Anodes for lithium and sodium batteries – and their challenging interfaces

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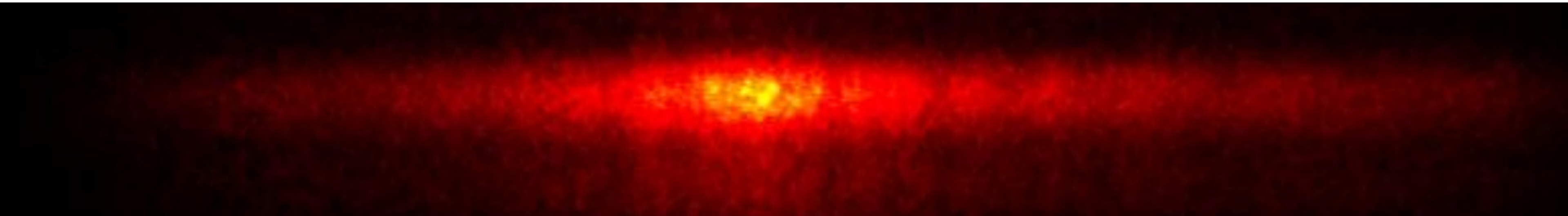
Ångström Advanced Battery Centre

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



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Not so far away

Ångström Advanced Battery Centre (since 2000)

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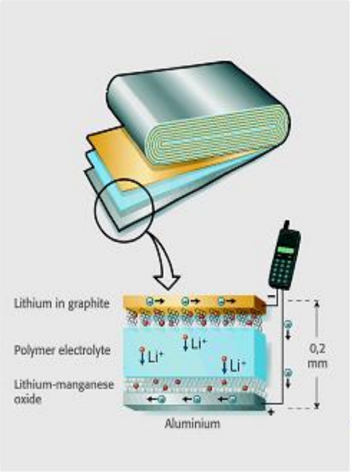
- The UU group started already at the end of the 1970:ies
- Started with the aluminium pouch cell concept – the ”coffee bag”
- Synthesise new materials, test them in Li- and Na-ion and beyond Li-batteries; study processes with *in situ and operando* methods. Intefaces are a prime interest
  - Today a 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

Det uppladdningsbara litiumjonbatteriet



- i mobila telefoner från ca. 1990

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A battery is all about interfaces

The interface between the current collector and electrode

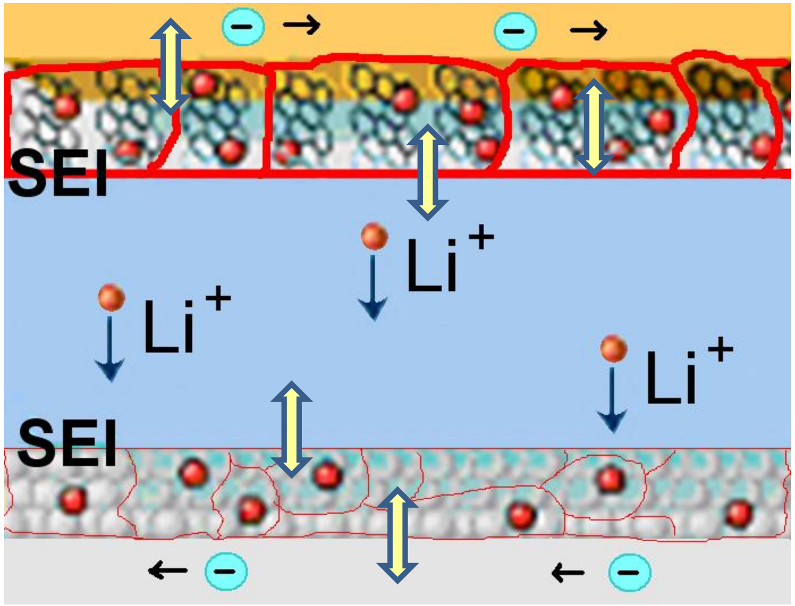
Between particles

Within particles

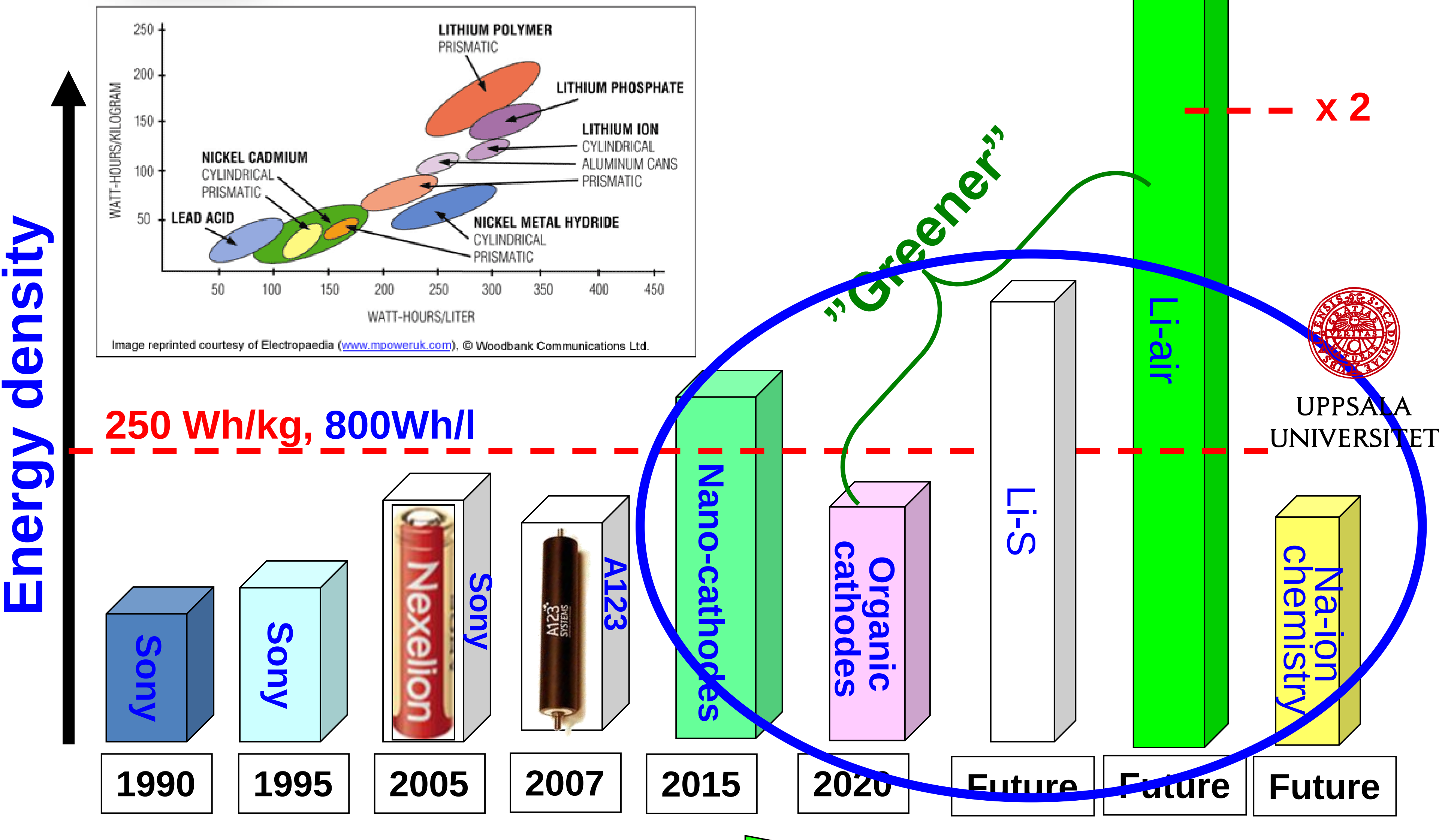
SEI formation

CEI (SPI) formation

And more…



Lithium and sodium batteries



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Anodes for lithium batteries, beyond lithium and Li-ion batteries

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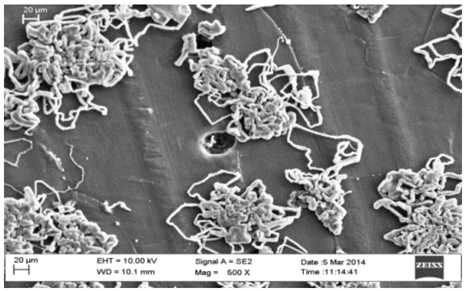
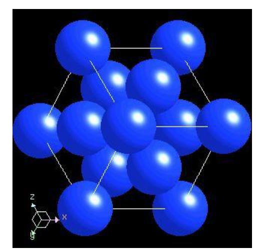


Lithium – 3862 $mAhg^{-1}$

Can new separators or electrolyte addivites 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. Fe_2O_3 - 1007 $mAhg^{-1}$

An low-cost environmental alternative?

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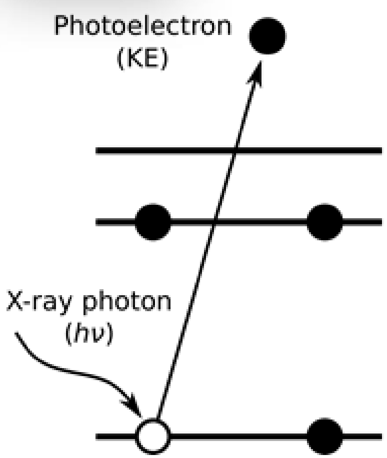
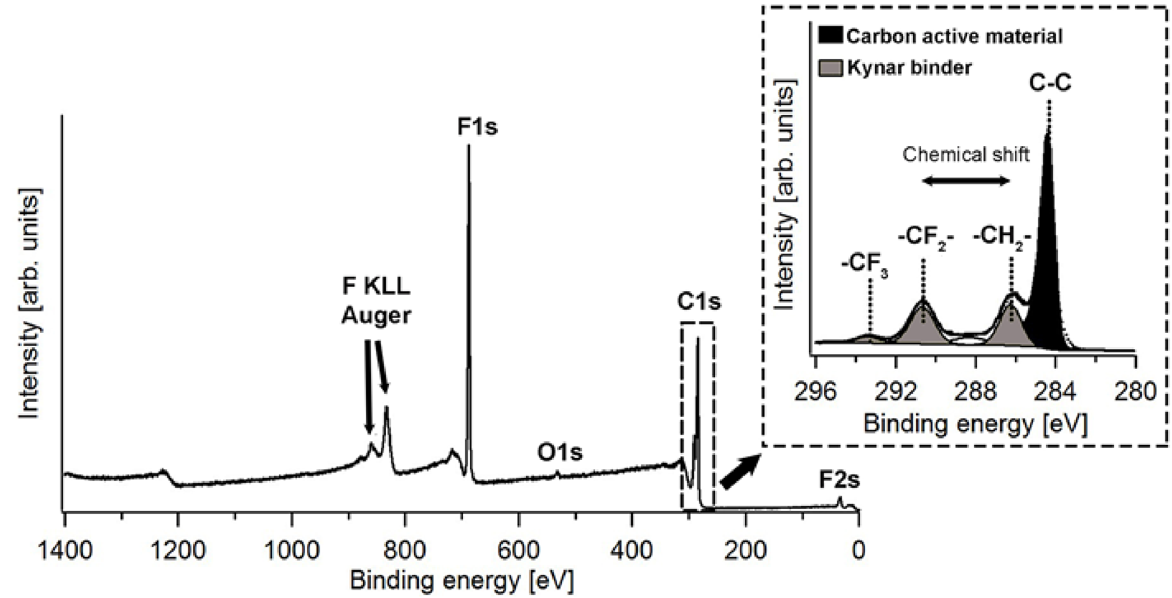
understanding interfaces is instrumental

Photoelectron spectroscopy (PES)





