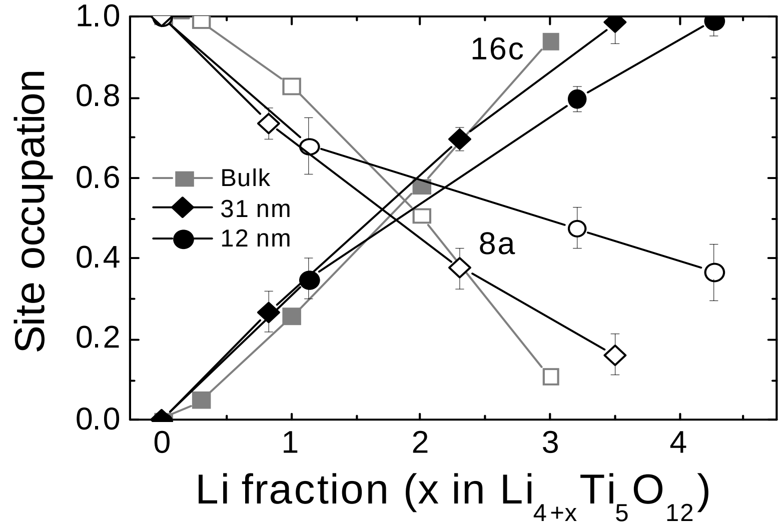
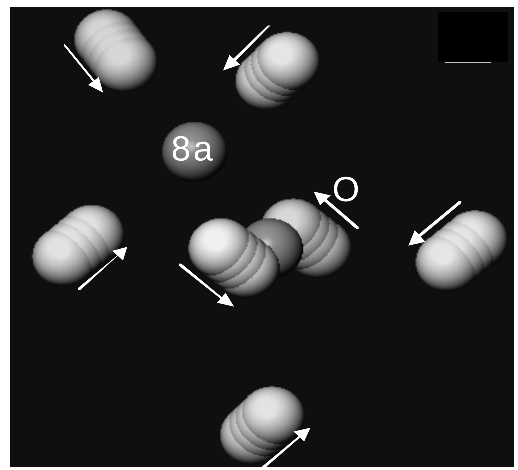
Neutron Diffraction ISIS (POLARIS)







In addition to maximum capacity $Li_7Ti_5O_{12}$ (all 16c) 8a occupancy in small particles

