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

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See also:

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

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

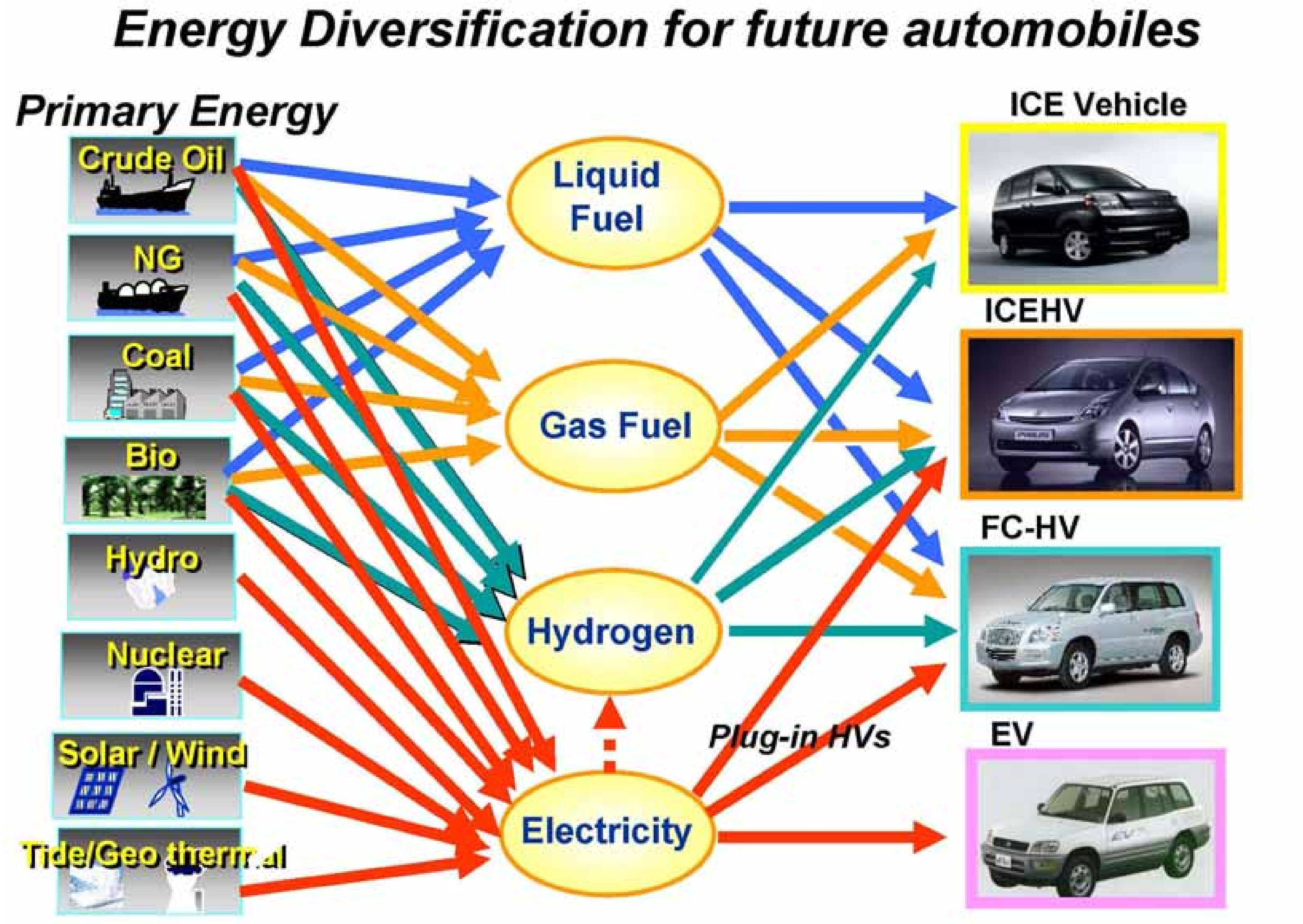
GCEP is GCEP

.... 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 killed the electric vehicle?” suspicions . . . . and our car industry is ”US owned”
- USA is capitalist – where private enterprise fluorishes . . . . Sweden is socialist - we look to ”the State” to make the moves

Sweden is more optimistic - but also more utopic and less realistic

A future vision borrowed from Toyota . . . .



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**

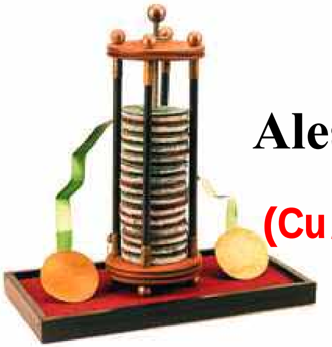
Time-scale ? *cf.* Joan Ogden (Day 1)

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 ?