$BE = h\upsilon - KE - \phi$

BE -binding energy

hυ -excitation energy

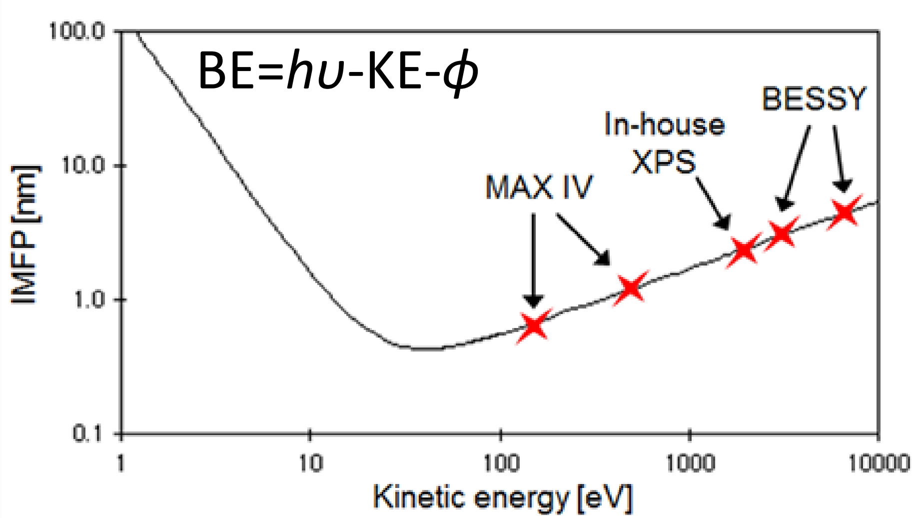
KE -kinetic energy

ϕ –work function

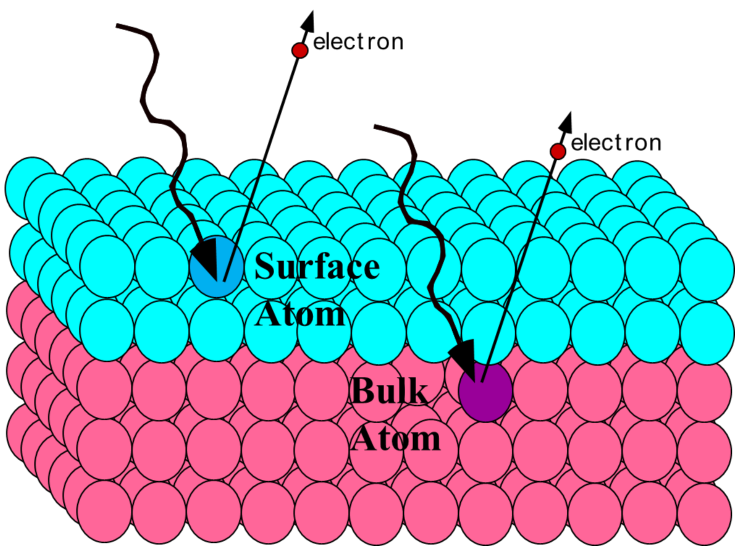
PES depth profiling:

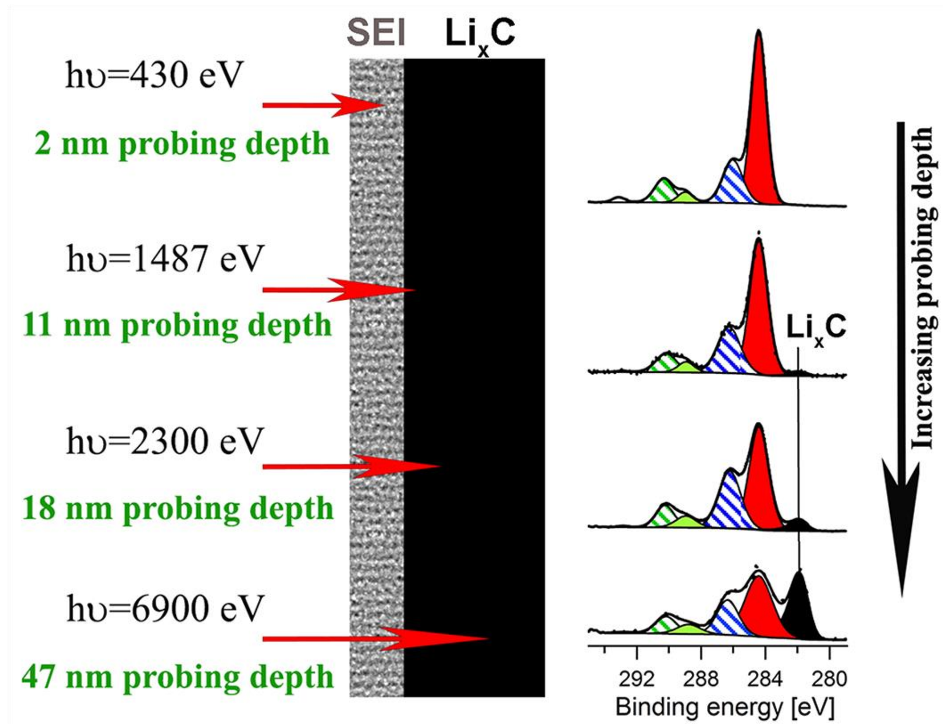
- Sputtering
- Angle-resolved X-ray photoelectron spectroscopy (ARXPS)
- Variation of the excitation energy

Non-destructive depth profiling



HAXPES or tender XPS





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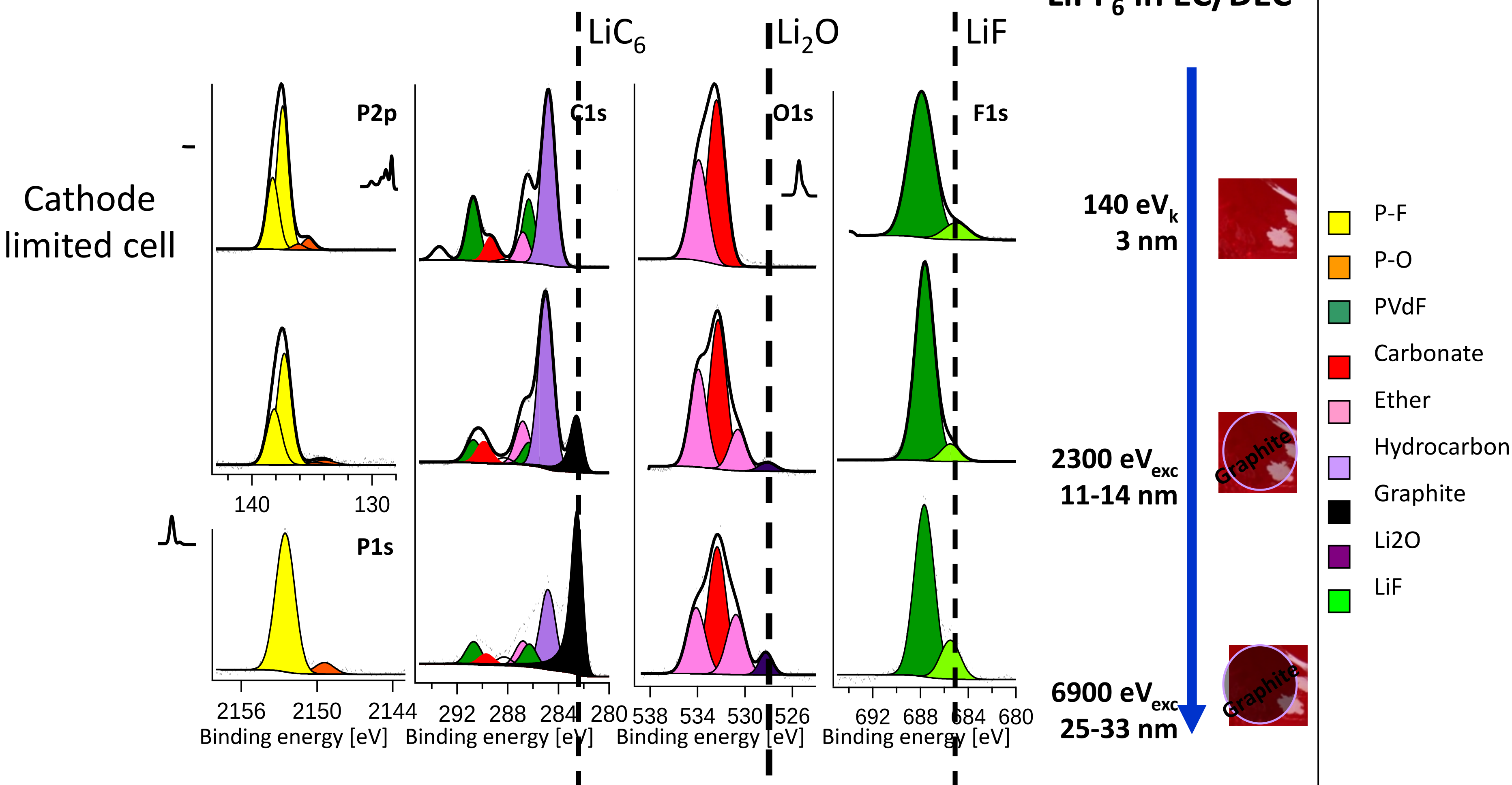
Li-ion batteryInterfaces in a typical cell

Is there a depth profile in the SEI?
From cells with graphite cycled vs. $LiFePO_4$



Deconvoluted lithiated **graphite** depth profiles

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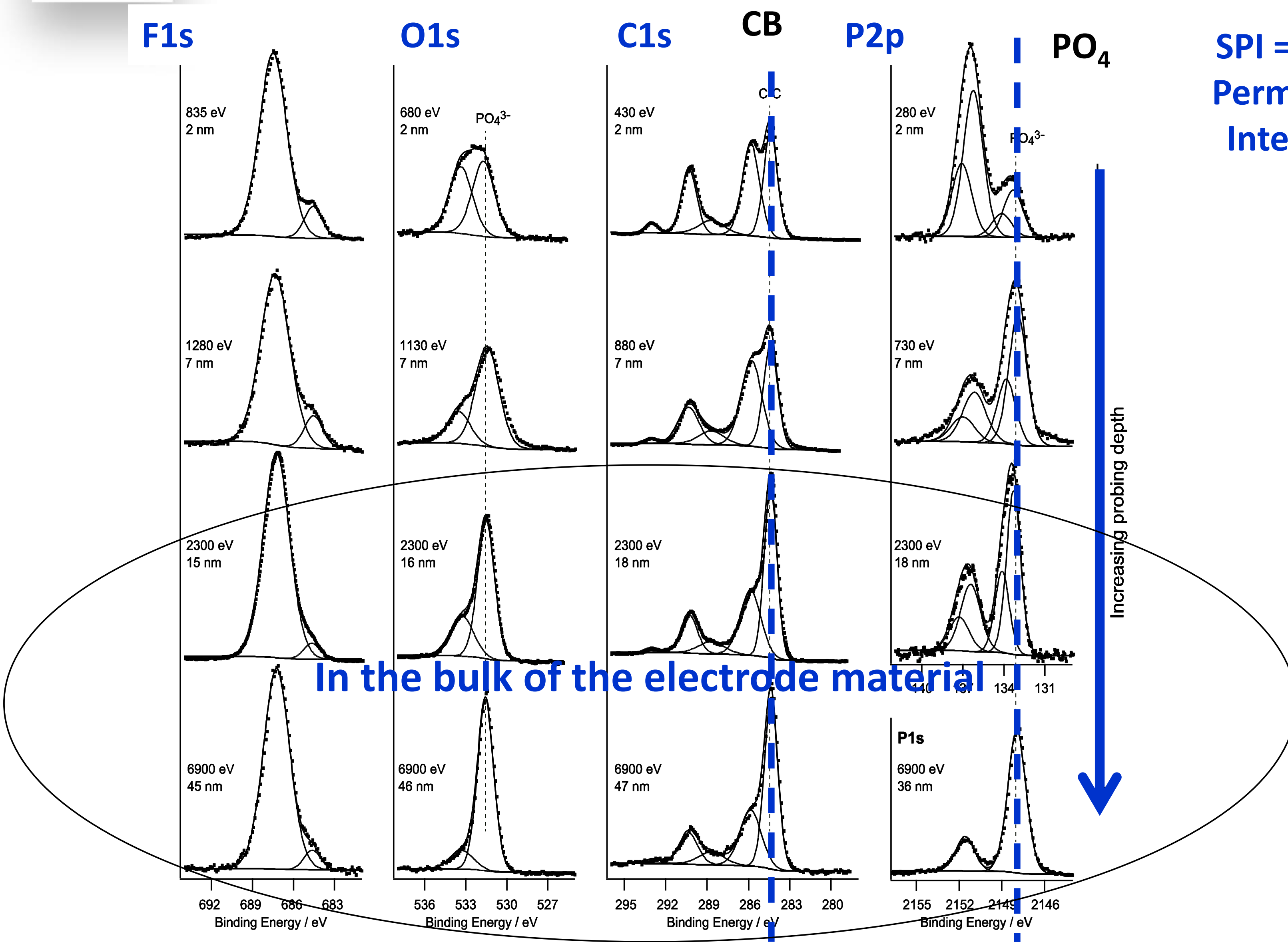
The outcome of the test

