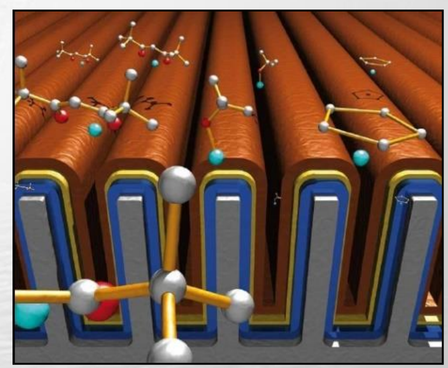
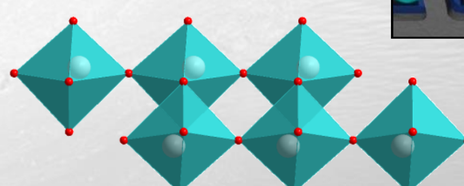
UiO : **Centre for Materials Science and Nanotechnology**

University of Oslo

Ola Nilsen, **Yang Hu**, **Jonas Sottmann**, **Knut B. Gandrud**, **Pushpaka Samarasingha**, **Annina Moser**, **Helmer Fjellvåg**

Electrons in motion



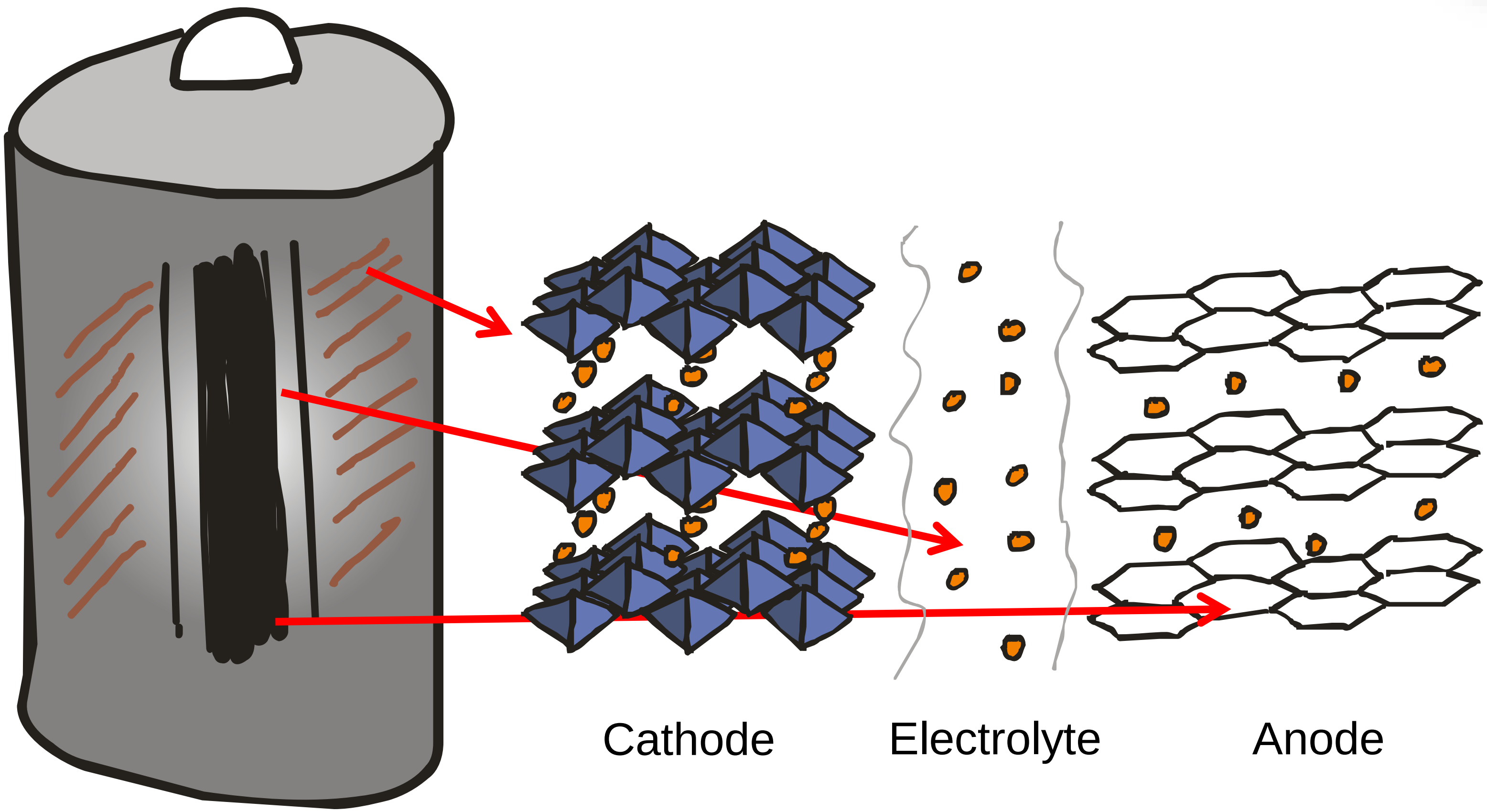


UiO : Centre for Materials Science and Nanotechnology
University of Oslo

NAFUMA

Nanostructured Functional Materials

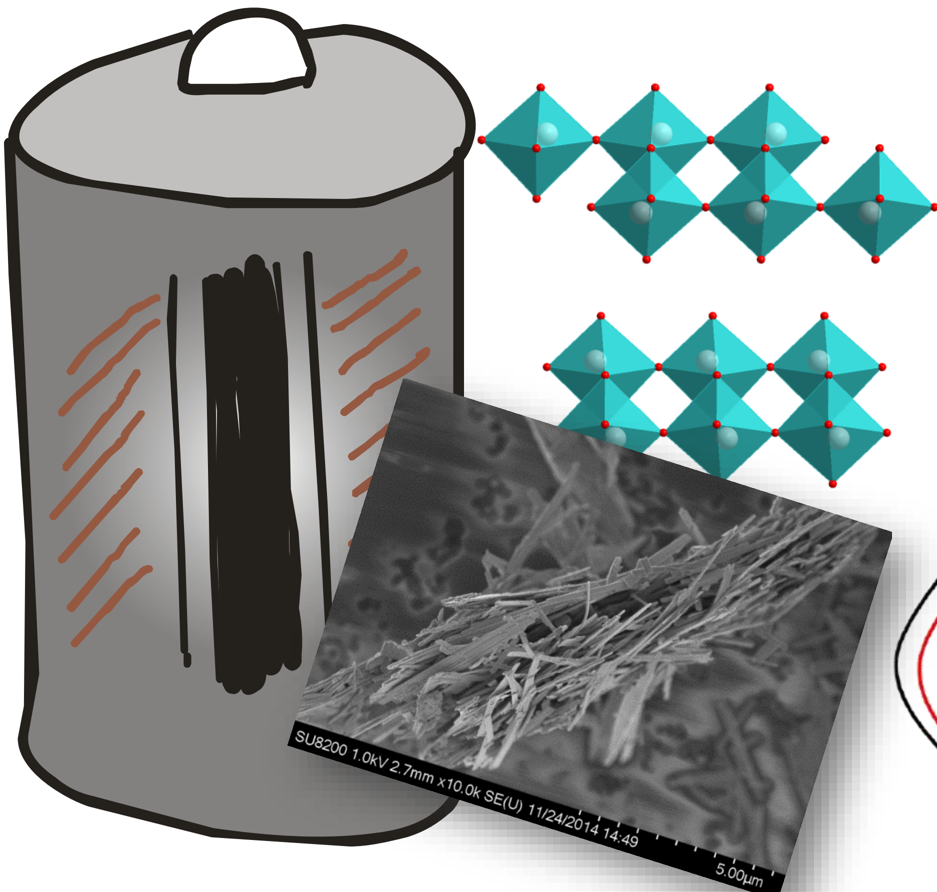
BATLAB

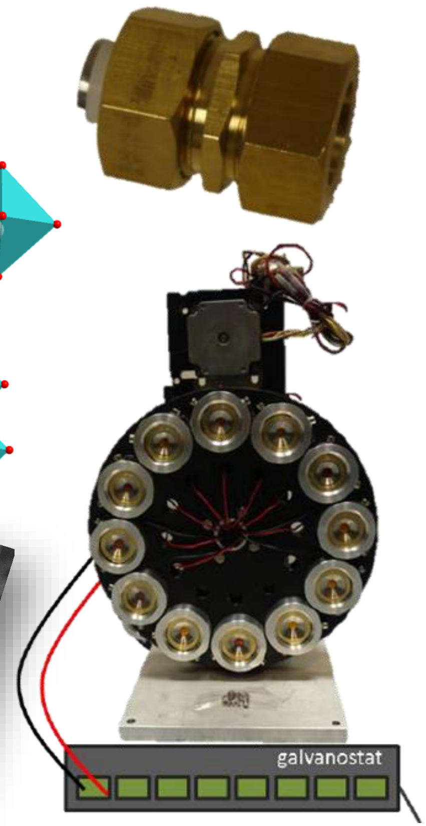


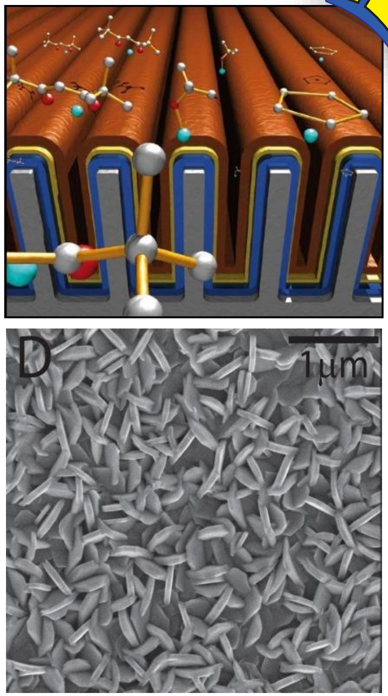
UiO : Centre for Materials Science and Nanotechnology
University of Oslo

NAFUMA

Nanostructured Functional Materials





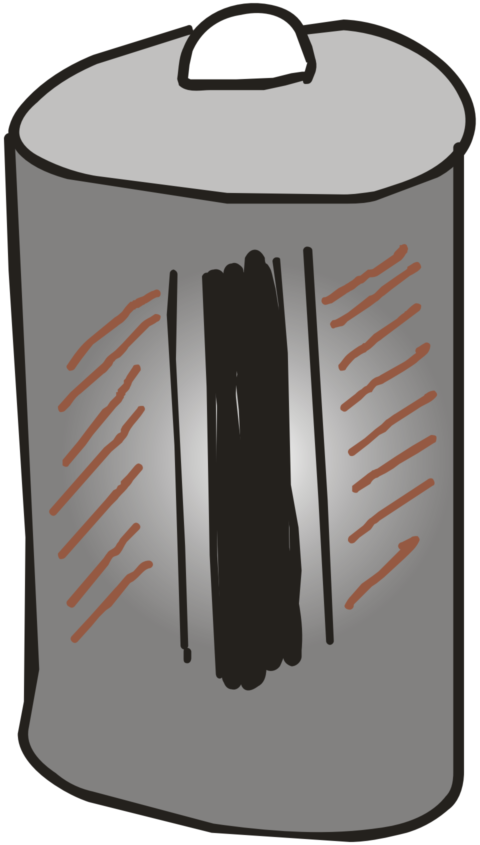


Powder

In situ

Thin film

The motion…



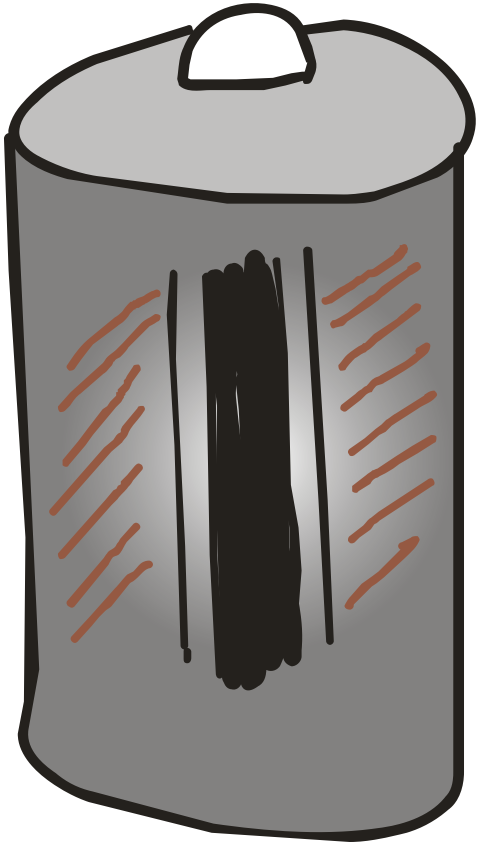
$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$ or $Li_2Mn_3NiO_8$?

MoO_3

Preussian blue $Na_xMn[Fe(CN)_6]_y$

Thin and solid

The motion…



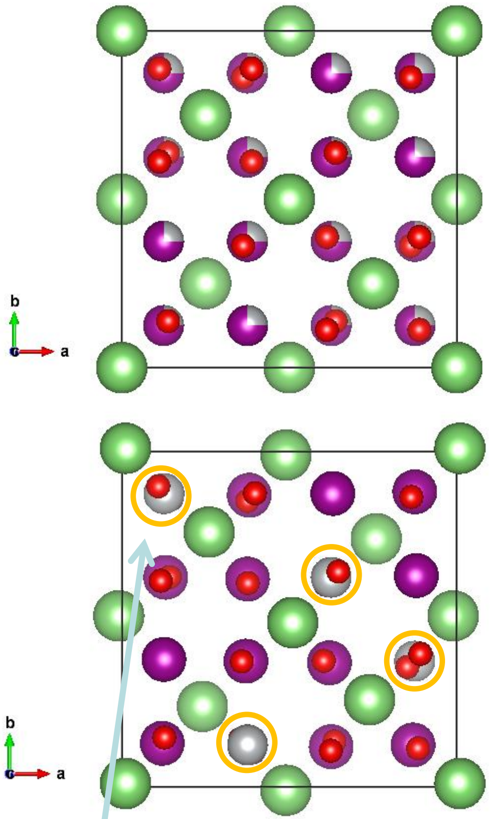
$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$ or $Li_2Mn_3NiO_8$?

$LiNi_{0.5}Mn_{1.5}O_4$ = 5 V ☺

The material exist with varying degrees of cation disorder in the spinel structure, where the disordered Fd-3*m* structure show a higher capacity over the ordered $P4_332$ structure.