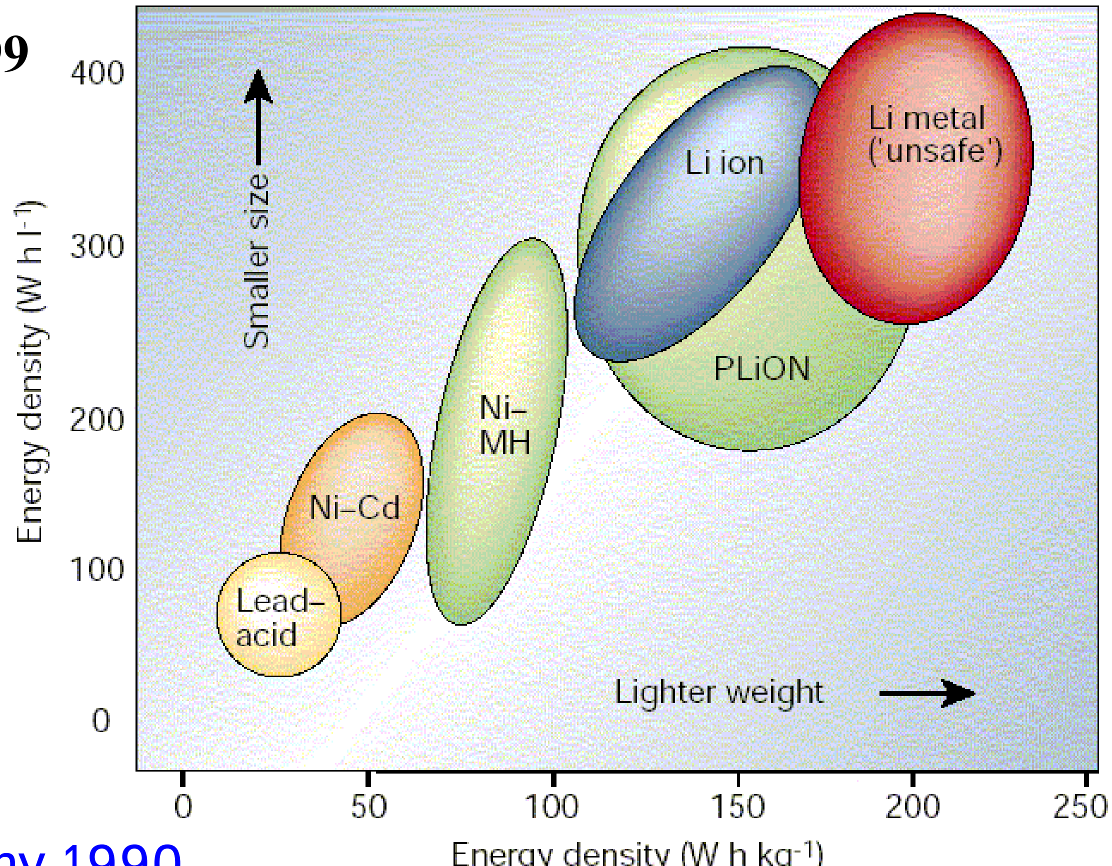
Where are batteries today – after two centuries ?



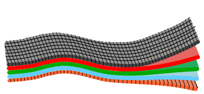
Alessandro Volta, 1799

(Cu/Zn)