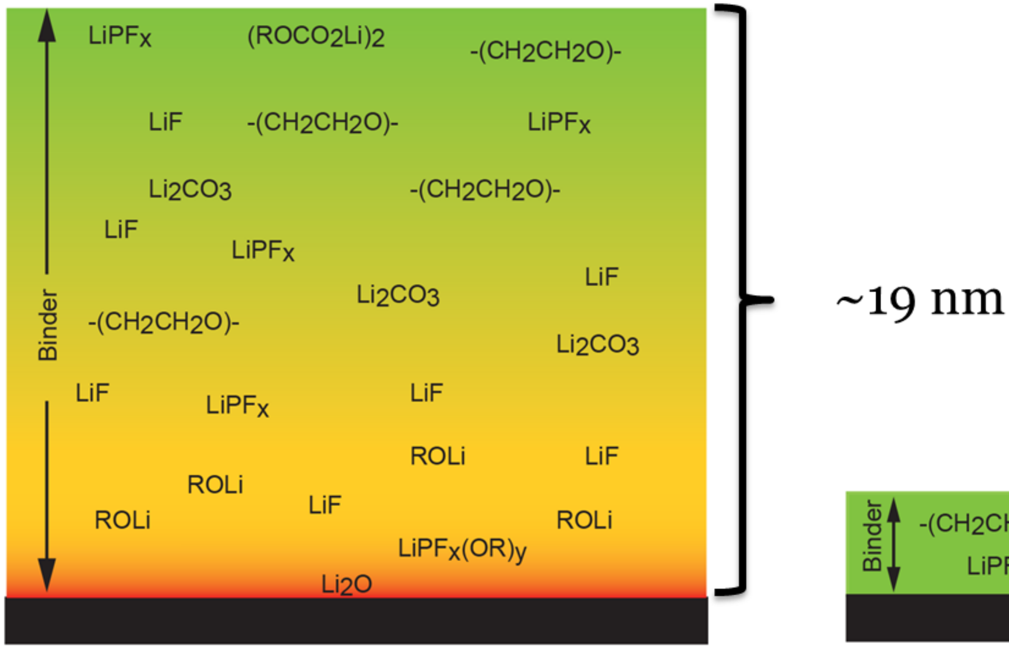
- LiF is seen through-out the whole SEI
- The organic reduction compounds have a clear depth profile
  - Li_2CO_3 is found medium deep in the SEI
  - Inorganic compounds such as Li_2O are found deep in the SEI
  - $(ROCO_2Li)_2$ and $-(CH_2CH_2O)-$ are found in the outer parts.
- Similar composition in the SEI for deintercalated graphite but slightly thinner layer

Delithiated $Li_{1-x}FePO_4$ spectra

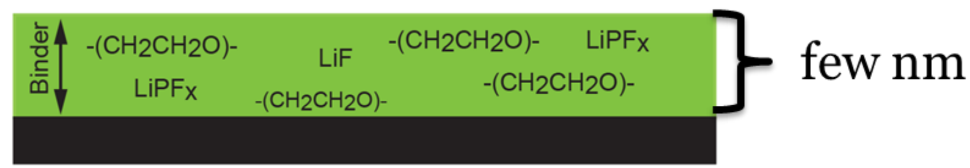


SPI = Solid Permeable Interface

Characterizing the surface with PES
Comparing cathode and anode interfaces



Graphite



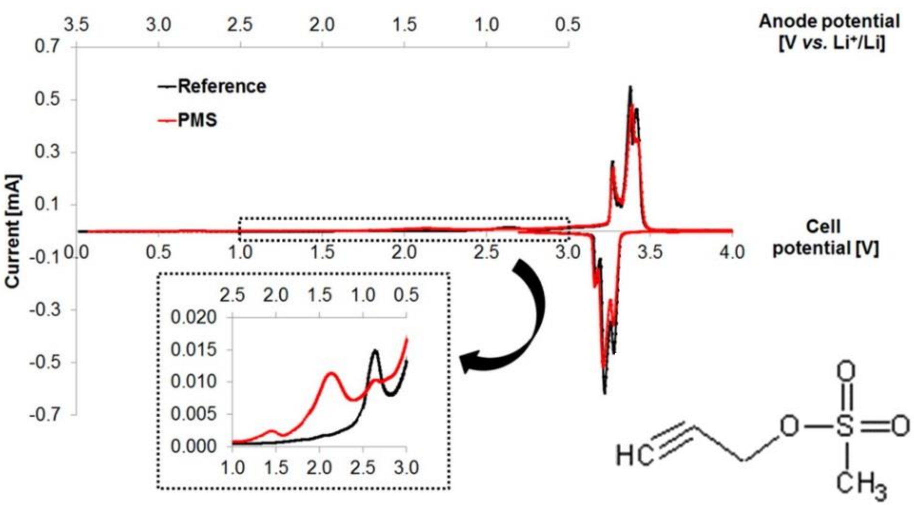
$LiFePO_4$

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.

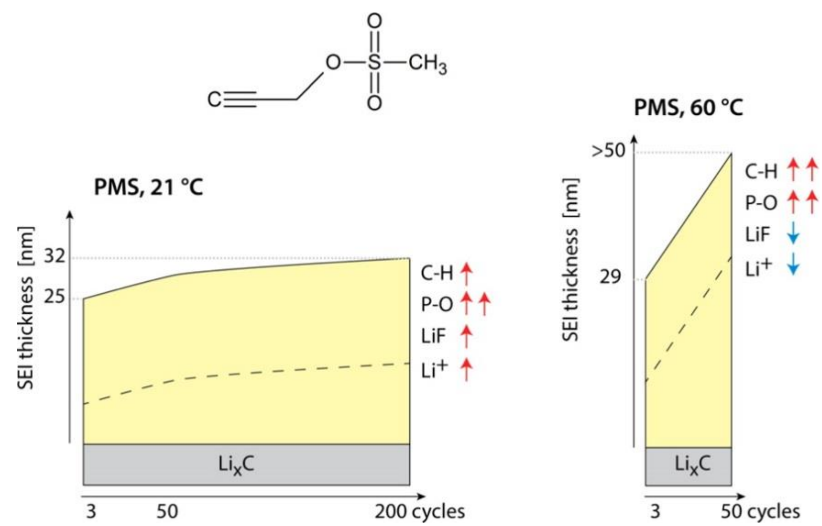
S. Malmgren, K. Ciosek, M. Hahlin, T. Gustafsson, M. Gorgoi, H. Rensmo, K. Edström *Electrochim. Acta* 97(2013) 23.

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[τ]



PMS



K. Ciosek Högström, S. Malmgren, M. Hahlin, H. Rensmo, F. Thébault, P. Johansson, K. Edström. *J. Phys. Chem. C* 117 (2013) 23476–23486.

*Thesis Anna Andersson 2001

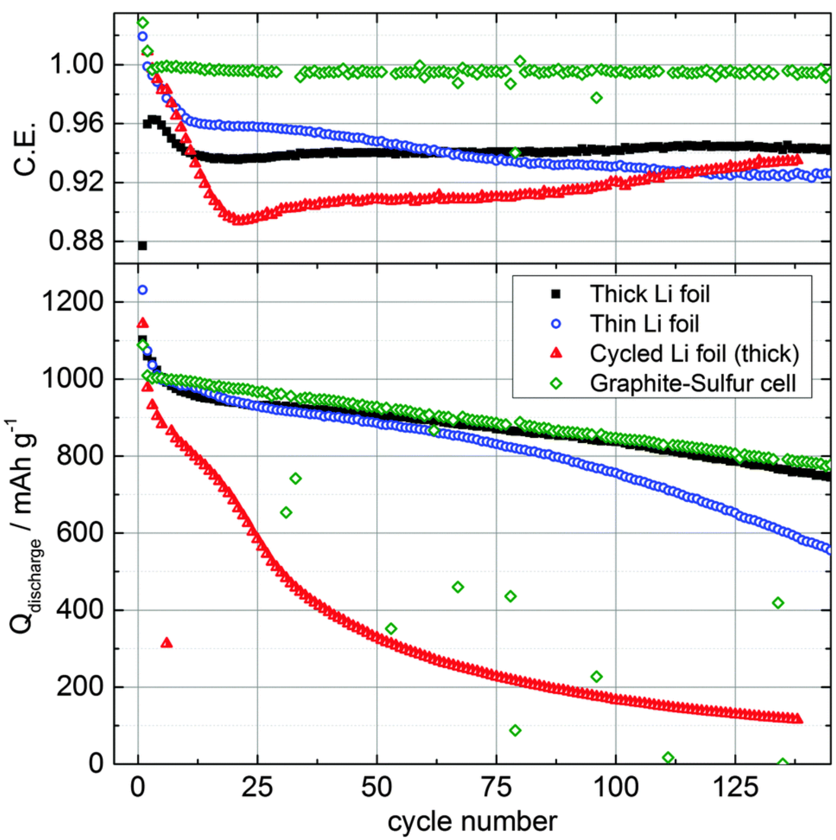
τ Thesis Katarzyna Ciosek Högström 2014

R. Younesi, G. Veith, P. Johansson, K. Edström, T. Vegge, Energy & Envir. (2015)

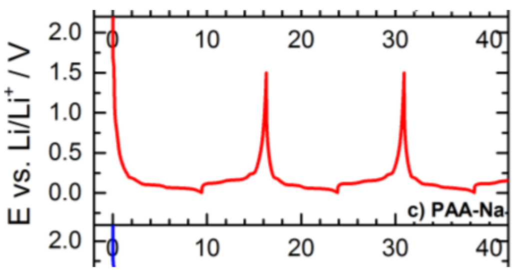
Binders and graphite

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

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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

Hi-C FP7

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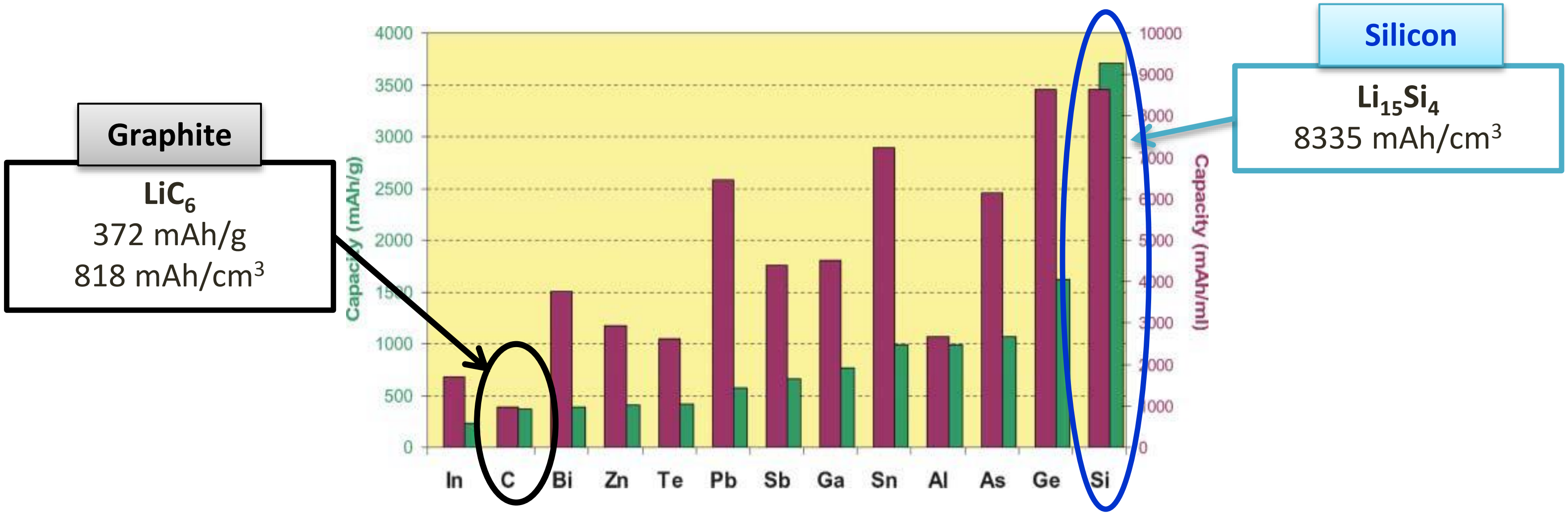
Silicon interfaces



Volume expansion 320%

D. Larcher, S. Beattle, M. Morcrette, K. Edstrom, J.-C. Jumas and J.-M. Tarascon
J. Mater. Chem, **17** (2007) 3759

Goal

Today 2-5% SiO_x is added to graphite anodes in commercial batteries to enhance capacity

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Model studies

Up-scaling in collaboration with the spin-off company LiFeSiZe

Depth-profiling the SEI of Silicon using PES

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From the extreme surface...