Disordered spinel; Fd-3m

$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$

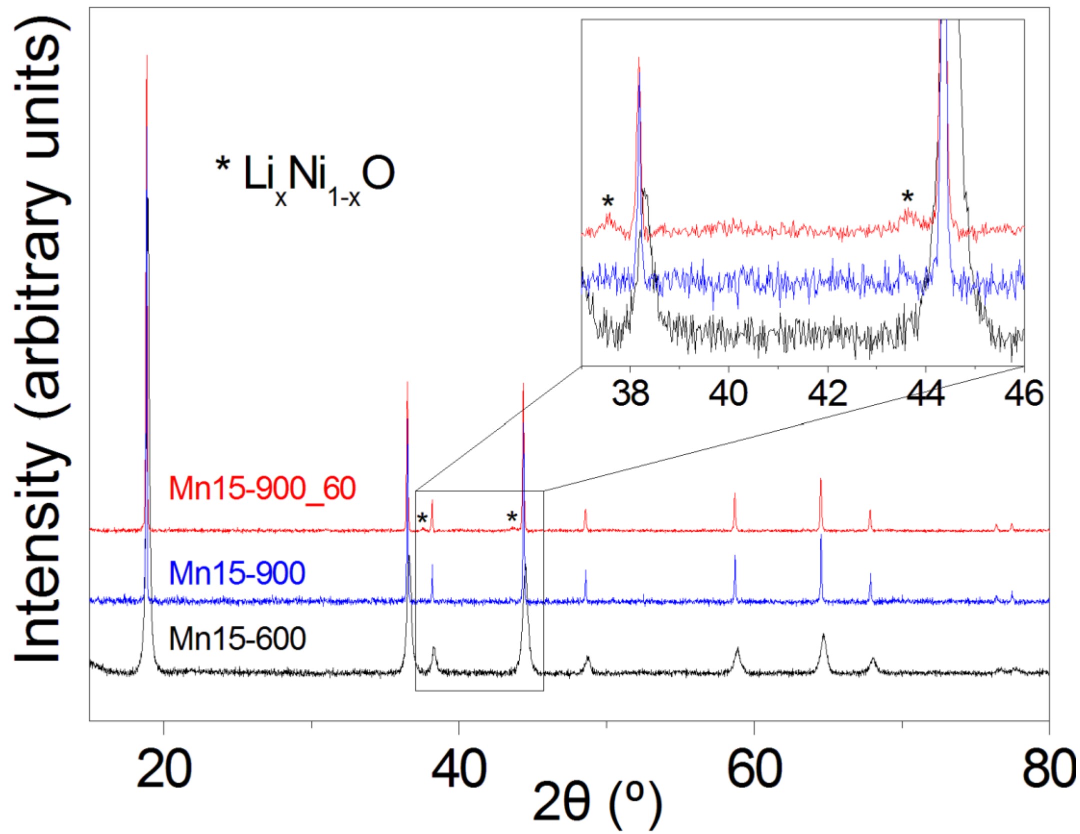


$Li_2Mn_3NiO_8$

Ordered spinel, $P4_332$

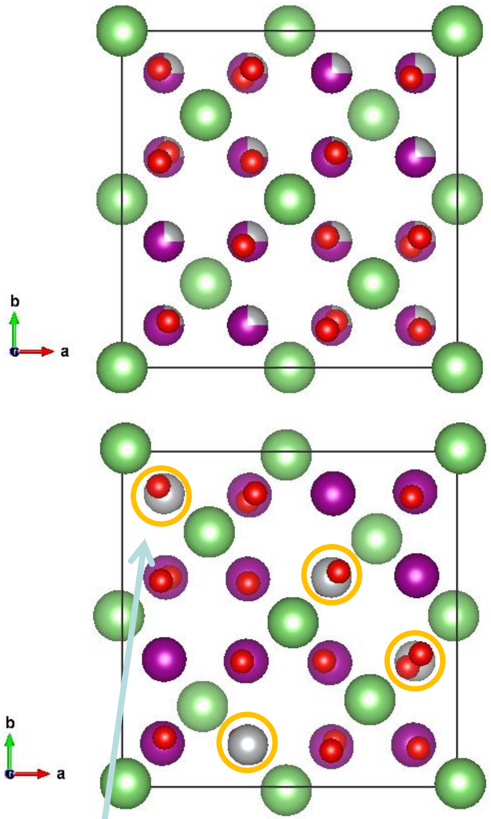
Mn, Ni ordering

Cu kα X-ray data



Disordered spinel; Fd-3m

$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$

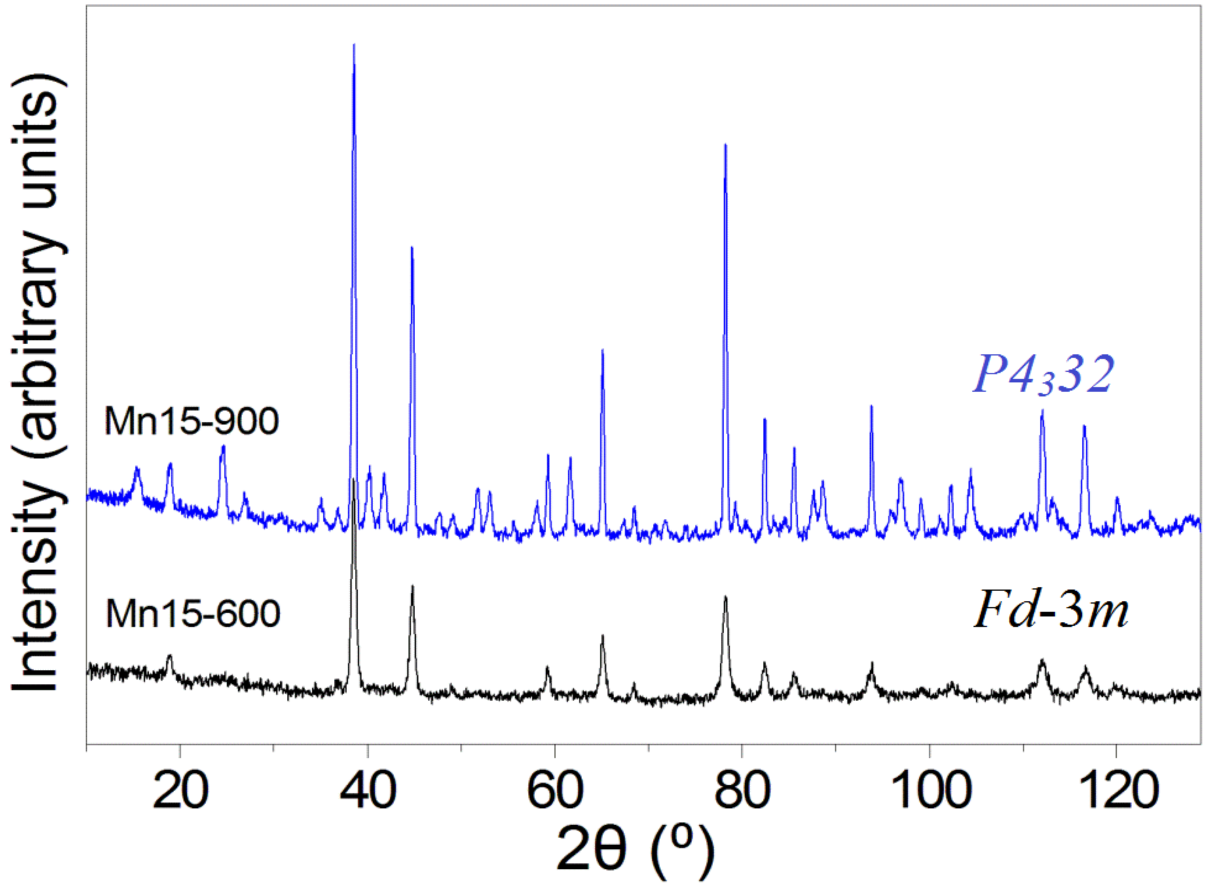


$Li_2Mn_3NiO_8$

Ordered spinel, $P4_332$

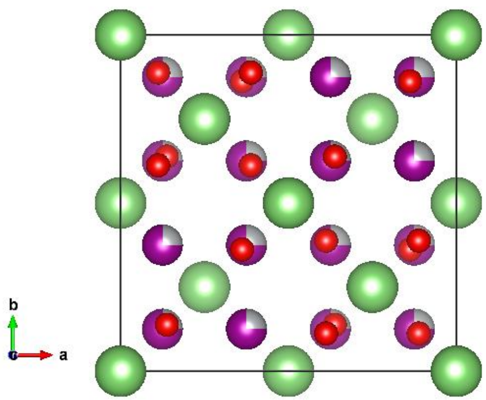
Mn, Ni ordering

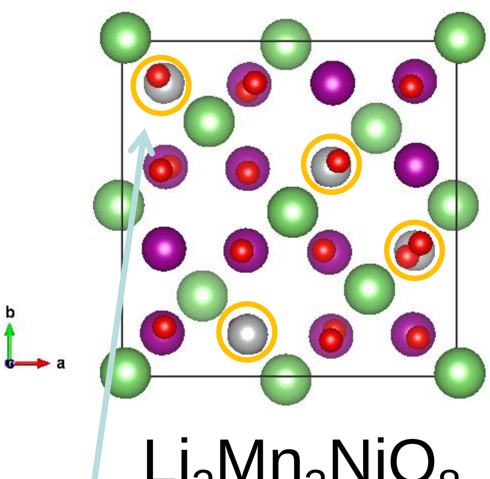
Neutron data



Disordered spinel; Fd-3m

$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$



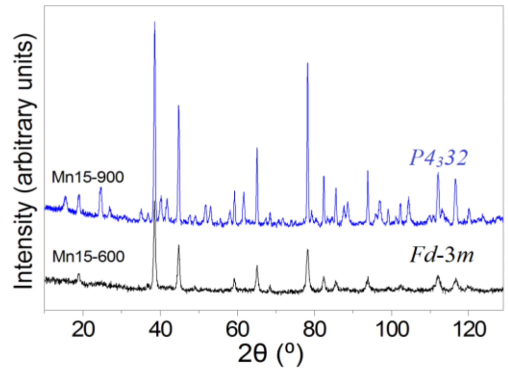


$Li_2Mn_3NiO_8$

Ordered spinel, $P4_332$

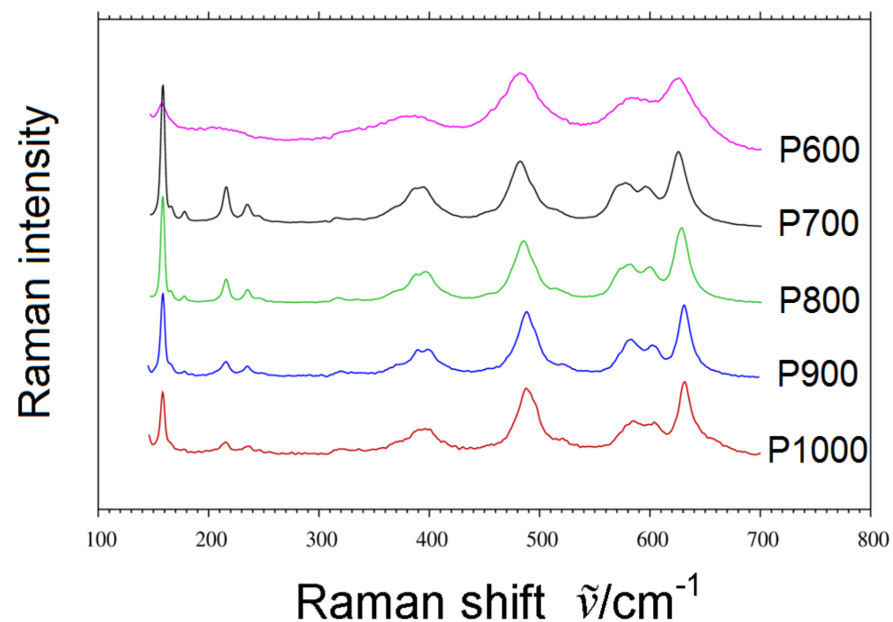
Mn, Ni ordering

Neutron data



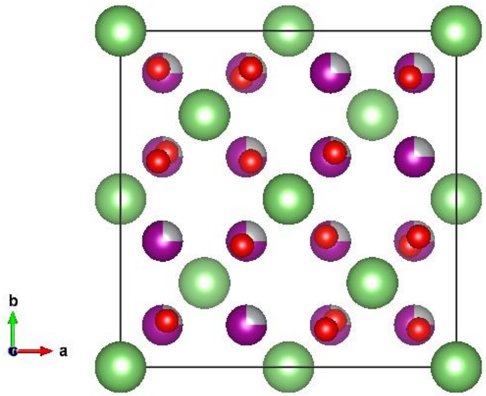
Synthesis at low-T give a disordered spinel with respect to Mn/Ni.

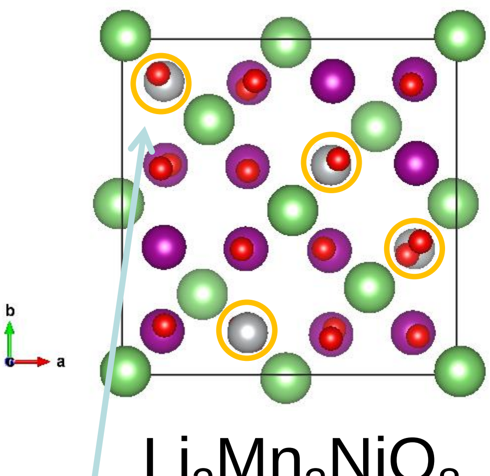
Intermediate temperatures and up (700°C) give complete Mn-Ni ordering



Disordered spinel; Fd-3m

$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$



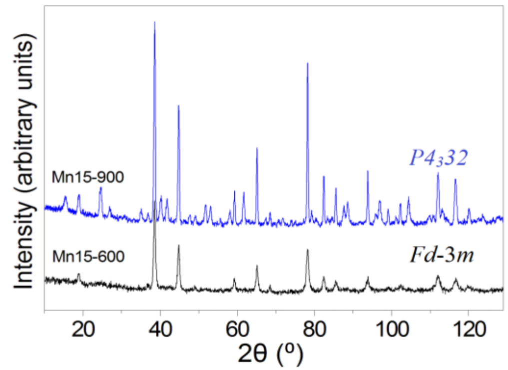


$Li_2Mn_3NiO_8$

Ordered spinel, $P4_332$

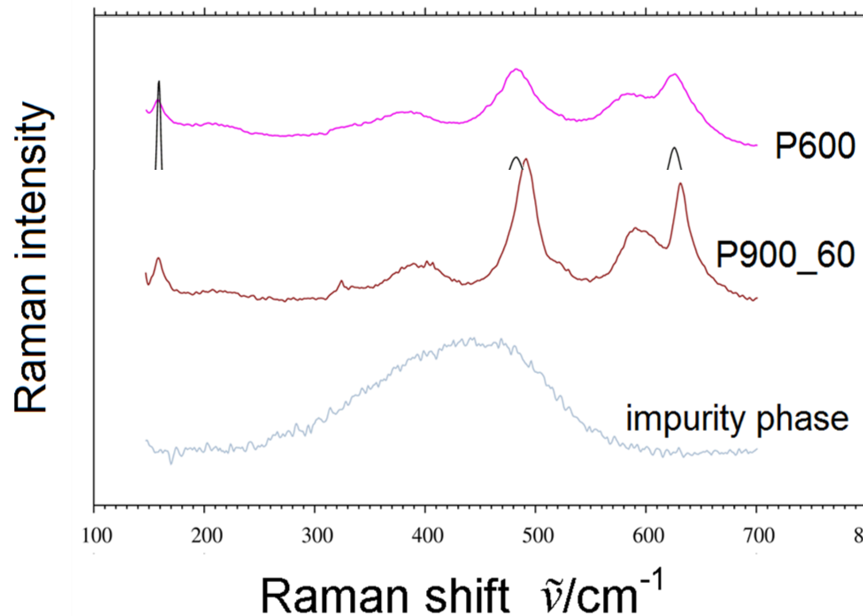
Mn, Ni ordering

Neutron data



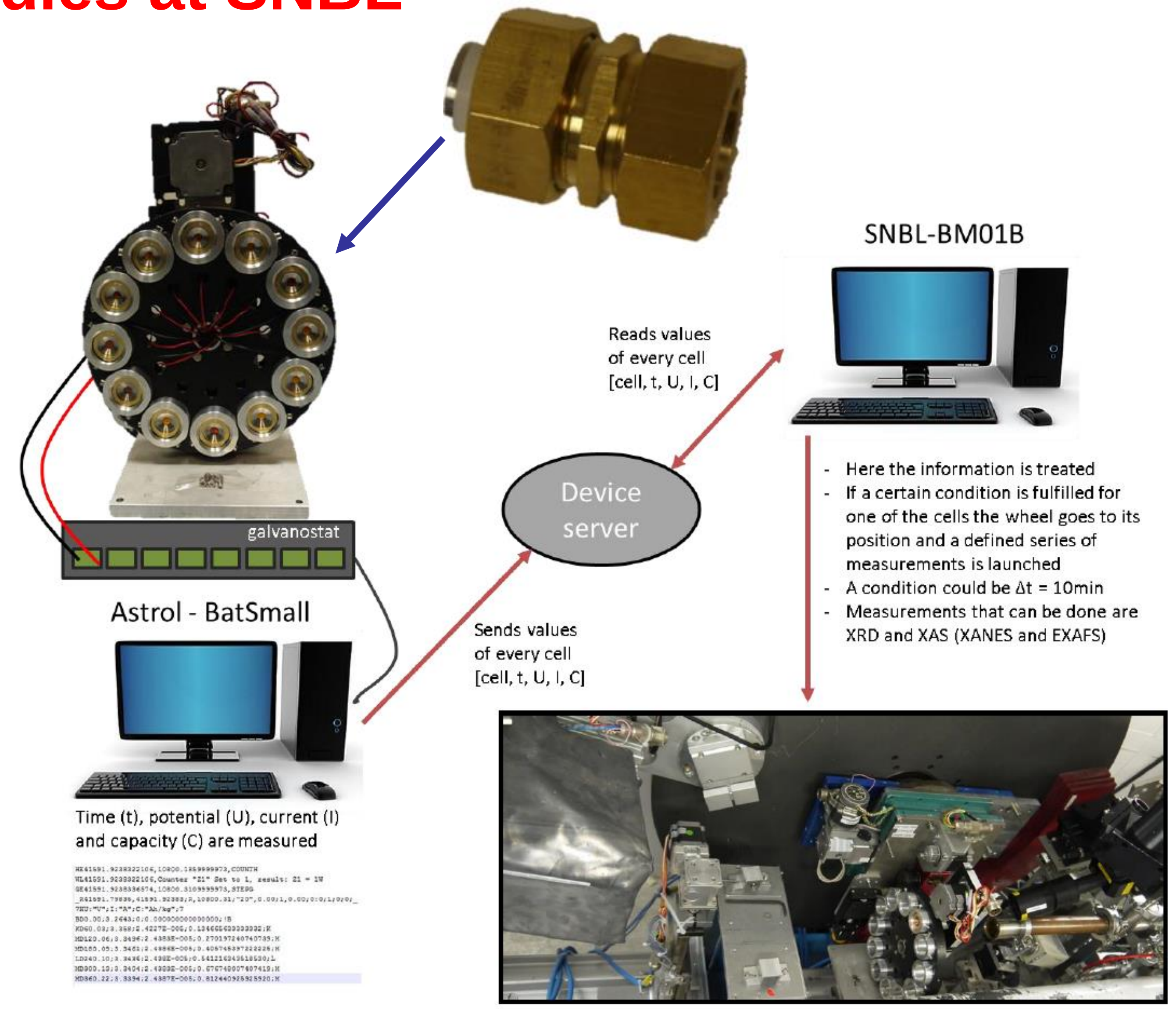
Synthesis at low-T give a disordered spinel with respect to Mn/Ni.

Intermediate temperatures and up (700ºC) give complete Mn-Ni ordering



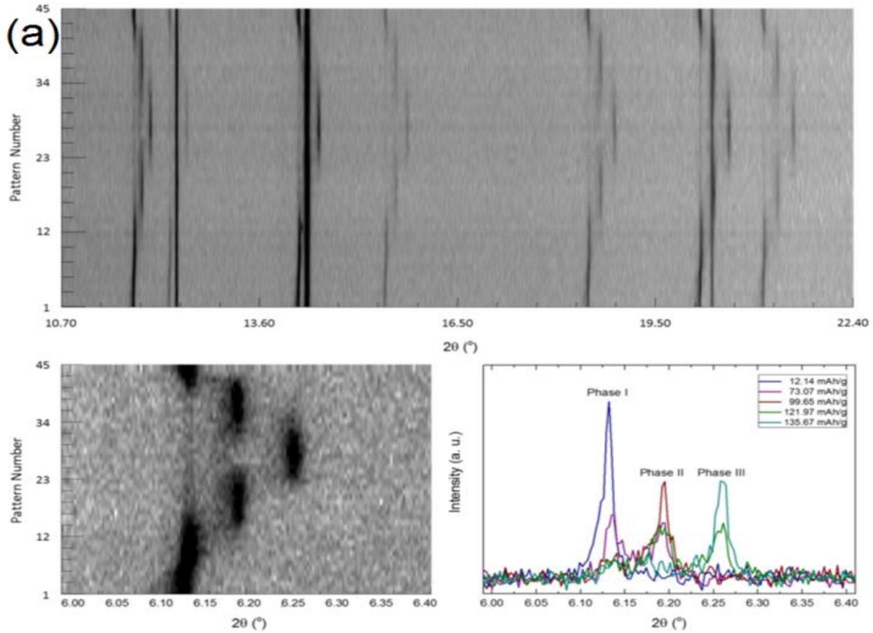
…or disordered at high temp over long time…

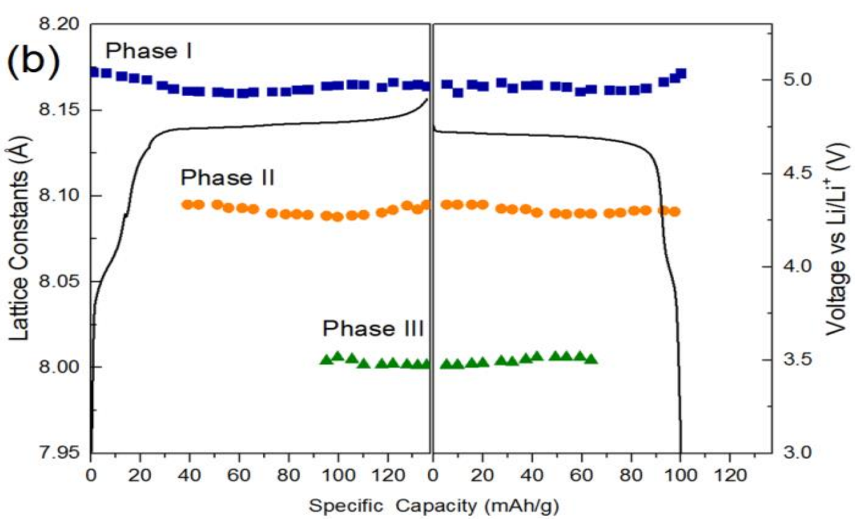
In-operando battery cell for synchrotron studies at SNBL