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



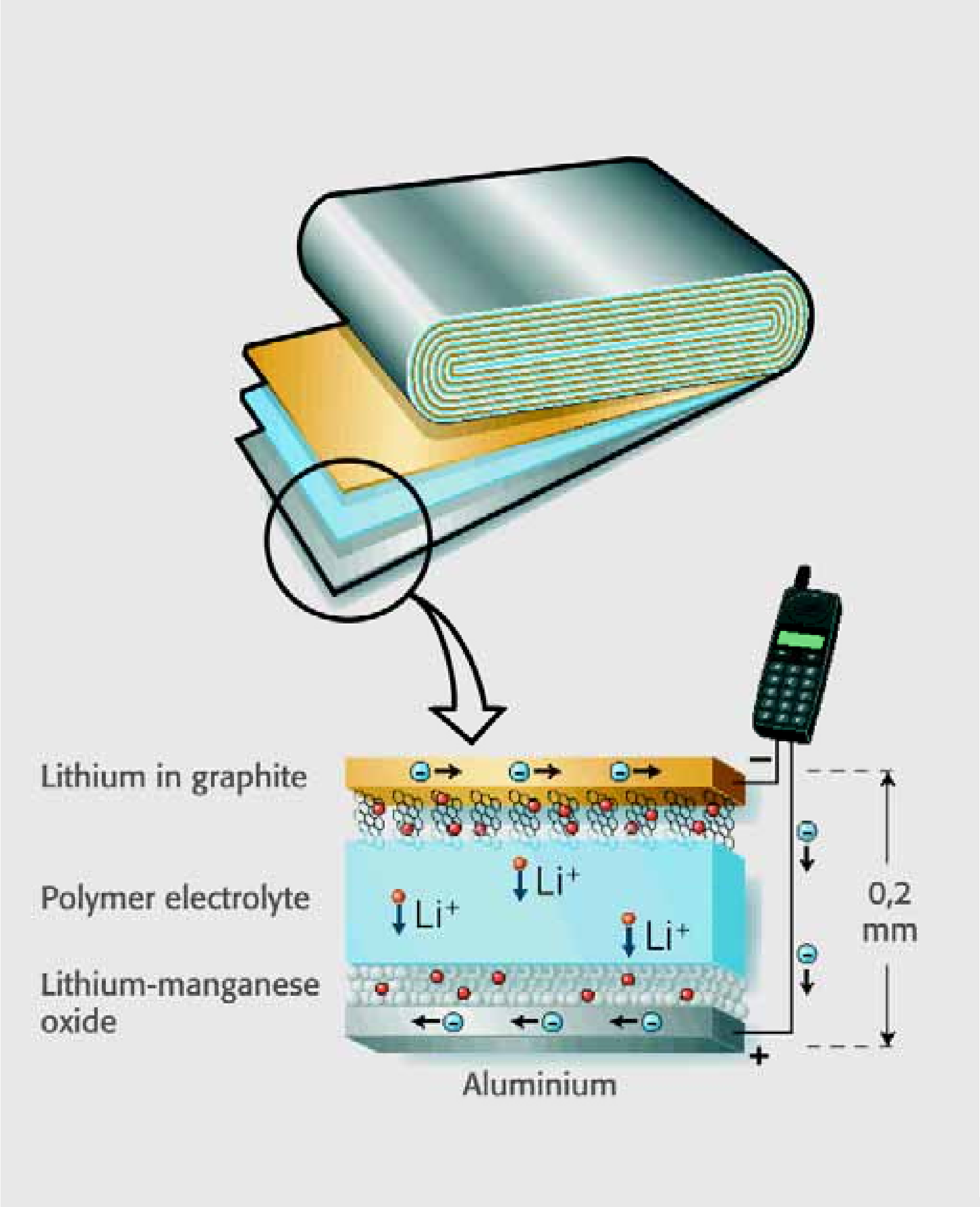
Li-ion: Sony 1990



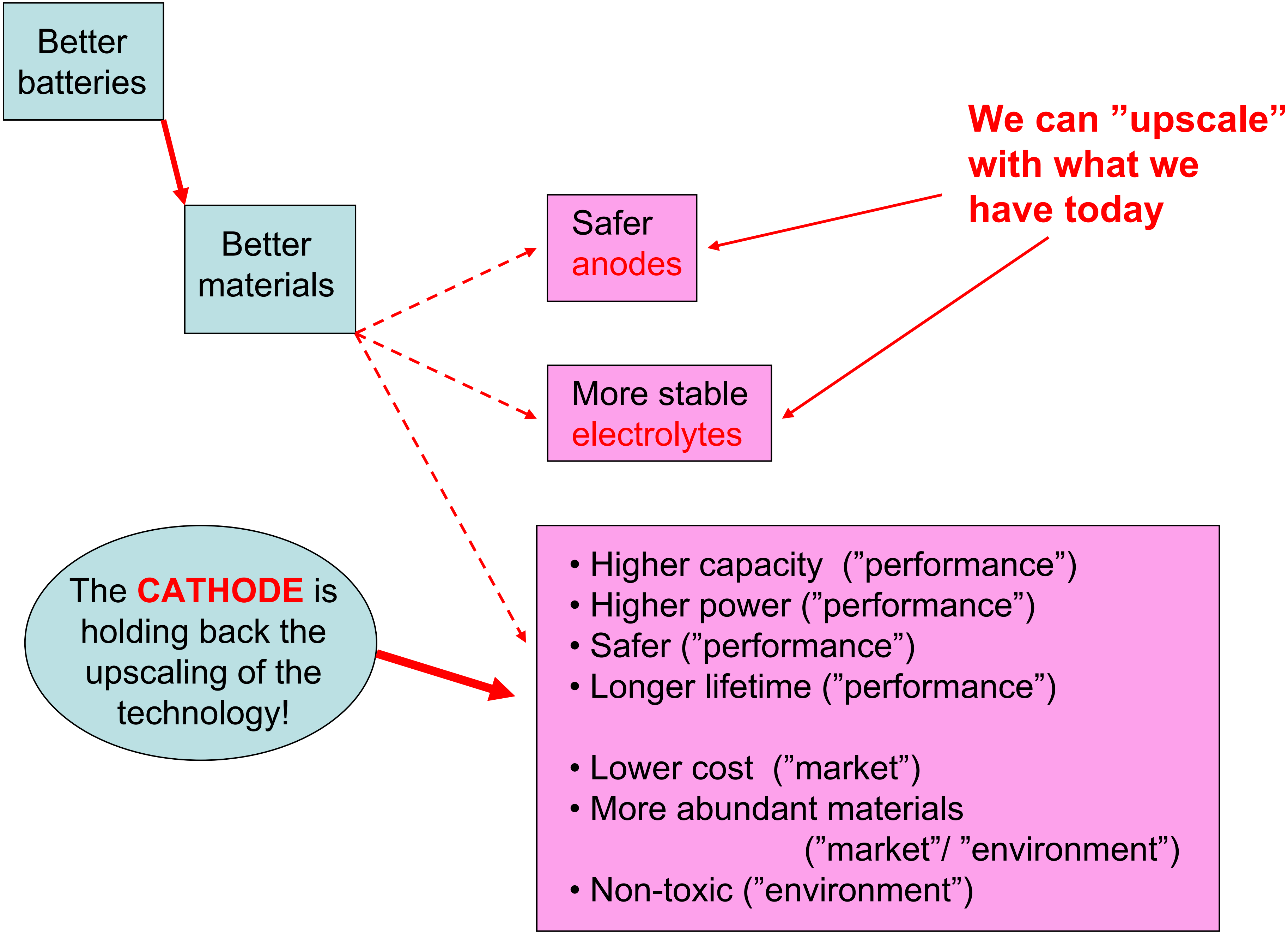
Li-ion polymer: 2000

The battery industry is clearly very conservative

The rechargable 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:

  $Li(Co,Ni)O_2$, $LiNi_{1-y-z}Co_yAl_zO_2$

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

  - $LiFePO_4$ (A123, *etc.)*
  - Li_2FeSiO_4 (our focus)

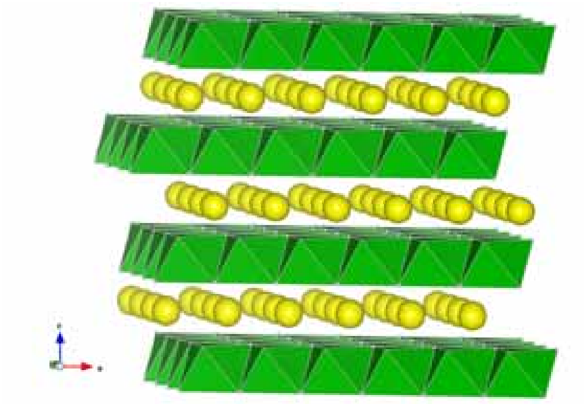
LiFeSiZE

(Fe- and Si-oxides make up >10% of the Earth's crust)

Cathode materials: a comparison

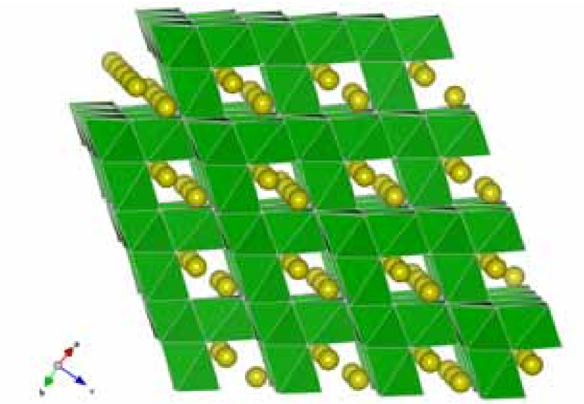
a) Layered:

$LiCoO_2$-> $Li_{0.5}CoO_2$: ~3.9V, ~140 mAh/g



b) Spinels:

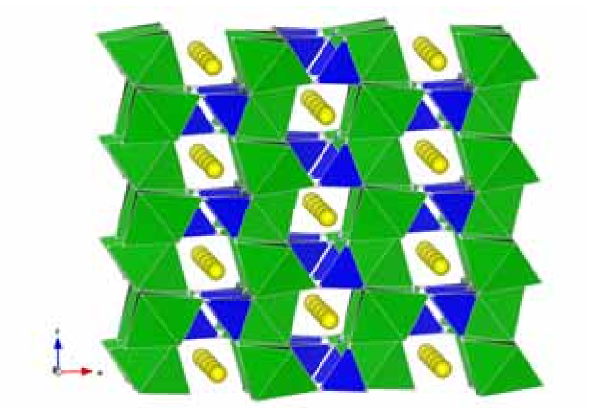
$LiMn_2O_4$-> Mn_2O_4: ~3V or ~4.0V, 148 mAh/g



Instabilitility !
Solution: doping

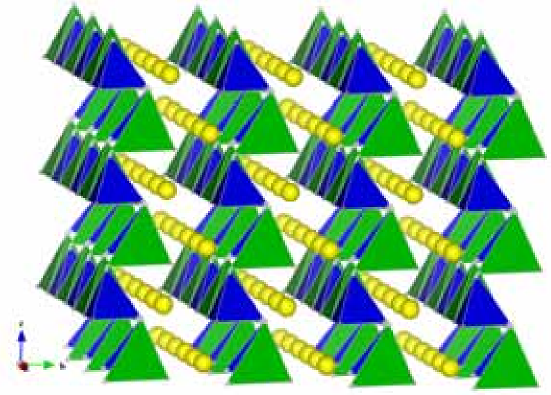
c) Olivines:

$LiFePO_4$ -> $FePO_4$, ~3.5V, ~170 mAh/g



d) Orthosilicates

Li_2FeSiO_4 -> $LiFeSiO_4$, ~2.85V, ~ 170 mAh/g



Poor el. conductivity !

Solutions:

- doping
- coating
- ”nano”-sizing

Our new Fe-based cathode material

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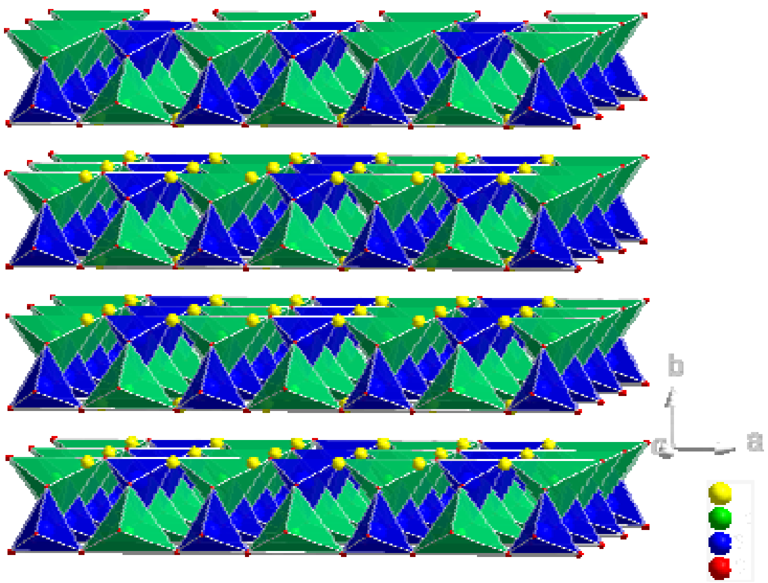
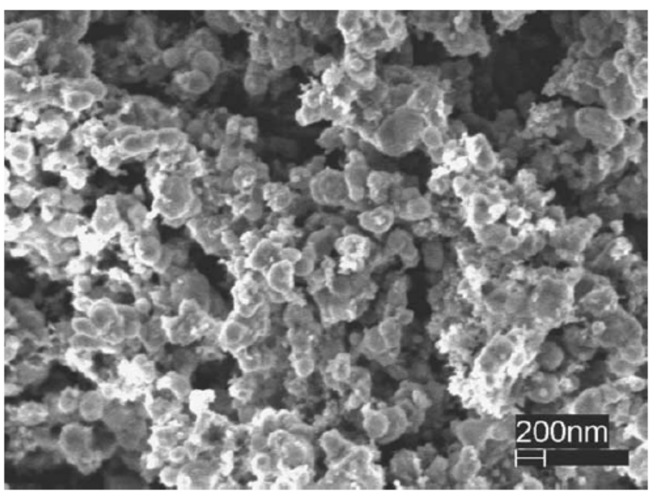
Li_2FeSiO_4 - an orthosilicate

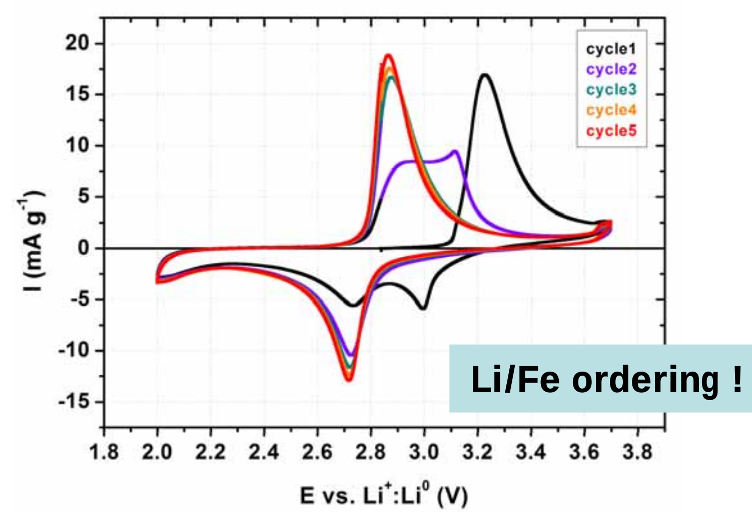


- $Li_2Fe^{2+}SiO_4 \leftrightarrow LiFe^{3+}SiO_4 + Li^+ + e^-$
- **E= 2.85 V vs. Li^+/Li (low!!)**
- **Q= 169 $mAh \cdot g^{-1}$**