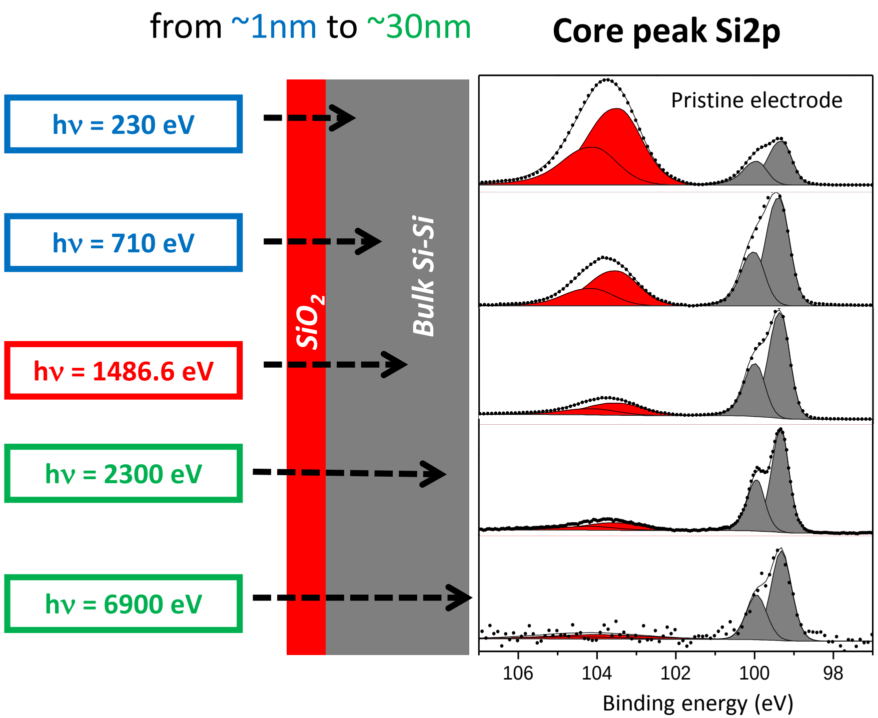
...to the "bulk"

Soft X-ray
hν = 100 to 1500 eV

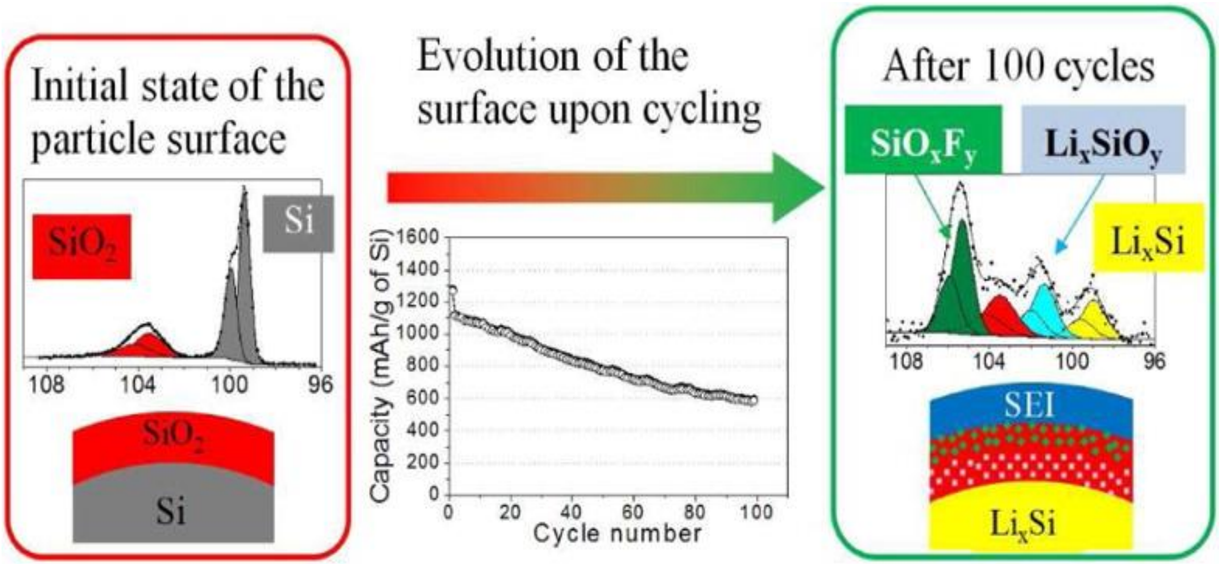
Al Kα ray
hν = 1486.6 eV

Hard X-ray
hν = 2000 to 10 000 eV

In-house XPS



What do we know from model system studies?



Standard electrolytes containing **$LiPF_6$ salt** is critical for cycling stability

So, change the salt

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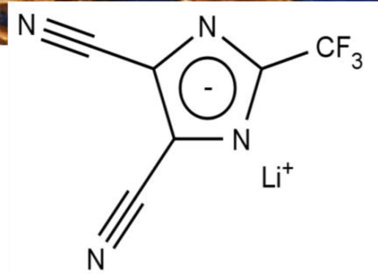
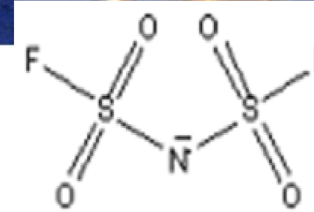
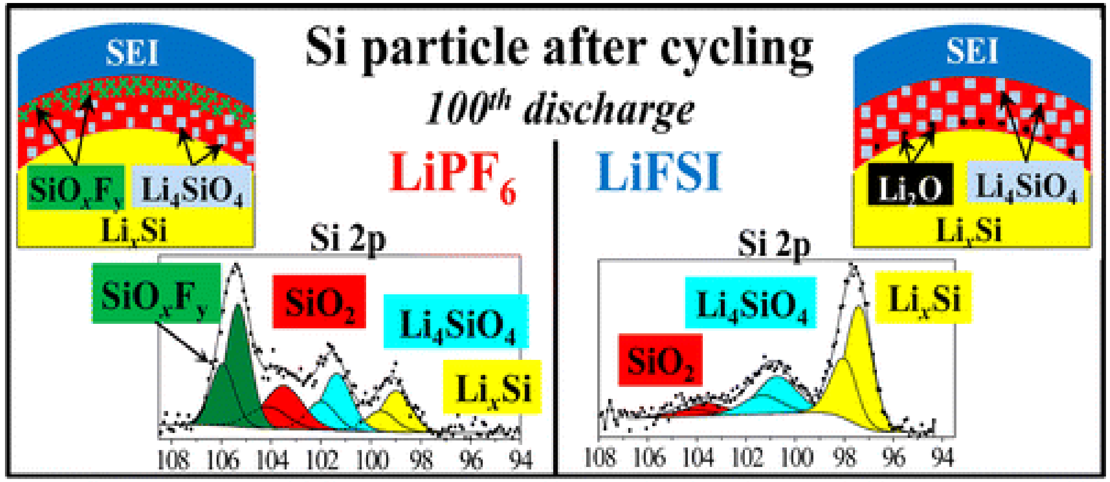




The role of the lithium salt

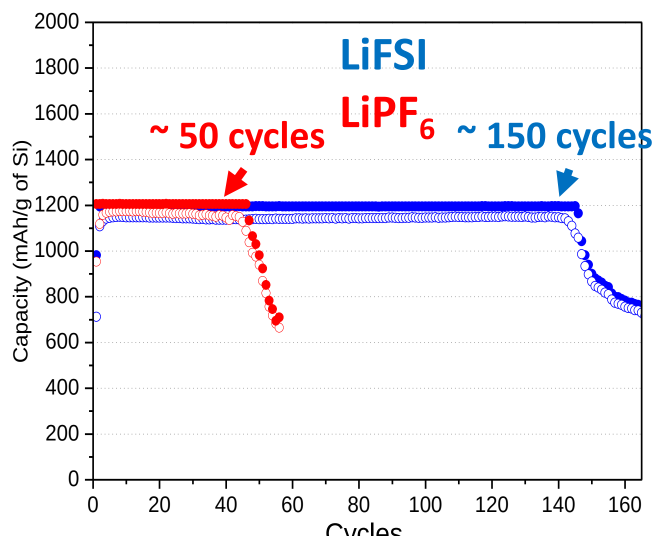


B. Philippe et al., *Chem. Mater*. **24** (2012) 1107

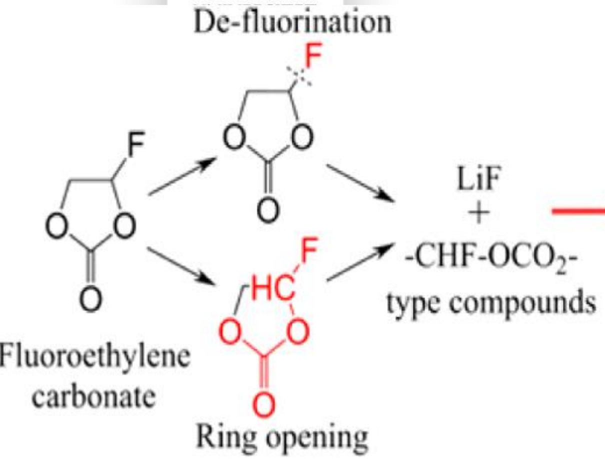
B. Philippe et al., *Chem. Mater*., **25** (2013) 394

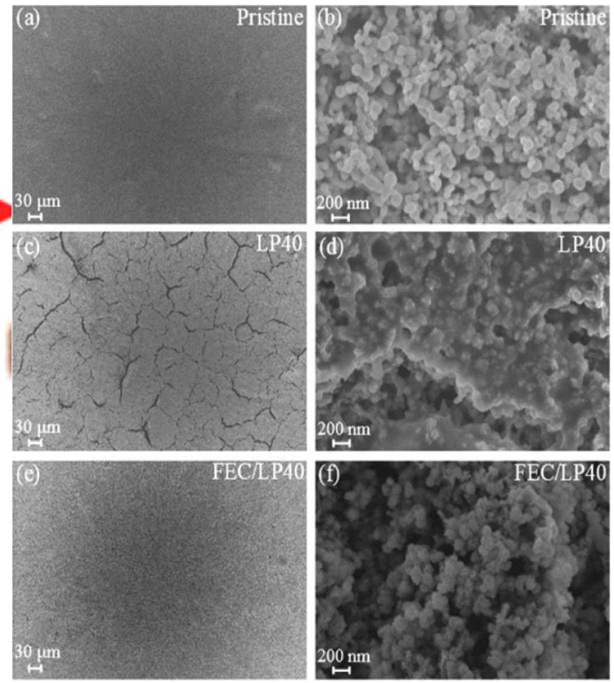
B. Philippe et al., *JACS* **135** (2013) 9829

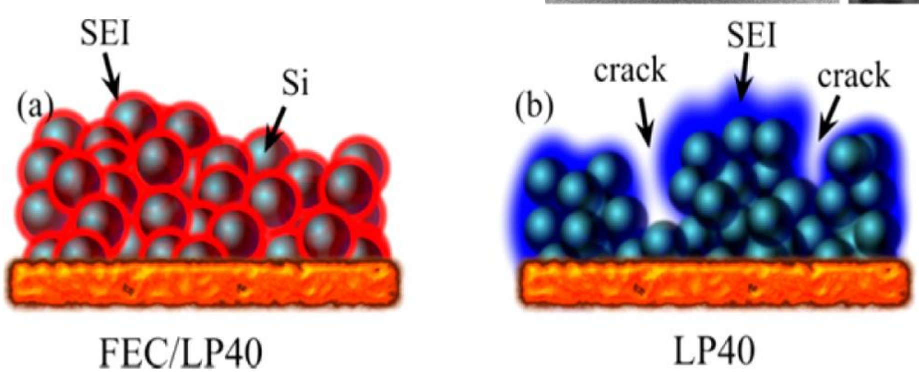
F. Lindgren et al., J. Power Sources 301 (2016) 105

