Synthesis and characterization of Li- and Na-ion batteries

Discussion session in the Danish Battery Society, Aarhus 2013
Battery-people at AU

Kirsten Marie Ø. Jensen – scattering techniques

Yanbin Shen – In operando studies, Li- and Na-ion batteries

Mette Filsø – PED void space calculations

Steinar Birgisson – in situ measurements

Bo B. Iversen

Morten B. Ley – H-storage and solid state electrolytes

Martin Søndergaard – synthesis and characterization

Supti Das – Solid state electrolytes

Troels L. Christiansen – LiMn$_2$O$_4$
Program

- 10.30-11.00: Introduction and TiO$_2$ - Martin
- 11.00-11.30: Procystal analysis - Mette
- 11.40-12.10: Lunch
- 12.10-12.40: Na-ion and in-operando - Yanbin
- 12.50-13.20: Scattering Techniques – Kirsten
- 13.30-13.45: LiMn$_2$O$_4$ nanoparticles - Troels
- 13.55-14.10: In-situ measurements - Steinar
- 14.20-14.35: Coffee break
- 14.35-15.00: Solid state electrolytes - Morten
- 15.00-16.00: Further discussion and lab tour
Inorganic chemistry department

Synthesis

Structure

Properties
Synthesis

• Conventional, 3-zone and induction furnaces, arc-melter, Spark Plasma Sintering, Ballmilling

• Autoclaves and in-house setups for fast-heated hydrothermal syntheses
Synthesis

• Single crystal growth

• Metastable phases

• Nanoparticles
Characterization

$I_{hkl} = S_{\varphi} \cdot Lp \cdot A \cdot j_{hkl} \cdot |F_{hkl}|^2$

$F_{hkl} = \sum f_j \cdot \exp \left( -B_j \frac{\sin^2 \theta_{hkl}}{\lambda^2} \right) \cdot \exp(2\pi i \cdot h \cdot r)$

$\lambda = 2d_{hkl} \sin(\theta_{hkl})$

$q / \text{Å}^{-1}$
Electrode changes during charge/discharge
Characterization at AU

Structural characterization

• 6 in-house X-ray diffractometers
• Partners at synchrotron and neutron facilities
• SEM & TEM

Additional

• ICP
• XRF
• XPS
• BET
• TGA/DSC
• UV + IR
Battery lab at AU

- Mixer
- Coater
- Compressor
- Cutter
- Crimping machine
- Battery Analyser
Electrochemical performance measurement

• Voltage/capacity
• Rate-ability
• High/low temperature discharge
• Cycle life
• Storage life
Battery lab at AU

Coin cell

In-situ cell

Split flat cell
Half-cell at AU

• Blue – stainless steel, top and bottom covers, spacer and springs
• Black – Lithium
• White – separator + electrolyte
• Red – working electrode coated on aluminum

Purple - insulation

ϕ, Li- 16 mm, 
t=0.6mm
ϕ, separators 19 mm, t=0.025mm
ϕ, electrode 15 mm
Half-cell at AU

1. Mixing active material and conductor, drying overnight. Drying PVDF and mixing with NMP, magnet stirring overnight.
2. Mixing and coating on Alu-foil, drying overnight
3. Cutting, (compressing) and assembling batteries
Commercial cathode materials

- LiCoO$_2$, LiNi$_{1-x}$Mn$_x$Co$_y$O$_2$, LiNi$_{1-x-y}$Al$_x$Co$_y$O$_2$
- LiMn$_2$O$_4$
- LiFePo$_4$

Lithium Ion Batteries, Advanced Materials and Technologies, Ed. By Yuan et al., CRC Press 2012
# Precursors

## Table 8.1

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Fe</th>
<th>P</th>
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</thead>
<tbody>
<tr>
<td>Li$_2$CO$_3$</td>
<td>Li$_2$CO$_3$</td>
<td>CoO</td>
<td>Ni(OH)$_2$</td>
<td>MnO$_2$</td>
<td>Fe</td>
<td>NH$_4$H$_2$PO$_4$</td>
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<td>LiOH</td>
<td>LiOH</td>
<td>Co$_2$O$_3$</td>
<td>NiO</td>
<td>Mn$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
<td>H$_3$PO$_4$</td>
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<tr>
<td>Alkyl Li</td>
<td>CoOOH</td>
<td>NiOOH</td>
<td>MnOOH</td>
<td>FeOOH</td>
<td>H$_3$PO$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co$_3$O$_4$</td>
<td>Ni oxalate</td>
<td>Mn$_3$O$_4$</td>
<td>Fe oxalate</td>
<td>P$_2$O$_5$</td>
<td></td>
</tr>
<tr>
<td>Li nitrate</td>
<td>Co nitrate</td>
<td>Ni nitrate</td>
<td>Mn nitrate</td>
<td>Fe$_3$O$_4$</td>
<td>(NH$_4$)$_2$HPO$_4$</td>
<td></td>
</tr>
<tr>
<td>Li sulfate</td>
<td>Co sulfate</td>
<td>Ni sulfate</td>
<td>Mn sulfate</td>
<td>Fe sulfate</td>
<td>HPO$_3$</td>
<td></td>
</tr>
<tr>
<td>Li halide</td>
<td>Co halide</td>
<td>Ni halide</td>
<td>Mn halide</td>
<td>Fe halide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li acetate</td>
<td>Co acetate</td>
<td>Ni acetate</td>
<td>Mn acetate</td>
<td>Fe acetate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Lithium Ion Batteries, Advanced Materials and Technologies, Ed. By Yuan et al., CRC Press 2012*
Quality of the product