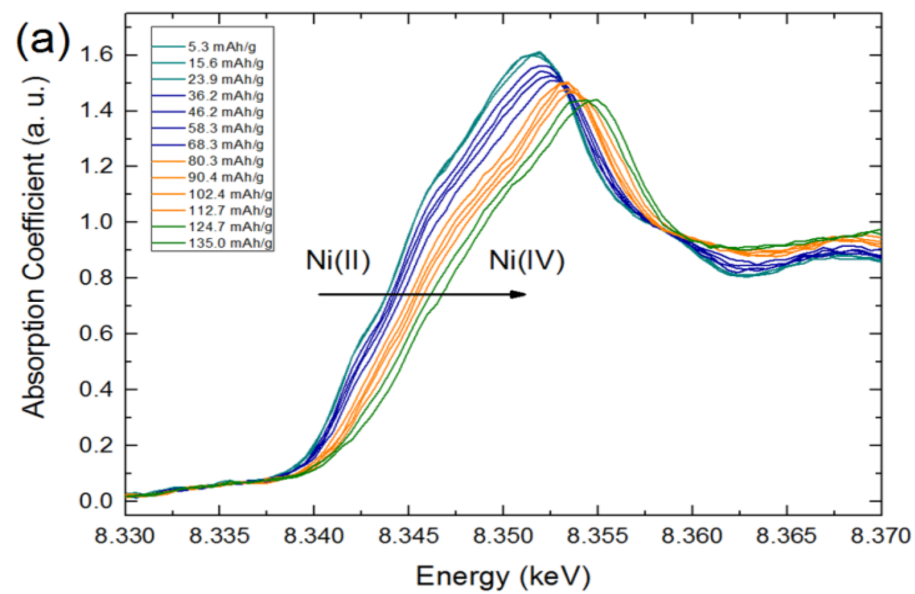


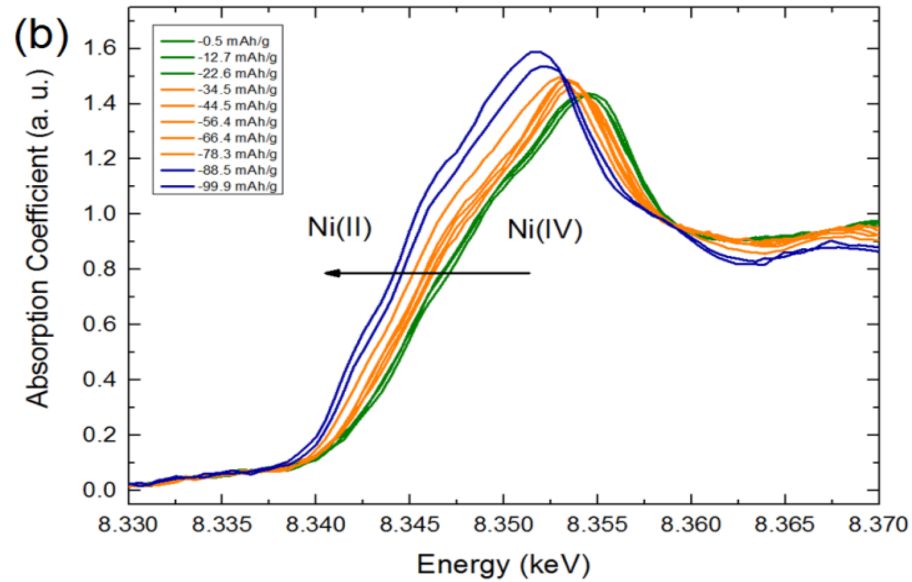
$Li_2Mn_3NiO_8$

In-operando synchrotron experiments



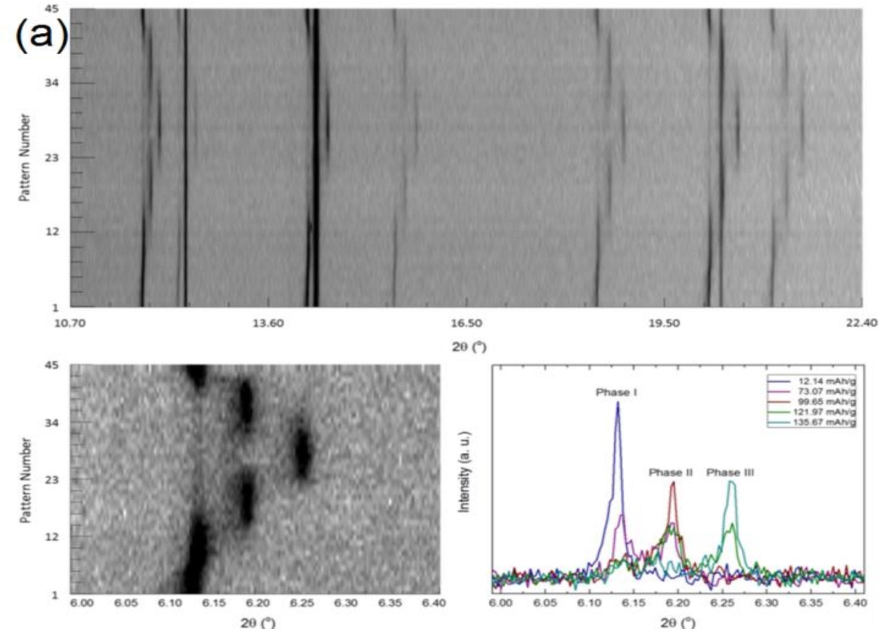


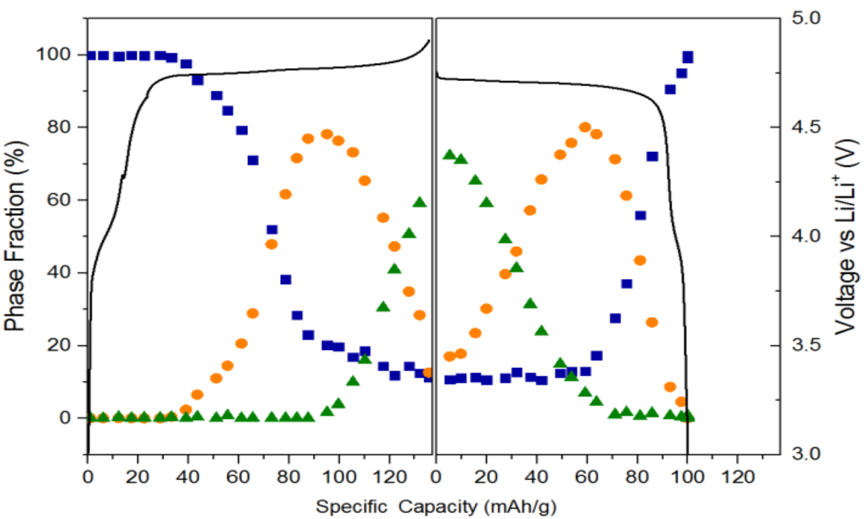


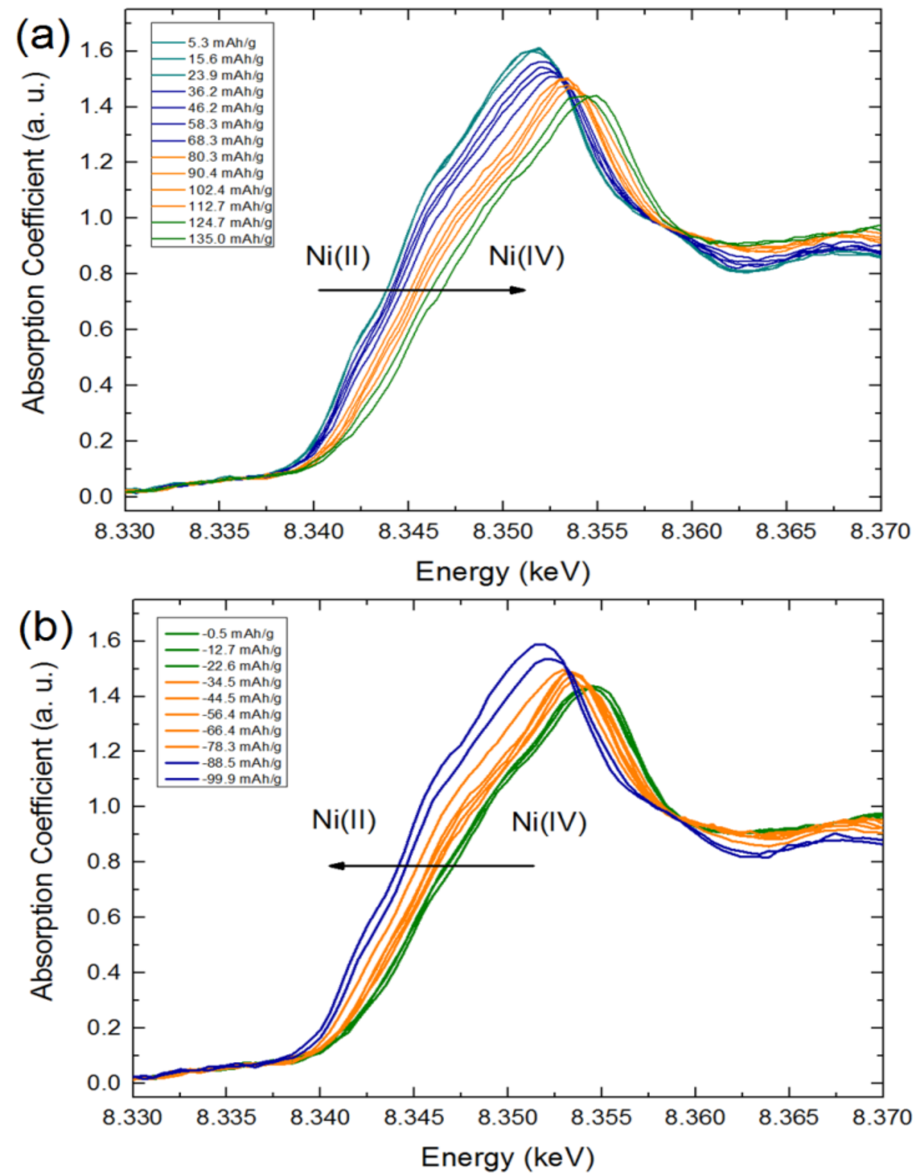


$Li_2Mn_3NiO_8$

In-operando synchrotron experiments

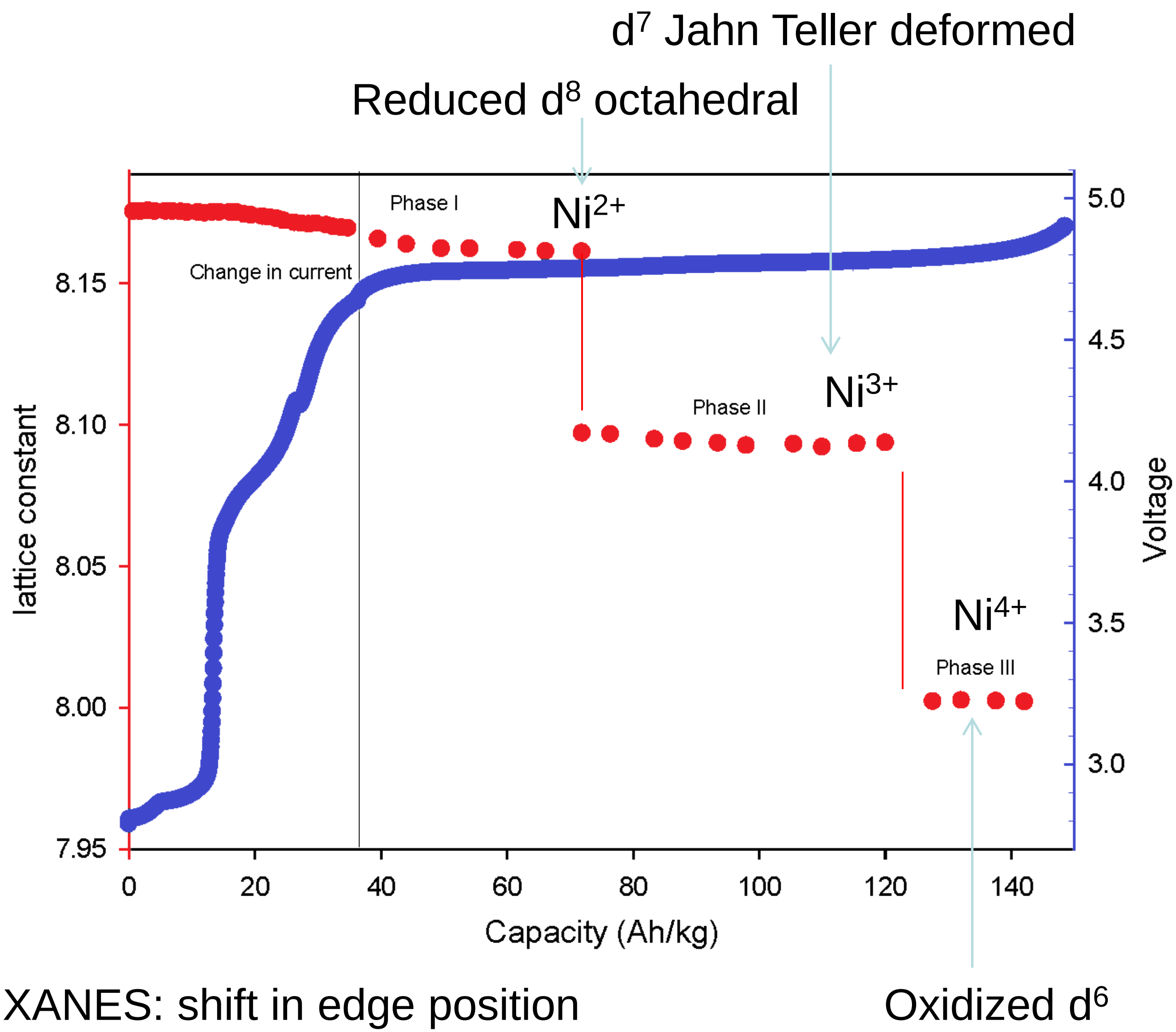






$Li_2Mn_3NiO_8$

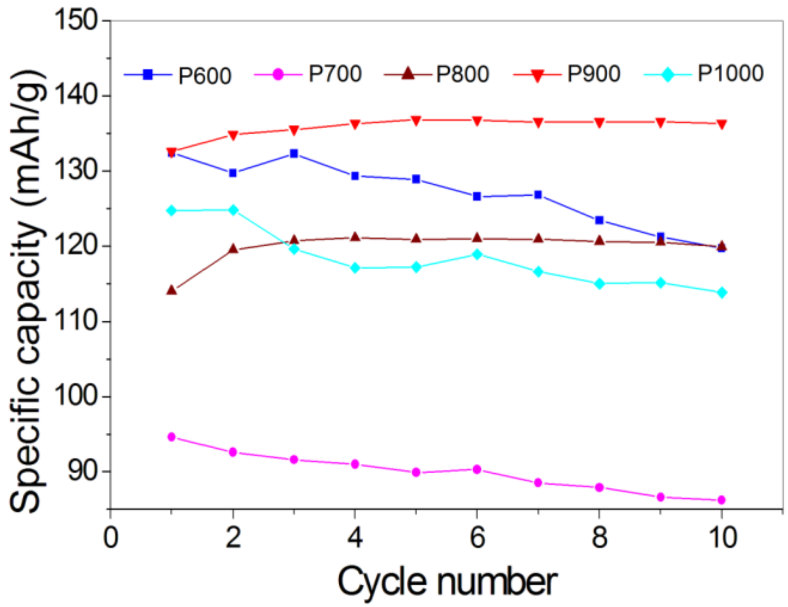
In-situ PXRD and XANES measurements

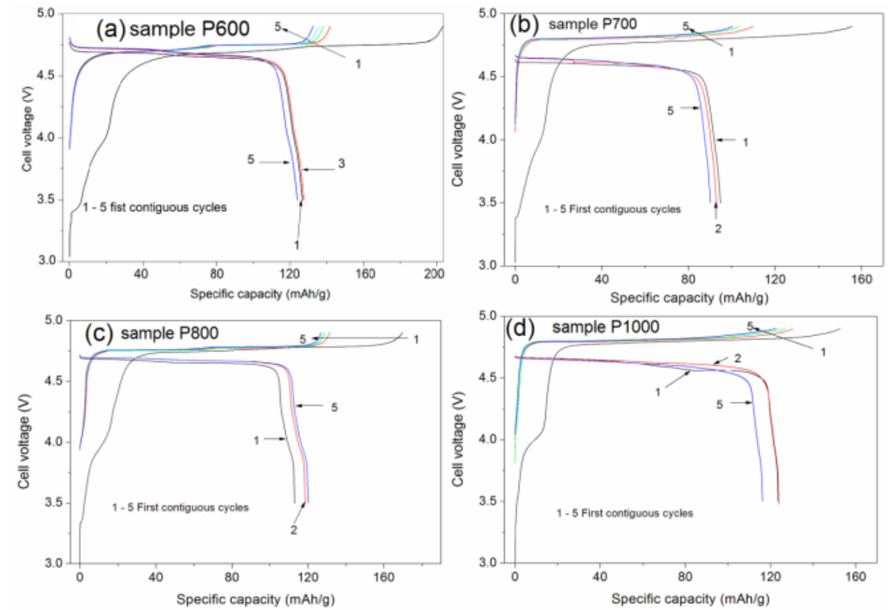


XANES: shift in edge position

EXAFS: change 1. coordination sphere

Cycling

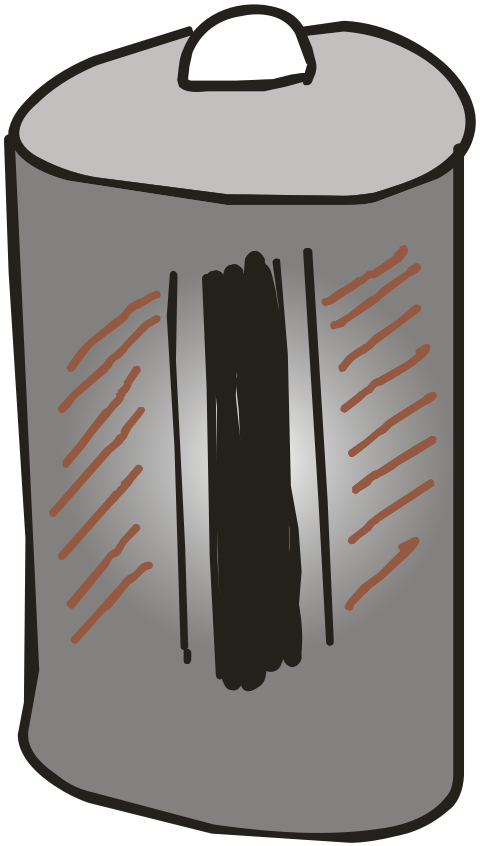




Discharge capacity versus cycle number for "type B" cathodes prepared from $LiMn_{1.5}Ni_{0.5}O_4$ powders. Discharge rates 15 mA/g (approximately 0.1 C); potential window 3.5 - 4.9 V. And Galvanostatic charge and discharge curves

We report the highest recorded specific capacity for the *ordered* phase, currently with submicron size particles as achieved by heat treatment at 900 °C for 10 h followed by 700 °C for another 10 h.

The motion…



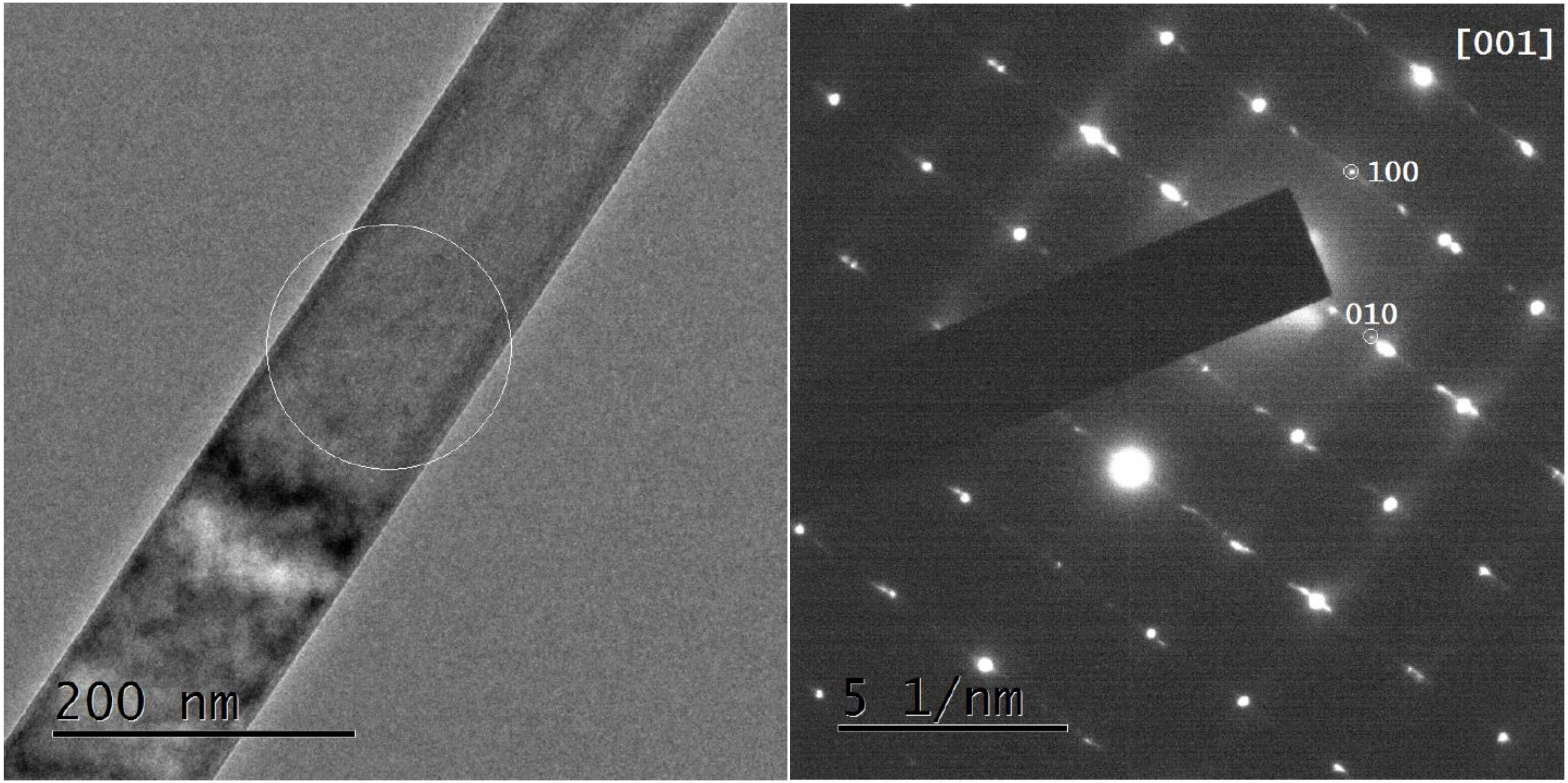
$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$ or $Li_2Mn_3NiO_8$?

