A "Quantum Leap" Forward for Li-Ion Battery Cathodes

Josh Thomas
Ångström Advanced Battery Centre, Uppsala University, Sweden.

josh.thomas@mkem.uu.se

GCEP Research Symposium: "Energy Research – Five Years and Beyond"
Stanford University, 1-3 October 2008
See also:

Poster #22:  Kinson Kam, Anti Liivat et al.

Poster #27:  David Ensling et al.  (esp. XPS/PES studies)
GCEP is GCEP

.... so a few ZEV-based perspectives on the general situation at some other spot on the industrially developed GLOBE:

• Sweden looks to CA for a lead . . . . . . yet tends to ”have all the answers”

• USA can make things happen . . . . . . Sweden can only follow

• Swedes share the same ”who . . . . . . . . and our car industry is ”US owned” killed the electric vehicle?”
  suspicions

• USA is capitalist – where . . . . . . . . Sweden is socialist - we look to
  private enterprise florishes ”the State” to make the moves

Sweden is more optimistic - but also more utopic and less realistic
A future vision borrowed from Toyota . . . .

**Energy Diversification for future automobiles**

ALL future vehicle concepts will need (better) batteries!
This is where our project comes in . . .

*Title:* A ”Quantum Leap” Forward for Li-Ion Battery Cathodes

A relatively uncontroversial consensus roadmap ahead towards ZEVs:

ICE ►► HEV ►► PHEV ►► FC-PHEV ►► (P-)EV

**Time-scale ?**  *cf. Joan Ogden (Day 1)*

*An estimate I saw somewhere a few months back:*

” . . . the last totally ICE vehicle will roll of the production lines in 2034 - give or take a year.”

**But why especially better cathodes ?**
Where are batteries today - after two centuries?

Alessandro Volta, 1799

1839 (Fuel cell)
1859 Pb-acid
1899 Ni-Cd (Swedish!)
1973 Li-metal
1975 Ni-MH
1979 Li-polymer

Li-ion: Sony 1990

Li-ion polymer: 2000

The battery industry is clearly very conservative
The rechargeable Li-ion (polymer) battery

"good rechargability" = the ability to extract and reinsert an optimal amount of Li many times (1000's) from the active particles without significant loss in capacity
Better batteries

Better materials

Safer anodes

More stable electrolytes

We can "upscale" with what we have today

The CATHODE is holding back the upscaling of the technology!

- Higher capacity ("performance")
- Higher power ("performance")
- Safer ("performance")
- Longer lifetime ("performance")
- Lower cost ("market")
- More abundant materials ("market"/ "environment")
- Non-toxic ("environment")
A lower-cost EV-cathode material?

- Today’s most common mobile phone/laptop material uses: 
  \[ \text{Li}(\text{Co}, \text{Ni})\text{O}_2, \text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2 \]

- Larger batteries demand lower-cost cathode materials ⇒ the obvious candidate . . .
  . . . some Fe-based material:

  - \( \text{LiFePO}_4 \) (A123, etc.)
  - \( \text{Li}_2\text{FeSiO}_4 \) (our focus)

(Fe- and Si-oxides make up >10% of the Earth’s crust)
Cathode materials: a comparison

a) Layered:
LiCoO$_2$ -> Li$_{0.5}$CoO$_2$: ~3.9V, ~140 mAh/g

b) Spinels:
LiMn$_2$O$_4$ -> Mn$_2$O$_4$: ~3V or ~4.0V, 148 mAh/g

Instability!
Solution: doping

c) Olivines:
LiFePO$_4$ -> FePO$_4$, ~3.5V, ~170 mAh/g

d) Orthosilicates
Li$_2$FeSiO$_4$ -> LiFeSiO$_4$, ~2.85V, ~170 mAh/g

Poor el. conductivity!

Solutions:
- doping
- coating
- ”nano”-sizing
Our new Fe-based cathode material

Li$_2$FeSiO$_4$ - an orthosilicate

- Li$_2$Fe$^{2+}$SiO$_4$ $\leftrightarrow$ LiFe$^{3+}$SiO$_4$ + Li$^+$ + e$^-$
- E = 2.85 V vs. Li$^+$/Li (low!!)
- Q = 169 mAh·g$^{-1}$

Advantages:
- Potentially lower cost, abundant, non-toxic
- High cycling efficiency
- High stability

Li/Fe ordering!
Strategies for improvement . . .

How can we extract >1 Li to give a higher capacity at a higher voltage?

\[
\text{Li}_2\text{FeSiO}_4 \Rightarrow \text{Li}^{+}(\text{Fe}^{2+}_{1-x}\text{Mn}^{2+}_x)\text{SiO}_4 + (1+x)\text{Li}^+ + (1+x)e^-
\]

e.g., for \(x = 0.5\)

![Graph showing voltage vs. specific capacity for different materials]

- \(\text{Li}_2\text{FeSiO}_4\)
- \(\text{Li}_{2}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4\)

**Transport**

- \(\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}\)
- \(\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}\)

Sustainable E-storage

Specific capacity (mAh.g\(^{-1}\))

Volts vs. Li\(^+\).Li\(^{10}\)

2.5

3.0

3.5

4.0

4.5

100

170

200

255

300
Our strategy for improving performance

A close interplay between DFT calculations and experiment!