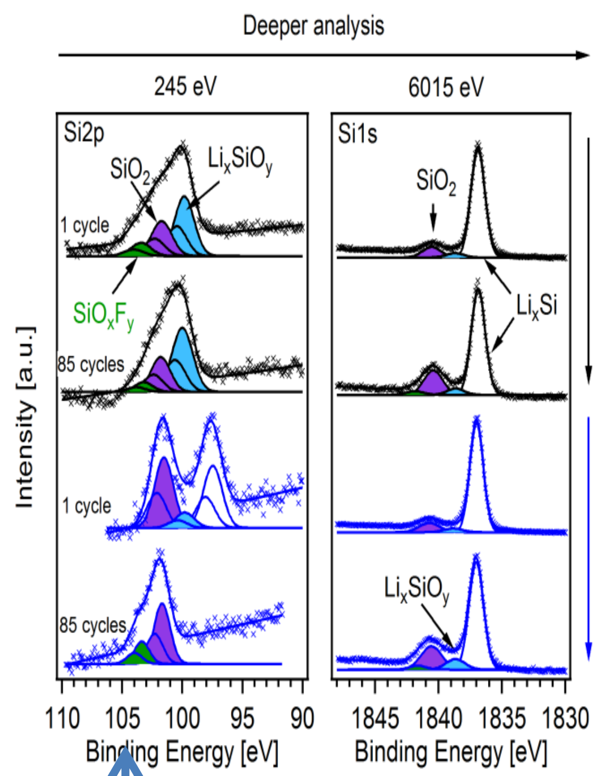


Silicon composite electrode, $LiPF_6$ and FEC









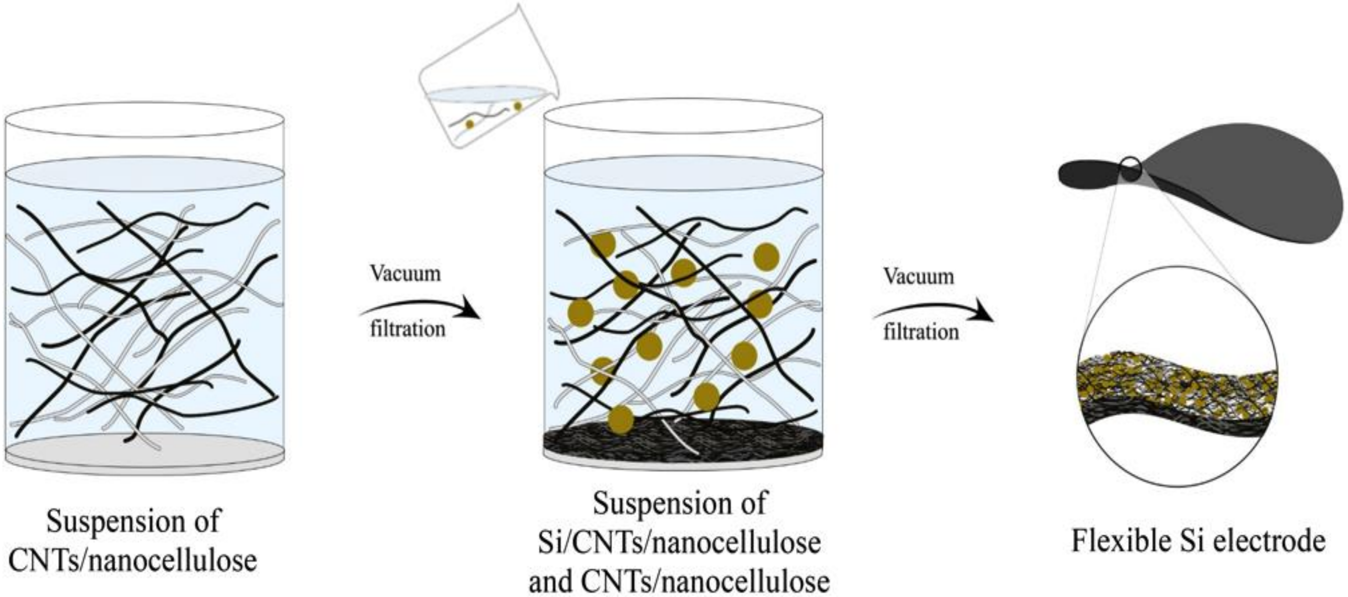
SiOFx forms later than for $LiPF_6$

Chao Xu et al., Chem. Mater. 27 (2015) 2591

Knowing this – what can we do?

Post Doc Z. Wang

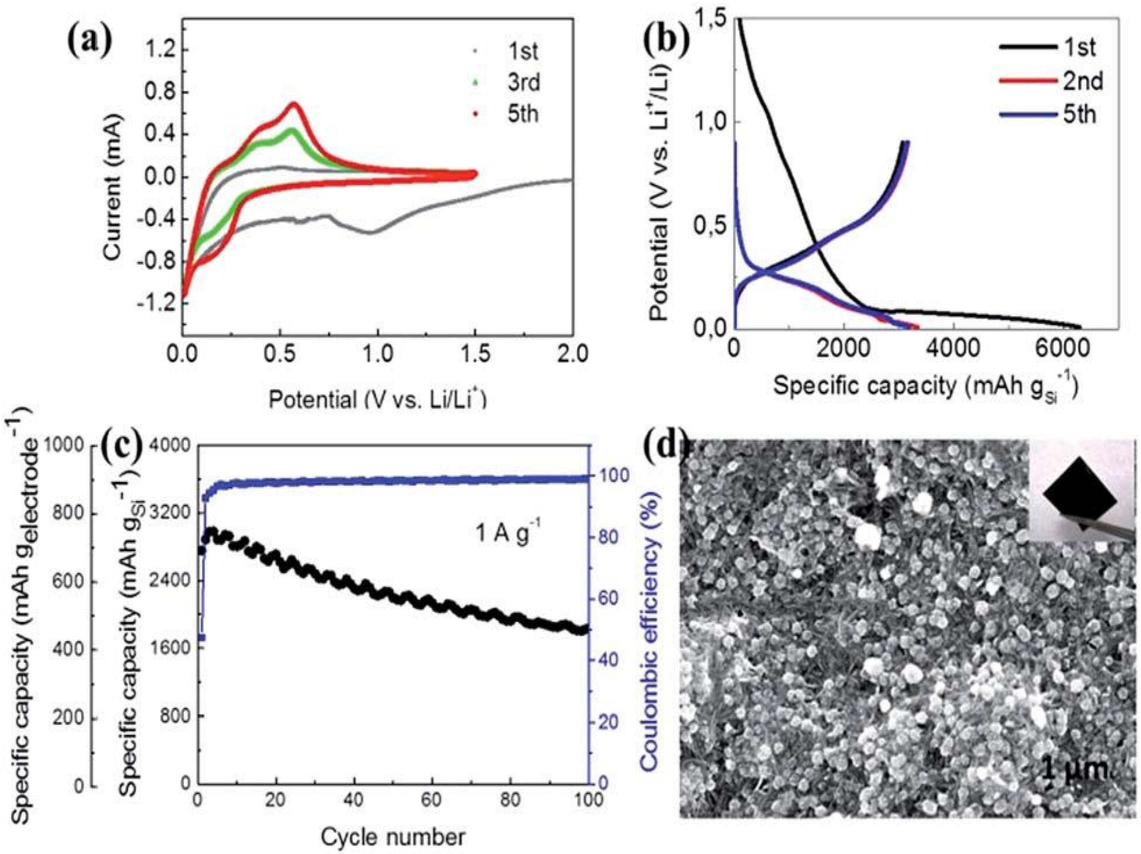
Flexible free-standing electrodes of cladophora nano cellulose



Simple paper making process

Z. Wang, C. Xu, P. Tammela, J. Huo, M. Strømme, K. Edström, T. Gustafsson and L. Nyholm.
J. Mater. Chem. A, 2015, 3, 14109

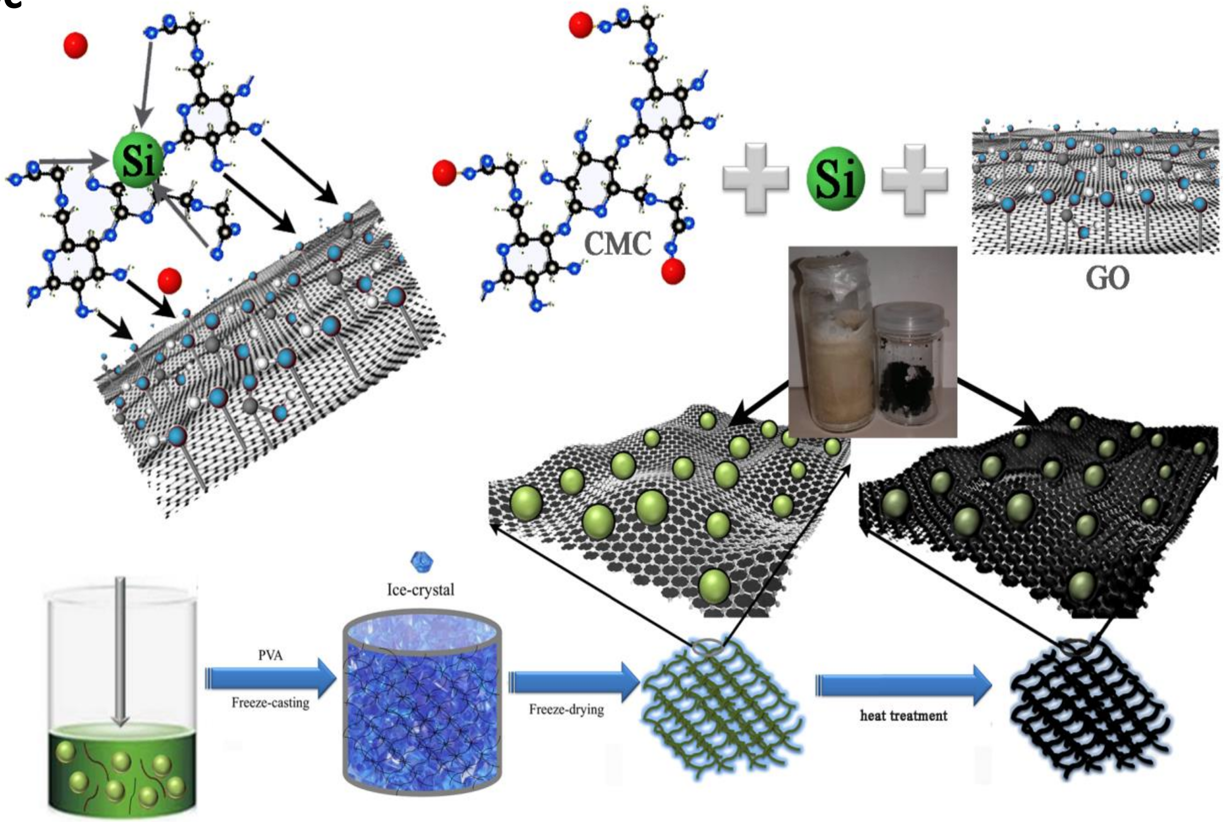
Electrochemical performance of the SiNP/CNT/CNC anodes



Z. Wang, C. Xu, P. Tammela, J. Huo, M. Strømme, K. Edström, T. Gustafsson and L. Nyholm.
J. Mater. Chem. A, 2015, 3, 14109

Knowing this – what can we do?

Post Doc Dr Yue (Mars)



Freeze drying!

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

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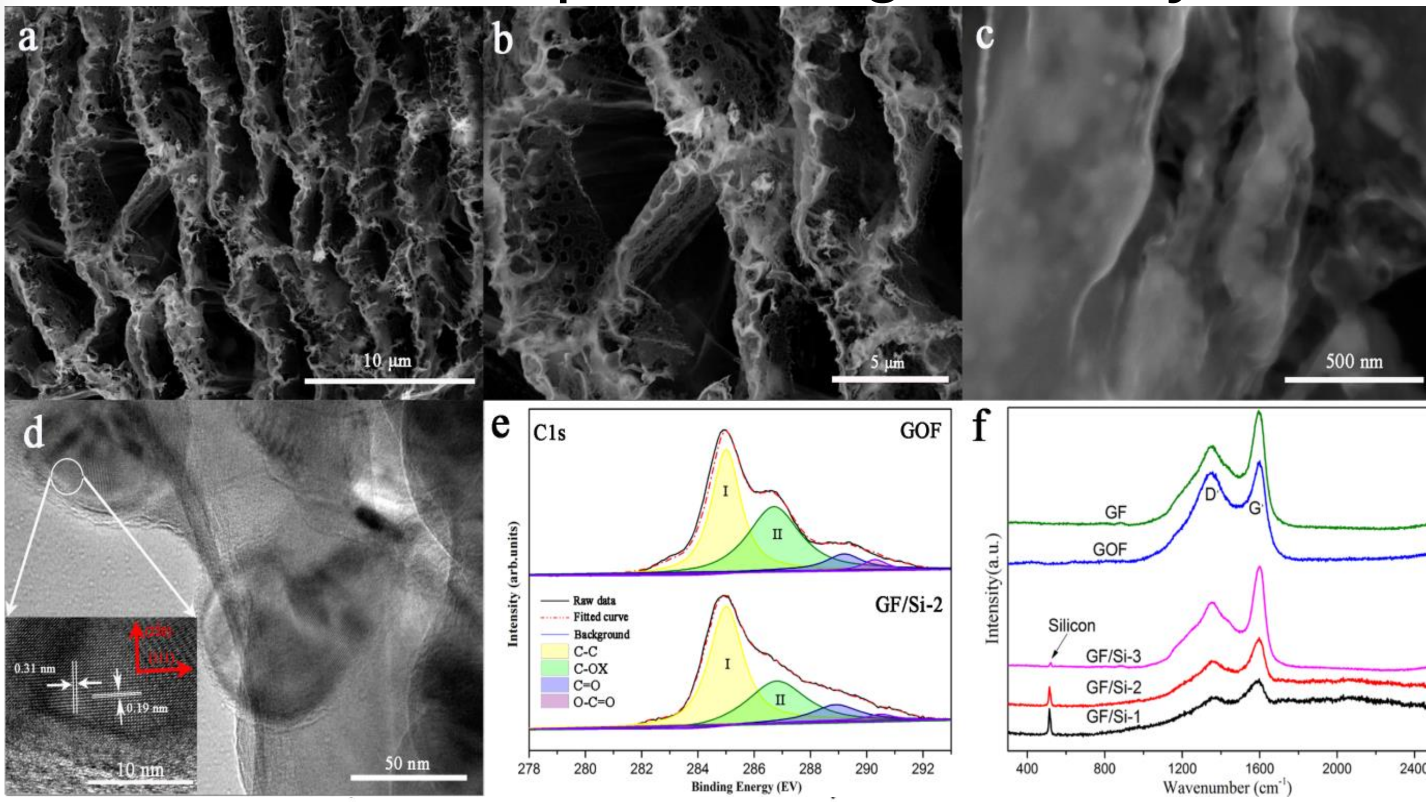
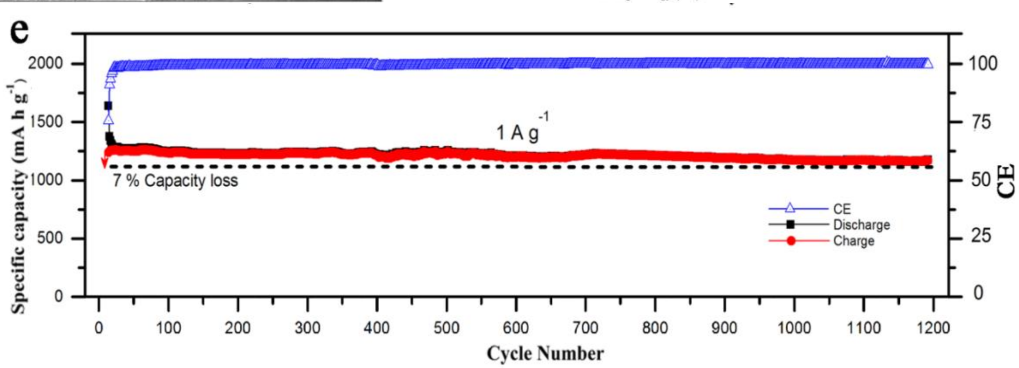
SEM