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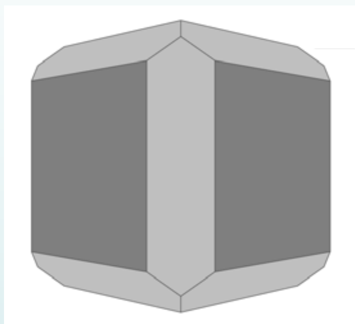
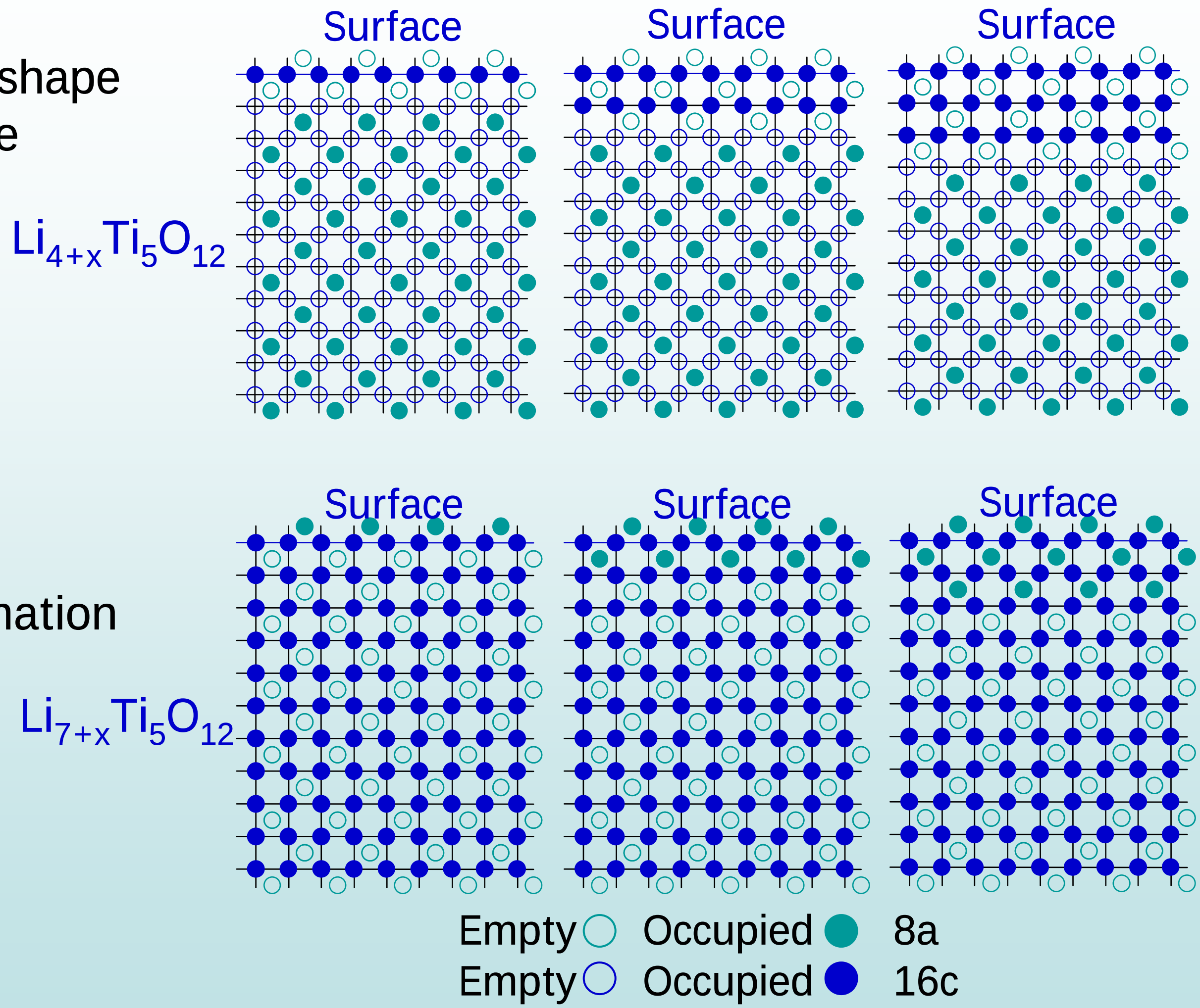
Surface storage spinel $Li_{4+x}Ti_5O_{12}$

Equilibrium Crystal (Wulff) shape
Dominated by (100) surface