Advantages:

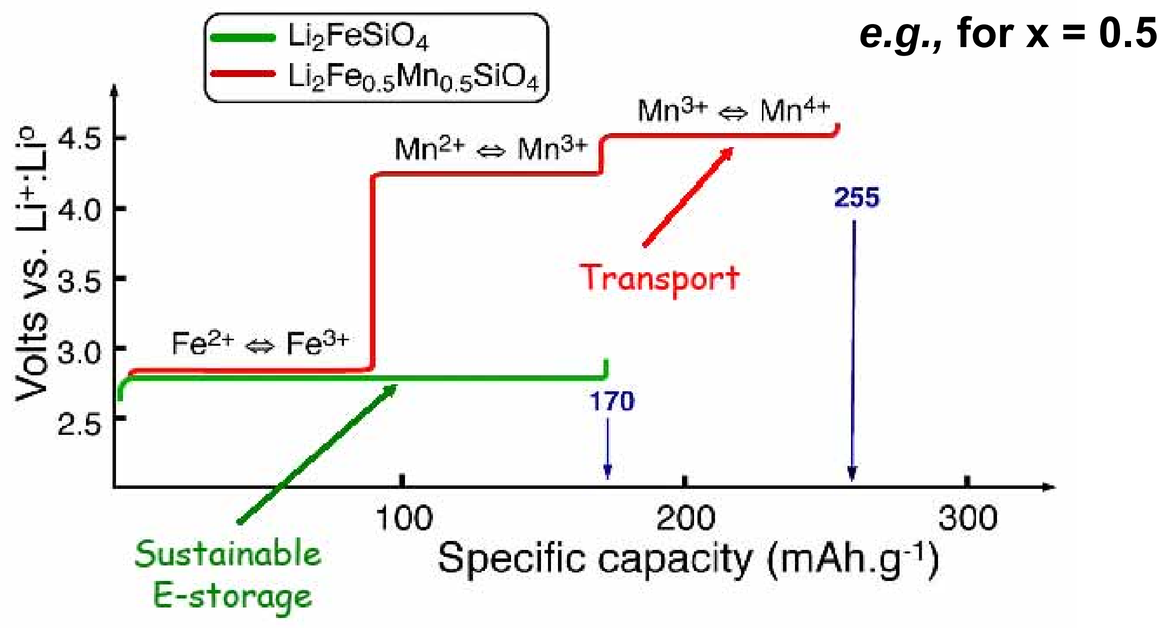
- Potentially lower cost, abundant, non-toxic
- High cycling efficiency
- High stability





Strategies for improvement . . .

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



$$Li^{+}_{2}(Fe^{2+}_{1-x}Mn^{2+}_{x})SiO_4 \Rightarrow Li^{+}_{1-x}(Fe^{3+}_{1-x}Mn^{4+}_{x})SiO_4 + (1+x)Li^{+} + (1+x)e^{-}$$

Our strategy for improving performance

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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, ...

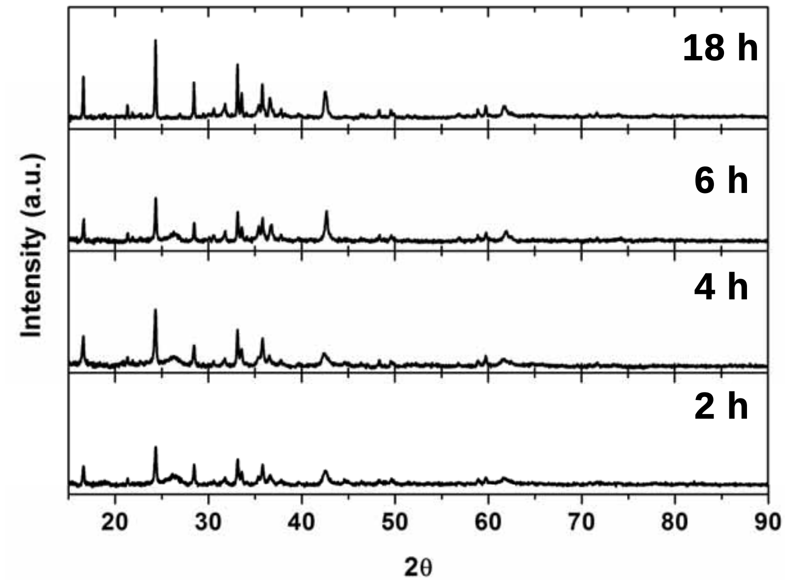
↓

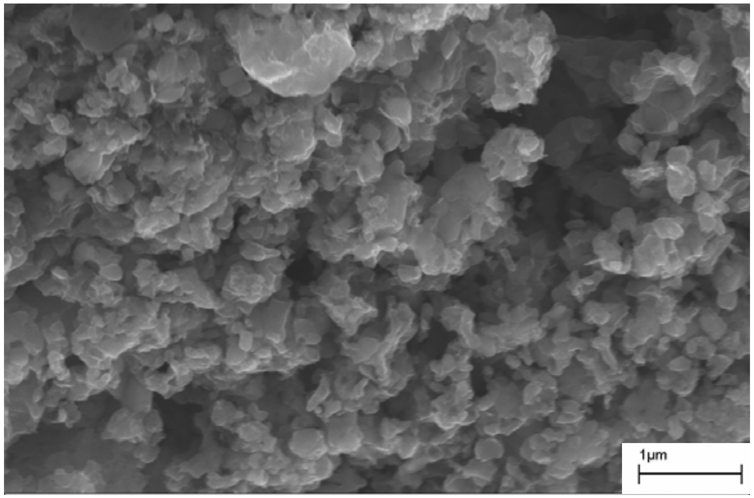
- **Materials screening and characterization:**
  - structure
  - surface properties (SEI layer?)
  - electrochemical performance

