

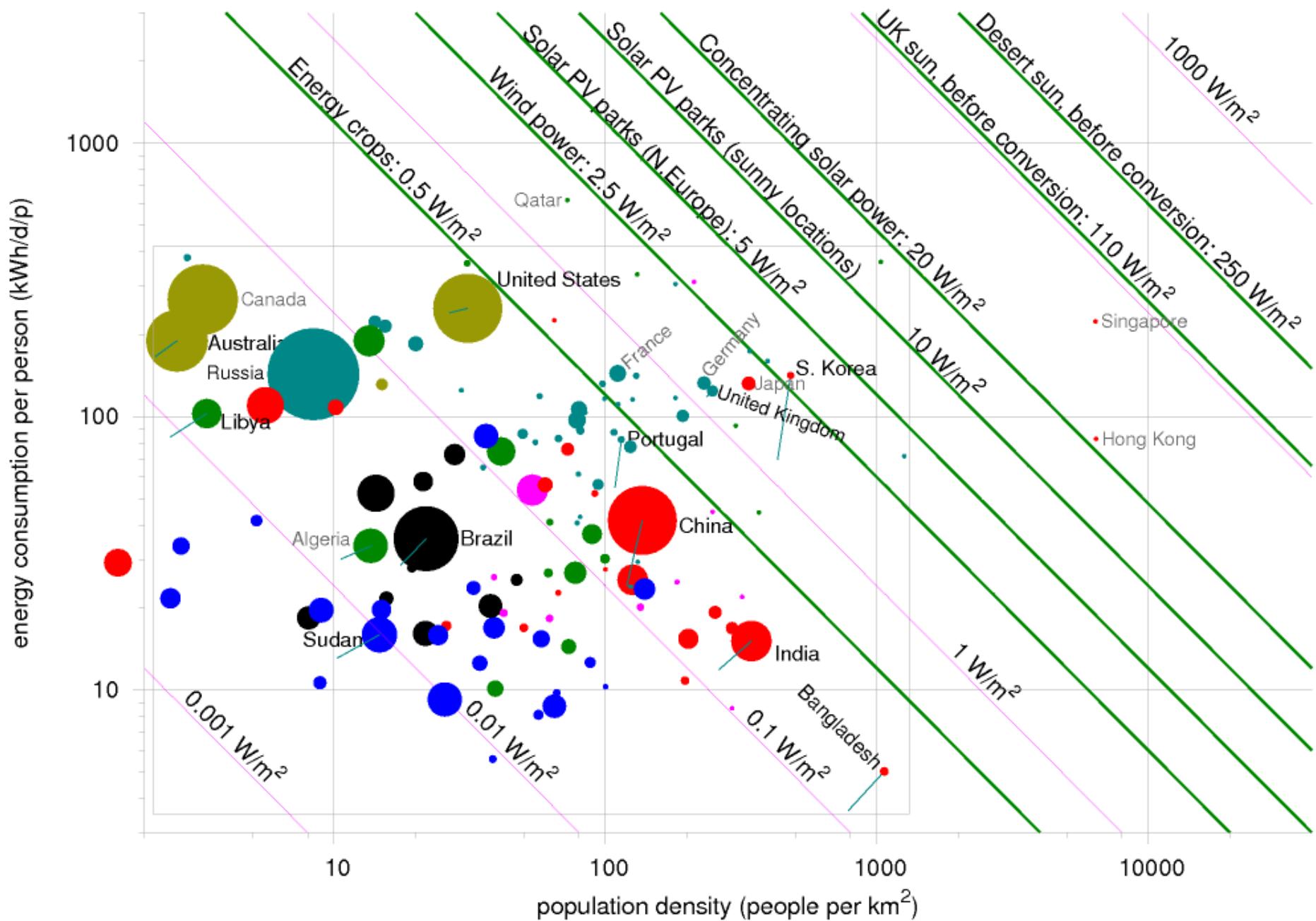
Following the transformation of individual crystallites in Li-ion batteries during cycling