Calculate voltage from formation energies (DFT) at the near surface environment

(100) Slabs 6.4 nm thick



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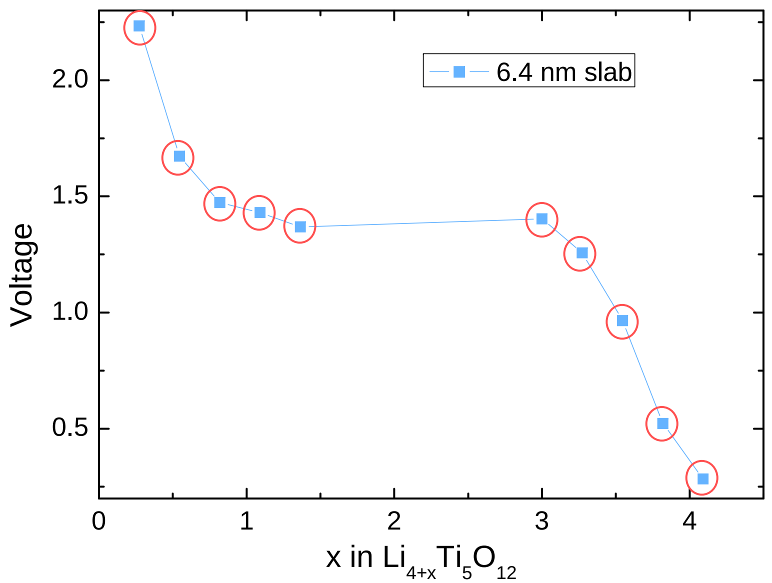
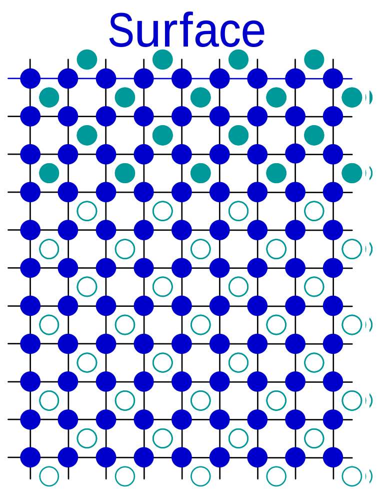
Surface storage spinel $Li_{4+x}Ti_5O_{12}$