TEM



1200 cycles of 66 wt% Si

$LiPF_6$ in EC/DEC + 10% FEC



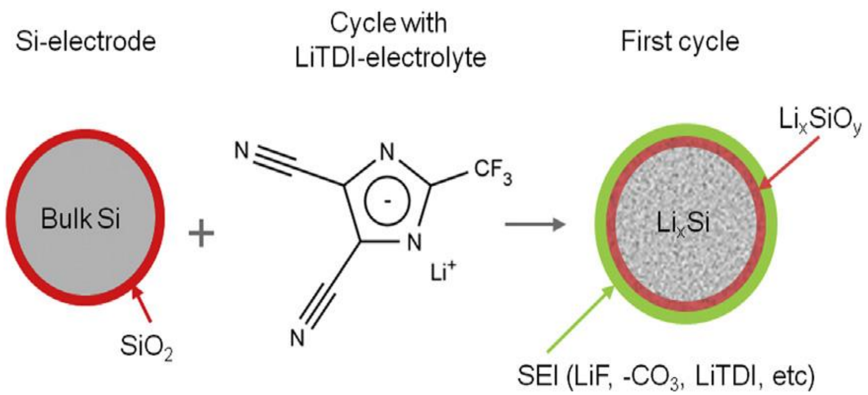
Ma Yue and K Edström, submitted

Next step

Upscaling: Composite electrodes using TDI salt and additives

Use the LiFeSiZe pilot line

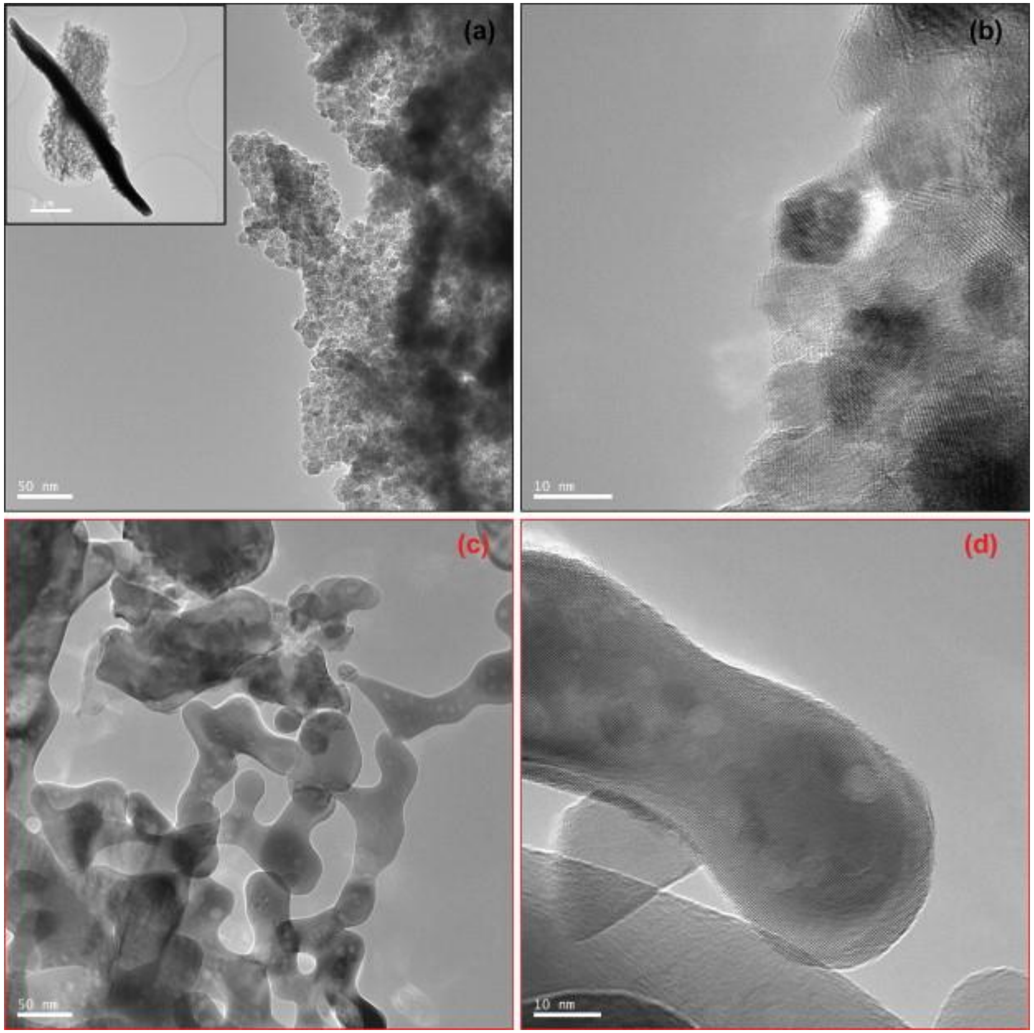
Continue the study of protection of the silicon particles



Conversion reactions
Li-ion vs. Na-ion

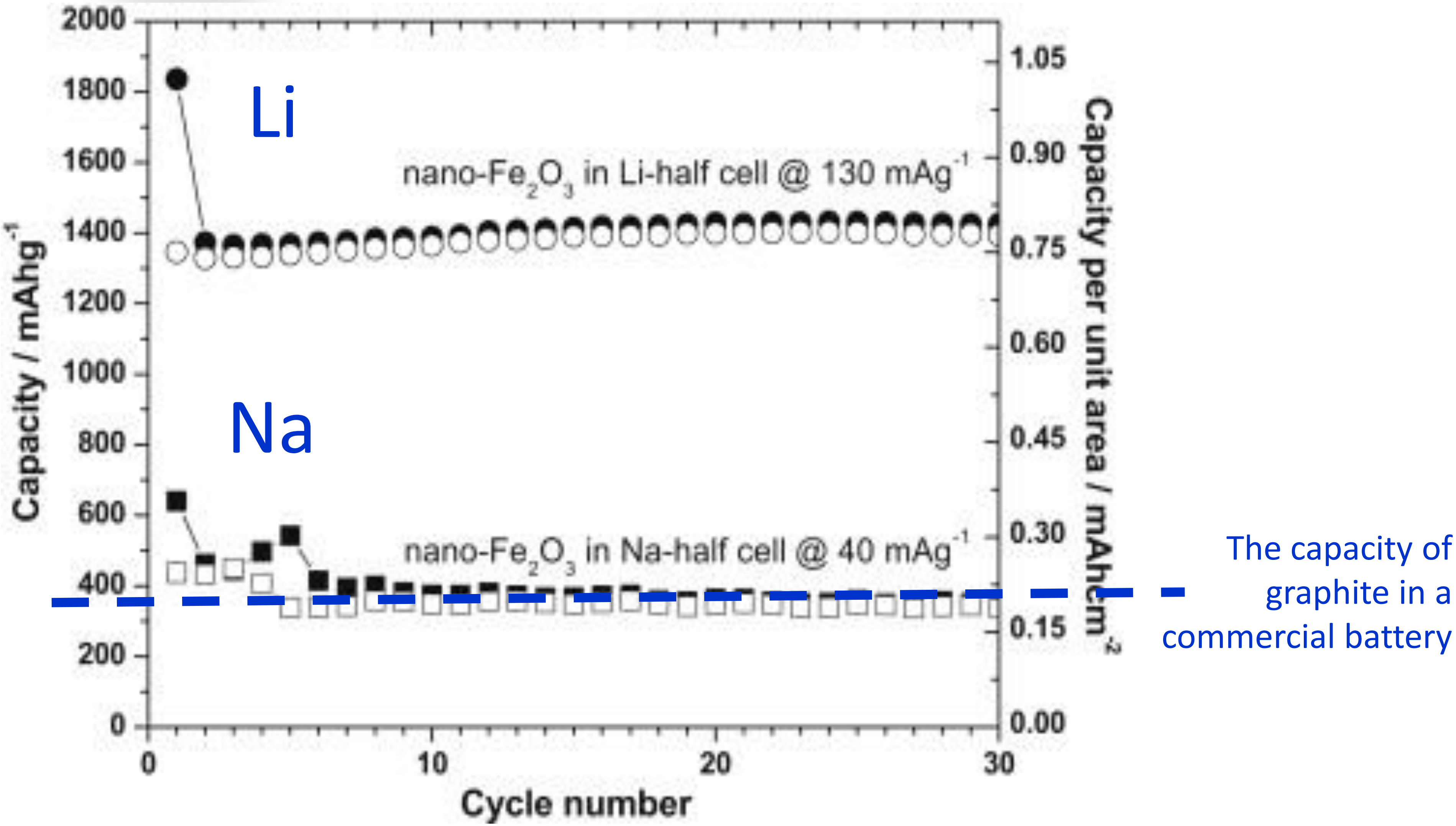
γ-Fe_2O_3 produced through pyrolisation of an Iron salt

$6Li + Fe_2O_3$
$= 3Li_2O + Fe$



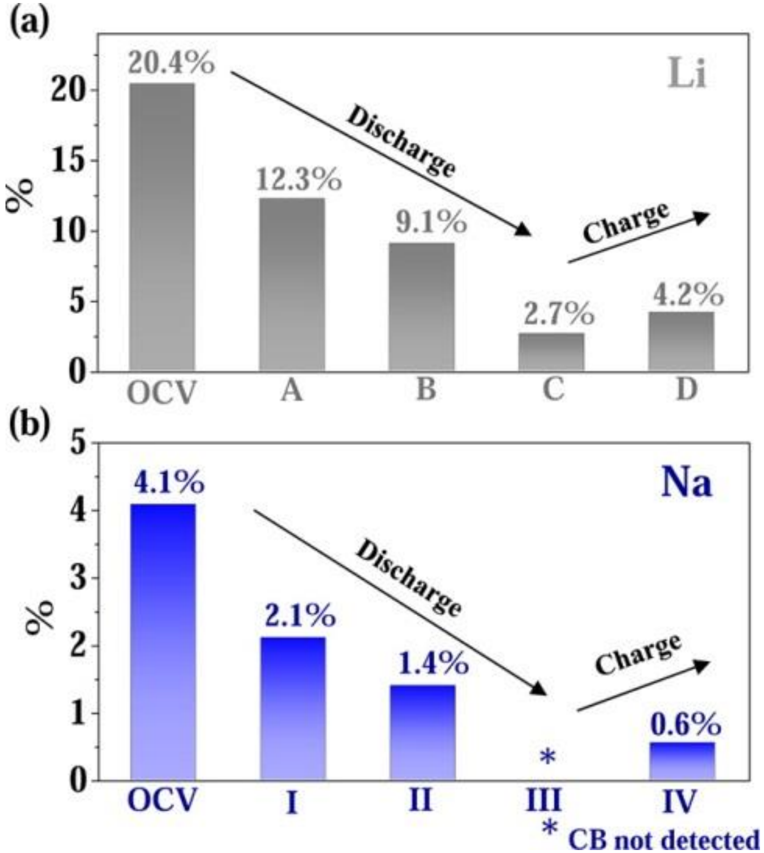
M. Valvo, F. Lindgren, U. Lafont, F. Björefors and K. Edström, *J. Power Sources* **245** (2014) 967.

Comparing Li and Na by cycling Fe_2O_3?



