Anodes for lithium and sodium batteries – and their challenging interfaces

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ÅABCB
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Results based om PhD students and post docs
Bertrand Philippe, Chao Xu, Daniel Brandell, Maria Hahlin, Fabian Jeschull, Matthew Lacey, Fredrik Lindgren, Julia Maibach, Sara Malmgren, Katarzyna Ciosek, Reza Younesi
Not so far away

Uppsala
Ångström Advanced Battery Centre (since 2000)

- The UU group started already at the end of the 1970:ies
- Started with the aluminium pouch cell concept – the "coffee bag"
- Synthesise new materials, test them in Li- and Na-ion and beyond Li-batteries; study processes with \textit{in situ} and \textit{operando} methods. Interfaces are a prime interest
- Today a group of \~40 people at UU
  
  Leader: Kristina Edström (anodes, interfaces and 3D)
  Pi Electrolytes, modelling, – Daniel Brandell
  Pi Cathodes and structure det. – Torbjörn Gustafsson
  Pi Electrochemistry and paper based – Leif Nyholm
  Pi Na-ion, Li-O2 and lithium – Reza Younesi
  Pi Fe-based batteries – Mario Valvo
  Pi Interfaces and new PES methods – Maria Hahlin
A battery is all about interfaces

The interface between the current collector and electrode

Between particles

Within particles

SEI formation

CEI (SPI) formation

And more...
Lithium and sodium batteries

Energy density

250 Wh/kg, 800 Wh/l

Sony 1990

Sony 1995

Nexelion 2005

Sony 2007

Nano-cathodes 2015

Organic cathodes 2020

Future Li-S

Future Na-ion chemistry

Li-air

"Greener"

Image reprinted courtesy of Electropedia (www.mpowesuk.com). © Woodbank Communications Ltd.
Anodes for lithium batteries, beyond lithium and Li-ion batteries

Lithium – 3862 mAhg\(^{-1}\)

Can new separators or electrolyte additives make lithium possible to use?

Graphite – 372 mAhg\(^{-1}\)

New electrolytes – can this improve safety?

Silicon 4200 mAhg\(^{-1}\)

Can we reach more than 5% mixed with graphite/graphene in a commercial cell?

Conversion materials, e.g. \(\text{Fe}_2\text{O}_3\) - 1007 mAhg\(^{-1}\)

An low-cost environmental alternative?
understanding interfaces is instrumental
Photoelectron spectroscopy (PES)

PES depth profiling:
- Sputtering
- Angle-resolved X-ray photoelectron spectroscopy (ARXPS)
- Variation of the excitation energy

\[ BE = h\nu - KE - \phi \]

$BE$ - binding energy
$h\nu$ - excitation energy
$KE$ - kinetic energy
$\phi$ - work function
Non-destructive depth profiling

\[ BE = h\nu - KE - \phi \]

- MAX IV
- In-house XPS
- BESSY

HAXPES or tender XPS

- \( h\nu = 430 \text{ eV} \)
- 2 nm probing depth
- \( h\nu = 1487 \text{ eV} \)
- 11 nm probing depth
- \( h\nu = 2300 \text{ eV} \)
- 18 nm probing depth
- \( h\nu = 6900 \text{ eV} \)
- 47 nm probing depth
Li-ion battery Interfaces in a typical cell
Is there a depth profile in the SEI?
From cells with graphite cycled vs. LiFePO₄
The outcome of the test

- LiF is seen throughout the whole SEI
- The organic reduction compounds have a clear depth profile
  - $\text{Li}_2\text{CO}_3$ is found medium deep in the SEI
  - Inorganic compounds such as $\text{Li}_2\text{O}$ are found deep in the SEI
  - $(\text{ROCO}_2\text{Li})_2$ and $-(\text{CH}_2\text{CH}_2\text{O})$- are found in the outer parts.
- Similar composition in the SEI for deintercalated graphite but slightly thinner layer
Delithiated Li$_{1-x}$FePO$_4$ spectra

In the bulk of the electrode material:

- F1s
- O1s
- C1s
- P2p

SPI = Solid Permeable Interface
SEI on anode is inhomogeneous and its thickness is in the order of twenty nanometers. The interface on the cathode is rather homogenous about a few nanometers thick.

What influences the SEI on graphite?

• The lithium salt – the *anion* influences the stability of the SEI*
• The surface composition of the graphite
• Corrosion of the cathode – cross talk
• The additives in the electrolyte\(\tau\)

*Thesis Anna Andersson 2001
\(\tau\) Thesis Katarzyna Ciosek Högström 2014

Binders and graphite

Binders could enhance coulmbic efficiency, protect the active material, provide mechanical integrity, good surface adhesion, and stable cycling of graphite in ’aggressive’ electrolyte environments.