• **Compositional variation:** transition-metal substitution, polyanion substitution, ”by-stander” ions to give structural support, etc.

• **DFT calculations:** gives indications of how to optimize electrochemical performance

• **Synthesis:** e.g., nanostructures, coating, ....

• **Materials screening and characterization:**
  - structure
  - surface properties (SEI layer?)
  - electrochemical performance
Nanostructures

e.g., solution-based synthesis:

- Precipitation of metal nitrate salts
- Similar redox behaviour as the bulk material
- Wide range of particle sizes can be tuned
Conductive enough to distribute e\(^-\) evenly

Thin enough to allow the passage of Li\(^+\)

carbon coated particles

Strategy to compensate for the low electronic conductivity of Li\(_2\)FeSiO\(_4\)–type materials

nano-painting with an electronic conductor
Nano-painting further improves particle contact . . .

Carbon coating ≈ 1nm thick, transparent to ions

- Structured carbon black nanoparticles
- Electrolyte
Going beyond Li$_2$FeSiO$_4$. . .

e.g., substitution

We want to make this box as small as possible!

Start material: Li$_2$FeSiO$_4$

Transition-metal substitution

Polyanion substitution

Kinetics! Reversibility!
The manganese-doped silicate?

\[ \text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4 \]

- Substitution of Fe by Mn facilitates a \( >1 \) Li\(^+\) transfer
  \( \text{Mn}^{2+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{4+} \)

- Similar X-ray diffraction patterns to undoped \( \text{Li}_2\text{FeSiO}_4 \)

- First redox reaction occurs at \( >4\text{V} \) (\( \text{Mn}^{2+} \rightarrow \text{Mn}^{3+} \))
  during 1st cycling
Polyanion substitution in Li$_2$FeSiO$_4$?

DFT modelling of substitutions: extra redox-activity VO$_4^{3-}$/VO$_4^{4-}$ at SiO$_4^{4-}$

- Complete delithiation!
- Less strain (bonds: $d_{Si-O} < d_{V-O} < d_{Fe-O}$)
- Higher $\sigma_{el}$ (smaller bandgap)

But . . .
- Volume expansion: ~10%
- Low V$^{4+}$/V$^{5+}$ voltage: 2.2V
Stability ????

XPS/PES surface analysis of Li$_2$FeSiO$_4$

We must probe the stability (“lifetime”) of the material for different electrolyte systems
e.g., a comparative study of performance for two commonly used salts: LiTFSI vs. LiPF$_6$
Why is this critical?

- **Surface chemistry** plays a crucial role in defining the cycling behaviour of Li-ion batteries - we can improve **cycling performance** if we understand the cathode-electrolyte interface (= the SEI layer).
Electrolyte systems studied . . .

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cut-off voltage [V]</th>
<th>Conc.</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiTFSI</td>
<td>2.0 – 3.7</td>
<td>1 M</td>
<td>Corrosion on Al current collector</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>2.0 – 3.7</td>
<td></td>
<td>Sensitive to H$_2$O</td>
</tr>
<tr>
<td>LiTDI</td>
<td>2.0 – 4.0</td>
<td></td>
<td>New !</td>
</tr>
<tr>
<td>LiPDI</td>
<td>2.0 – 4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBOB</td>
<td>2.0 – 4.2</td>
<td></td>
<td>Studied on the anode side</td>
</tr>
</tbody>
</table>

Solvents: EC : DEC 2:1
Electrochemical performance . . .

- a - charge capacity
- b - discharge capacity
Comparative study: LiTFSI vs. LiPF$_6$

Li$_2$FeSiO$_4$/C cycled with two electrolytes:

(a) 1M LiTFSI (2:1) EC:DEC
(b) 1M LiPF$_6$ (2:1) EC:DEC

Measured with XPS on both lithiated and delithiated precycled electrodes.

**Safe transfer** from cell to XPS analysis:
Comparative study: LiTFSI vs. LiPF$_6$

Solvent reaction: EC → polymer

- Salt degradation: PF$_6$ → P-F-O
- LiF formation
- Corrosion of electrode: Si-F bonds
SEI models deduced (schematic)

LiTFSI electrolyte
- Decomposition of the solvent

LiPF₆ electrolyte
- Degradation of the salt/electrode
Conclusions

A combination of DFT and selective synthesis is proving a most fruitful route towards understanding how the full promise of the Li$_2$FeSiO$_4$ system can be realized in a lower-priced Li-ion battery cathode material.

XPS/PES is helping us tune the optimal electrolyte to use for a given cathode in a battery.
Thank you - GCEP!