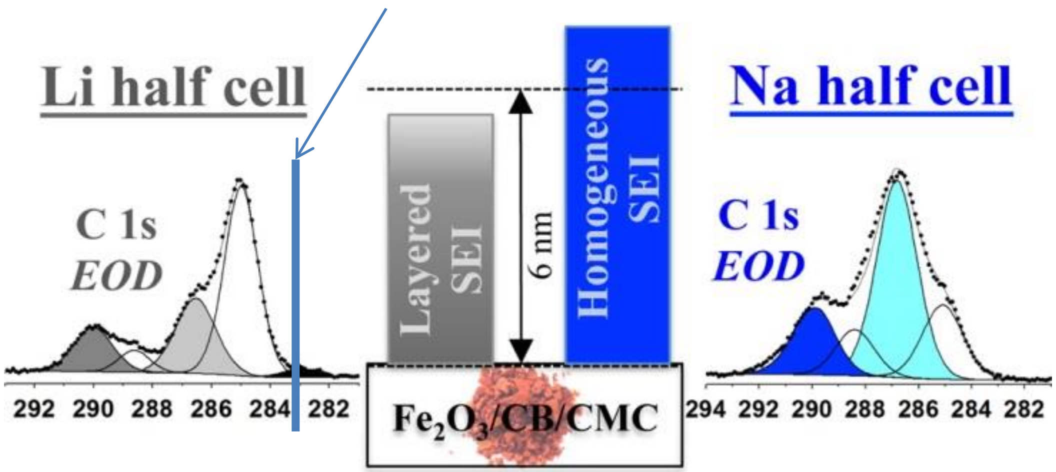
M. Valvo, F. Lindgren, U. Lafont, F. Björefors and K. Edström, *J. Power Sources* **245** (2014) 967.

The difference in SEI between Fe_2O_3 cycled *vs.* Li or Na



The amount of visible CB through the SEI layer

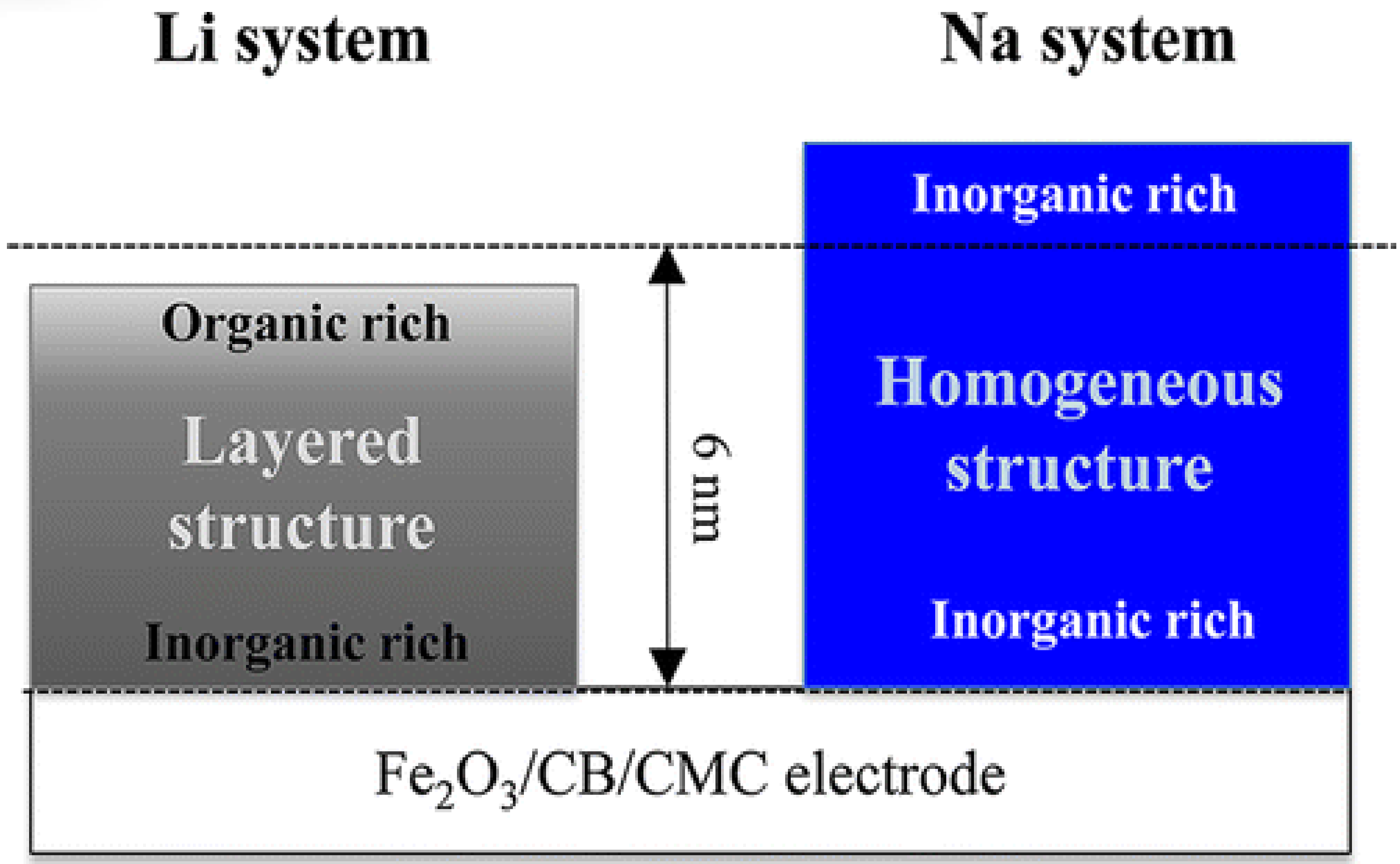
The peak from carbon black in the composite electrode is a probe of ”SEI thickness”



C1s peaks for the SEI layer of Fe_2O_3 cycled with lithium (left) and sodium (right)

Bertrand Philippe, Mario Valvo, Fredrik Lindgren, Håkan Rensmo, and Kristina Edström, *Chem. Mater.*, **2014**, *26* (17), 5028–5041

The losses – electrode/electrolyte surface reactions

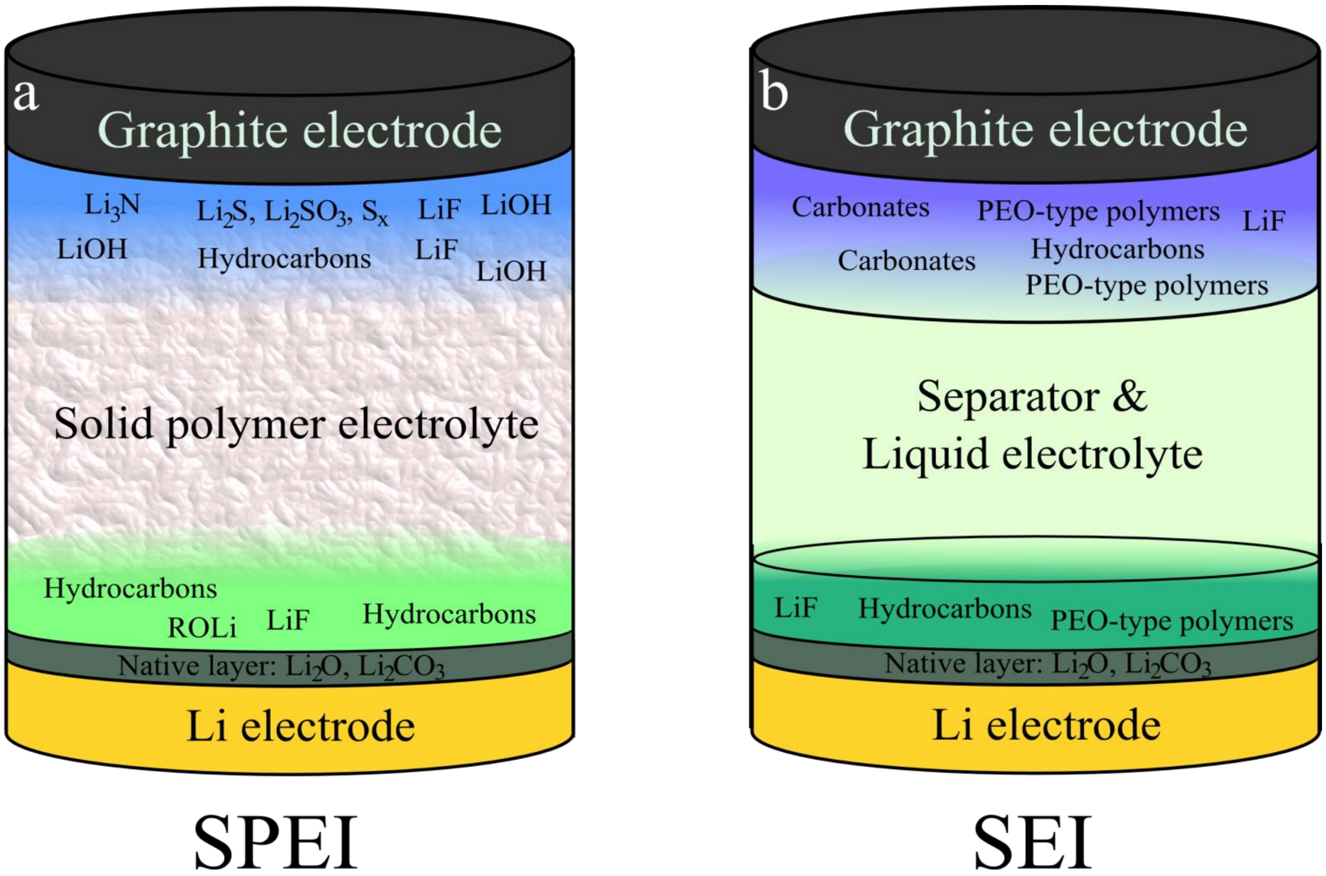


M. Valvo, F. Lindgren, U. Lafont, F. Björefors and K. Edström, *J. Power Sources* **245** (2014) 967.

Lithium interfaces

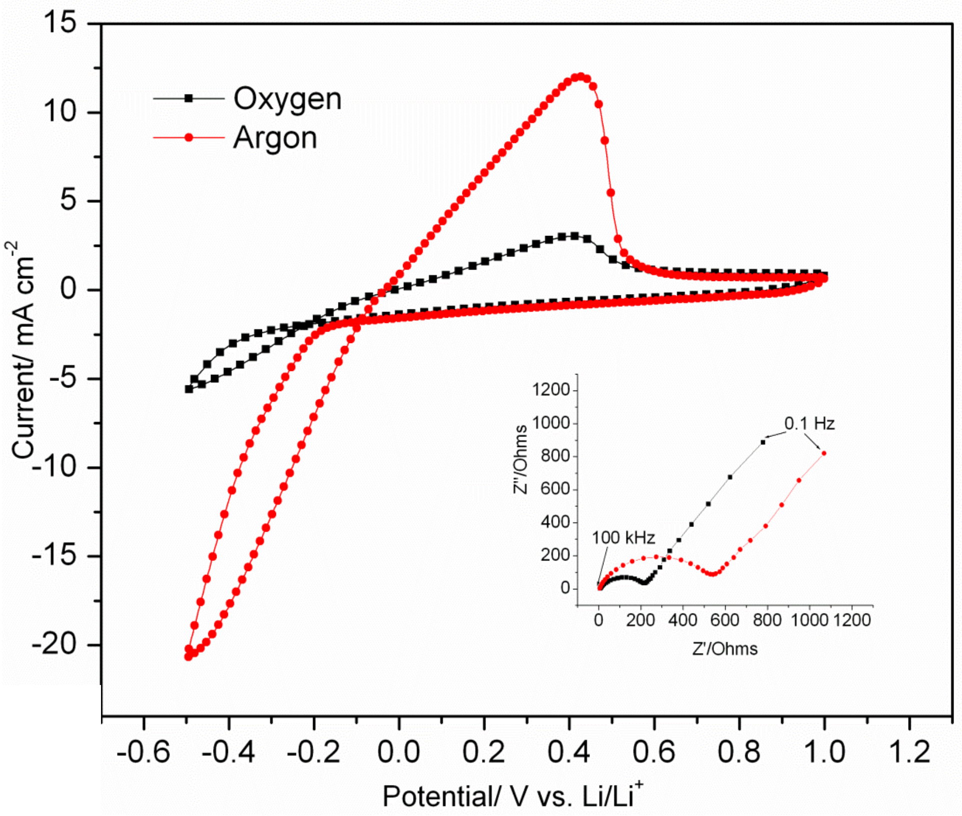
Comparing a cell with a polymer electrolyte and a cell with organic solvents

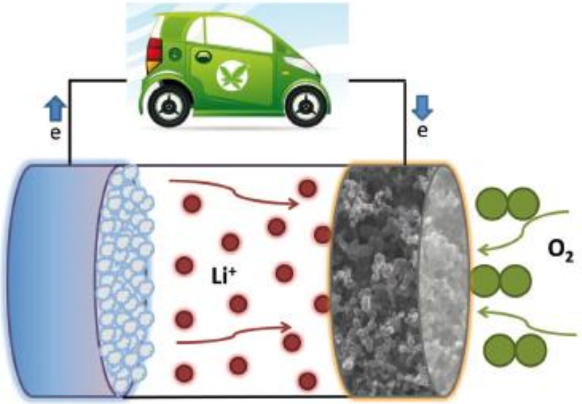
Based on PES-studies



C. Xu, B. Sun, T. Gustafsson, K. Edström, D. Brandell and M. Hahlin, *J. Mater. Chem. A* **2** (2014) 7256

Compare to the surface of lithium in a Li-O_2 cell





S.R. Younesi, M. Hahlin, M. Roberts, and K. Edström, *J. Power Sources*, **225** (2013) 40.