Nanostructures

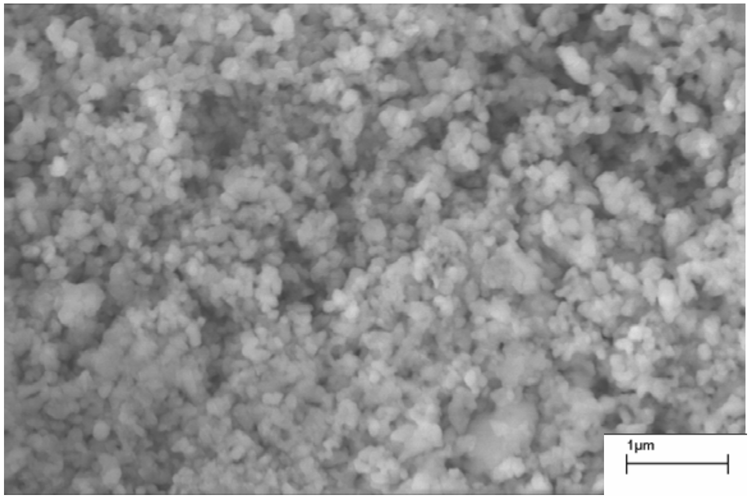
e.g., solution-based synthesis:

- **Precipitation of metal nitrate salts**
- **Similar redox behaviour as the bulk material**
- **Wide range of particle sizes can be tuned**





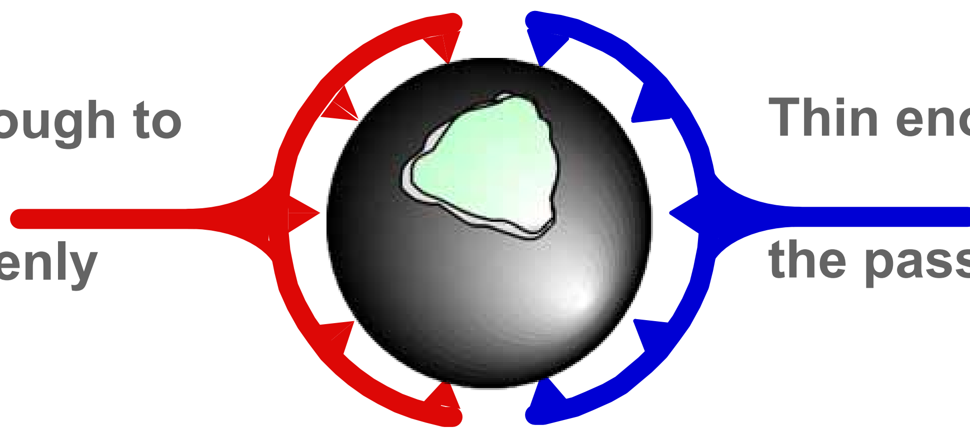
Varying synthesis conditions



Strategy to compensate for the low electronic conductivity of Li_2FeSiO_4 –type materials

nano-painting with an electronic conductor

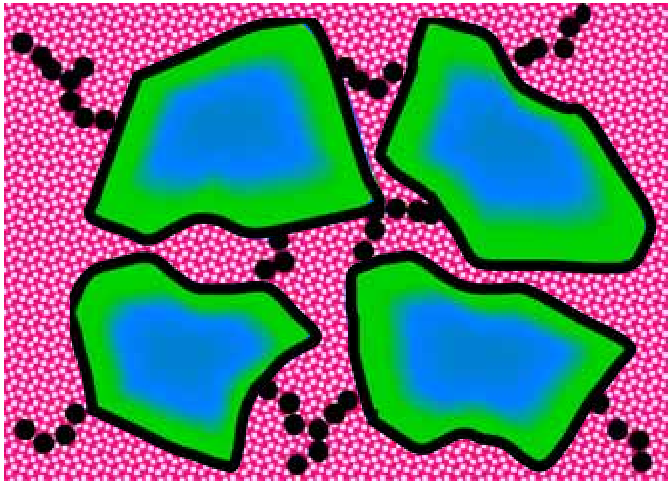
Conductive enough to distribute e^- evenly



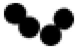
Thin enough to allow the passage of Li^+

carbon coated particles

Nano-painting further improves particle contact . . .