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Marnix Wagemaker¹

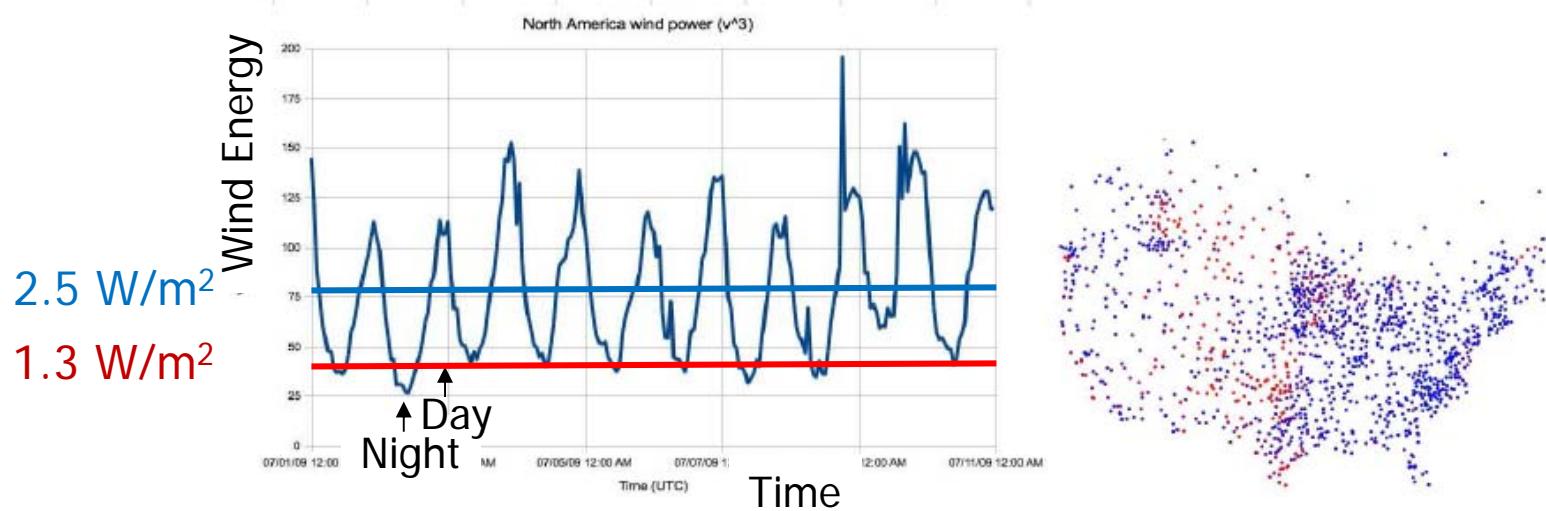


Battery Research
Group Delft, The Netherlands



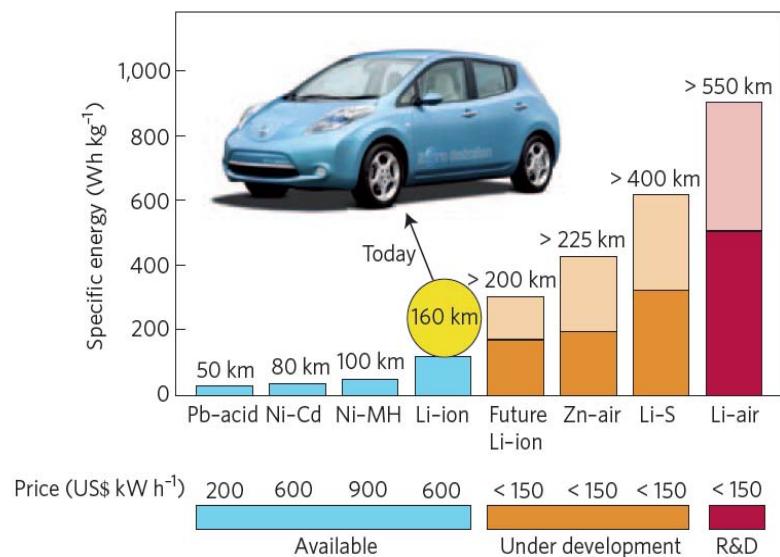


Fluctuations in energy production

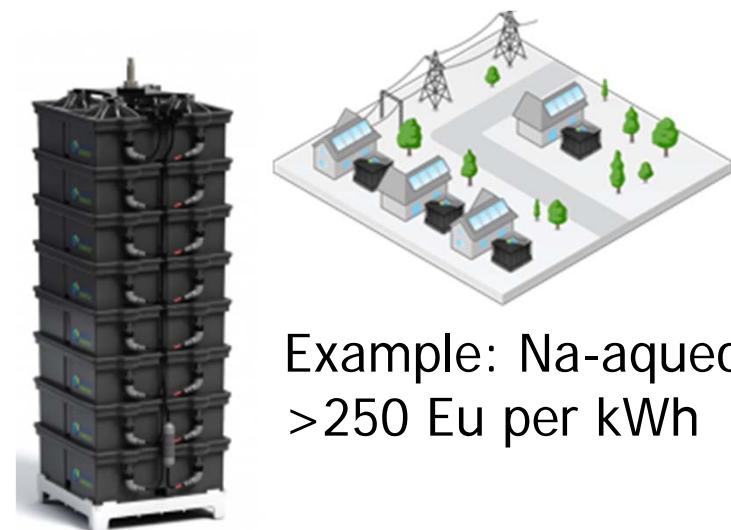


Batteries

Mobility:
High Energy Density



Storage Renewables:
Low price

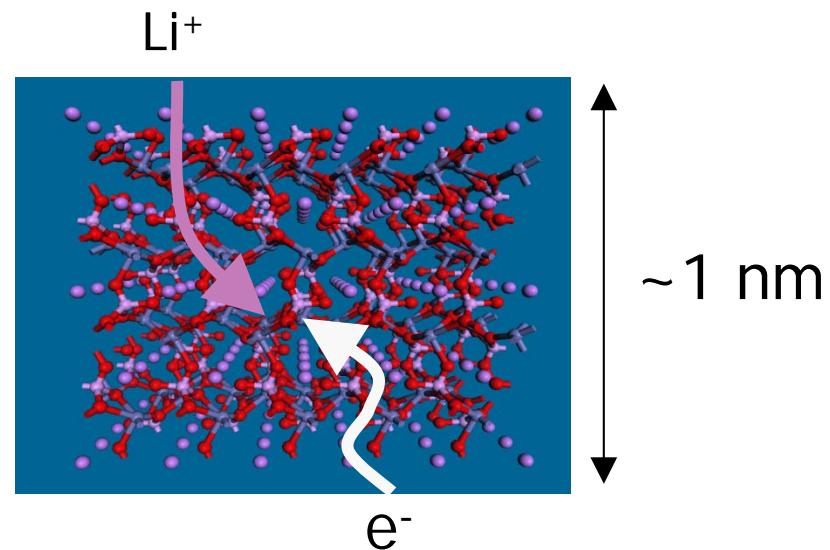


Example: Na-aqueous
>250 Eu per kWh

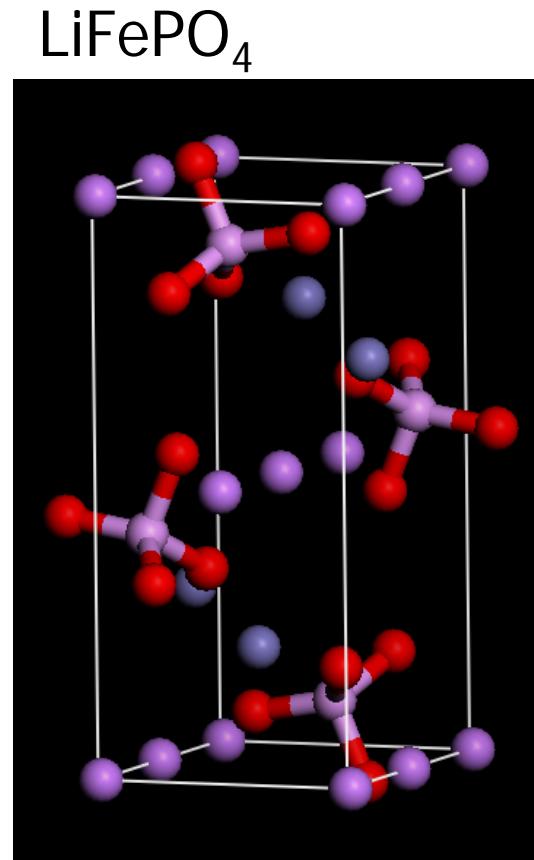
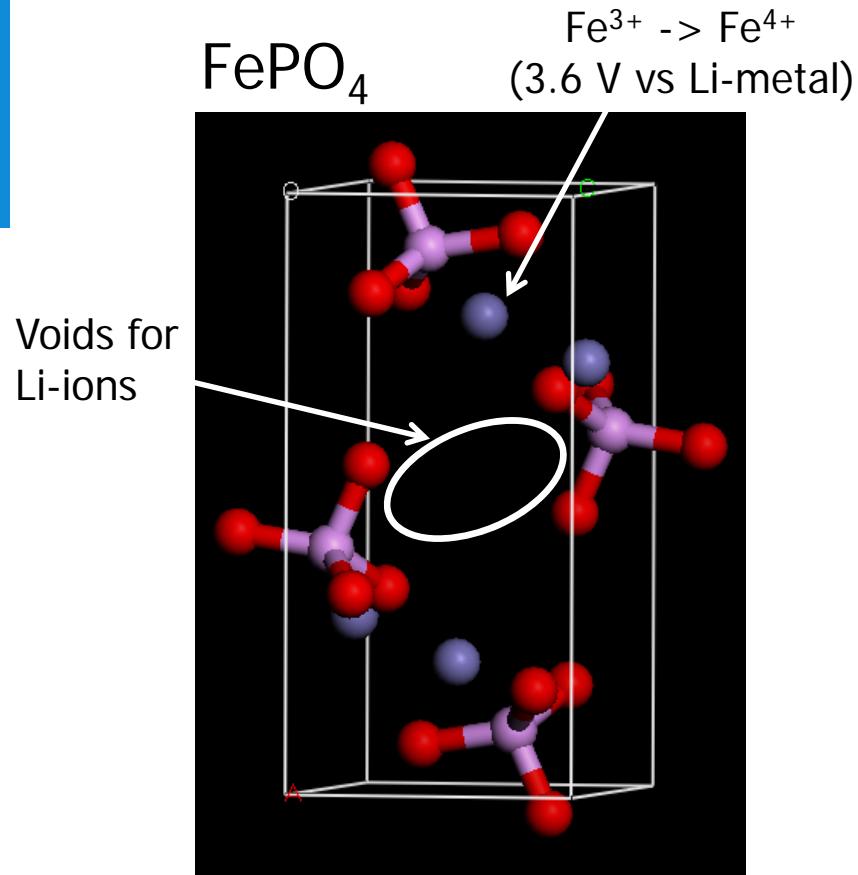
Li-ion Batteries

LiFePO_4 replacing LiCoO_2

Cheaper and more stable

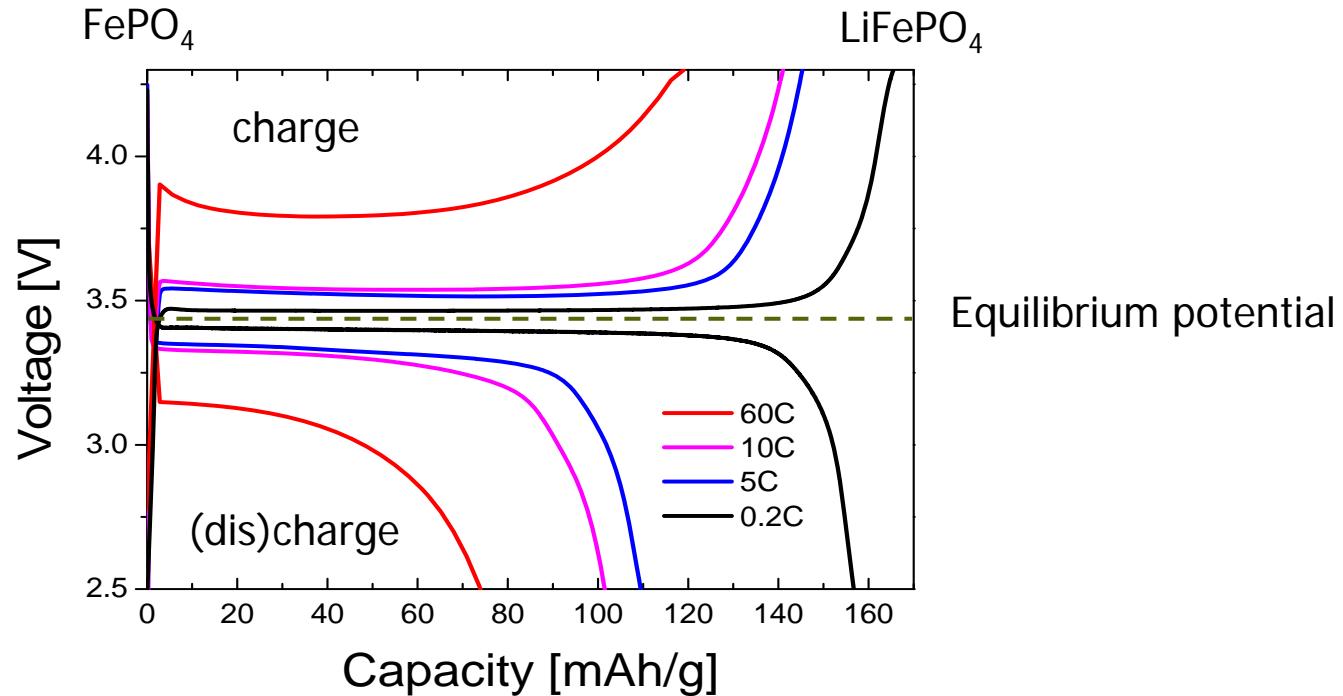


LiFePO_4 as positive electrode material



Li-ion insertion => 1st order phase transition
Remains orthorhombic, volume change: ~ 5 %