MoO_3

TEM and SAED on MoO_3 nanobelt

Nice belts with well defined reflections…

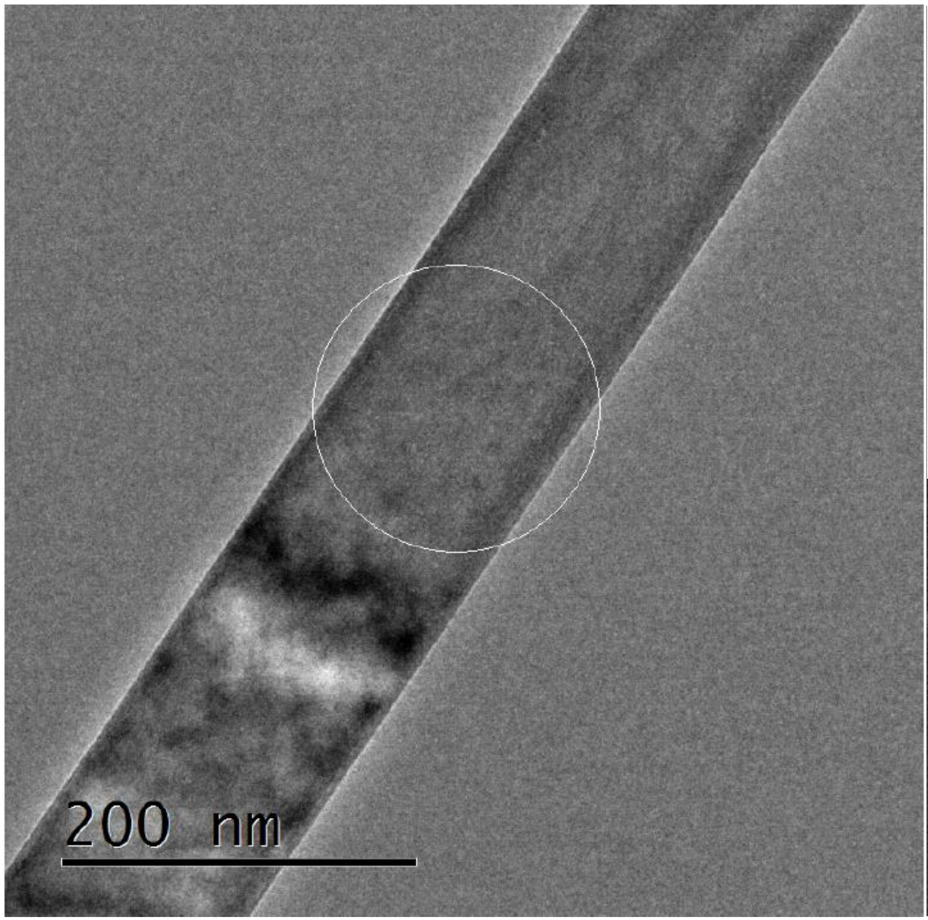
…in one direction…

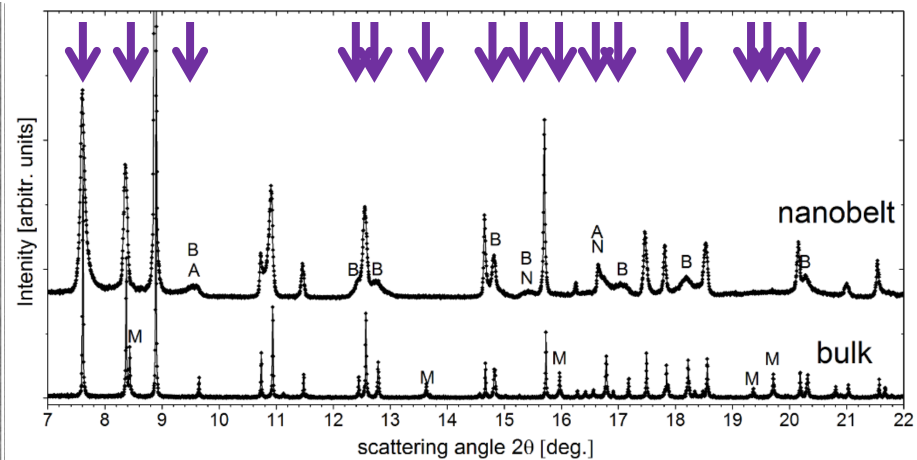


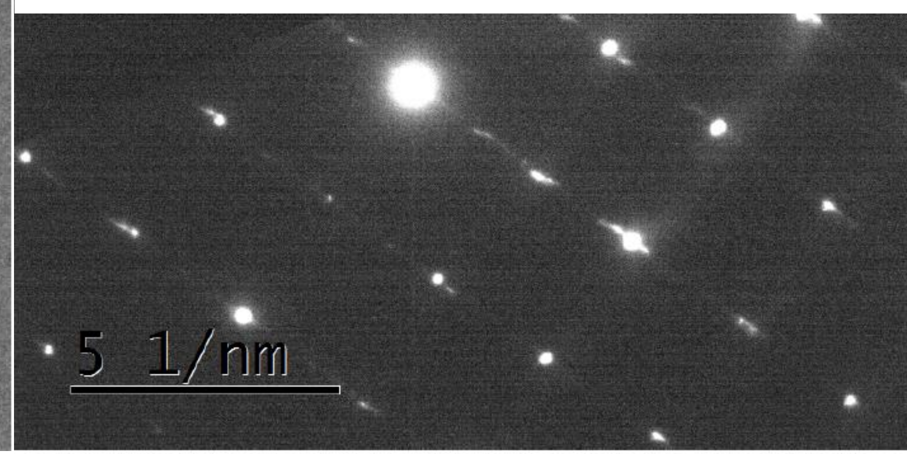
TEM and SAED on MoO_3 nanobelt

Nice belts with well defined reflections…

…in one direction…

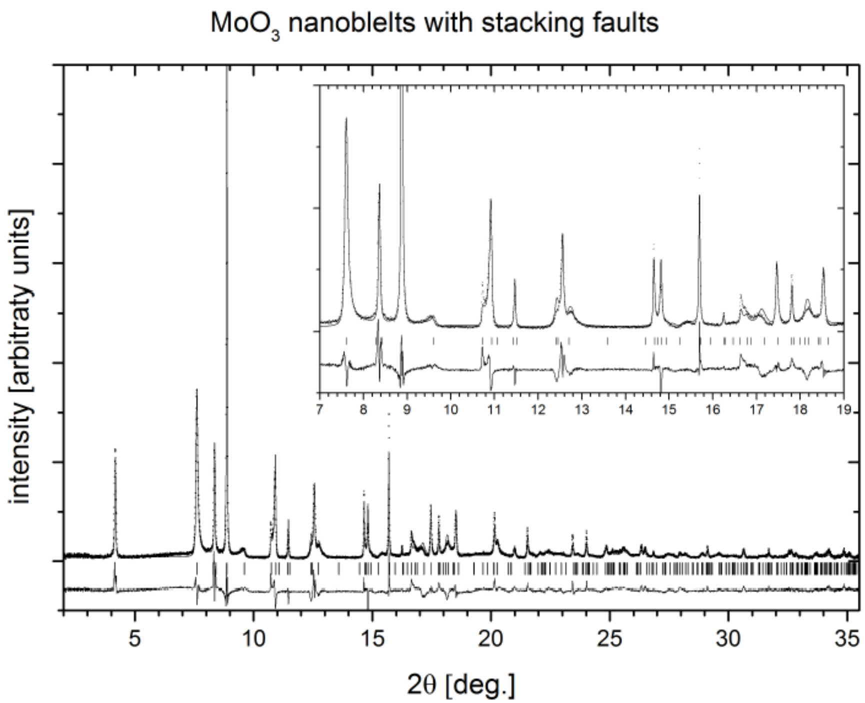


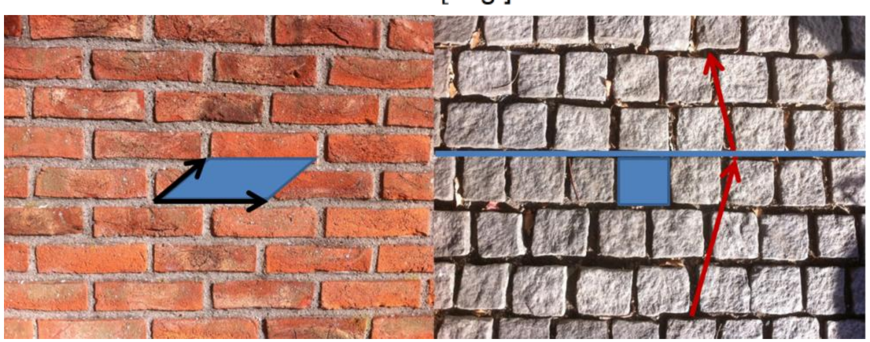


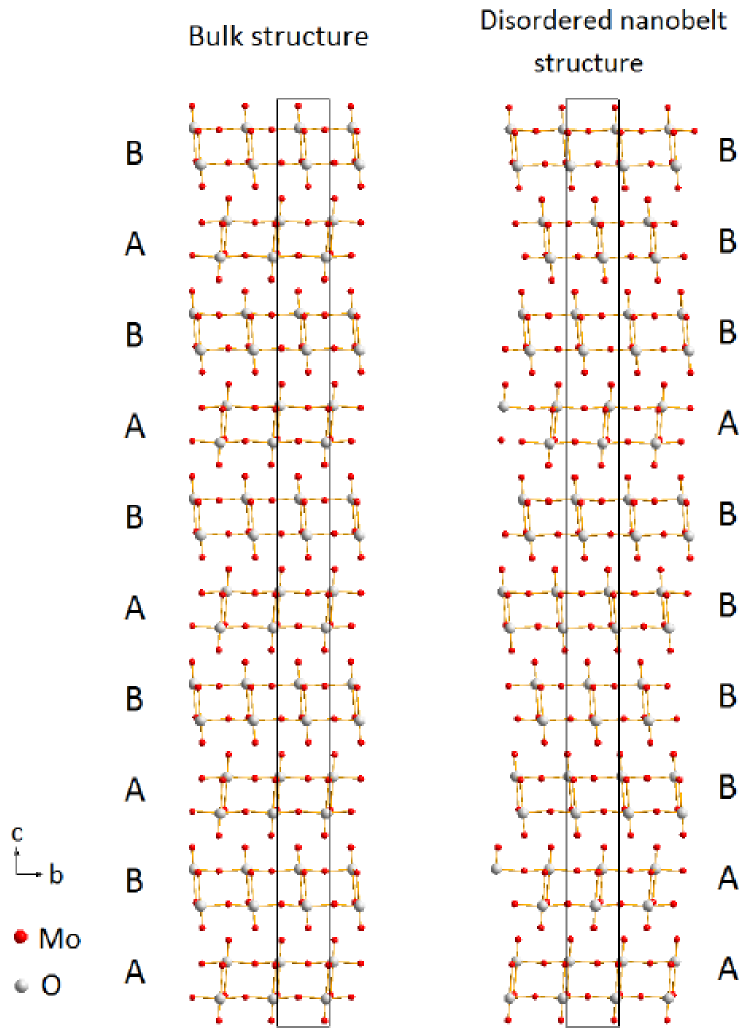


Structural differences at nanoscale MoO_3 nanobelts vs bulk

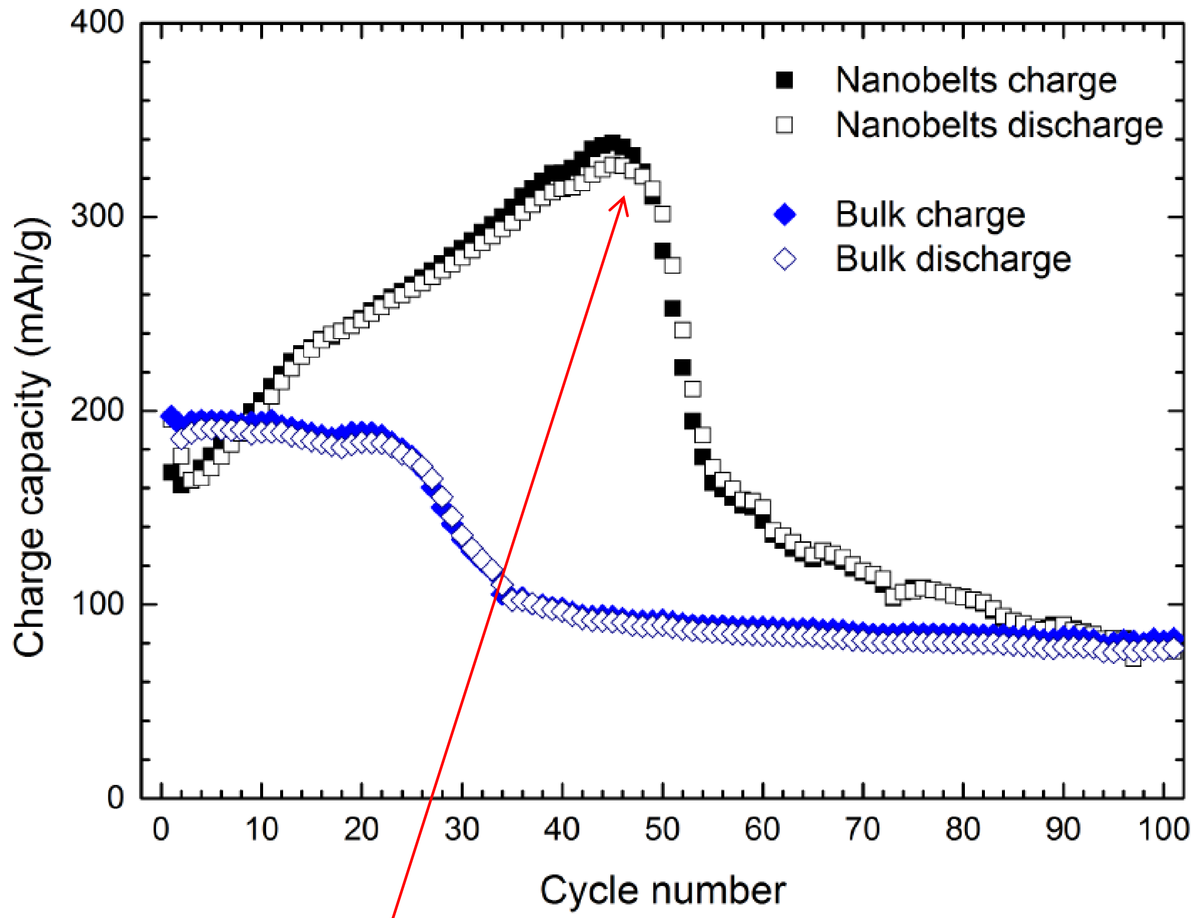
Structural differences at nanoscale Stacking faults







High capacity cathode materials: Bulk and nanobelt MoO_3

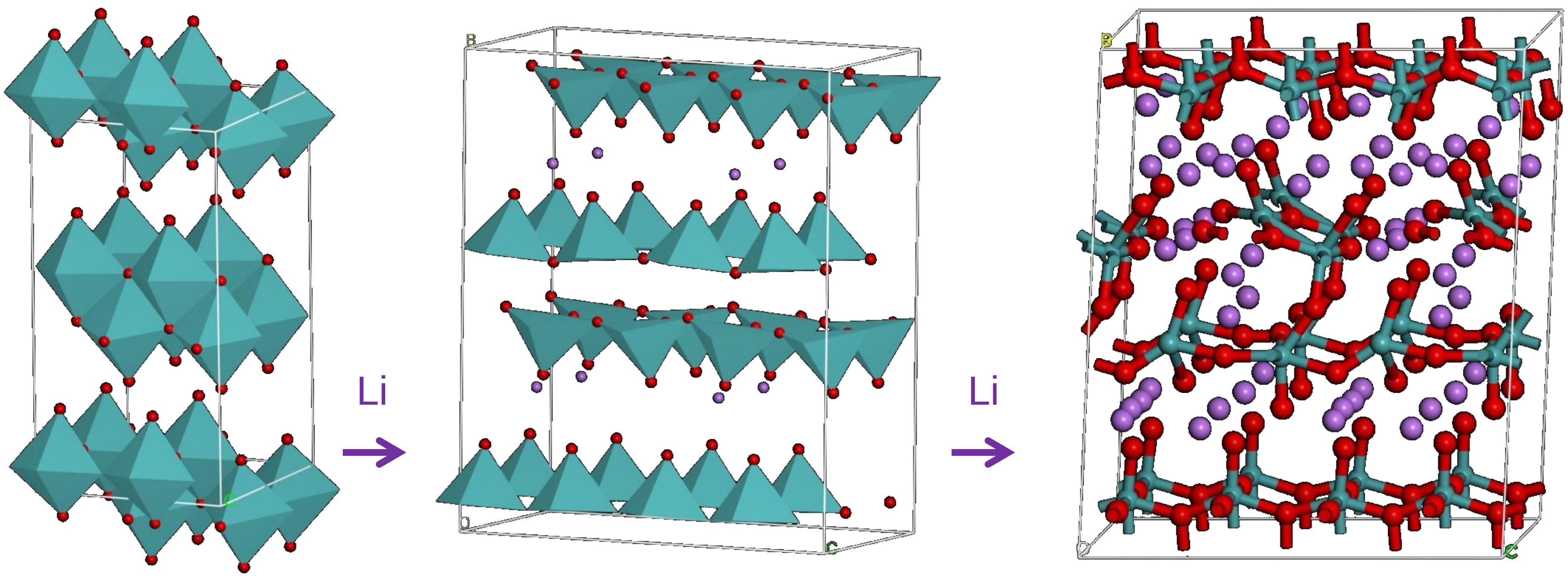


Commercial state-of-the art cathode material $LiFePO_4/LiCoO_2$ spinel,…

Must solve stability issue: degradation mechanism

Li insertion process for MoO_3

Computational modeling:



MoO_3 $Li_{0.25}MoO_3$ $Li_{1.75}MoO_3$

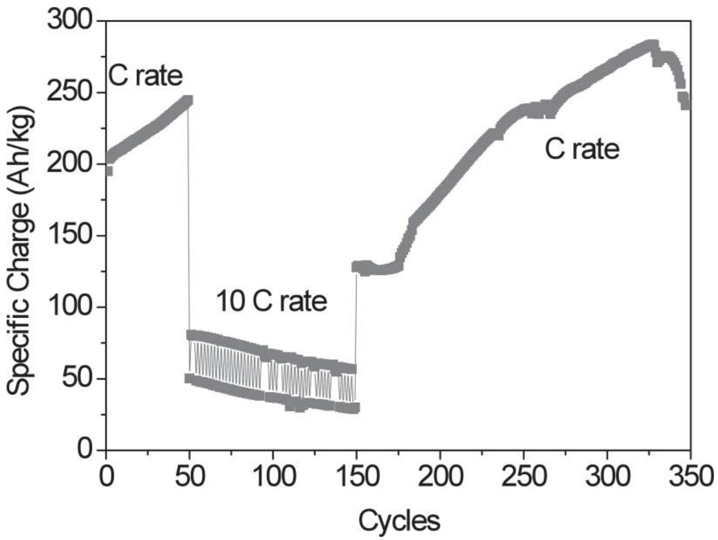
In-situ diffraction:
Rapid «amorphization» (loss of diffraction peaks)

α-MoO_3 as cathode material

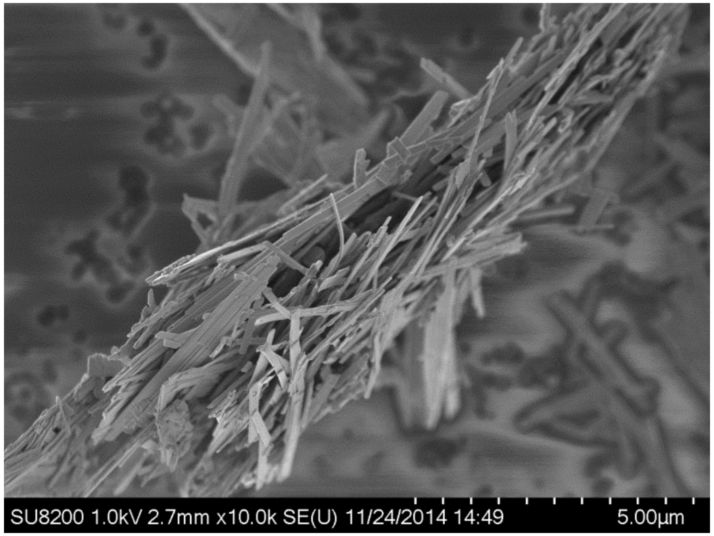
N-doped α-MoO_3 nanobelts gives the highest capacity to date