Surface analysis of the Li anode

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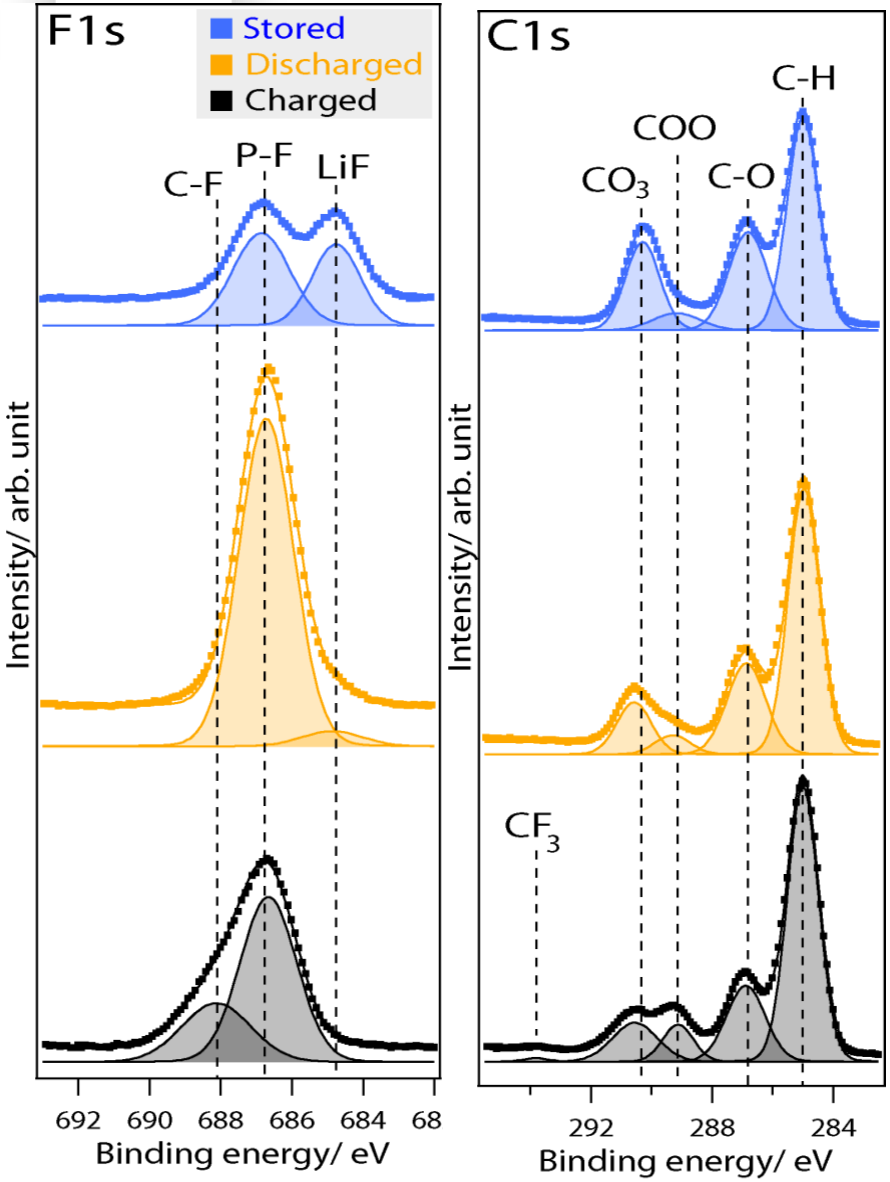
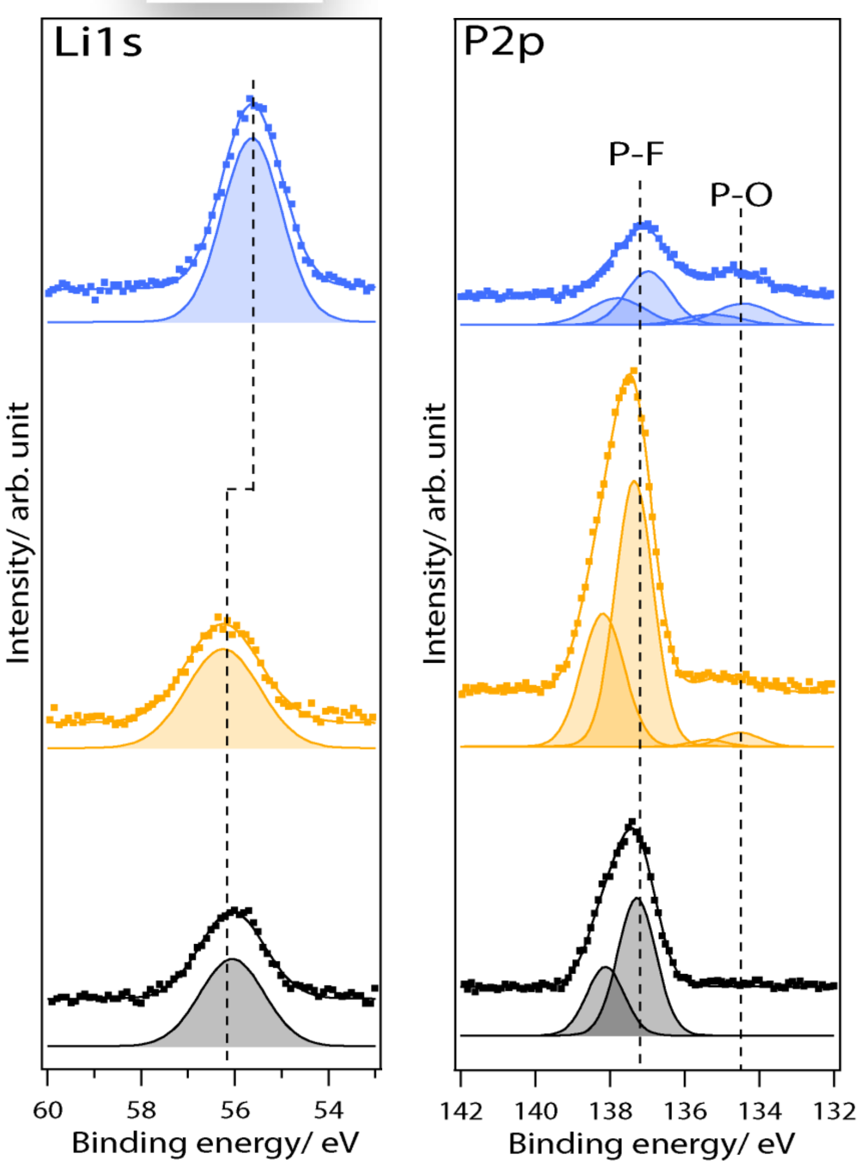


- Constantly evolving SEI on the Li anode in the Li-O_2 battery
- The composition of the surface layer **change** after discharging and again after charging.
- Decomposition of PC to lithium alkyl carbonates, PEO and carboxylate species
- Decomposed Kynar binder on Li anode

No dramatic difference between discharge and charge

S.R. Younesi, M. Hahlin, M. Roberts, and K. Edström, *J. Power Sources*, **225** (2013) 40.

Surface analysis of the Li anode

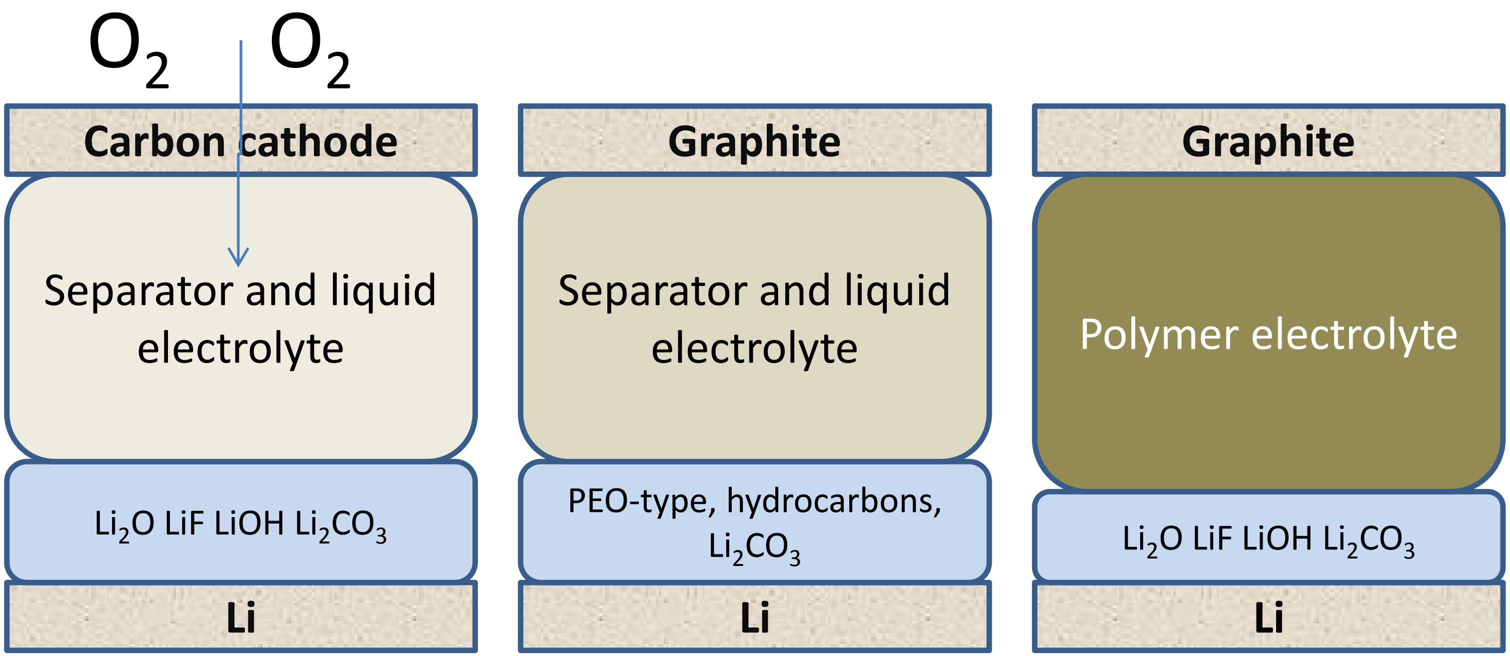


- Increase of the relative amounts of F and P from the stored Li anode to the discharged and charged samples
- Decomposed $LiPF_6$ salt on the stored Li anode, but negligible on the discharged and charged samples.
- $LiPF_6$ found on the Li anode of discharged and charged cells.

S.R. Younesi, M. Hahlin, M. Roberts, and K. Edström, *J. Power Sources*, **225** (2013) 40.

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

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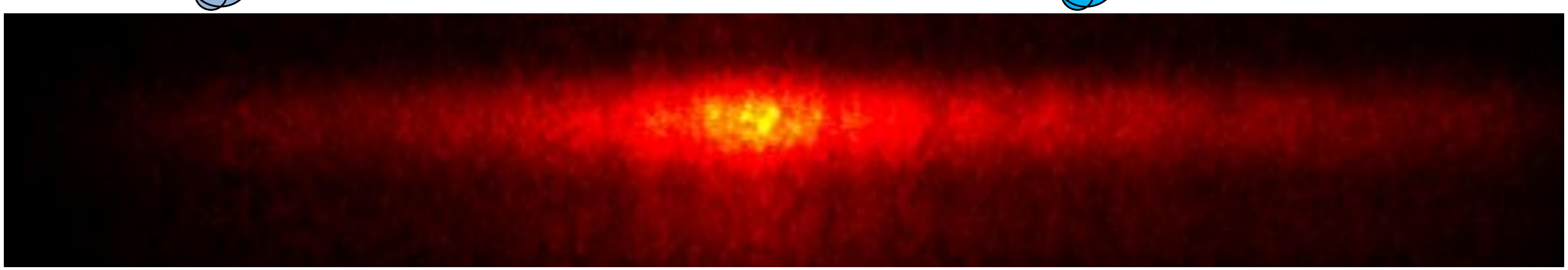
Conclusions

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?



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Research Funding

VINNOVA

formas

SEVENTH FRAMEWORK PROGRAMME

ALISTORE-ERI and French Ministry

AVFALL SVERIGE

ÅFORSK

Vetenskapsrådet

STandUP for ENERGY

Swedish Energy Agency

Multi-project grant, basic energy research + ”normal” grants

STINT
Stiftelsen för internationalisering av högre utbildning och forskning

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High Voltage Valley