LiFePO₄ as positive electrode material



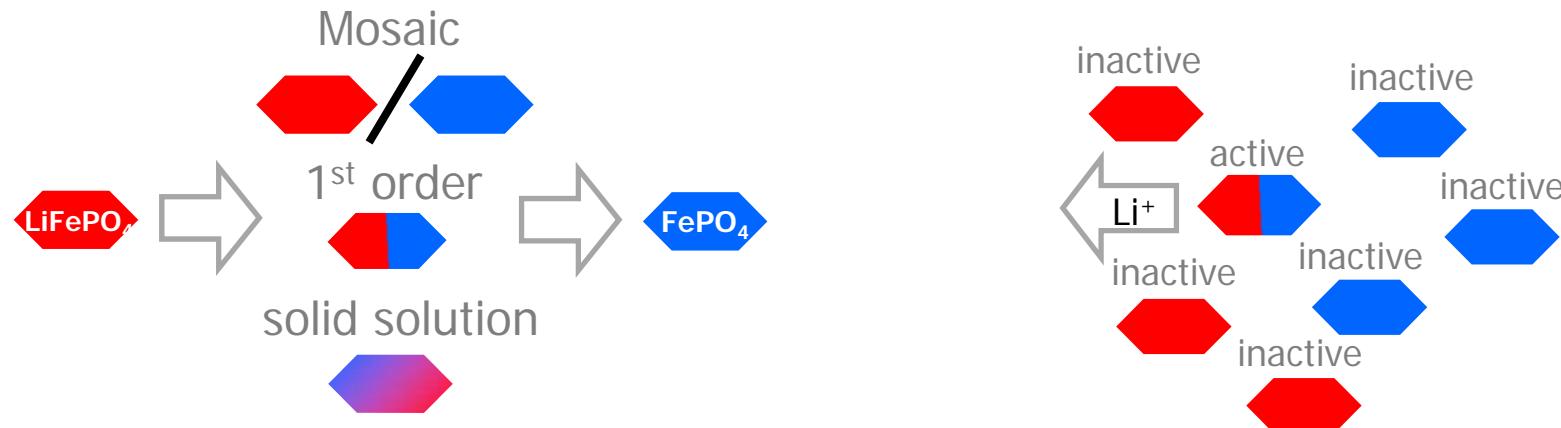
C/n (dis)charge rate, n: # hours to reach full capacity

LiFePO₄ as positive electrode material

Fundamental questions

Why can LiFePO₄ deliver such high currents?

How is the total current carried by the ensemble of crystallites?