Calculated Voltage Slab 6.4 nm
Measured size dependence





Empty ○ Occupied ● 8a
Empty ○ Occupied ● 16c

- Surface storage leads to intrinsic change voltage curve (Gibbs Free Energy)
- Explains curved shape and large capacity

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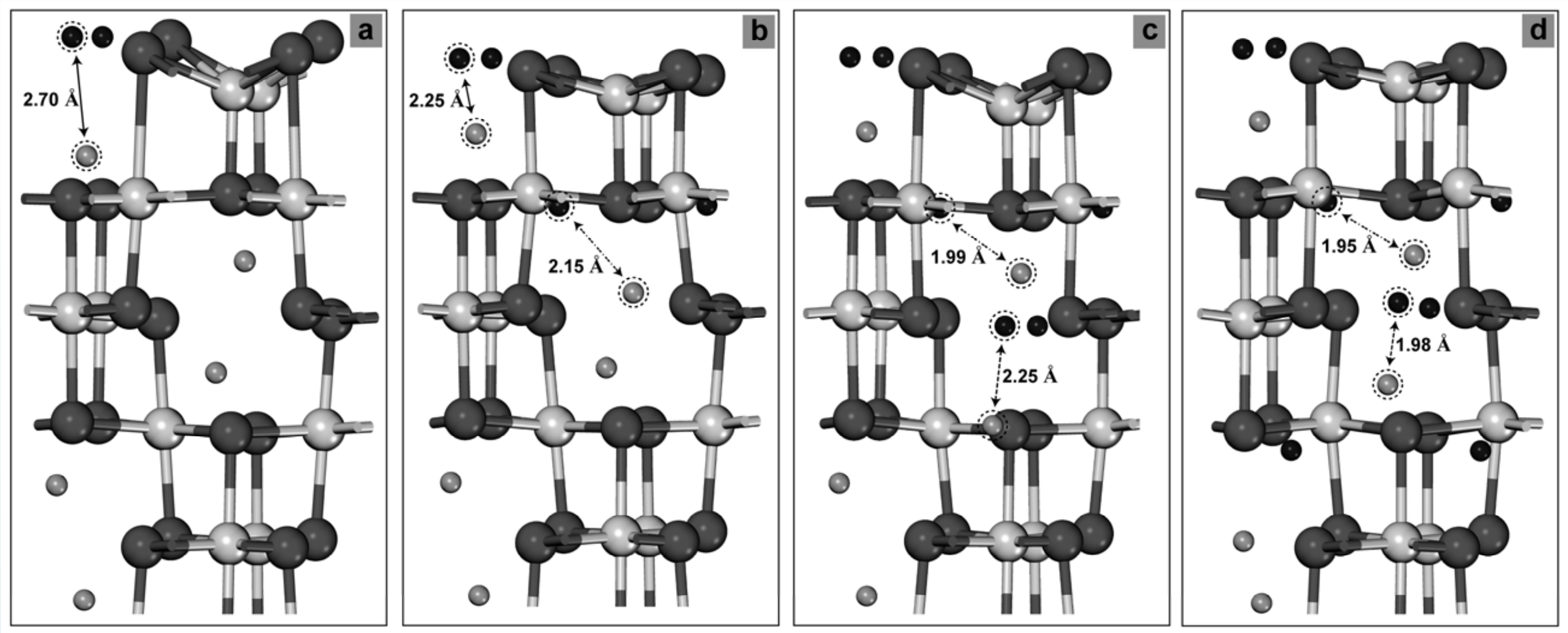
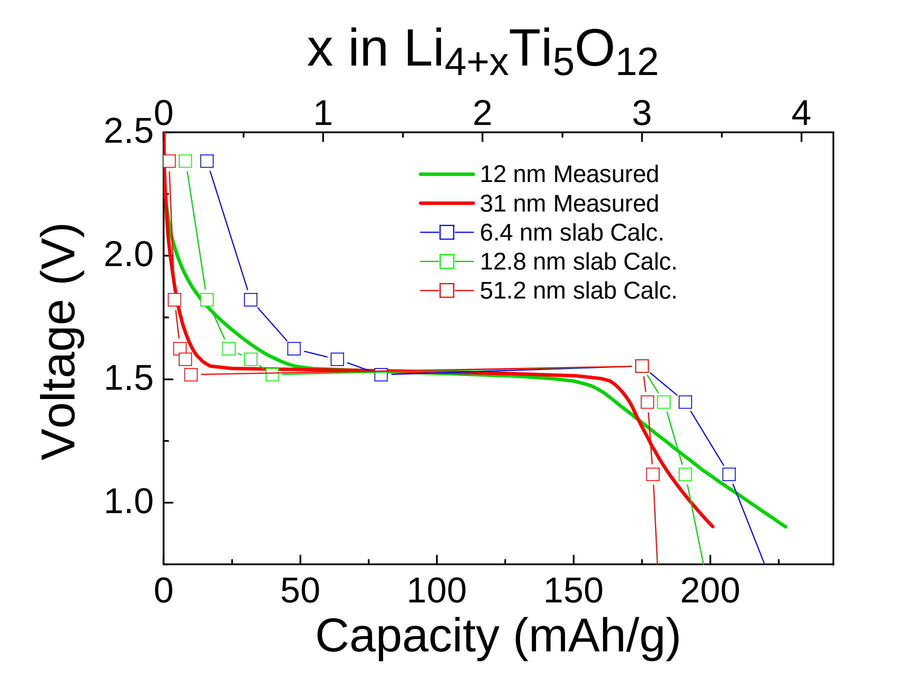
Origin: Surface relaxation