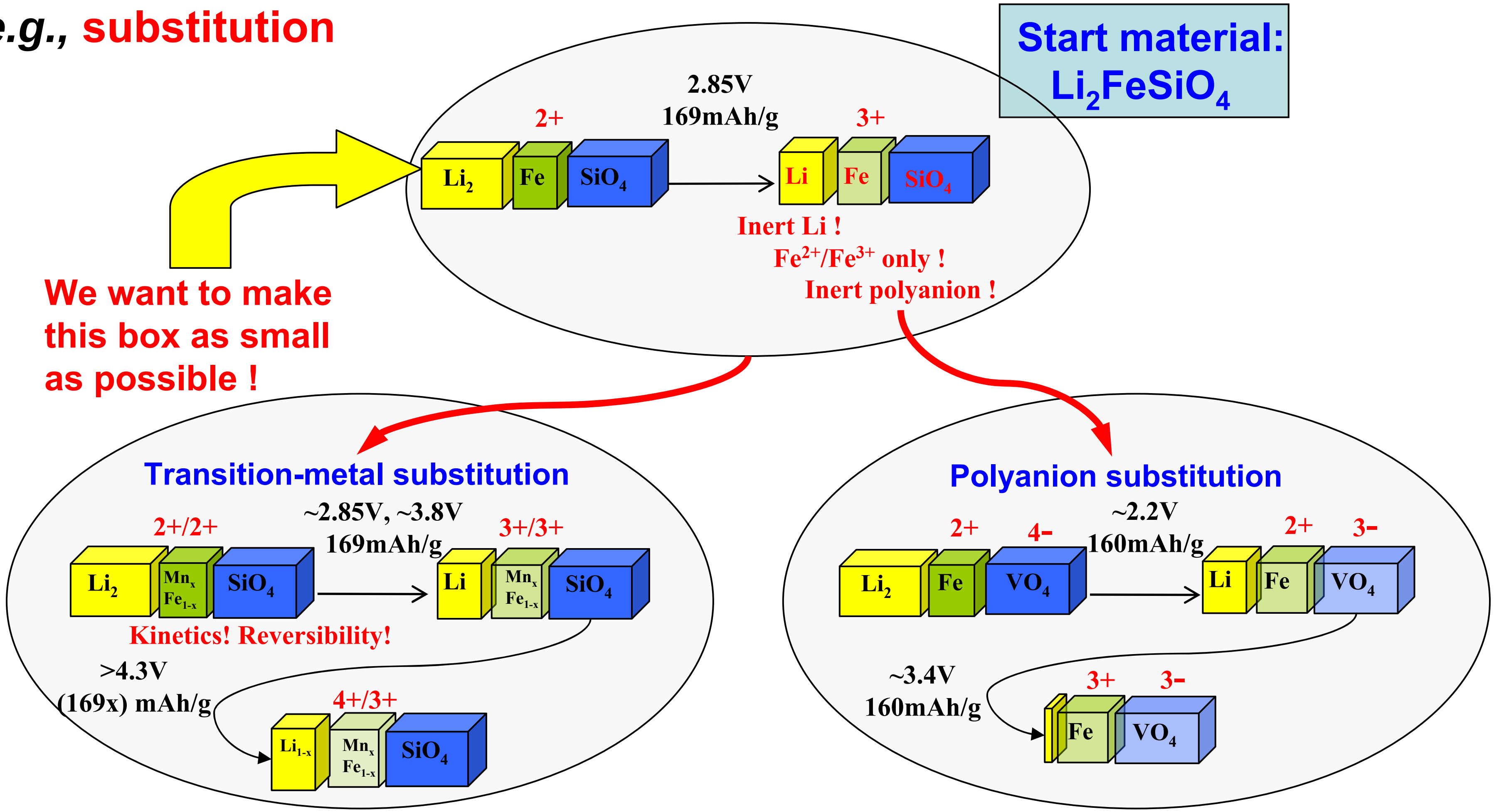
Carbon coating ≈ 1nm thick, transparent to ions

 Structured carbon black nanoparticles

 Electrolyte

Going beyond Li_2FeSiO_4 . . .

***e.g.*, substitution**



The manganese-doped silicate ?

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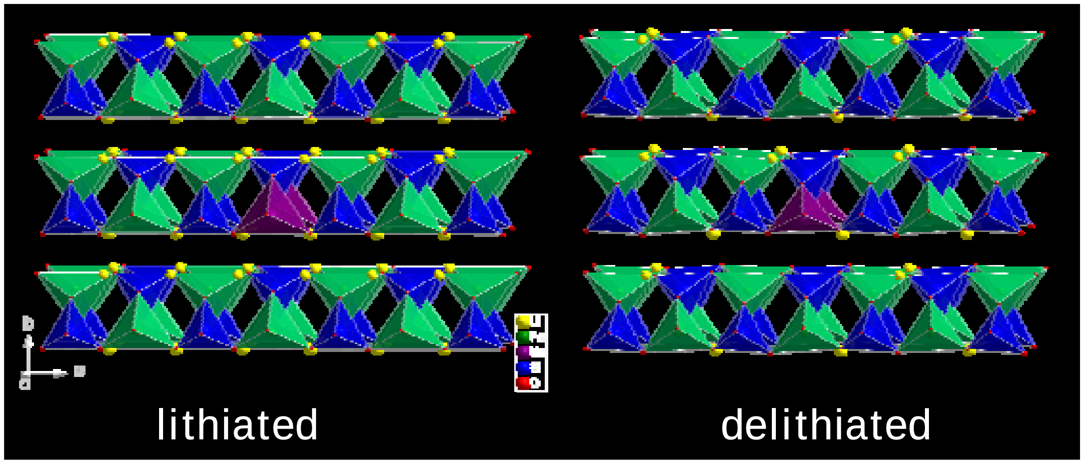
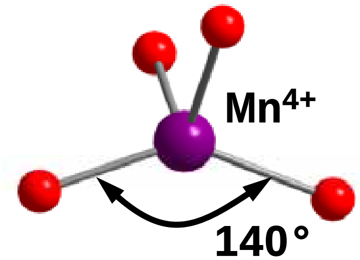
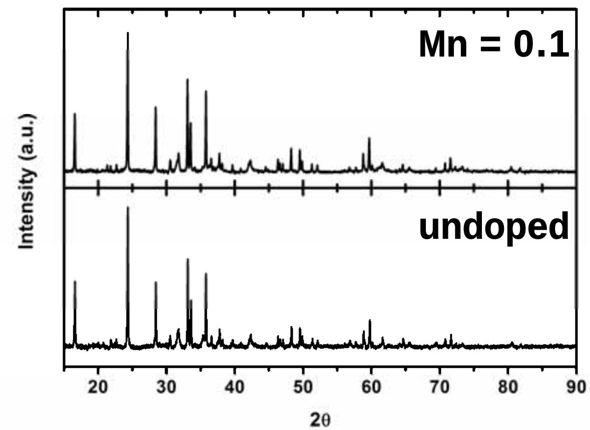
$Li_2Mn_xFe_{1-x}SiO_4$