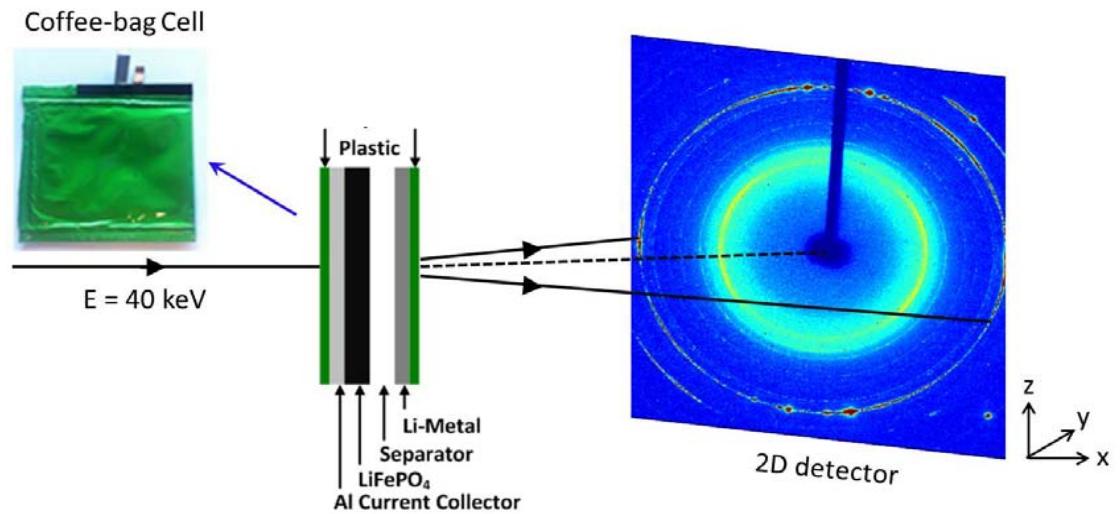


Operando powder diffraction

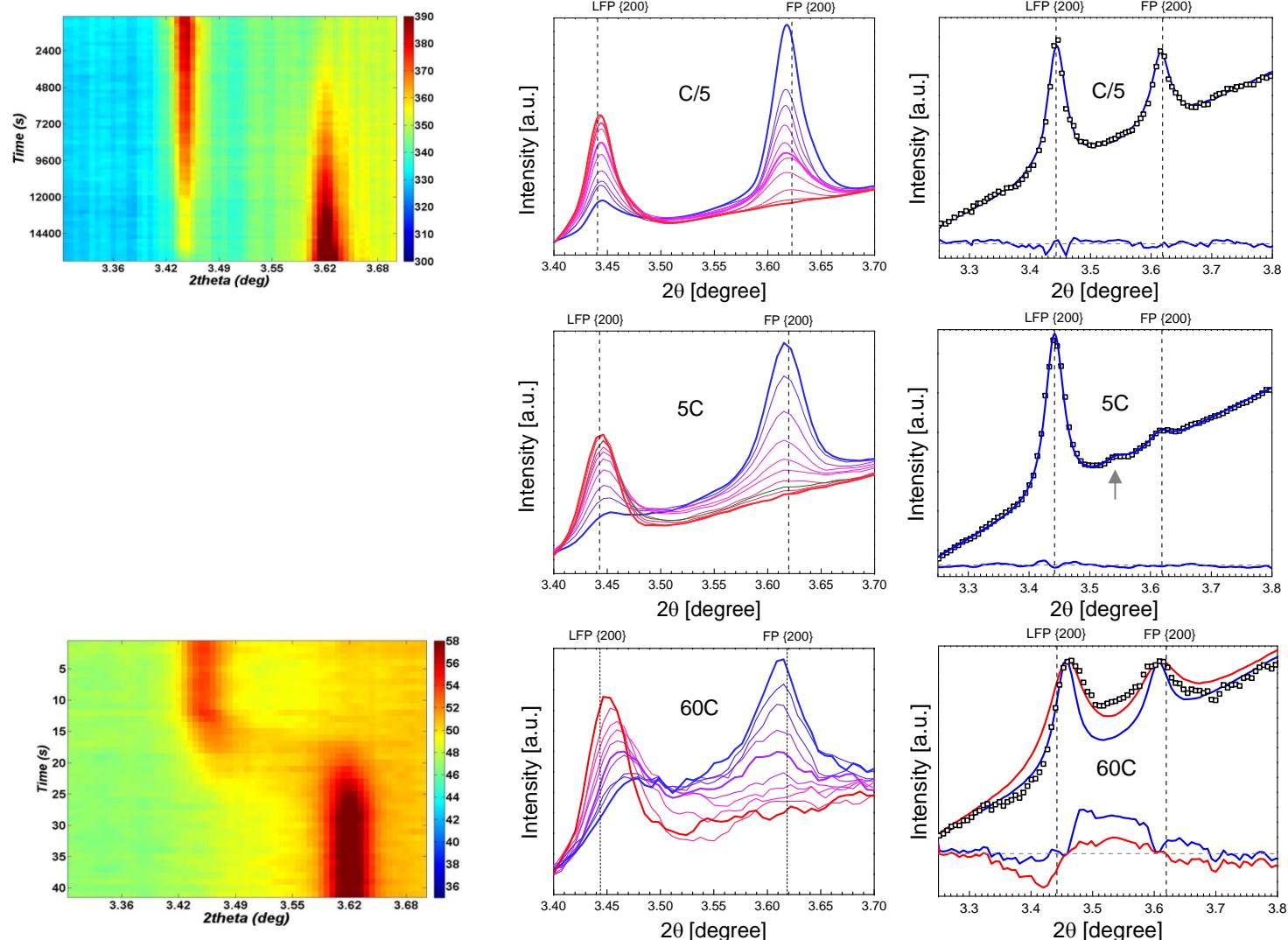
Operando powder diffraction



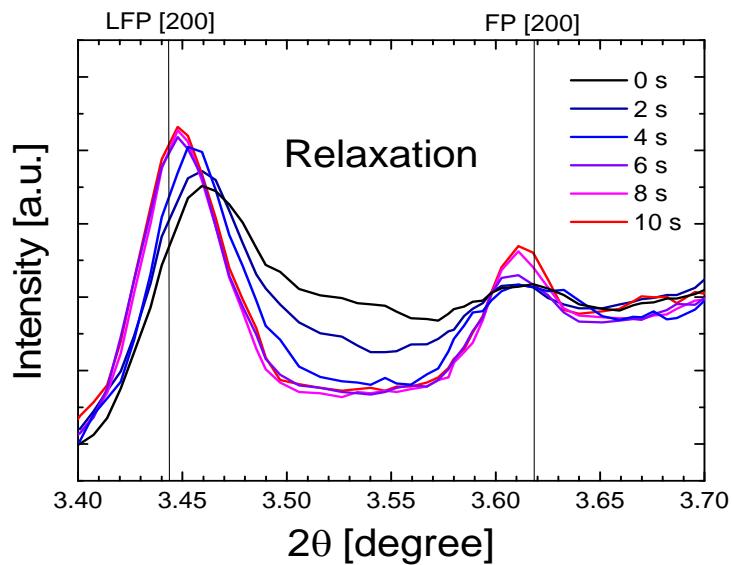
ESRF, ID11



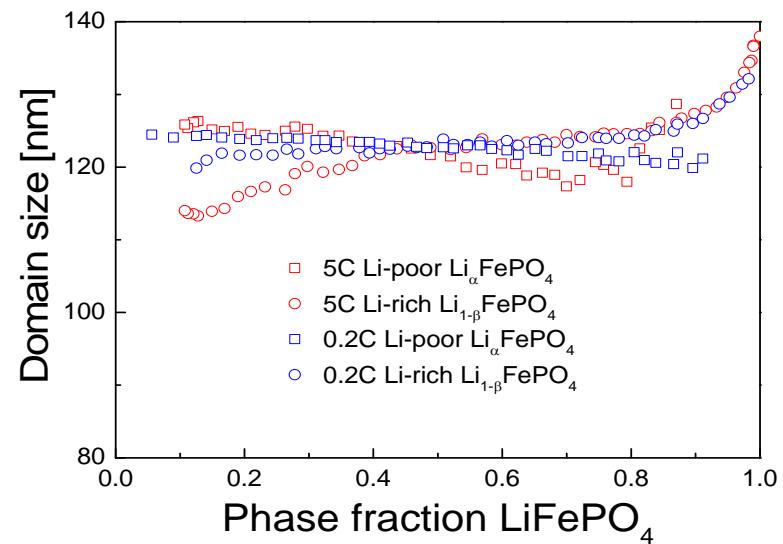
Operando powder diffraction



Operando powder diffraction

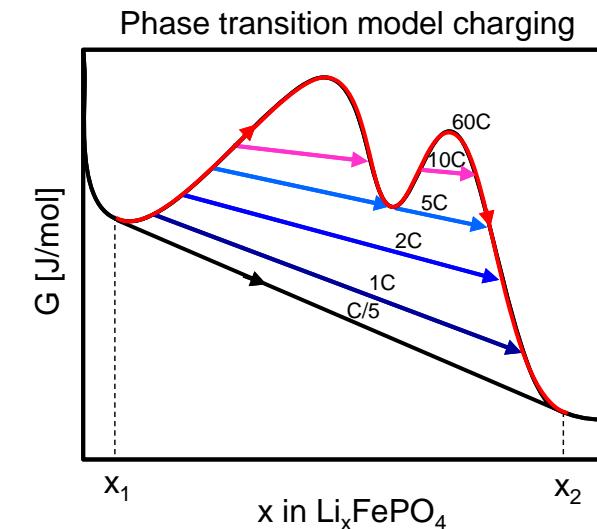
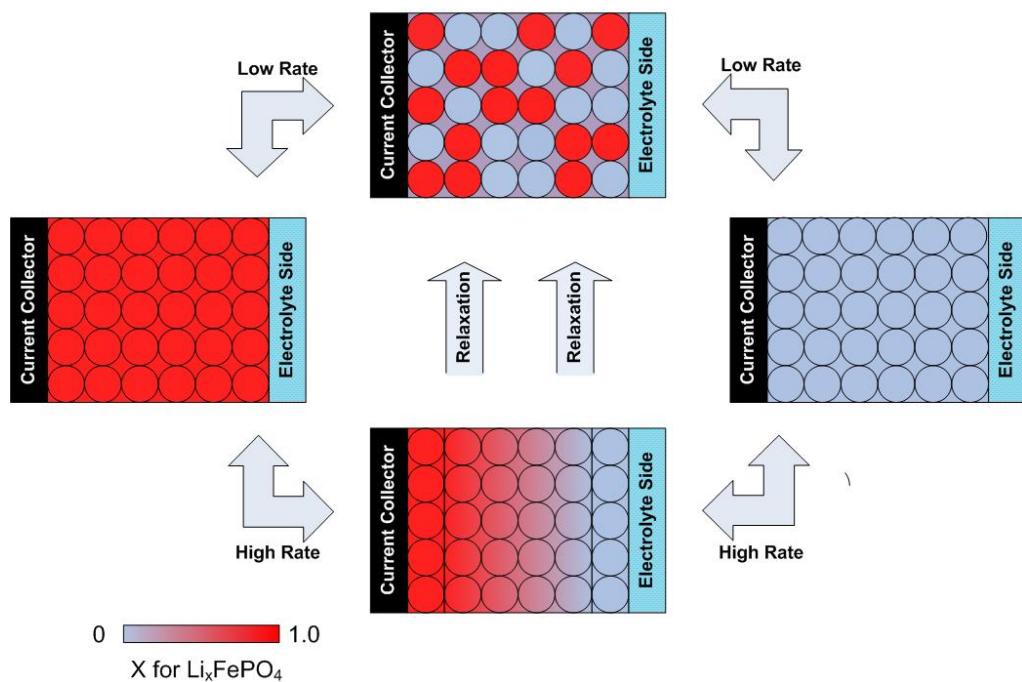


Solid solution phases are unstable



Low rates mosaic transformation

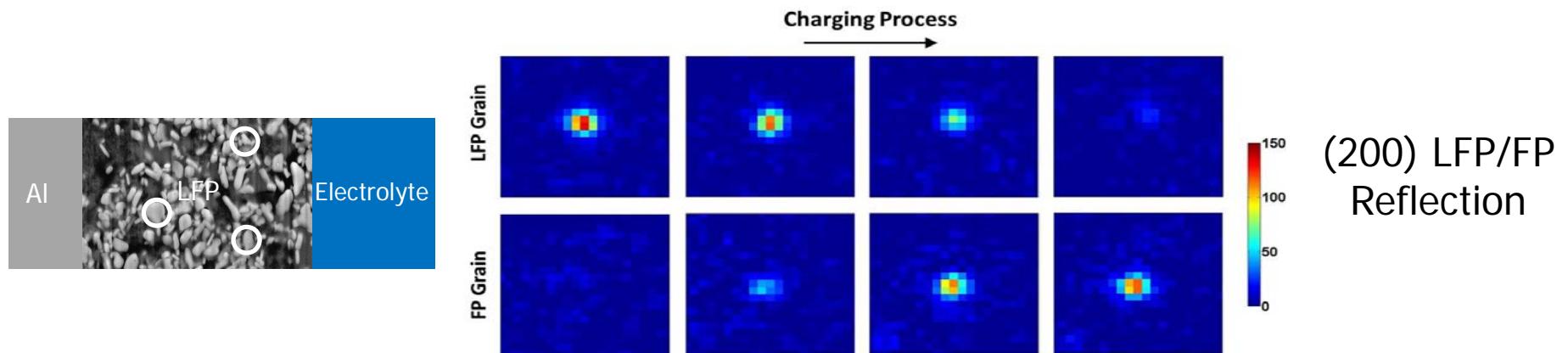
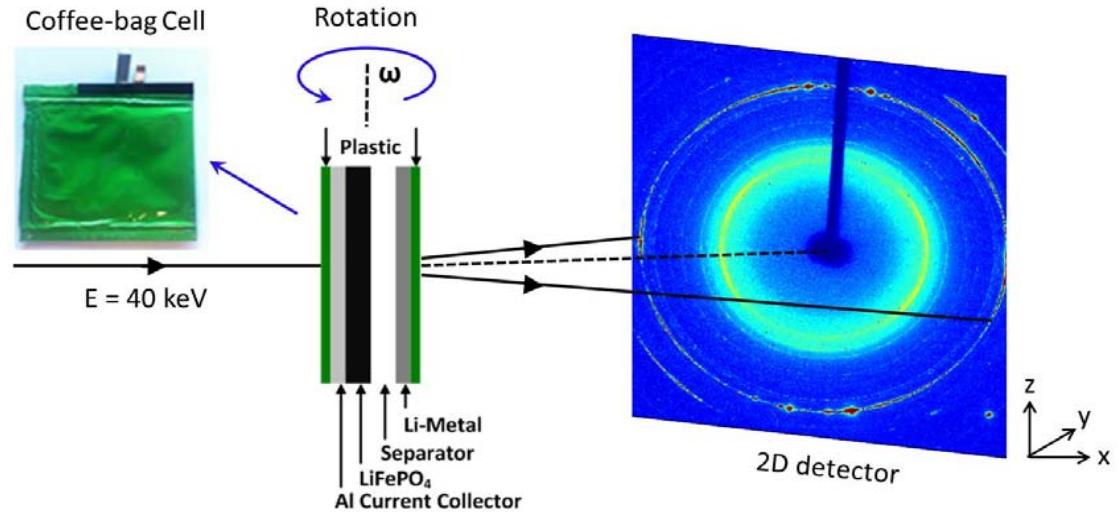
Operando powder diffraction