Crystal structure
- Anti-sites
- Vacancies
- Dislocations
- Stacking faults
- Grain Boundaries
- Doping

Microstructure
- Particle sizes
- Particle morphologies
- Agglomoration
- Crystallinity

- Precursors, mixing, heat treatment, atmosphere, cooling rate, post-modification e.g. coating
Anode materials

• Carbonaceous materials
  Natural or synthetic graphite, soft, hard

• $\text{Li}_4\text{Ti}_5\text{O}_{12}$
  increased safety, reduced energy density

• Alloys and metal anodes, e.g. Sn-Co-C in 2005

Lithium Ion Batteries, Advanced Materials and Technologies, Ed. By Yuan et al., CRC Press 2012
Synthetic graphite

FIGURE 8.6
A sample flowchart for the production of synthetic graphite from either a petroleum or coal source.

Lithium Ion Batteries, Advanced Materials and Technologies, Ed. By Yuan et al., CRC Press 2012
Hydrothermal synthesis

the dielectric constant drops from 78.4 to 2 (a value similar to hexane) when the temperature is increased from room temperature to 400°C at 250 bar
Continuous hydrothermal flow synthesis

Li$_4$Ti$_5$O$_{12}$ nanocrystals for Li-ion battery applications

Continuous hydrothermal flow synthesis
Continuous hydrothermal flow synthesis

- Control of parameters: Temperature, pressure, flow rate, pH, concentration

- Various particle sizes, crystallinities and morphologies

- Possibility of adding extra pump for e.g. core-shell synthesis
TiO$_2$ as alternative anode material

Possible Anode materials

Figure from M. Pfanzelt dissertation, University of Ulm, 2012
TiO₂ as alternative anode material
Initial TiO$_2$ results left out
## Some different formulations


<table>
<thead>
<tr>
<th>Active material</th>
<th>% active by mass</th>
<th>% binder by mass</th>
<th>% carbon black (and/or graphite) by mass</th>
<th>Compressed</th>
<th>Reference</th>
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<tbody>
<tr>
<td>NMC</td>
<td>96</td>
<td>2</td>
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<tr>
<td>$\text{Li}<em>{1.11}\text{Mn}</em>{1.9}\text{O}_4$</td>
<td>$\sim 96$</td>
<td>$\sim 2$</td>
<td>$\sim 2$</td>
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<td>LiMn$_2$O$_4$</td>
<td>85</td>
<td>5</td>
<td>10 (graphite)</td>
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<tr>
<td>Li$<em>{1.04}$Mn$</em>{1.96}$O$_4$</td>
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<td>5</td>
<td>20</td>
<td>Not clear</td>
<td>4</td>
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<td>7</td>
<td>7</td>
<td>No</td>
<td>5</td>
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<td>LiCoO$_2$</td>
<td>92</td>
<td>4</td>
<td>4</td>
<td>No</td>
<td>6</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>92</td>
<td>6</td>
<td>2</td>
<td>No</td>
<td>7</td>
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<td>LiCoO$_2$</td>
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<td>No</td>
<td>9</td>
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<td>8 (4 carbon and 4 graphite)</td>
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<tr>
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<tr>
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<td>11 (7 carbon and 4 graphite)</td>
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<td>12</td>
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<tr>
<td>LiCoO$_2$</td>
<td>85</td>
<td>5</td>
<td>10</td>
<td>No</td>
<td>13</td>
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<tr>
<td>LiCoO$_2$</td>
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<tr>
<td>LiCoO$_2$</td>
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<td>70</td>
<td>5</td>
<td>25</td>
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<td>16</td>
</tr>
</tbody>
</table>

Carbon content 2 to 25% and binder 4 to 12% commercial electrodes contain just 2% of each (surface area - 0.26 m$^2$/g)
Standardization in cell tests

- Within what limits is it possible to standardize tests for a given electrode material?
  E.g. different surface area may require very different amounts of binder and carbon conductor.

- How thick should a coating be for a power test?
- If cells differ, is it reasonable to pick the best one and assume the rest had some problems?
- We employ two membranes to reduce risk of short-circuit, however, it may impair the rate-ability
- “Forum” on DBS for experiences with coating?