α-MoO_3 nanobelts are difficult to study because of preferred orientation

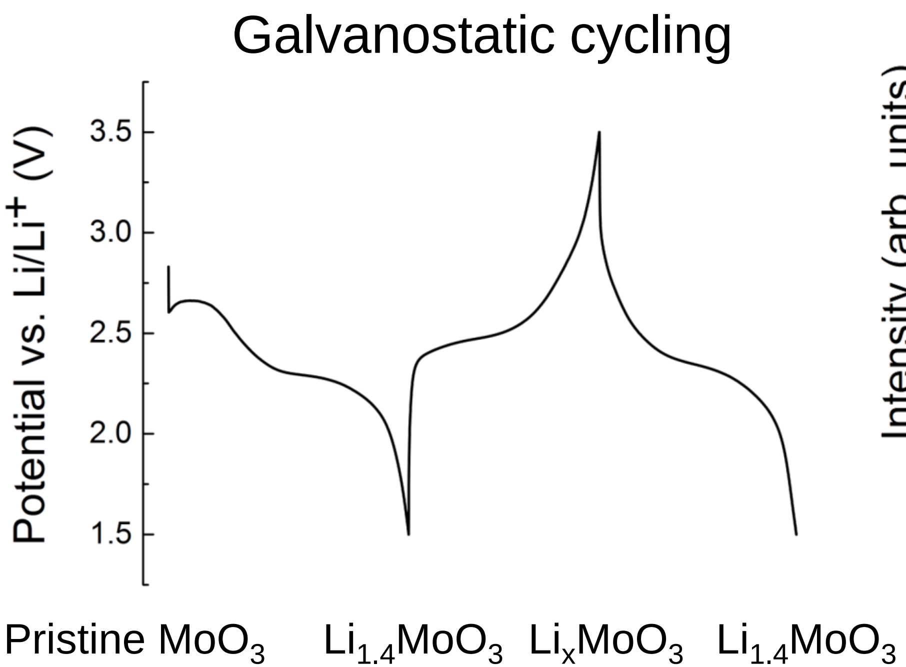
Using bulk α-MoO_3 as a model material for in situ diffraction studies

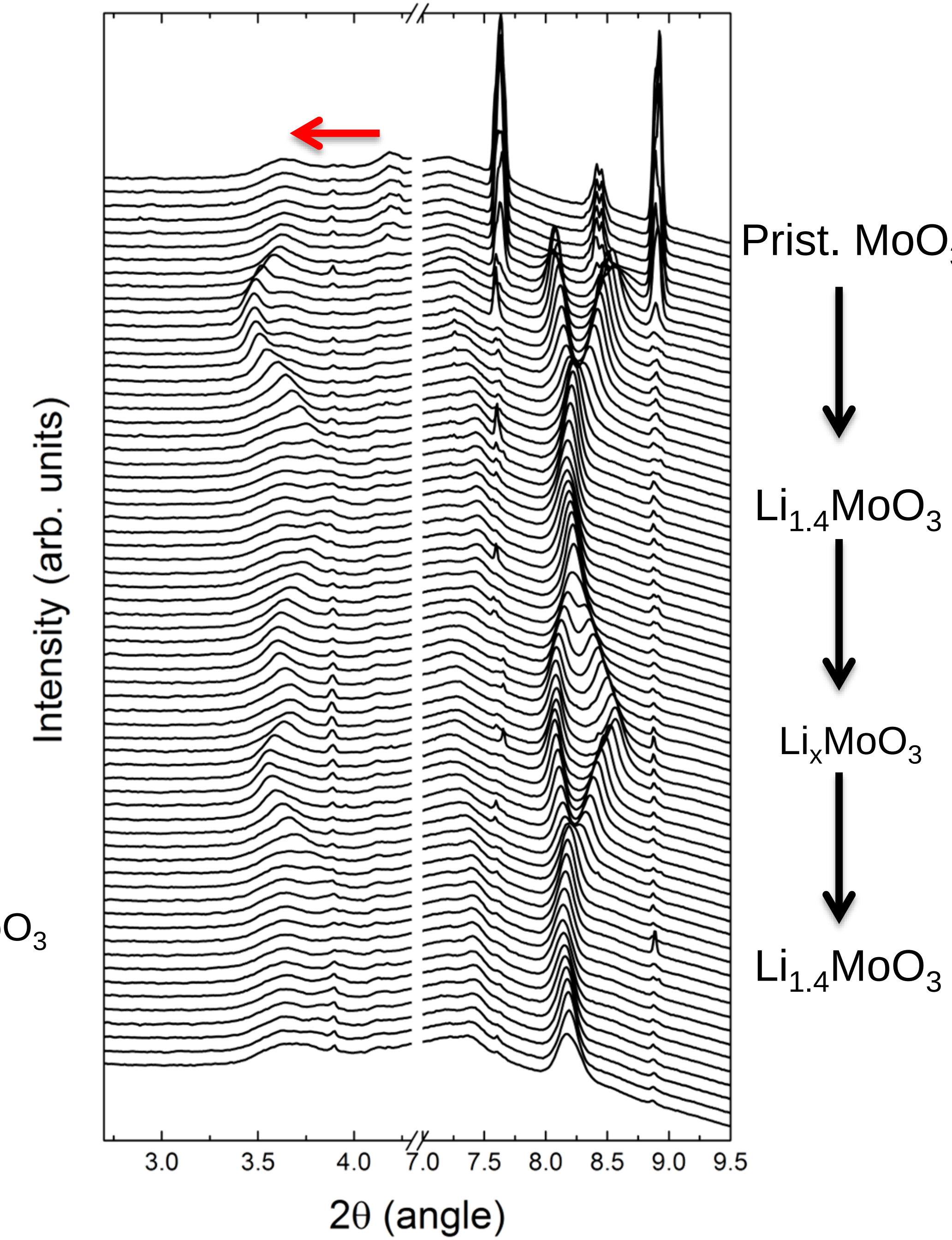


Wang et. al. Vol. 3, is. 5, pg. 606-614 , Adv. Energy Mater. **2012**

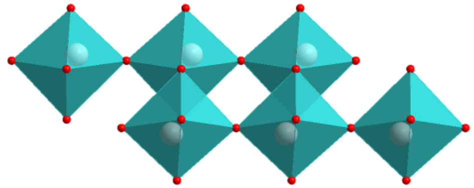


Phase transformation



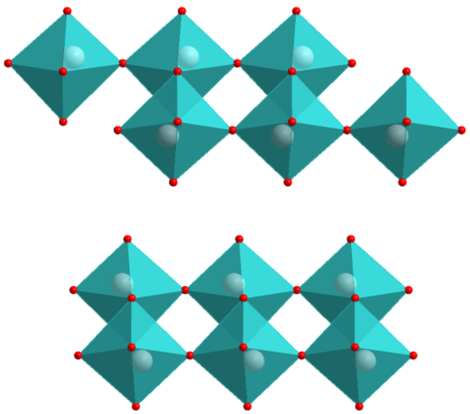


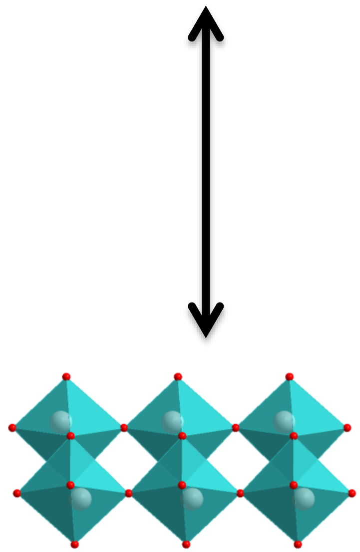
$Li_{0.2}MoO_3$

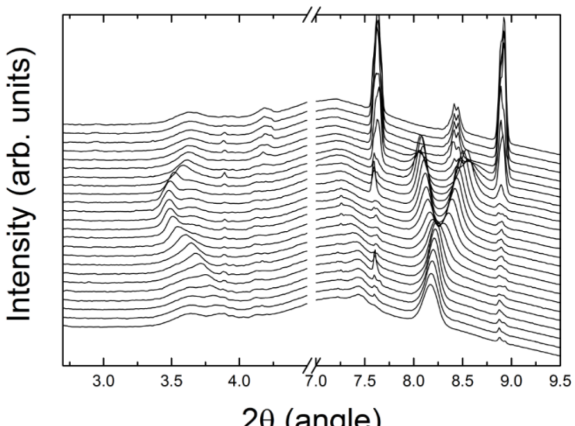


$Li_{1.4}MoO_3$

α-MoO_3

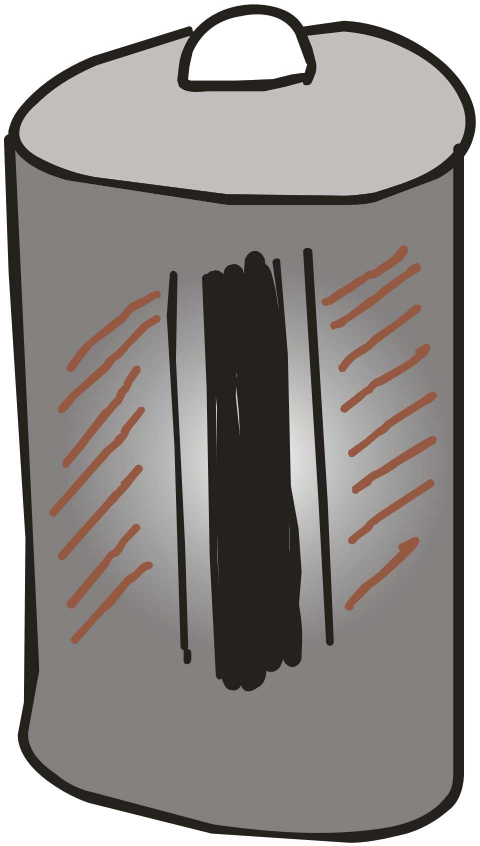






Layer expansion and contraction during lithiation

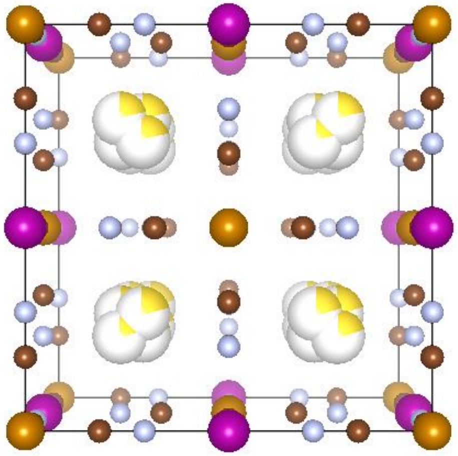
The motion…



$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$ or $Li_2Mn_3NiO_8$?

MoO_3

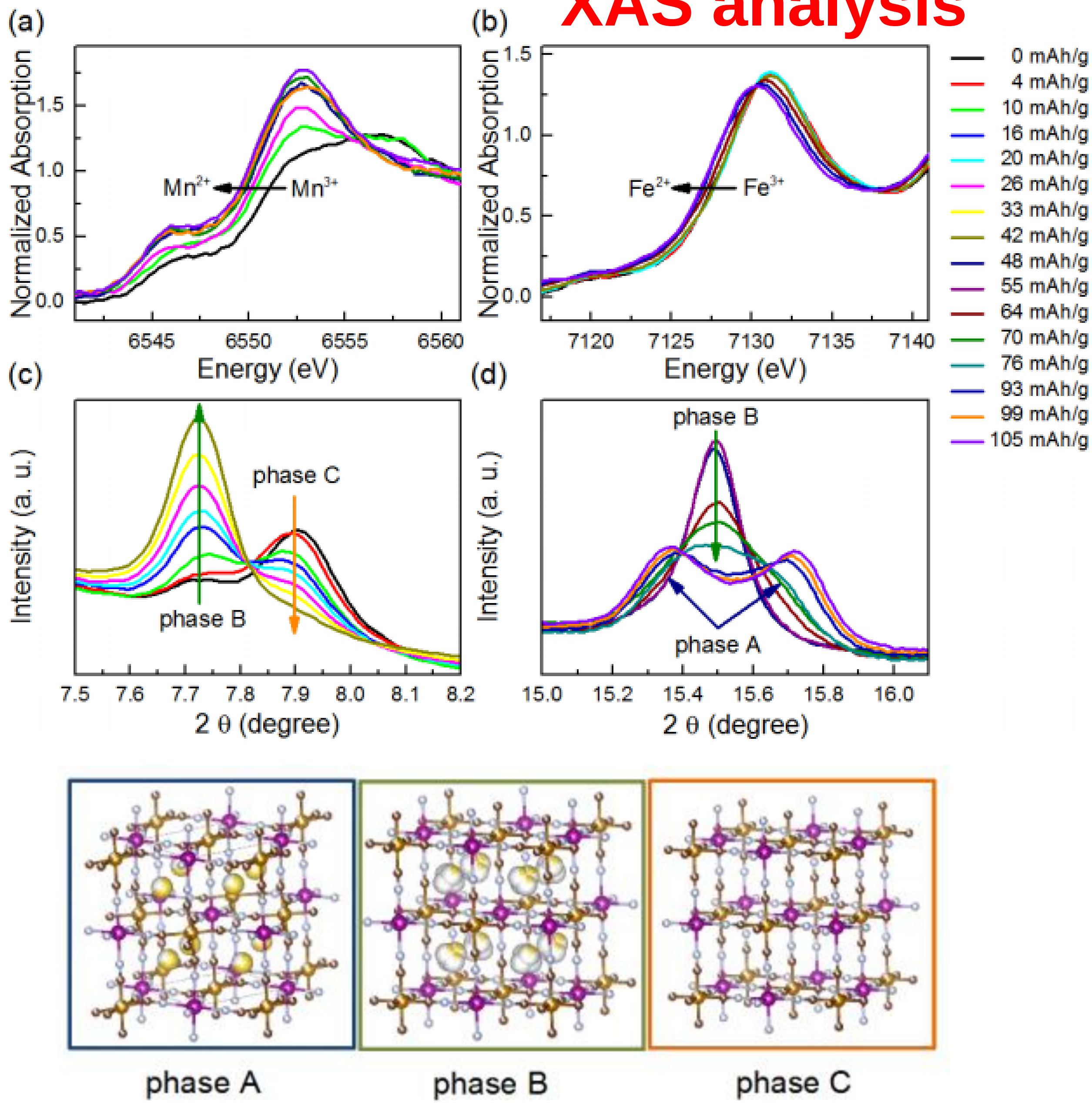
Preussian blue $Na_xMn[Fe(CN)_6]_y$



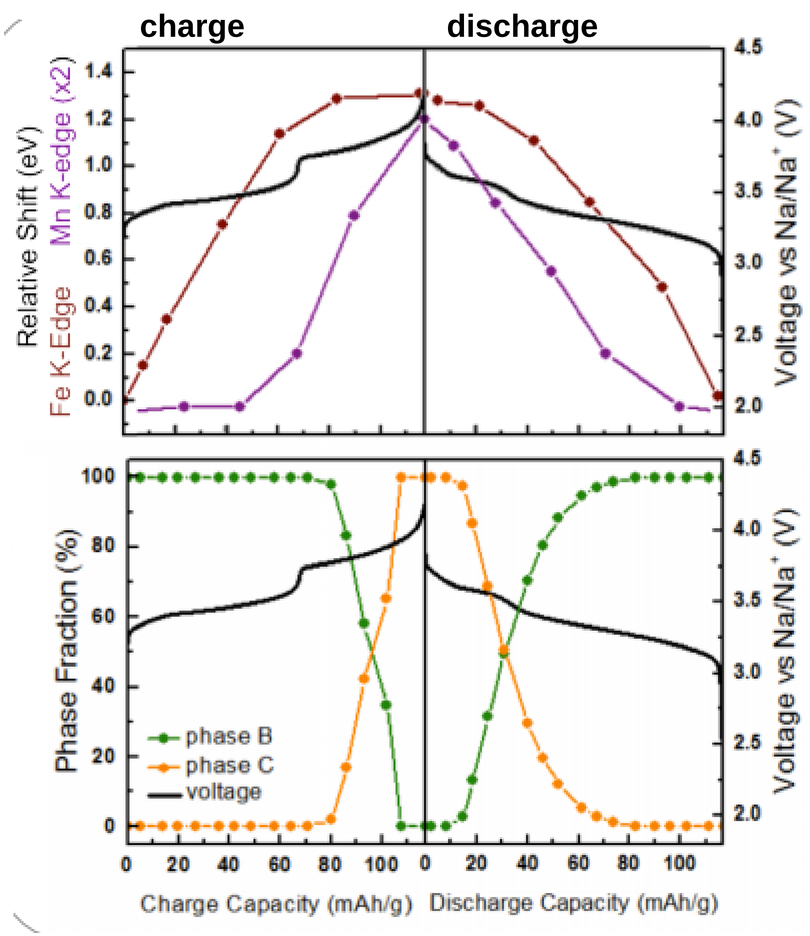
Combined XRD and XAS analysis

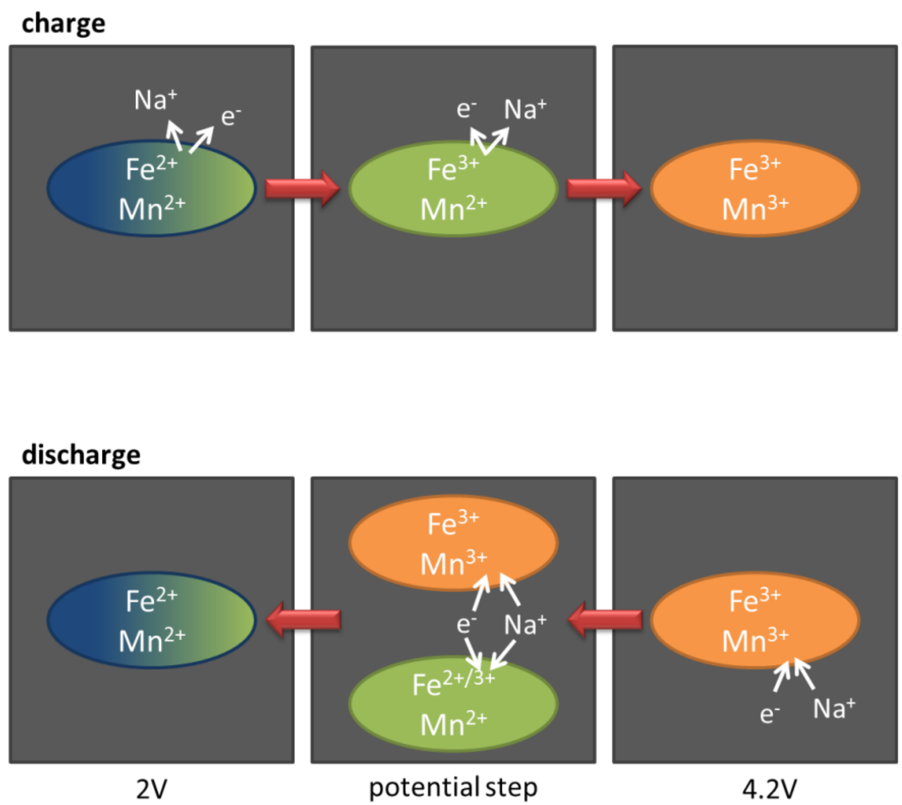
Follow Oxidation State

Identify Phases

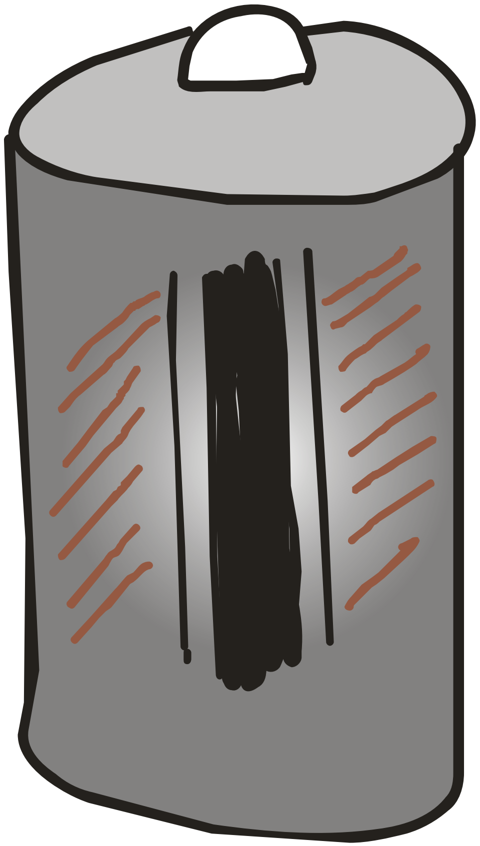


Na (de)insertion mechanism in $Na_xMn[Fe(CN)_6]_y$





The motion…

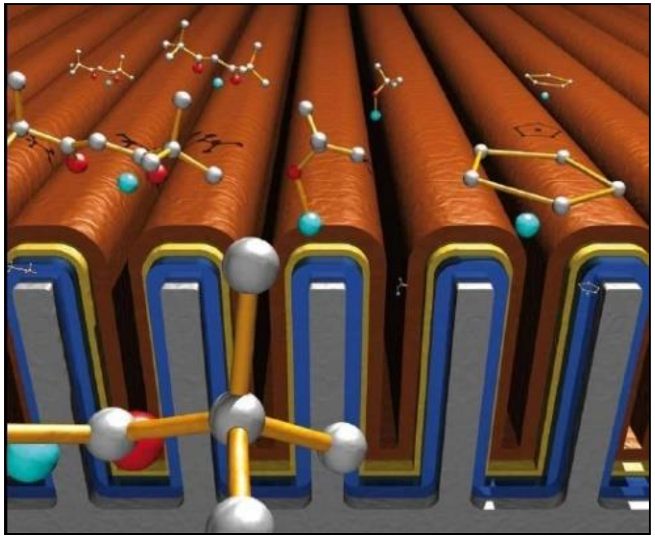


$Li_2(Mn_{0.75}Ni_{0.25})_4O_8$ or $Li_2Mn_3NiO_8$?