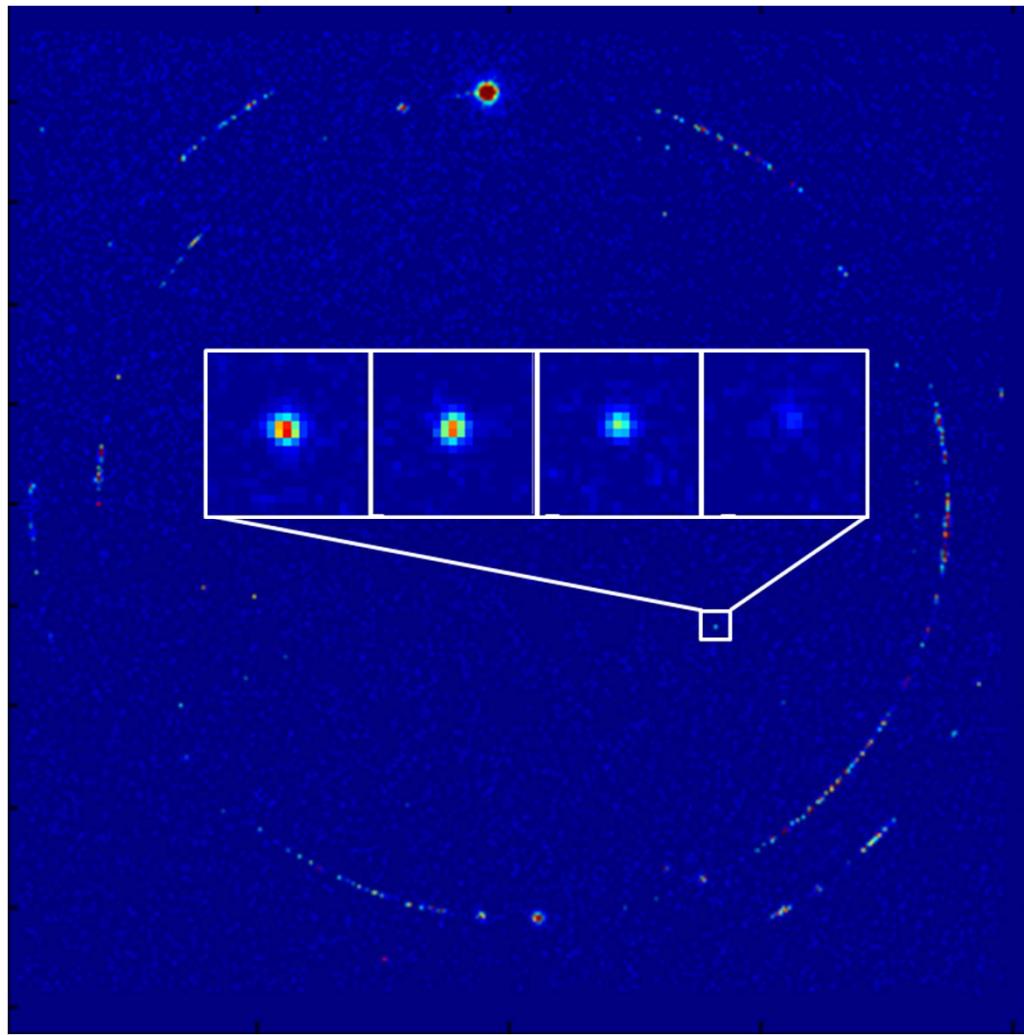
Overpotential drives the solid solution behavior
Solid solution behavior is responsible for fast (dis)charging LiFePO_4

Operando Microbeam diffraction

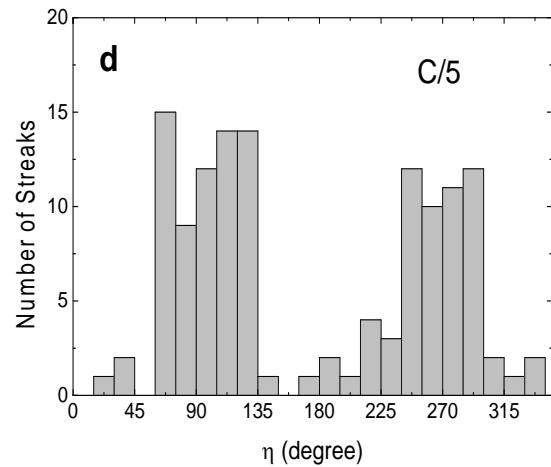
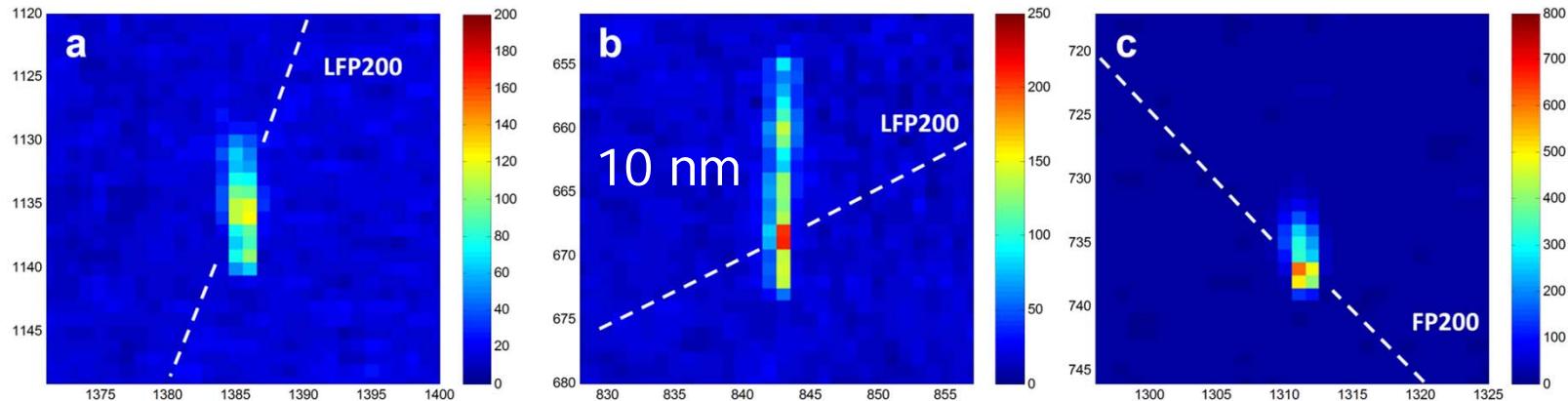
Following individual LiFePO₄ grains in-situ with micro beam diffraction