A stable graphite negative electrode for the lithium–sulfur battery

Graphite-sulfur cell cycled in ether-based (DME and DOL) electrolytes. A protective electrode binder, polyacrylic acid sodium salt (AAP-Na).

Lithium–sulfur cells with different negative electrodes (“thick” Li, “thin” Li, and “cycled” Li) cycled at a constant rate of C/10.

Jeschull, Brandell, Edström, Lacey, Chem. Commun. 2015, 51, 17100-17103
Conclusions

• Graphite is here to stay
  – It might be mixed with silicon or tin
  – Graphene may also be added
  – It might be that EC/DMC or EC/EMC solvent can be exchanged for other solvents
  – New binders might also stabilize the graphite
Silicon interfaces
Graphite

LiC$_6$
372 mAh/g
818 mAh/cm$^3$

Silicon

Li$_{15}$Si$_4$
8335 mAh/cm$^3$

Volume expansion 320%

D. Larcher, S. Beattle, M. Morcrette, K. Edstrom, J.-C. Jumas and J.-M. Tarascon

Goal

Today 2-5% $\text{SiO}_x$ is added to graphite anodes in commercial batteries to enhance capacity.

Model studies

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Up-scaling in collaboration with the spin-off company LiFeSiZe
Depth-profiling the SEI of Silicon using PES

From the extreme surface... ...to the “bulk”

Soft X-ray  
$\nu = 100 \text{ to } 1500 \text{ eV}$

Al Kα ray  
$\nu = 1486.6 \text{ eV}$

Hard X-ray  
$\nu = 2000 \text{ to } 10000 \text{ eV}$

Core peak Si2p

Pristine electrode

Bulk Si-Si

SiO₂

from $\sim 1 \text{ nm}$ to $\sim 30 \text{ nm}$

Binding energy (eV)
What do we know from model system studies?

Standard electrolytes containing LiPF$_6$ salt is critical for cycling stability

So, change the salt
The role of the lithium salt


B. Philippe et al., *JACS* **135** (2013) 9829

F. Lindgren et al., J. Power Sources **301** (2016) 105
Silicon composite electrode, LiPF$_6$ and FEC

Chao Xu et al., Chem. Mater. 27 (2015) 2591
Flexible free-standing electrodes of cladophora nano cellulose

Simple paper making process

J. Mater. Chem. A, 2015, 3, 14109
Electrochemical performance of the SiNP/CNT/CNC anodes

J. Mater. Chem. A, 2015, 3, 14109
Knowing this – what can we do?

Spatially confined silicon nanocrystals within an oriented macroporous graphene monolith

Synthetic procedures for the graphene foam monolith encapsulation of silicon nanoparticles

Ma Yue and K Edström, submitted
Graphene oxide with 66 wt% silicon – preventing electrolyte contact

SEM

TEM

1200 cycles of 66 wt% Si

LiPF$_6$ in EC/DEC + 10% FEC

Ma Yue and K Edström, submitted
Next step

Upscaling: Composite electrodes using TDI salt and additives

Use the LiFeSiZe pilot line

Continue the study of protection of the silicon particles
Conversion reactions
Li-ion vs. Na-ion
γ-Fe₂O₃ produced through pyrolysis of an Iron salt

\[ 6\text{Li} + \text{Fe}_2\text{O}_3 = 3\text{Li}_2\text{O} + \text{Fe} \]

Comparing Li and Na by cycling Fe\textsubscript{2}O\textsubscript{3}?  

The capacity of graphite in a commercial battery  

The difference in SEI between Fe$_2$O$_3$ cycled vs. Li or Na

The peak from carbon black in the composite electrode is a probe of "SEI thickness"

The amount of visible CB through the SEI layer

The losses – electrode/electrolyte surface reactions

Lithium interfaces
Comparing a cell with a polymer electrolyte and a cell with organic solvents

Based on PES-studies

Compare to the surface of lithium in a Li-O₂ cell

Surface analysis of the Li anode

- Constantly evolving SEI on the Li anode in the Li-O₂ battery

- The composition of the surface layer **change** after discharging and again after charging.

- Decomposition of PC to lithium alkyl carbonates, PEO and carboxylate species

- Decomposed **Kynar** binder on Li anode

No dramatic difference between discharge and charge

Surface analysis of the Li anode

- Increase of the relative amounts of F and P from the stored Li anode to the discharged and charged samples

- Decomposed LiPF₆ salt on the stored Li anode, but negligible on the discharged and charged samples.

- LiPF₆ found on the Li anode of discharged and charged cells.

Conclusion

SEI comparison of Li and graphite

Li-anode in a LiO$_2$ battery and a carbonate based electrolyte

Li-anode and carbonate based electrolyte

Li-anode and polymer electrolyte
Conclusions

Will more realistic techniques (ambient pressure XPS) give us more useful information?

How will we best translate the information we have to better battery performance?
Research Funding

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