Bulk Li_{8a}-Li_{16c} 1.81 Å



Larger Li_{8a}-Li_{16c} distances near the surface -> lower energy/higher voltage

Conclusions LTO



- Surface storage explains higher capacity smaller particles
- Surface storage explains curved voltage shape (apparent decrease miscibility gap)
- Surfaces may be used to tailor the electrode properties

General Conclusions

Size effects in Electrode Materials:

(1) Solubility limits are not only changed, also not constant, will impact the Li-ion diffusion and phase behavior

(2) Surface storage shows potential to tune electrode properties

Acknowledgments

DISE

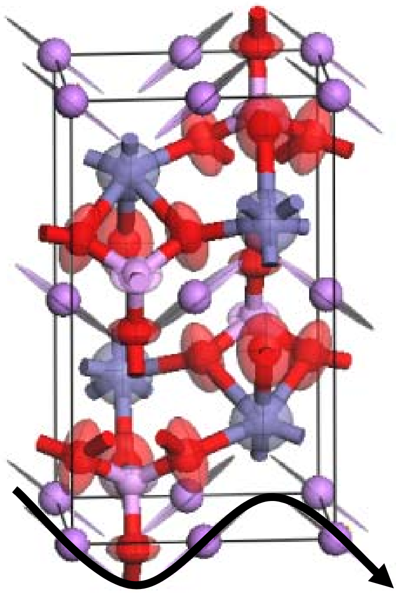
Delft Institute for Sustainable Energy

NWO
Netherlands Organisation for Scientific Research

VIDI, and beamtime ISIS

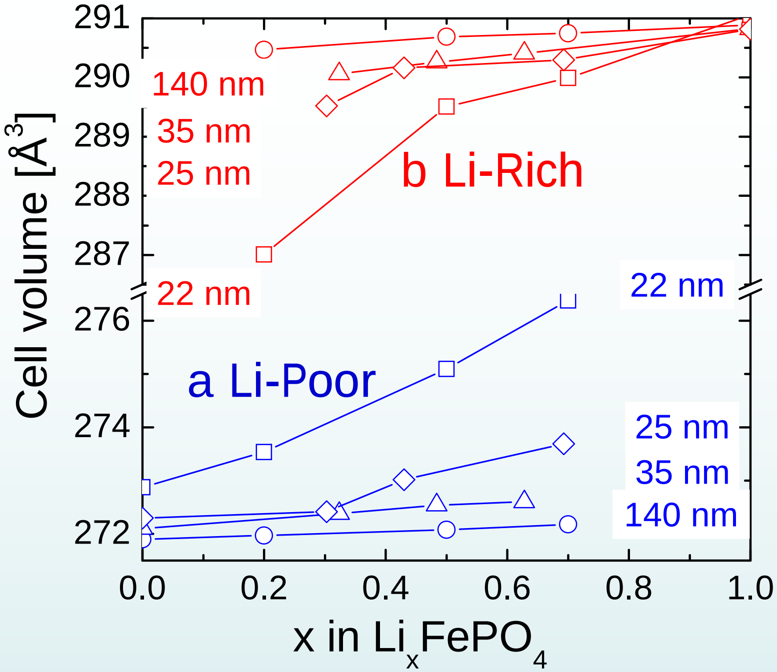
ISIS/PSI/ILL/ANSTO Support at beamlines

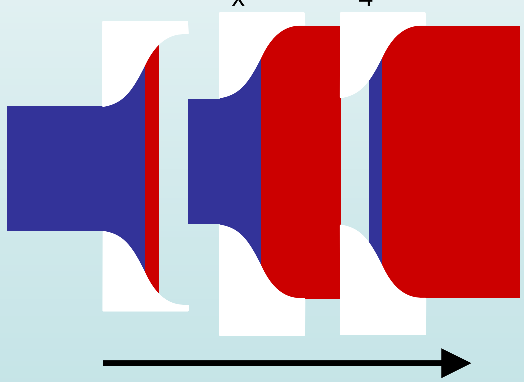
Anisotropic temperature factors



Curved Li-ion diffusion path *b*-direction

Nishimura et al, Nat. Mat. 2008, 7, 707

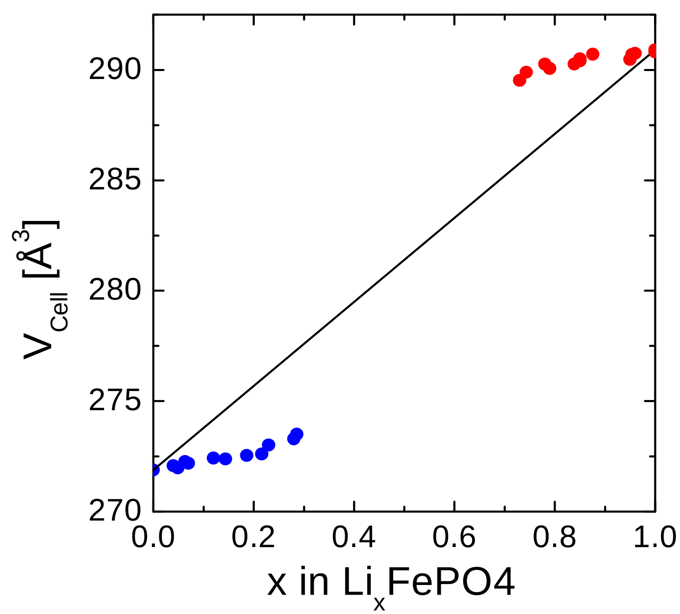




Increasing overall composition

Vegard's Law

In the Miscibility gap: No



Outside the Miscibility gap: Yes

(Kobayashi et al. Adv. Func. Mat. 2009 19 395)