Following individual LiFePO₄ grains in-situ with micro beam diffraction

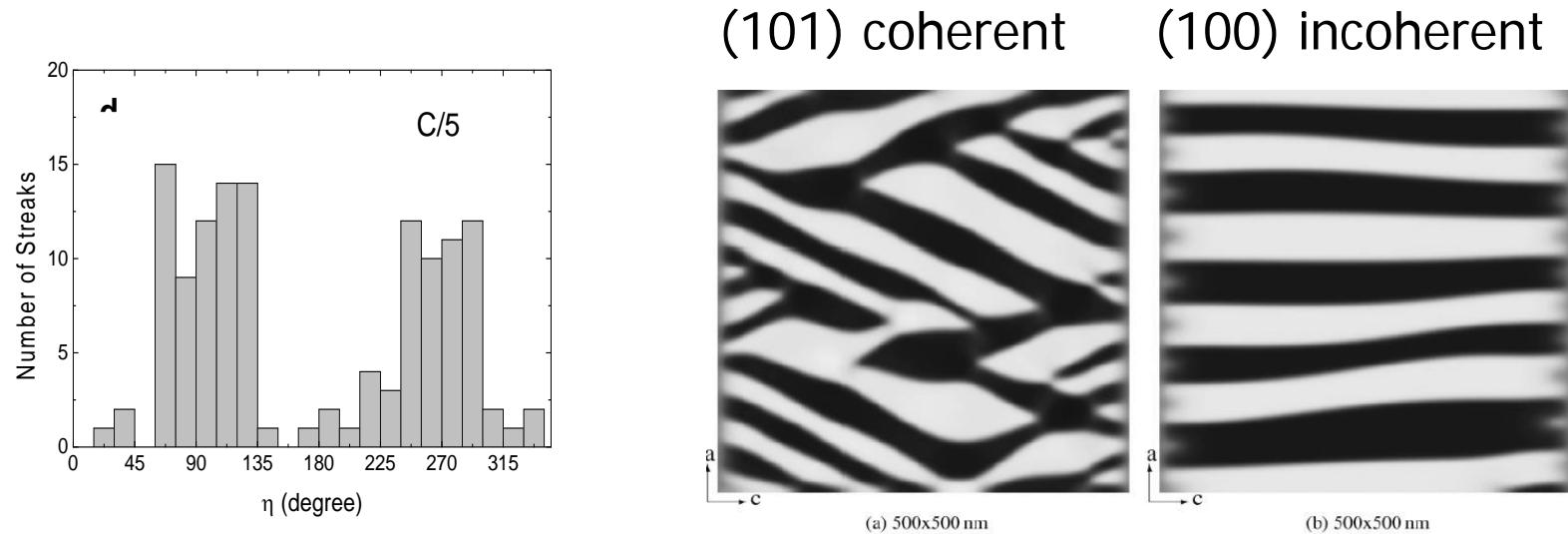
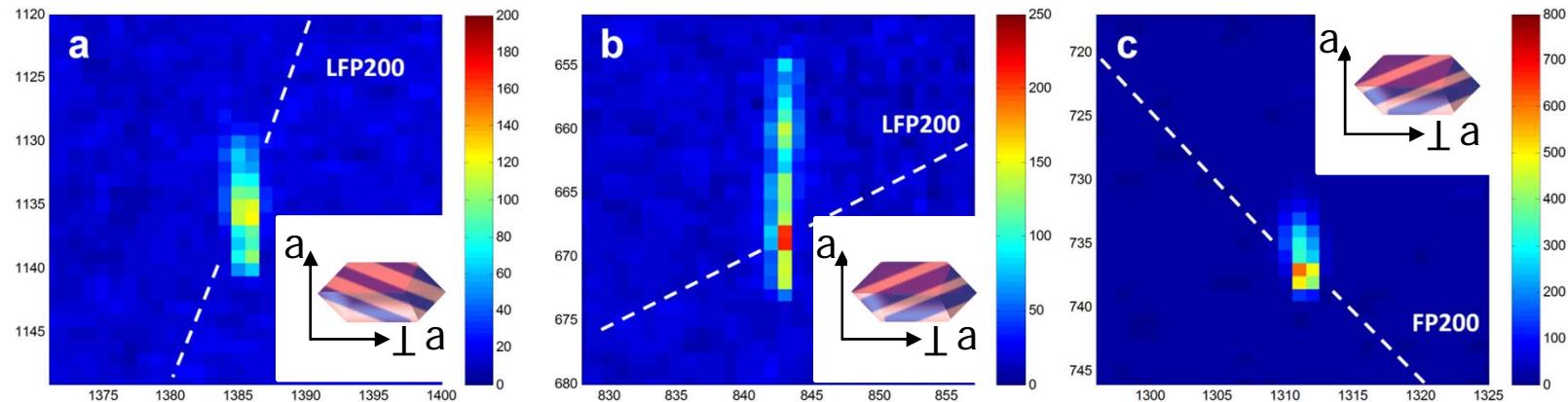


Low Rate (C/5): internal domain structure in 140 nm LiFePO₄



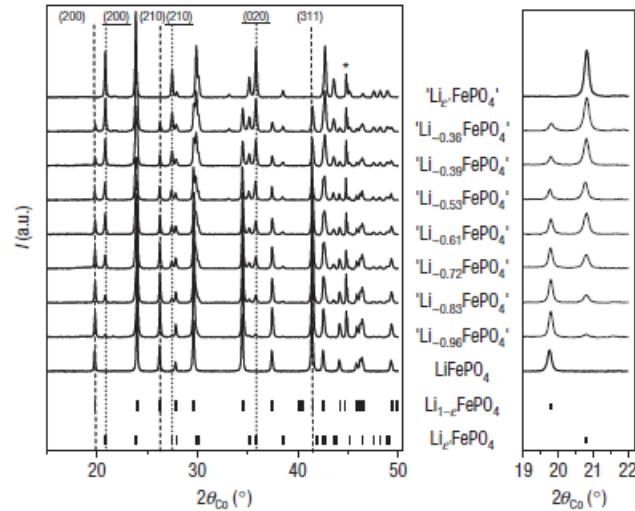
1D broadening: Platelet shaped LFP/FP domains
Position on ring: Interface orientation between platelet LFP/FP domains

Phase field modelling single grain:



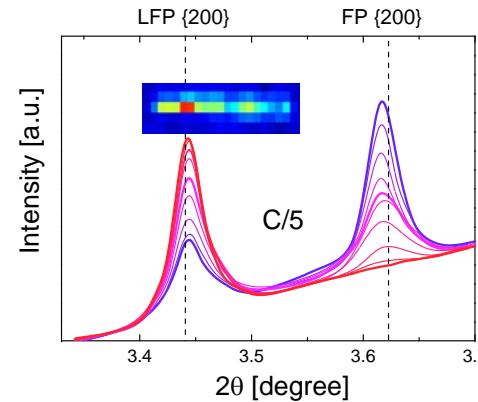
Source: Cogswell et al, ACS Nano 6 (2012) 2215

But what about the mosaic transformation?

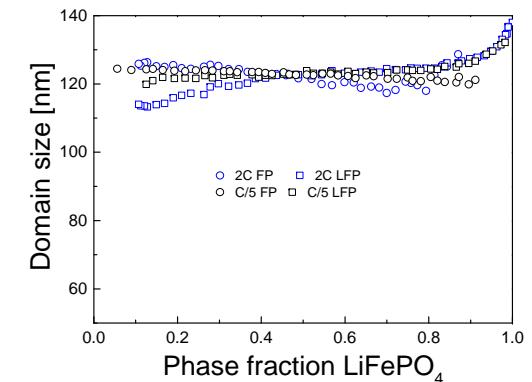


Source:
Delmas et al, Nature Materials 7 (2008) 665

Integrated (powder) diffraction
Operando microbeam experiments

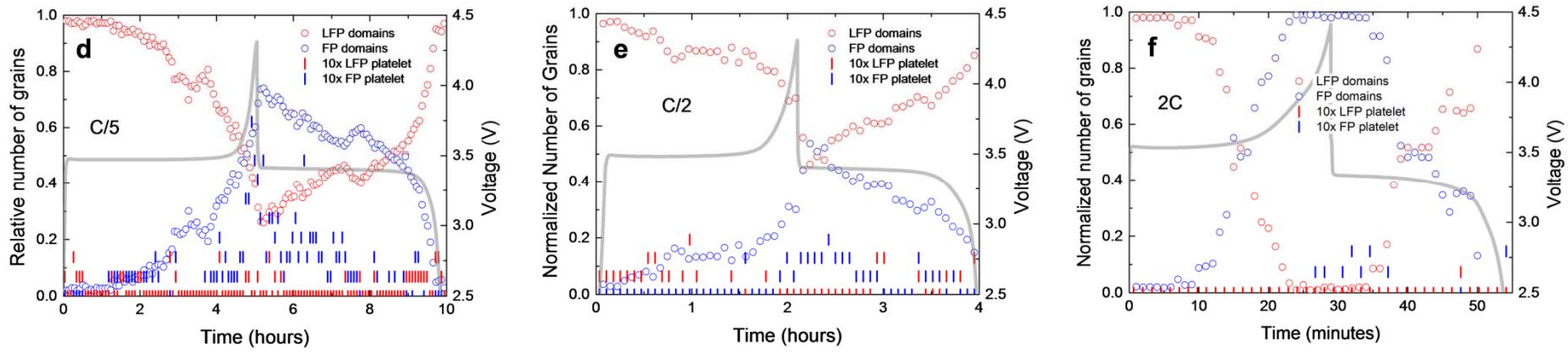


Zhang et al, Nano Letters (2014)