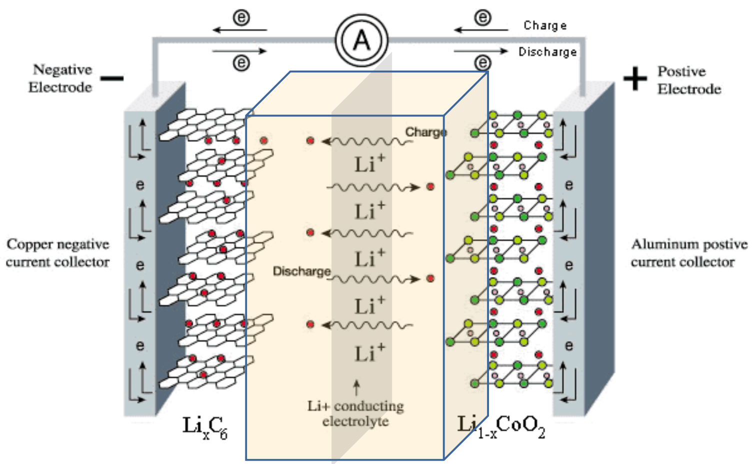
MoO_3

Preussian blue $Na_xMn[Fe(CN)_6]_y$

Thin and solid

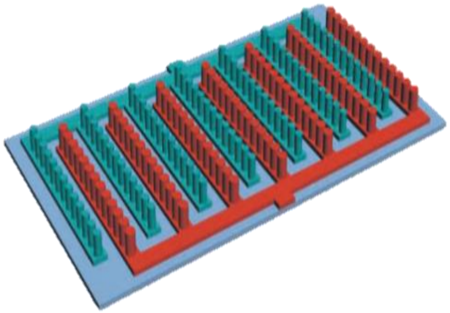


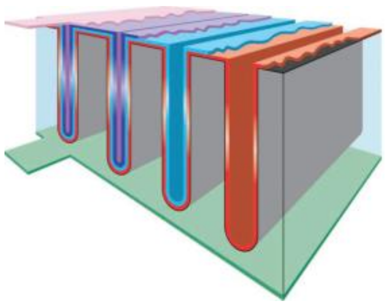
3D all-solid-state Li-ion batteries



http://www.ict.fhg.de/deutsch/scope/ae/Libattery.gif)

- Solid state Li-ion batteries
  - Safter, more environment friendly
  - Low Li^+ conductivity
- Thin film electrolytes
  - Compensate the low conductivity
  - Facilitate architecture design
- 3-dimentional (3D) structure
  - Desired power density
  - Require suitibable thin film deposition technology

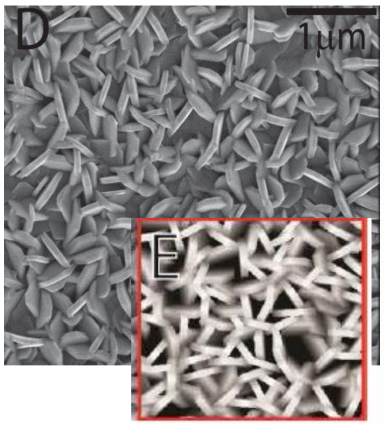


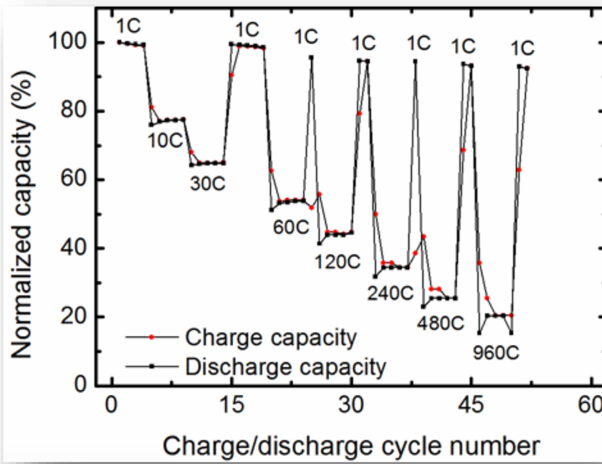


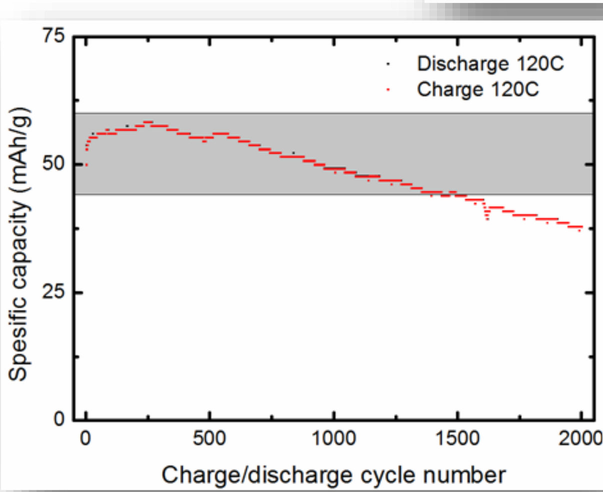
Advanced Energy Materials **2011**, *1*, 10-33. *Adv. Funct. Mater.* **2008** , *18* , 1057 .

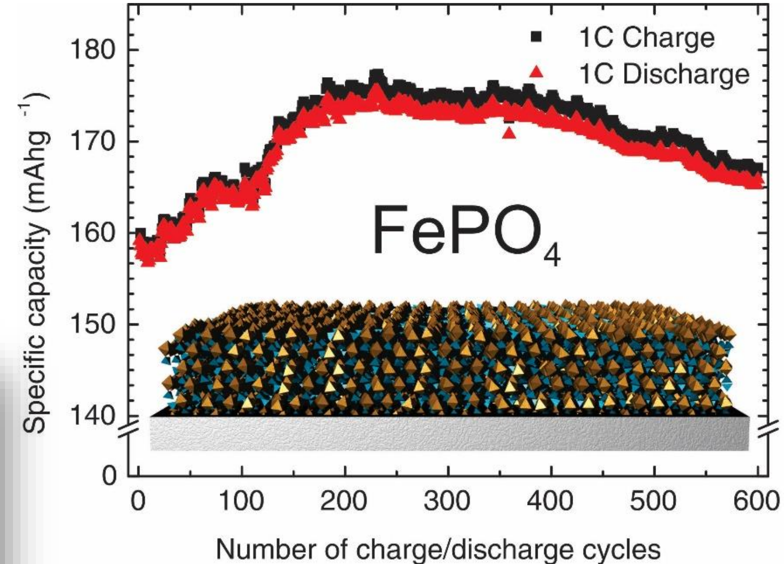
Cathode materials

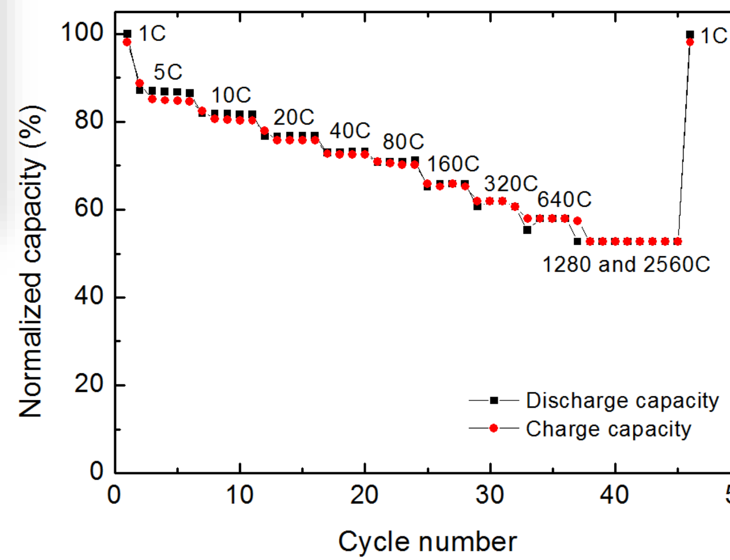
V_2O_5 E. Østreng, …, H. Fjellvåg,
J. Mater. Chem. A, **2** (2014) 15044







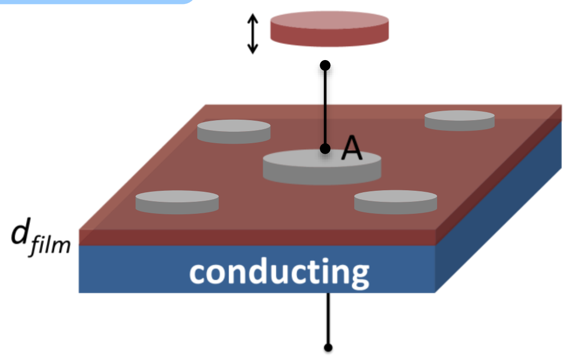




$FePO_4$ K.B. Gandrud, …, H. Fjellvåg,
J. Mater. Chem A. **1** (2013) 9054

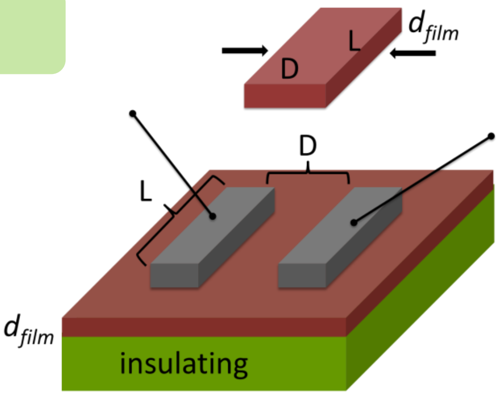
Conductivity measurements

Cross-plane



$$\sigma_{cross} = \frac{L}{R \times A} = \frac{d_{film}}{R \times A_{electrode}}$$

In-plane

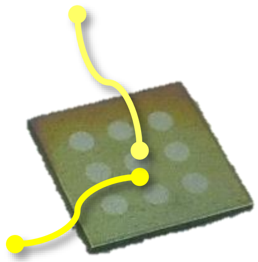


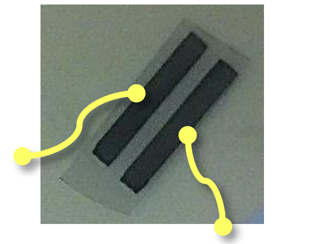
$$\sigma_{in} = \frac{L}{R \times A} = \frac{D_{electrode}}{R \times (d_{film} \times L)}$$

- More practical interests
- Challenges: short-circuiting
- Difficult to carry out

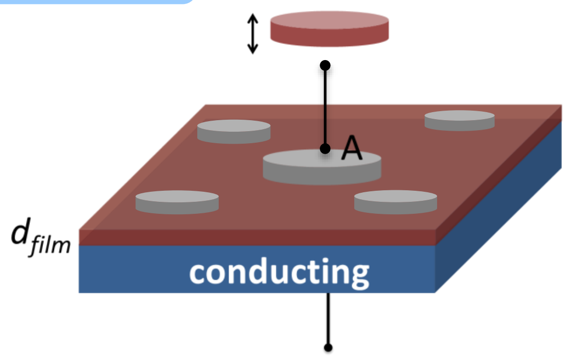
- Circumvent the short-circuitings
- Significant resistance
- More sensitive to parasitics

Conductivity measurements



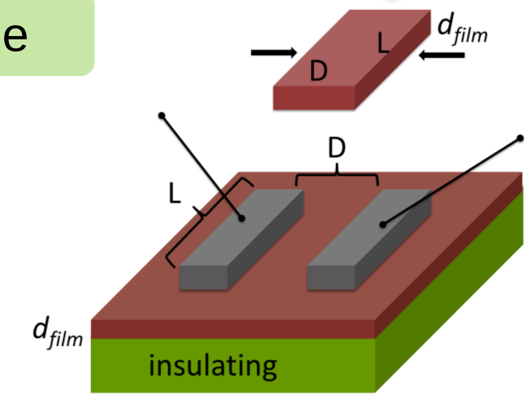


Cross-plane



$$\sigma_{cross} = \frac{L}{R \times A} = \frac{d_{film}}{R \times A_{electrode}}$$

In-plane

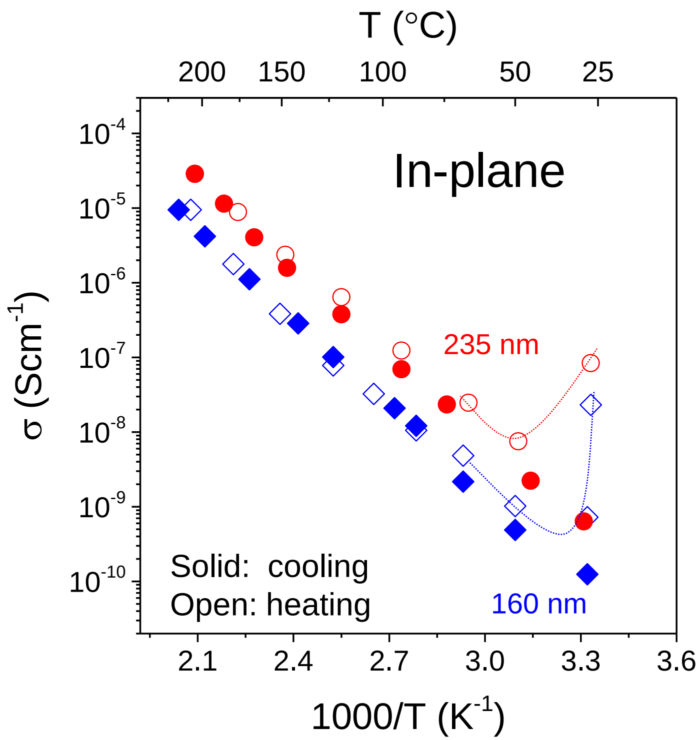


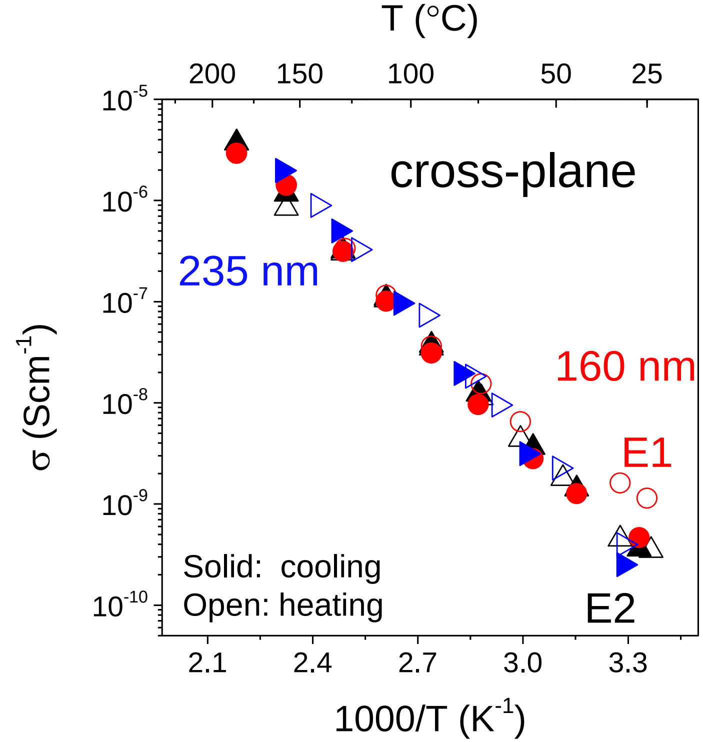
$$\sigma_{in} = \frac{L}{R \times A} = \frac{D_{electrode}}{R \times (d_{film} \times L)}$$

- More practical interests
- Challenges: short-circuiting
- Difficult to carry out

- Circumvent the short-circuitings
- Significant resistance
- More sensitive to parasitics

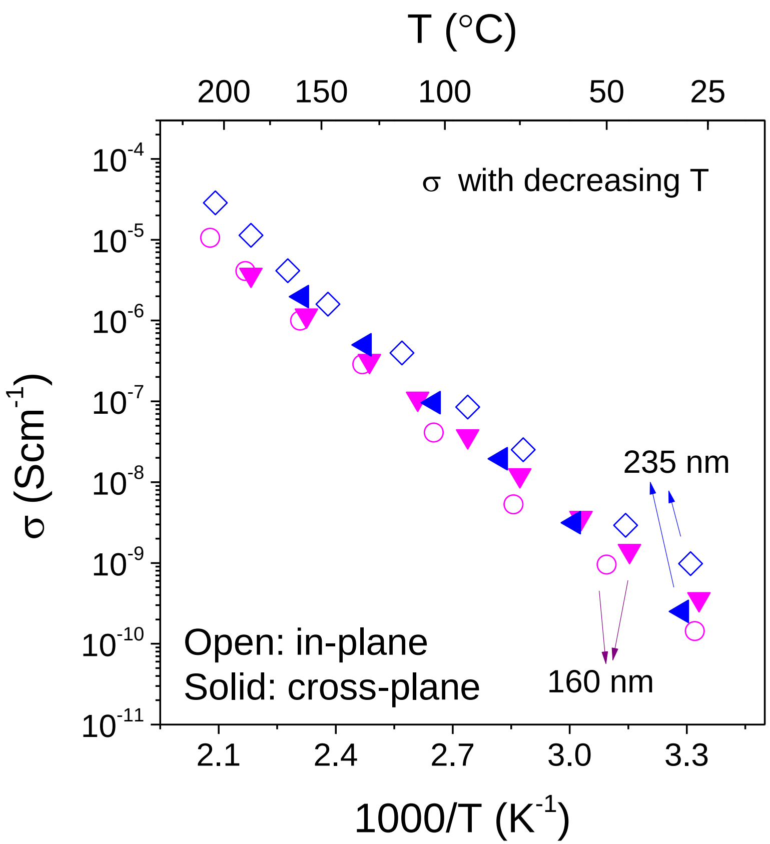
Conductivity of $LiAlO_2$ films





- Thermally activated ionic characteristics → Arrhenius relation: $\sigma = \frac{\sigma_0}{T}\exp(-\frac{E_a}{kT})$
- Larger thickness-dependence for in-plane method: *surface, interface*
- σ @ room temperature: $10^{-10} \sim 10^{-9}$ Scm^{-1}

