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Electrons in motion
NAFUMA Nanostructured Functional Materials

Cathode
Electrolyte
Anode
NAFUMA

Nanostructured Functional Materials

Powder  In situ  Thin film
The motion...

Li$_2$(Mn$_{0.75}$Ni$_{0.25}$)$_4$O$_8$ or Li$_2$Mn$_3$NiO$_8$?

MoO$_3$

Preussian blue Na$_x$Mn[Fe(CN)$_6$]$_y$

Thin and solid
The motion...

Li$_2$(Mn$_{0.75}$Ni$_{0.25}$)$_4$O$_8$ or Li$_2$Mn$_3$NiO$_8$?

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$_3$32 structure.
Disordered spinel; Fd-3m

\[ \text{Li}_2(\text{Mn}_{0.75}\text{Ni}_{0.25})_4\text{O}_8 \]

Ordered spinel, P4<sub>3</sub>32

\[ \text{Li}_2\text{Mn}_3\text{NiO}_8 \]

Mn, Ni ordering

Cu kα X-ray data

Intensity (arbitrary units)

* \( \text{Li}_x\text{Ni}_{1-x}\text{O} \)

\[ \text{Mn}_{15-900\_60} \]

\[ \text{Mn}_{15-900} \]

\[ \text{Mn}_{15-600} \]
Disordered spinel; Fd-3m

Li$_2$(Mn$_{0.75}$Ni$_{0.25}$)$_4$O$_8$

Ordered spinel, P4$_3$32
Mn, Ni ordering

Neutron data

Intensity (arbitrary units)

2θ (°)

Mn15-900
Mn15-600

P4$_3$32
Fd-3m
Disordered spinel; Fd-3m

\[ \text{Li}_2(\text{Mn}_{0.75}\text{Ni}_{0.25})_4\text{O}_8 \]

Ordered spinel, P4\text{3}32

\[ \text{Li}_2\text{Mn}_3\text{NiO}_8 \]

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

\[ \text{Li}_2(\text{Mn}_{0.75}\text{Ni}_{0.25})_4\text{O}_8 \]

Ordered spinel, P4_332

\[ \text{Li}_2\text{Mn}_3\text{NiO}_8 \]

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

…or disordered at high temp over long time…
In-operando battery cell for synchrotron studies at SNBL
In-operando synchrotron experiments
In-operando synchrotron experiments

Li$_2$Mn$_3$NiO$_8$
In-situ PXRD and XANES measurements

Reduced $d^8$ octahedral

$d^7$ Jahn Teller deformed

Ni$^{2+}$

Phase I

Change in current

Phase II

Ni$^{3+}$

Phase III

Ni$^{4+}$

XANES: shift in edge position
EXAFS: change 1. coordination sphere

Li$_2$Mn$_3$NiO$_8$
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$_{0.25}$)$_4$O$_8$ or Li$_2$Mn$_3$NiO$_8$?

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

MoO₃ nanobelts with stacking faults
High capacity cathode materials: **Bulk and nanobelt MoO₃**

Commercial state-of-the-art cathode material LiFePO₄/LiCoO₂ spinel,…

Must solve stability issue: degradation mechanism
Li insertion process for MoO₃

Computational modeling:

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

Phase transformation

Galvanostatic cycling

Potential vs. Li/Li⁺ (V)

Pristine MoO₃  Li₁.₄MoO₃  LiₓMoO₃  Li₁.₄MoO₃

Intensity (arb. units)

2θ (angle)

Prist. MoO₃  Li₁.₄MoO₃  LiₓMoO₃  Li₁.₄MoO₃
Layer expansion and contraction during lithiation
The motion...

Li$_2$(Mn$_{0.75}$Ni$_{0.25}$)$_4$O$_8$ or Li$_2$Mn$_3$NiO$_8$?

MoO$_3$

Preussian blue Na$_x$Mn[Fe(CN)$_6$]$_y$
Combined XRD and XAS analysis

Follow Oxidation State

Identify Phases
Na (de)insertion mechanism in Na$_x$Mn[Fe(CN)$_6$]$_y$
The motion...

Li$_2$(Mn$_{0.75}$Ni$_{0.25}$)$_4$O$_8$ or Li$_2$Mn$_3$NiO$_8$?

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Preussian blue Na$_x$Mn[Fe(CN)$_6$]$_y$

Thin and solid
3D all-solid-state Li-ion batteries

- **Solid state Li-ion batteries**
  - Safer, more environment friendly
  - Low Li⁺ conductivity

- **Thin film electrolytes**
  - Compensate the low conductivity
  - Facilitate architecture design

- **3-dimentional (3D) structure**
  - Desired power density
  - Require suitable thin film deposition technology

**References**

Cathode materials

V$_2$O$_5$  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

\[ \sigma_{\text{cross}} = \frac{L}{R \times A} = \frac{d_{\text{film}}}{R \times A_{\text{electrode}}} \]

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

In-plane

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

• Circumvent the short-circuitings
• Significant resistance
• More sensitive to parasitics
Conductivity measurements

Cross-plane

\[ \sigma_{\text{cross}} = \frac{L}{R \times A} = \frac{d_{\text{film}}}{R \times A_{\text{electrode}}} \]

In-plane

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

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

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

\( \sigma \) @ room temperature: \( 10^{-10} \sim 10^{-9} \text{Scm}^{-1} \)
### Conductivity of LiAlO$_2$ films

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\sigma_{RT}$ (S cm$^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-crystalline $\gamma$-LiAlO$_2$</td>
<td>$\sim 1 \times 10^{-17}$ *</td>
<td>1.14(1)</td>
<td>1</td>
</tr>
<tr>
<td>Polycrystalline $\gamma$-LiAlO$_2$</td>
<td>$2 \times 10^{-14}$ *</td>
<td>0.81 (extrinsic)</td>
<td>2</td>
</tr>
<tr>
<td>$\gamma$-LiAlO$_2$ film on quartz substrate</td>
<td>$5.6 \times 10^{-8}$ *</td>
<td>0.56</td>
<td>3</td>
</tr>
<tr>
<td>Quenched glass</td>
<td>$3 \times 10^{-11}$ *</td>
<td>0.88</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{-8}$ *</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>ALD LiAlO$_2$ films, sapphire and Ti substrates</td>
<td>$1 \sim 5 \times 10^{-10}$</td>
<td>0.7~0.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

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

• 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.
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$_2$ on structured surface

Carbon structured surface

with TiO$_2$ (black), TiC and TiO$_2$ (red) and soot. The cell with soot batteries with and without soot. The cell with soot is lower at first.
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Nanocubes of Co$_3$O$_4$.

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

Charge

Discharge

Cathode

Electrolyte

Anode

UiO: Centre for Materials Science and Nanotechnology
University of Oslo
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 $\rightarrow$ **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

Nanocubes of Co₃O₄.
ALD advantages:
- Low process temperature (25 – 400 °C)
- Conformal coverage, 3D
- Easily scalable
Batcave @ NAFUMA

Automated sample changer – battery cycling, diffraction and XAS