Strong anisotropic broadening disappears in the background of powder diffraction

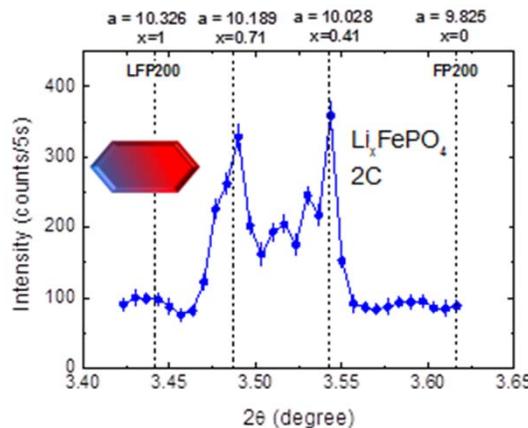
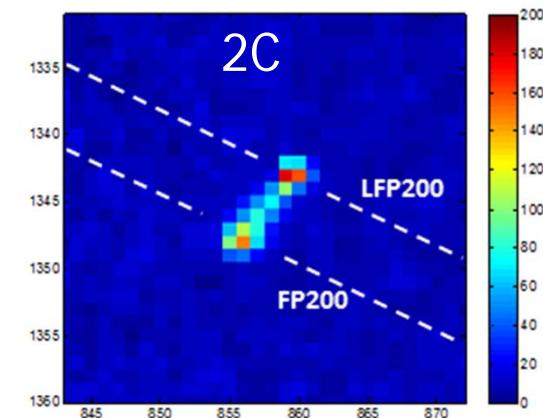
Increasing the rate



Platelet shaped LFP/FP domain
structure disappears

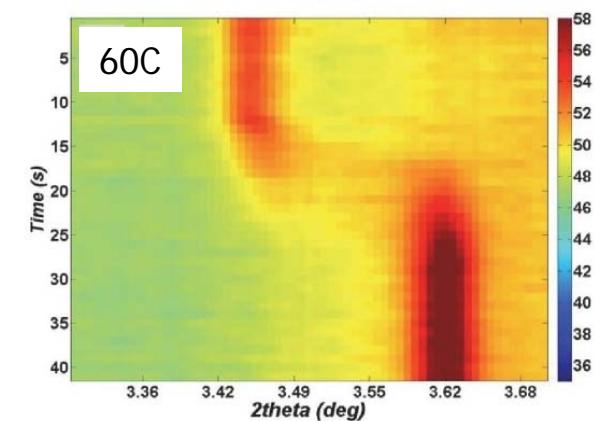
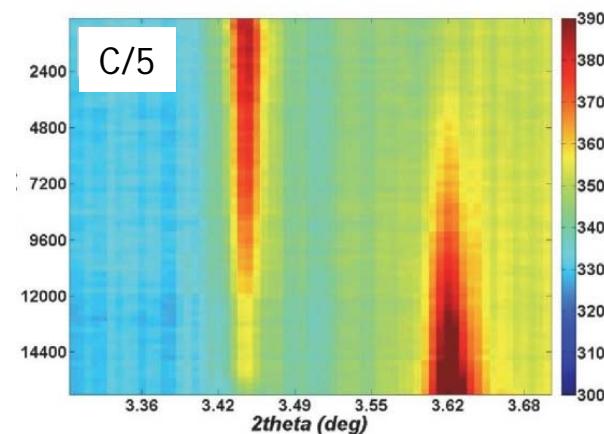
Suppression of the first order phase transition

Micro-beam XRD



Solid solution phases exist
within single 140 nm crystallite

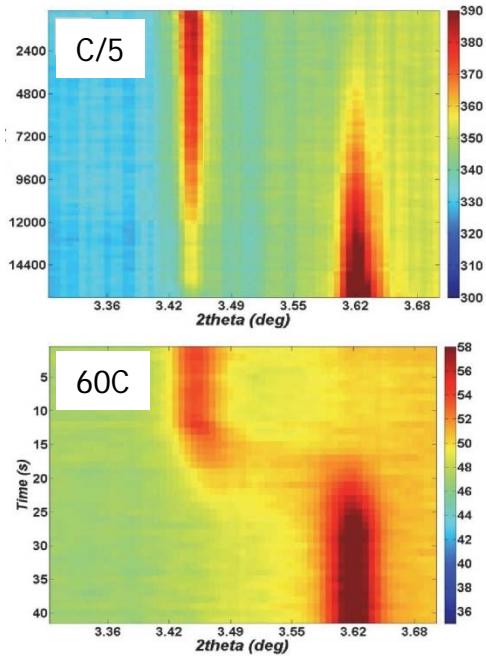
Powder XRD



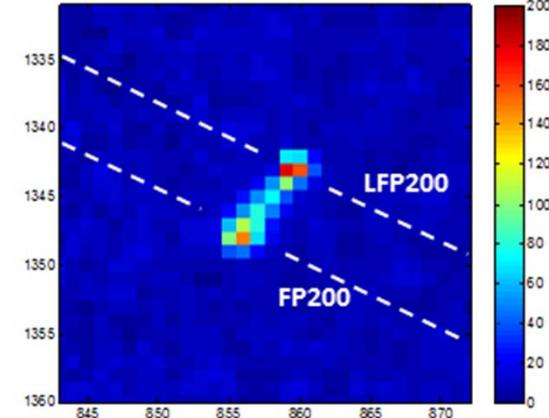
Presence of solid
solution phases

Suppression of the first order phase transition

Powder XRD



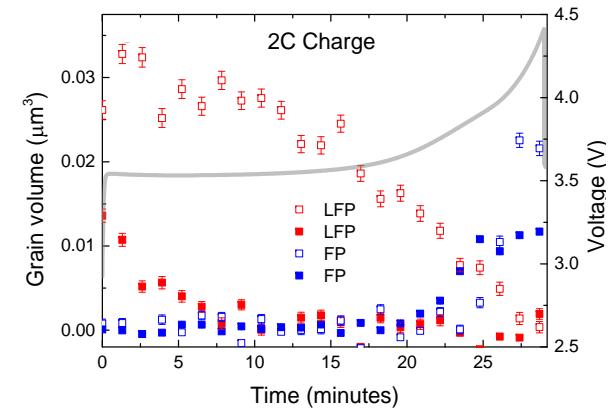
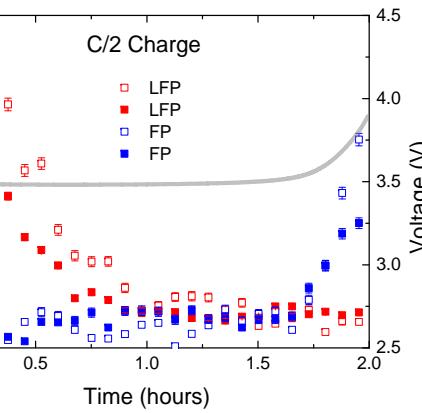
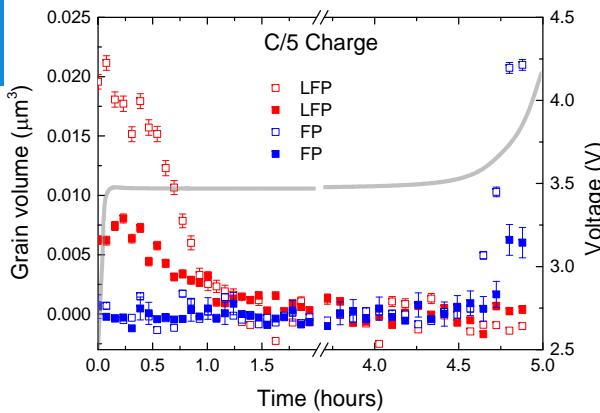
Micro-beam XRD