Conductivity of $LiAlO_2$ films

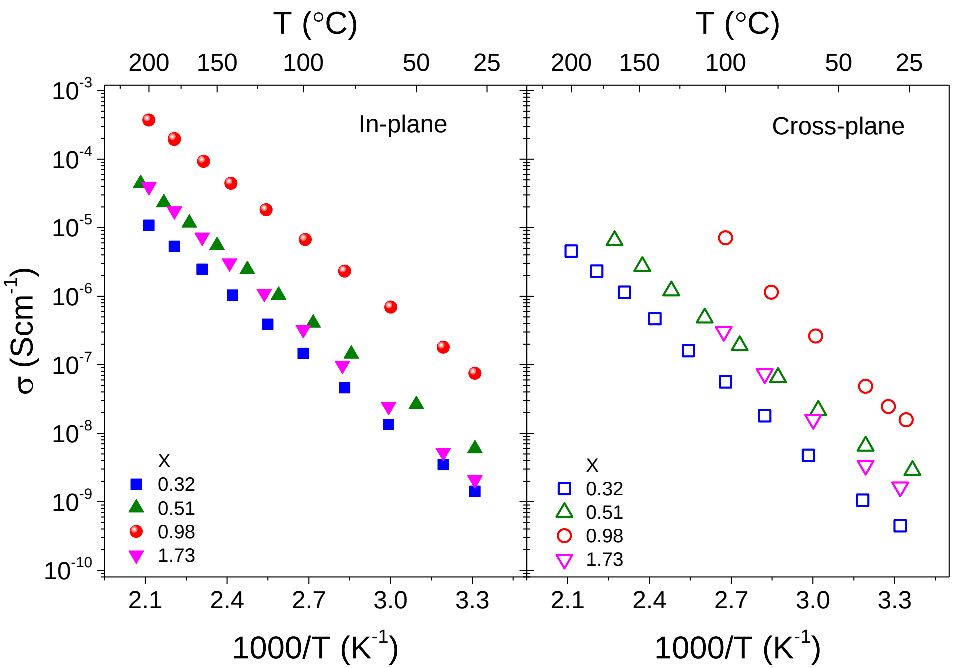


Materials	σ_{RT} (S cm^{-1})	E_a (eV)	Ref.
Single-crystalline γ-LiAlO2	~1×10^{-17} *	1.14(1)	1
Polycrystalline γ-$LiAlO_2$	2×10^{-14} *	0.81 (extrinsic) 1.3 (intrinsic)	2
ALD $LiAlO_2$ film on quartz substrate	5.6×10^{-8} *	0.56	3
Quenched glass $0.6Li_2O–0.4Al_2O_3$ $0.7Li_2O–0.3Al_2O_3$	3×10^{-11} * 5×10^{-8} *	0.88 0.57	4
ALD $LiAlO_2$ films, sapphire and Ti substrates	$1\sim5\times10^{-10}$	0.7~0.8	**This work**

- Room temperature conductivity was rarely reported
- Disordered amorphous/glassy Li_xAlO_y → higher conductivity
- Improved conductivity can be expected with increasing Li content

1. *The Journal of Physical Chemistry C* **2012**, *116*, 14243
2. *J. Am. Ceram. Soc.* **1984**, *67*, 418-41
3. J. *Chem. Mater.* **2014**, *26*, 3128-3134.
4 . *J. Appl. Phys.* **1980**, *51*, 3756-3761.

Li_xTaO_y with Li content variation



- Increasing Li content x from 0.32 to 0.98 results in improved conductivity.
- Compatible in-plane and cross-plane conductivities with acceptable deviations (< 1 order of magnitude).
- The film with highest Li content does not show a pronounced conductivity enhancement, probably due to the H/C surface enrichment.

x in Li_xTaO_y	In-plane		Cross-plane	
	σ_{RT} (Scm^{-1})	E_a (eV)	σ_{RT} (Scm^{-1})	E_a (eV)
0.32	2.1×10^{-9}	0.68	1.6×10^{-9}	0.70(1)
0.51	6.0×10^{-9}	0.66	2.9×10^{-9}	0.65(1)
0.98	7.5×10^{-8}	0.64	1.6×10^{-8}	0.82(2)
1.73	1.4×10^{-9}	0.74	4.5×10^{-10}	0.73(3)

TiO_2 on structured surface

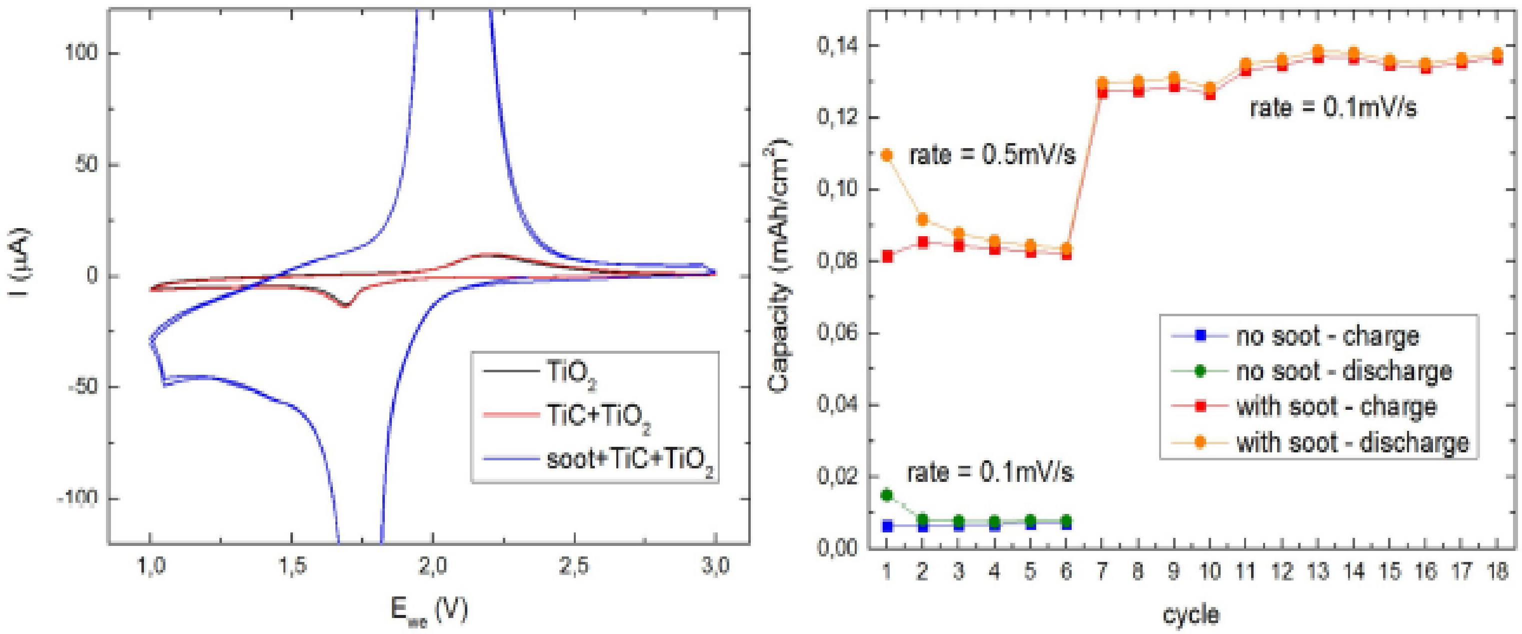
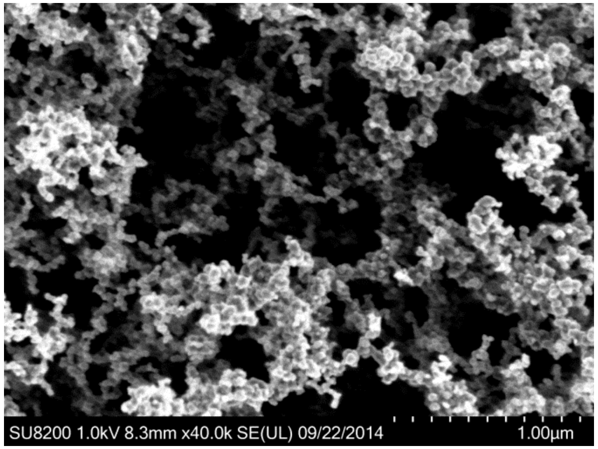


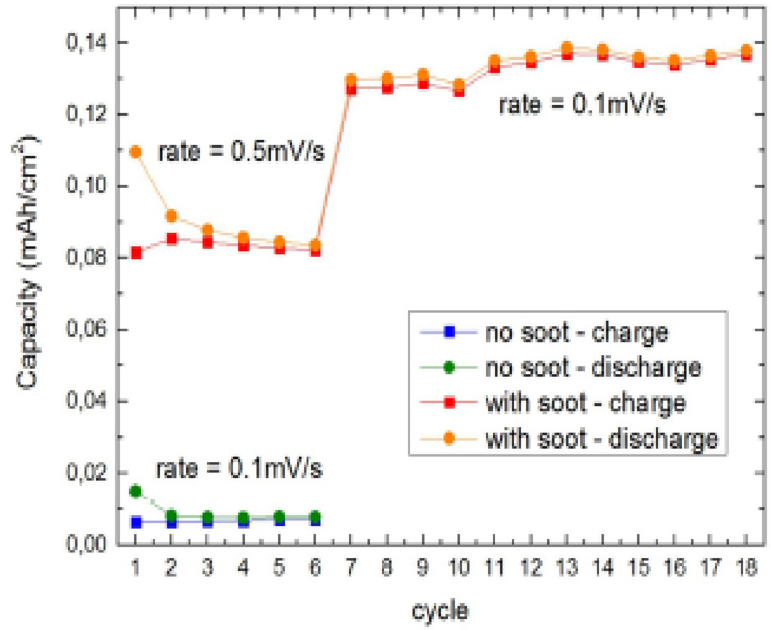
Figure 31: left: cyclic voltammetry of batteries with TiO_2 (black), TiC and TiO_2 (red) and soot with TiC and TiO_2 (blue). right: capacity of the batteries with and without soot. The cell with soot was first cycled at a higher rate, which is why the capacity is lower at first.

TiO_2 coated

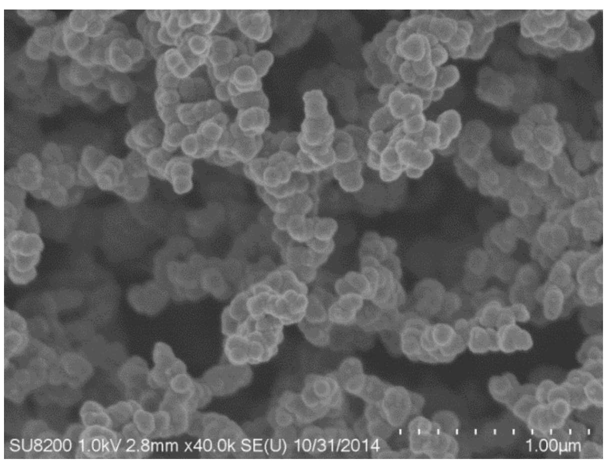
TiO_2 on structured surface



Carbon structured surface



with TiO_2 (black), TiC and TiO_2 (red) and soot
e batteries with and without soot. The cell with
vhy the capacity is lower at first.



TiO_2 coated

Acknowledgements

BATLAB

Helmer Fjellvåg

Mari Alnes
Matti Putkonen
Titta Aaltonen
Ville Miikkulainen

Knut B Gandrud
Erik Østreng
Anders Pettersen
Amund Ruud
Annina Moser

Yang Hu
Jonas Sottmann
Ponniah Vajeeston
Pushpaka Samarasingha

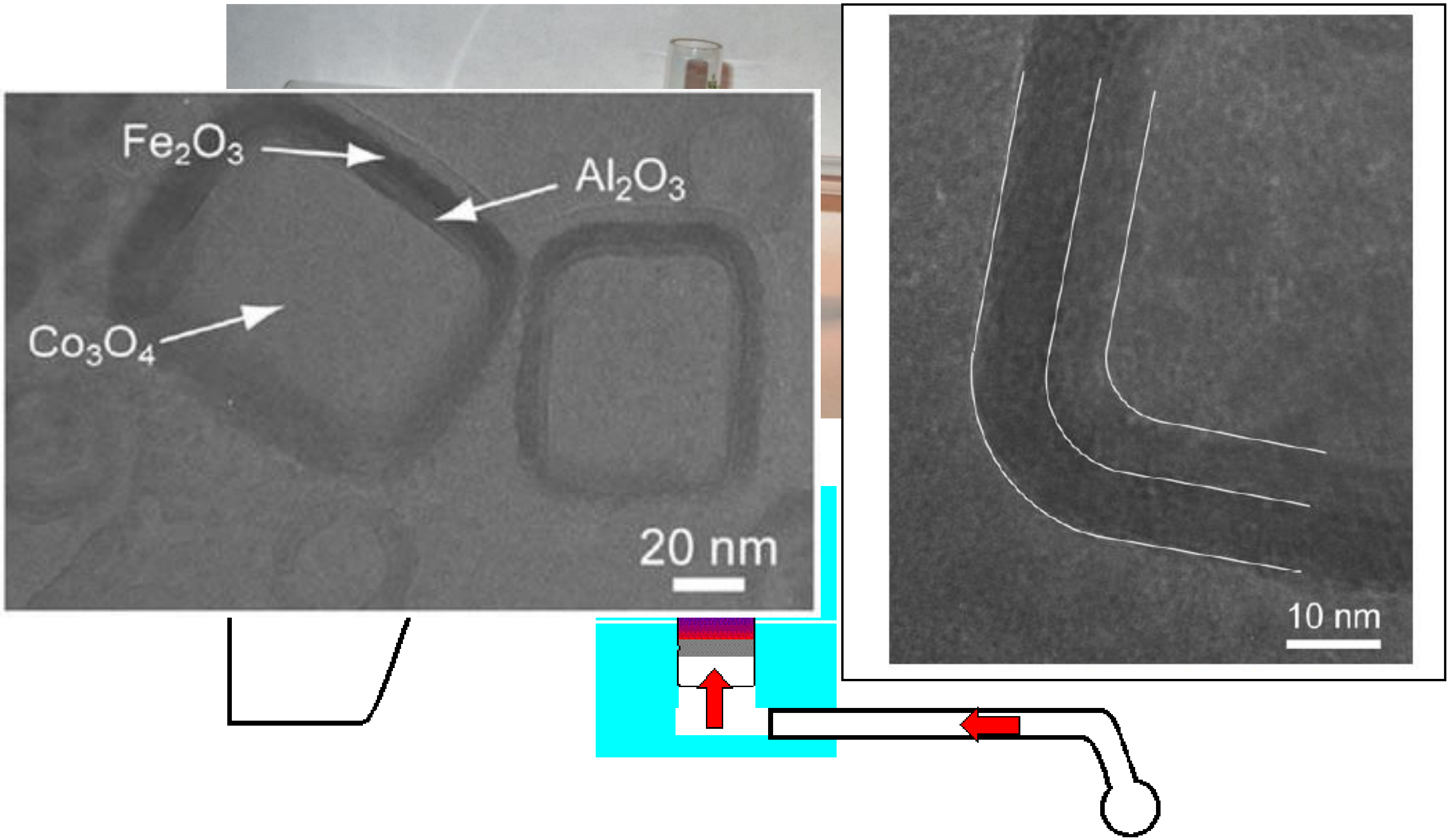
Martin Sunding
Anna Magraso
Alexander Azarov
Timo Sajavaara
Leila Costelle
Niels H. Andersen

baldur
BALDUR COATINGS AS

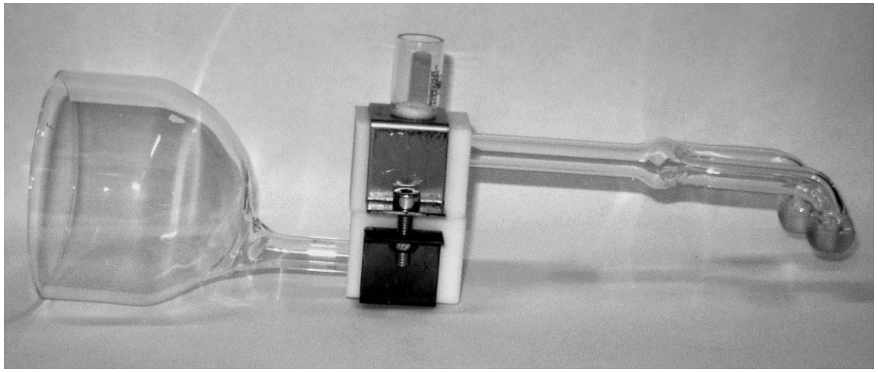
The Research Council of Norway

ALD reaction chambers – Powder

Skjematisk oppsett for pulvercelle



ALD reaction chambers – powder - mini

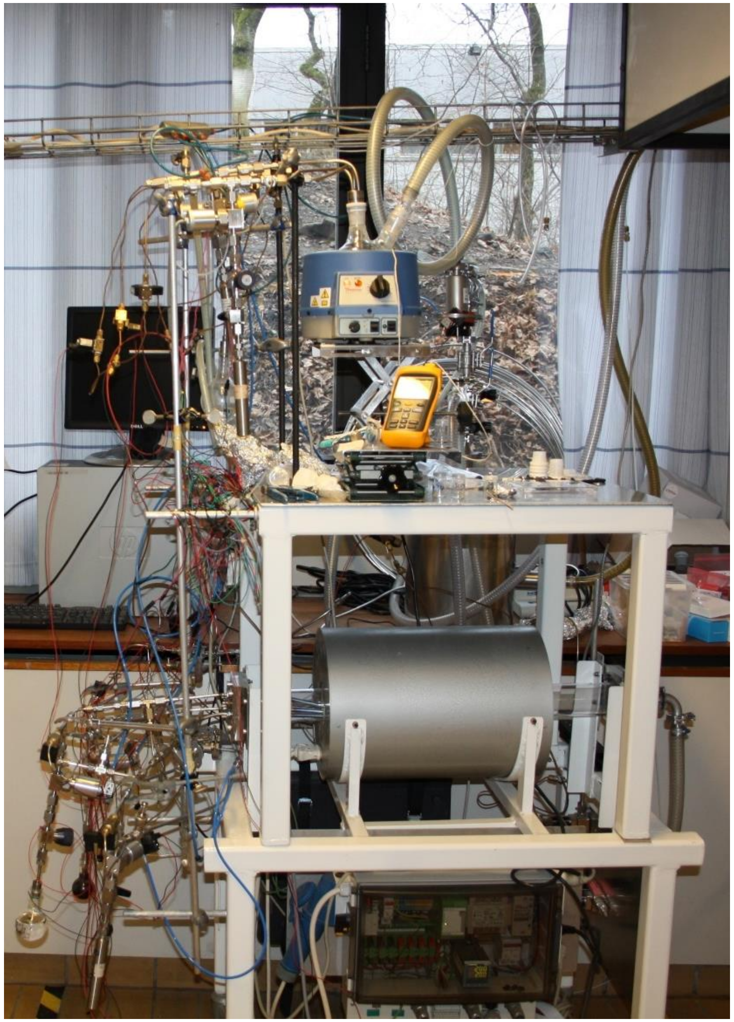


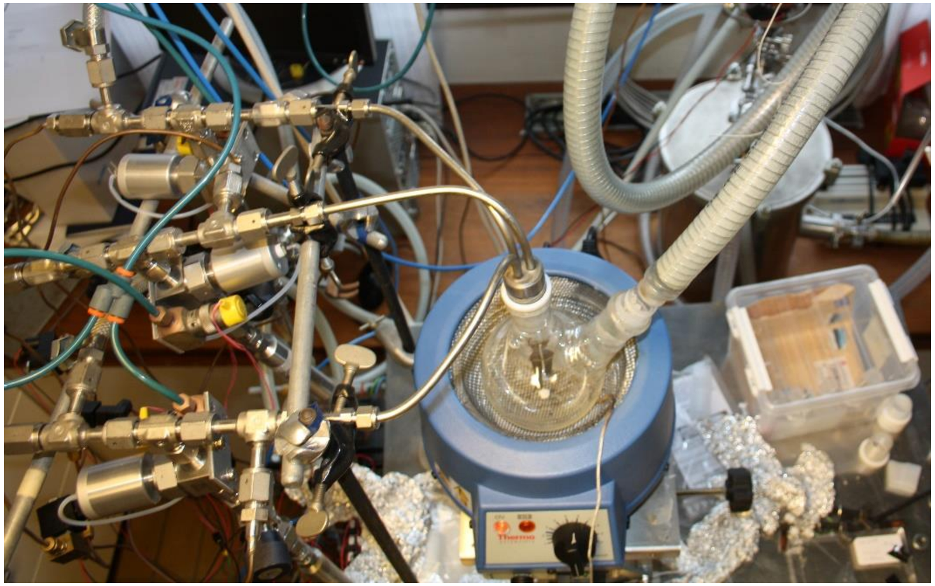
2 powder cells:

Small = 1.5 ml

Large = ca. 30 ml

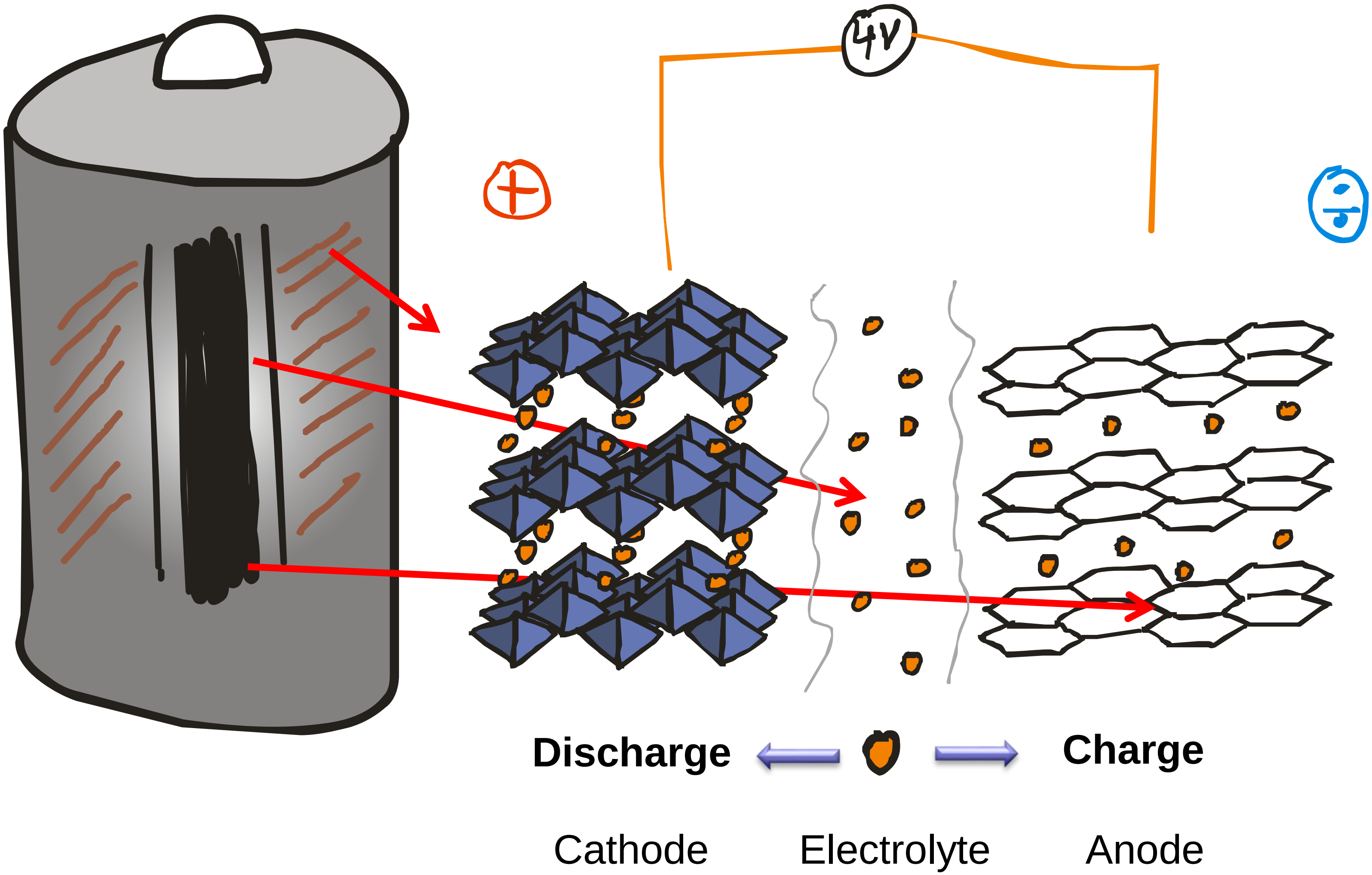
ALD reaction chambers – powder - maxi





500 ml

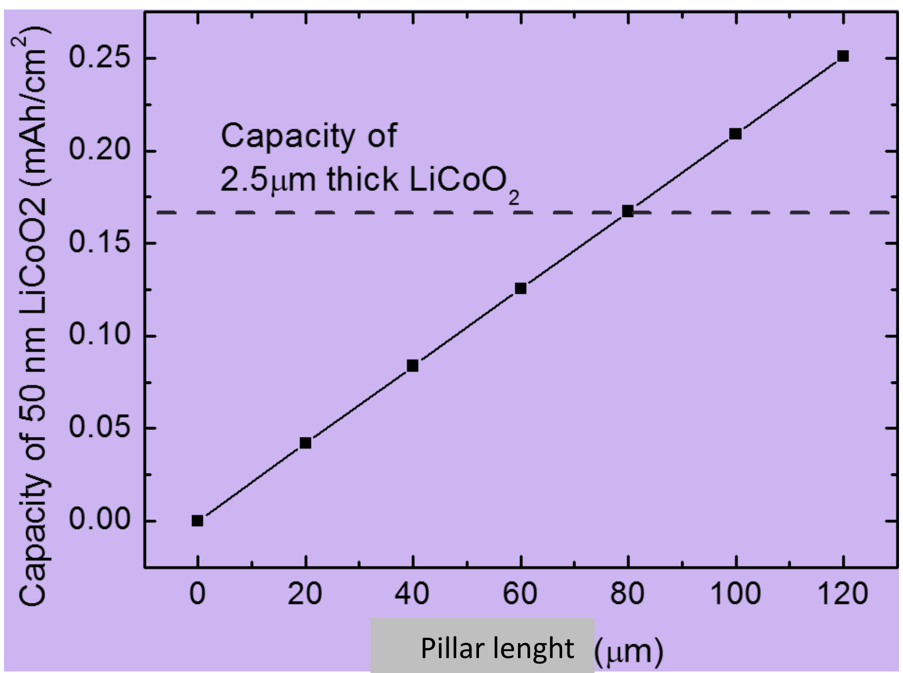
Li-battery

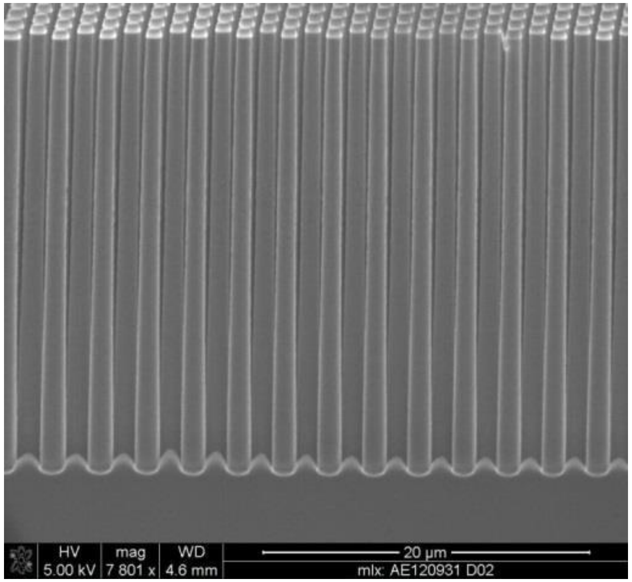


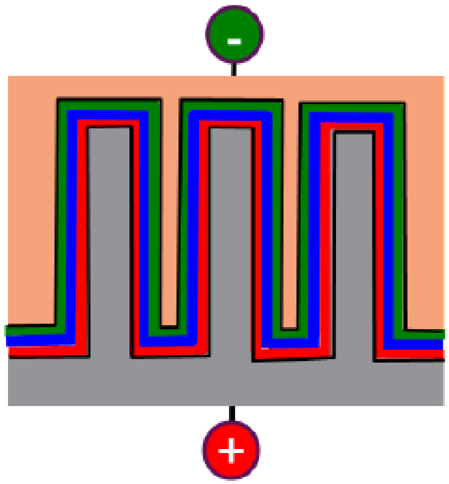
3D Batteries: Power and Energy

- 50 nm $LiCoO_2$ on 80 µm long pillars
  - 1.3 µm in diameter, 1.3 µm distance between pillars
- 0.003 mAh/cm^2 x 56 → **0.168 mAh/cm^2**

- **Bonus:** Enhanced kinetics!
  - Got both good power and energy density!

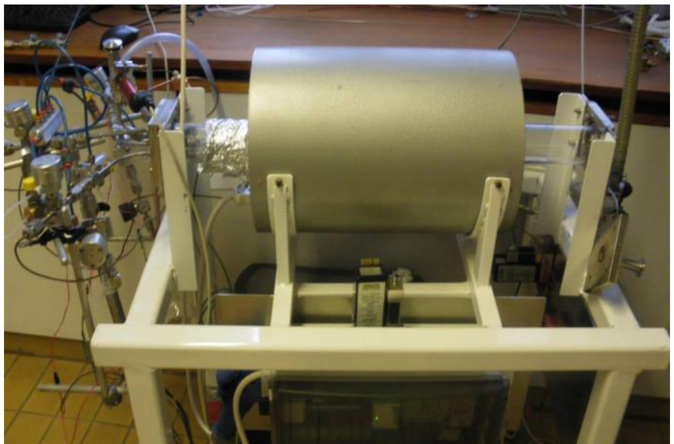






Reactors for coatings & thin films
Atomic Layer Deposition

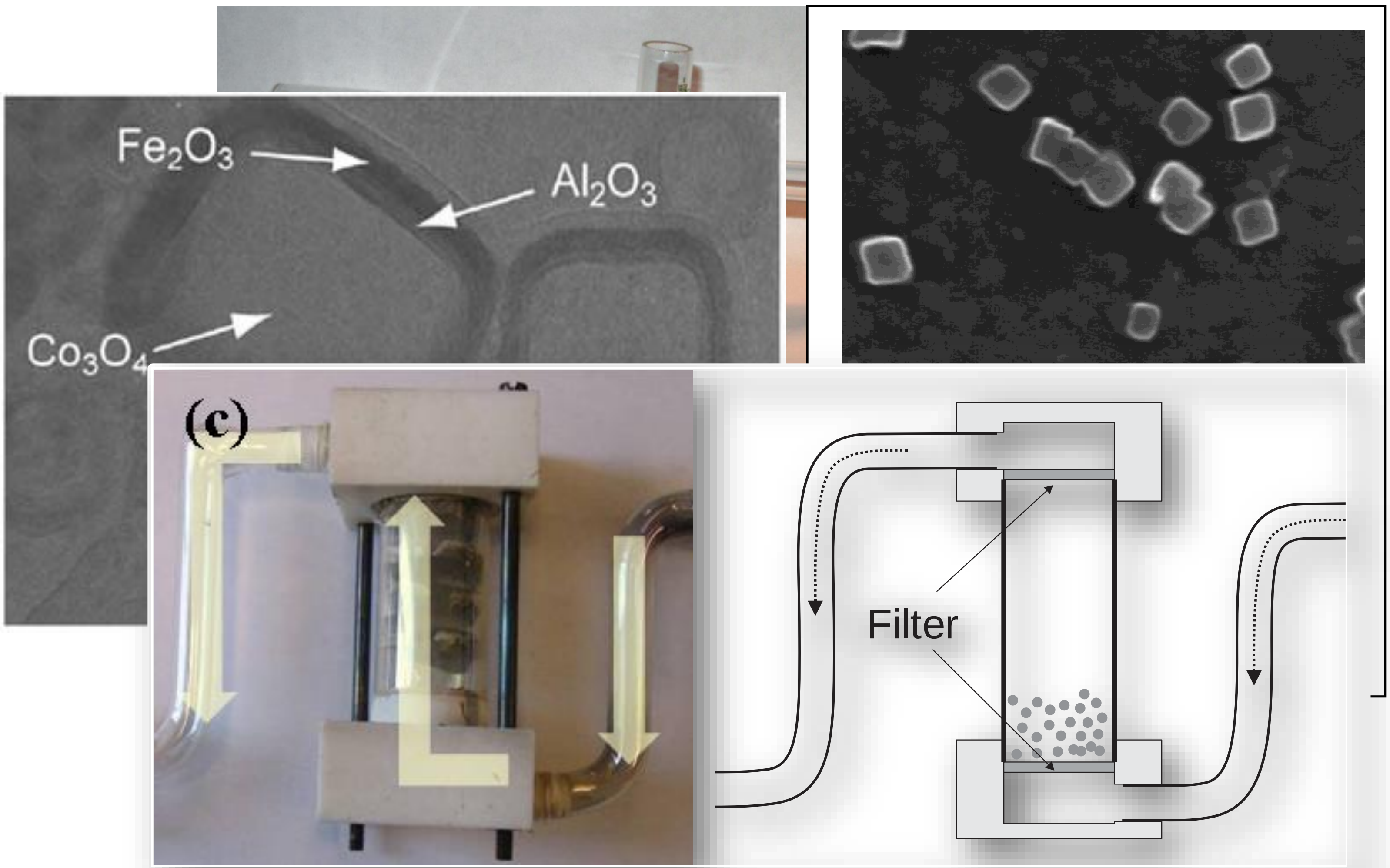
Home made reactor
Hybrid Closed/flow type reactor



TSF 500 (BENEQ)
Flow type reactor

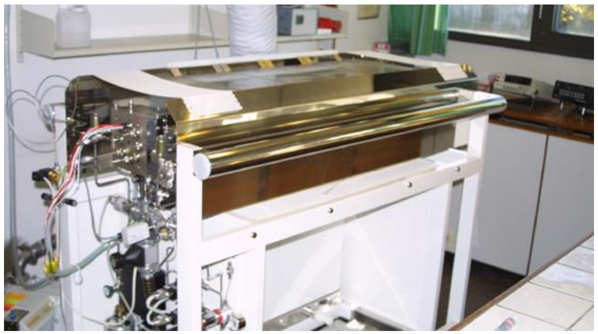
Coating of powder

Skjematisk oppsett for pulvercelle



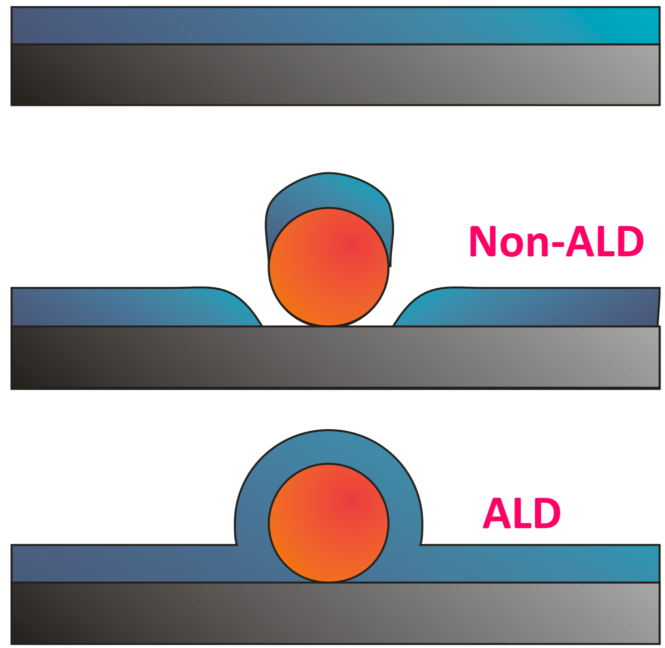
ALD

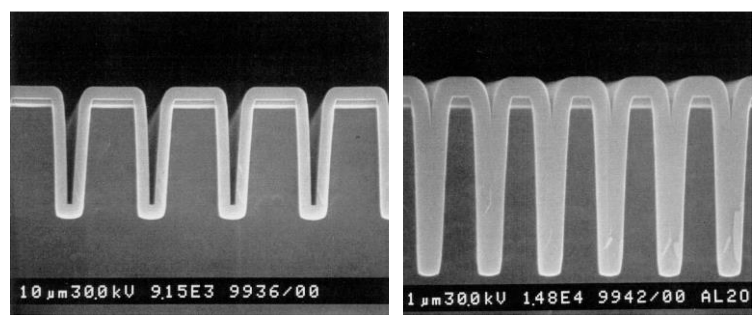
ALD



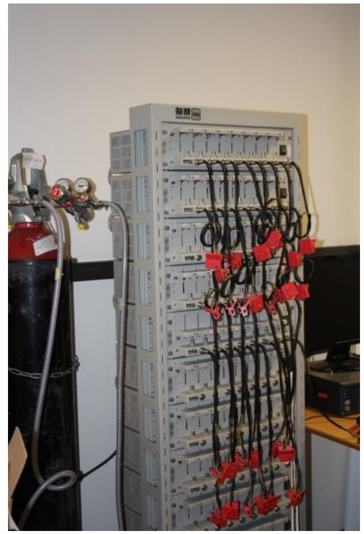
ALD advantages:

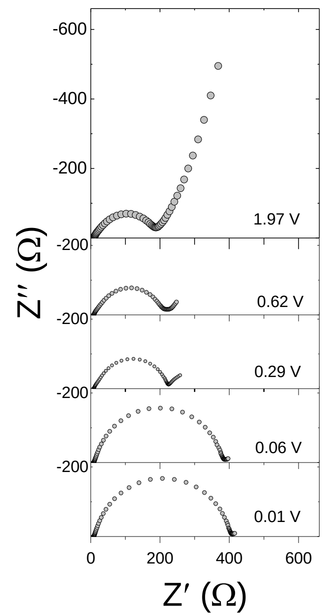
- -Low processtemperature (25 – 400 ºC)
- -Confromal coverage, 3D
- -Easily scalable

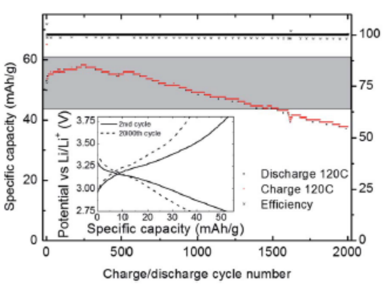


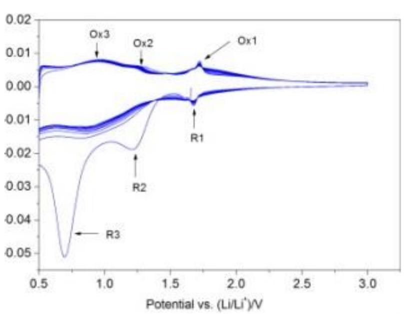


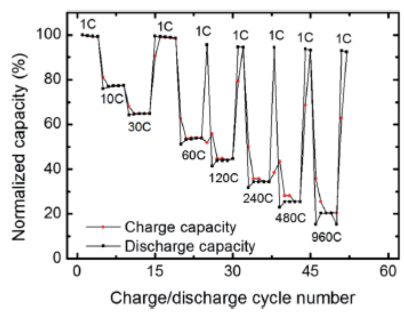
Batcave @ NAFUMA

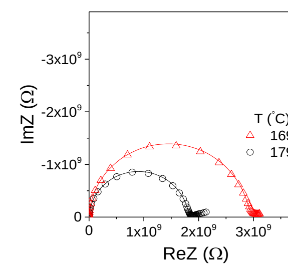












1. *Electrochim. Acta* **2015**, *153*, 232-237 2. *J. Mater. Chem. A* **2014**, *2*, 15044-15051

Automated sample changer – battery cycling, diffraction and XAS