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

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Fluctuations in energy production

2.5 W/m²
1.3 W/m²
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

~1 nm
LiFePO$_4$ as positive electrode material

Li-ion insertion $\Rightarrow$ 1$^{\text{st}}$ order phase transition
Remains orthorhombic, volume change: $\sim$ 5%
LiFePO$_4$ as positive electrode material

\[ \text{Graph: Voltage [V] vs. Capacity [mAh/g]} \]

- FePO$_4$
- LiFePO$_4$

C/n (dis)charge rate, n: # hours to reach full capacity
LiFePO$_4$ as positive electrode material

Fundamental questions

Why can LiFePO$_4$ 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

Nano Letters 2014
Operando powder diffraction

Solid solution phases are unstable

Low rates mosaic transformation

Relaxation
Operando powder diffraction

Overpotential drives the solid solution behavior
Solid solution behavior is responsible for fast (dis)charging LiFePO₄
Operando Microbeam diffraction
Following individual LiFePO₄ grains in-situ with micro beam diffraction
Following individual LiFePO$_4$ 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:

(101) coherent  (100) incoherent

Source: Cogswell et al, ACS Nano 6 (2012) 2215
But what about the mosaic transformation?

Source:
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

Nature Comm. 2015
Suppression of the first order phase transition

Powder XRD

Presence of solid solution phases

Micro-beam XRD

Solid solution phases exist within single 140 nm crystallite
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}
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\[
\langle \Delta t_{LFP} \rangle = 18 \text{ min}
\]

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