Solid solution phases exist
within single 140 nm crystallite

Presence of solid
solution phases

Rate dependent transformation times individual 140 nm LFP grains

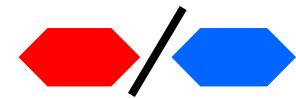


$$\langle \Delta t_{LFP} \rangle = 66 \text{ min}$$

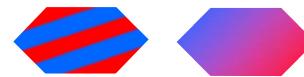
$$\langle \Delta t_{LFP} \rangle = 50 \text{ min}$$

$$\langle \Delta t_{LFP} \rangle = 18 \text{ min}$$

Mosaic transformation: fast transformation individual spots

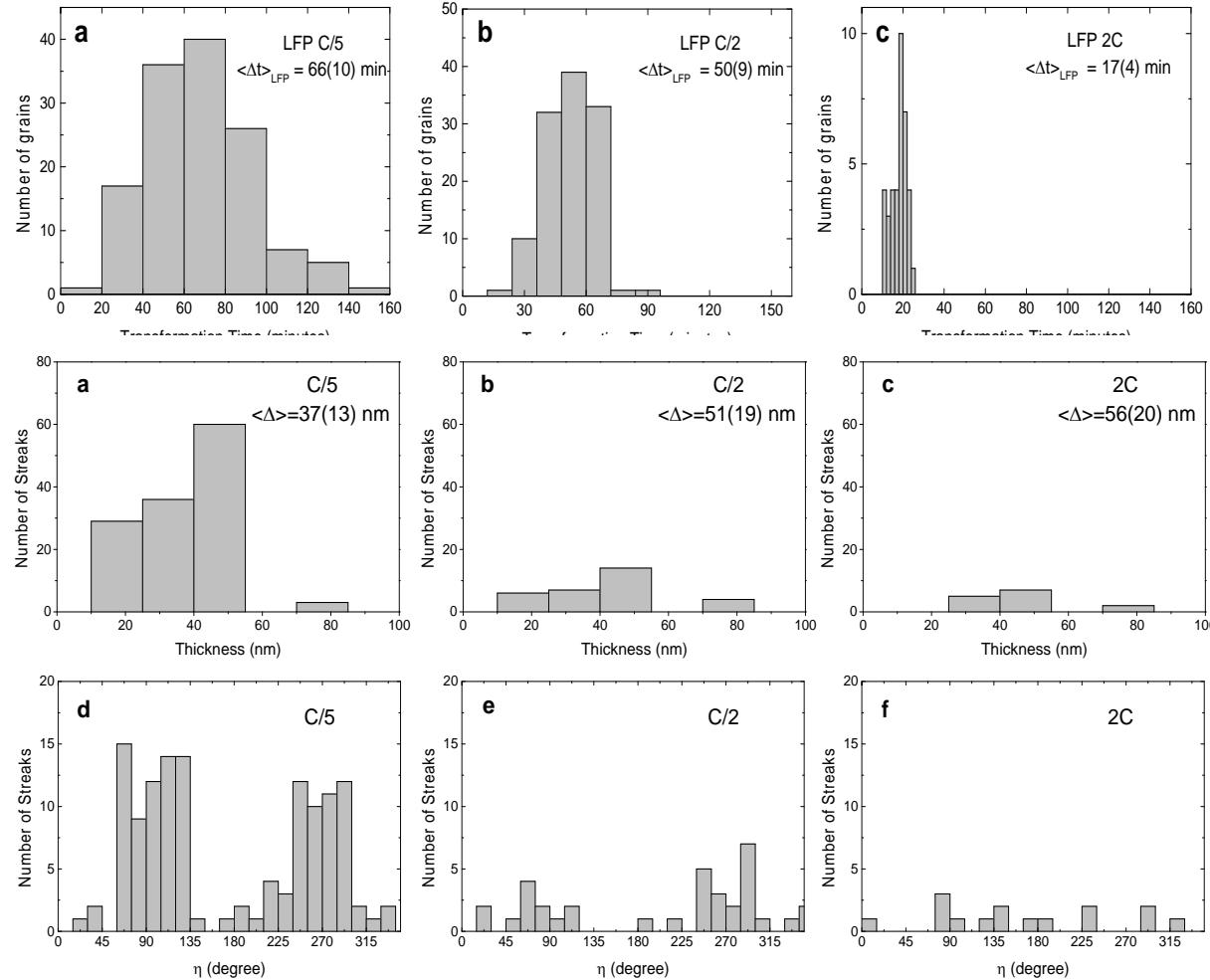


Observed: Slow transformation



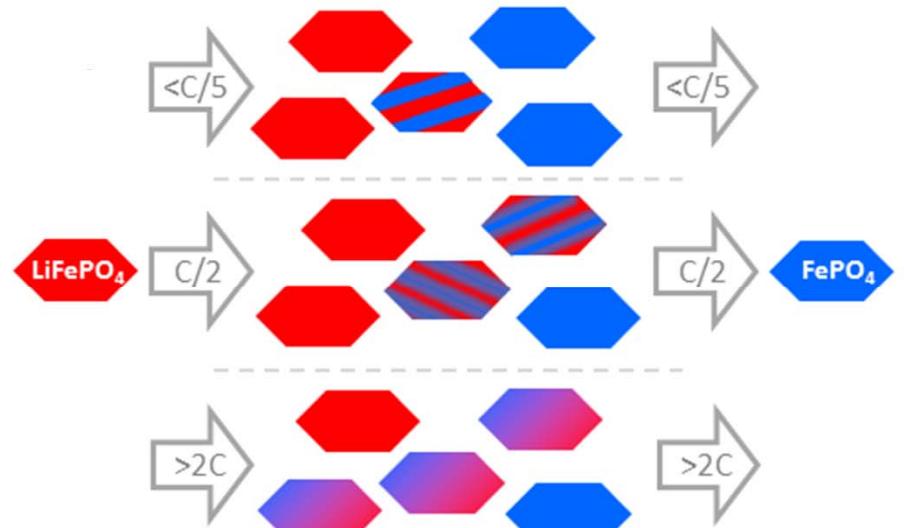
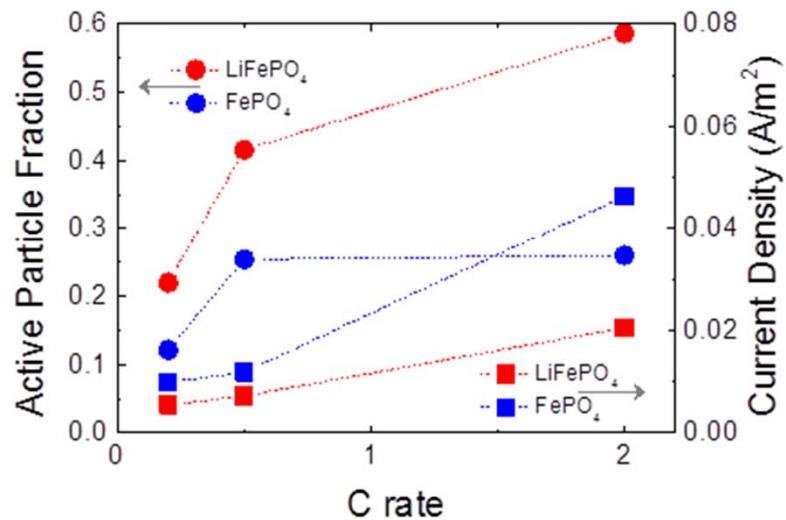
With increasing rate: Faster transformation, more concurrent

Statistics on individual grains



Rate induced faster transformation,
and disappearing internal platelet domains structure

Rate dependent transformation mechanism LFP

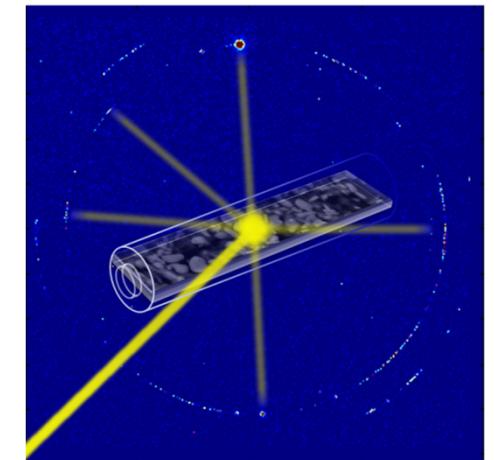
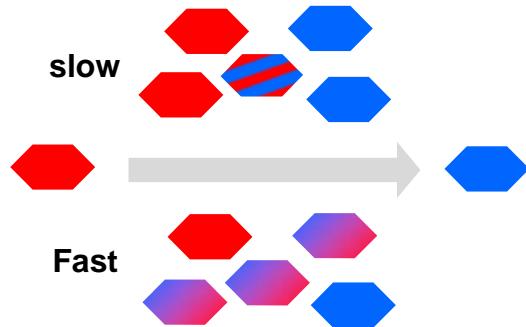


Low rate => Concurrent slow transformation via coexisting domains

Increasing the rate => more diffuse interfaces, increasing active fraction and increase in transformation rate (local current density)

Conclusions

- Powder diffraction: (dis)charge rate induced solid solution phases
- Micro-beam diffraction: Direct operando view on the phase transformation of *individual* grains in the electrodes
- LiFePO₄:
 - Low rates: No mosaic transformation, platelet internal phase morphology
 - High rates: Diffuse interface in single grains
- What determines transformation rate of individual grains
 - Role charge transfer?
 - Pinning interfaces?



Acknowledgements



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