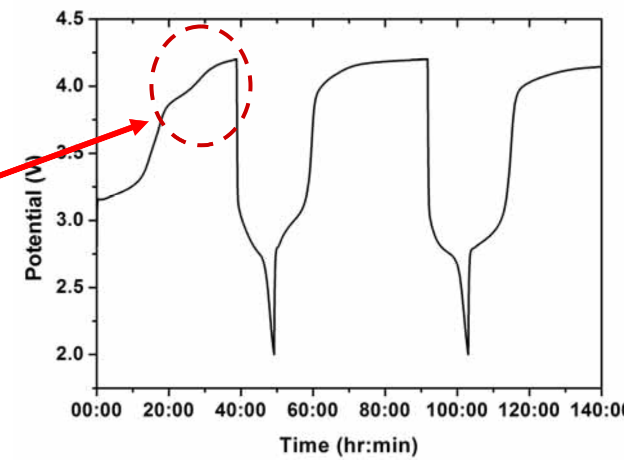




Distortion in MnO_4



- Substitution of Fe by Mn facilitates a **>1 Li^+ transfer** ($Mn^{2+} \rightarrow Mn^{3+} \rightarrow Mn^{4+}$)
- Similar X-ray diffraction patterns to undoped Li_2FeSiO_4
- First redox reaction occurs at > 4V ($Mn^{2+} \rightarrow Mn^{3+}$) during 1st cycling



Polyanion substitution in Li_2FeSiO_4 ?

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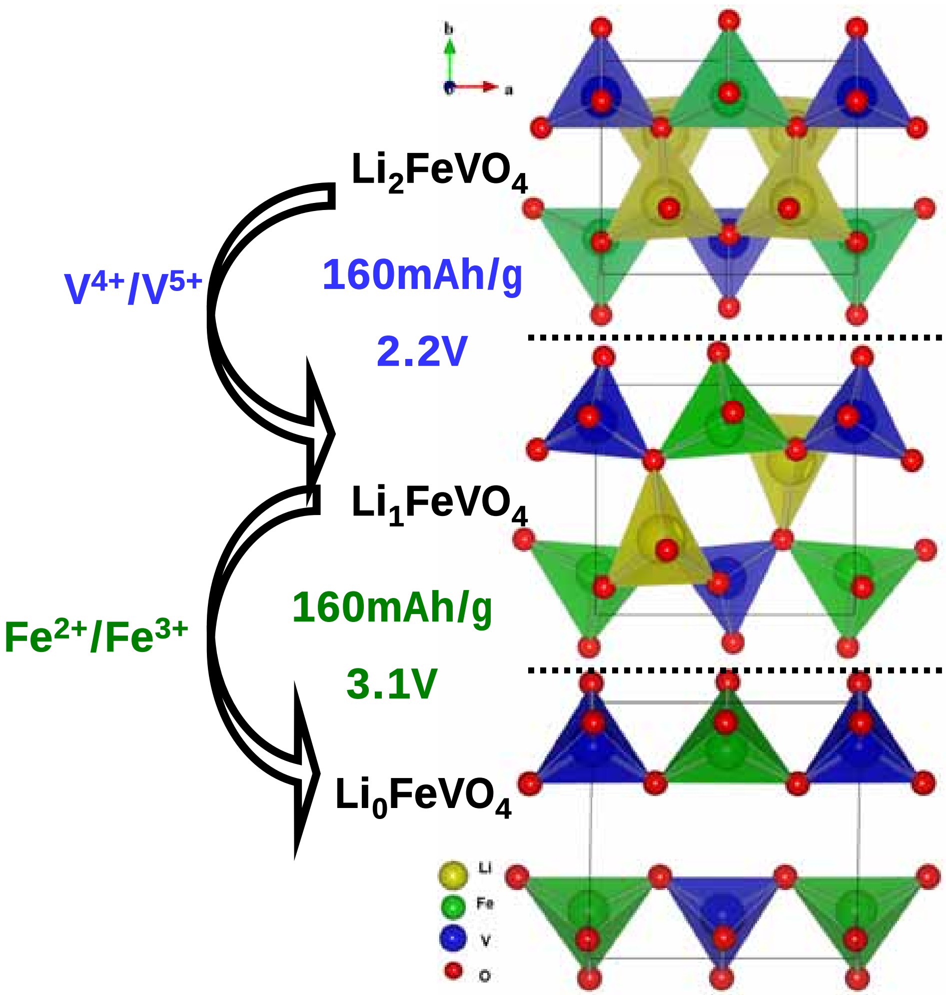
DFT modelling of substitutions: extra redox-activity VO_4^{3-}/VO_4^{4-} at SiO_4^{4-}



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

But . . .

- Volume expansion: ~10%
- Low V^{4+}/V^{5+} voltage: 2.2V

Stability ????

XPS/PES surface analysis of Li_2FeSiO_4

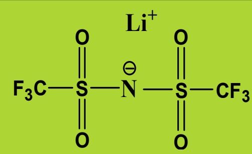
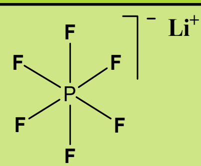
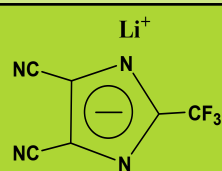
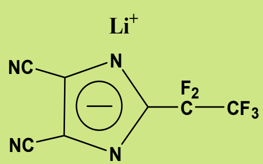
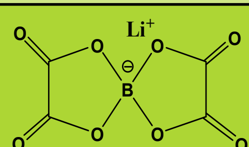
We must probe the stability ("lifetime") of the material for different electrolyte systems

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)

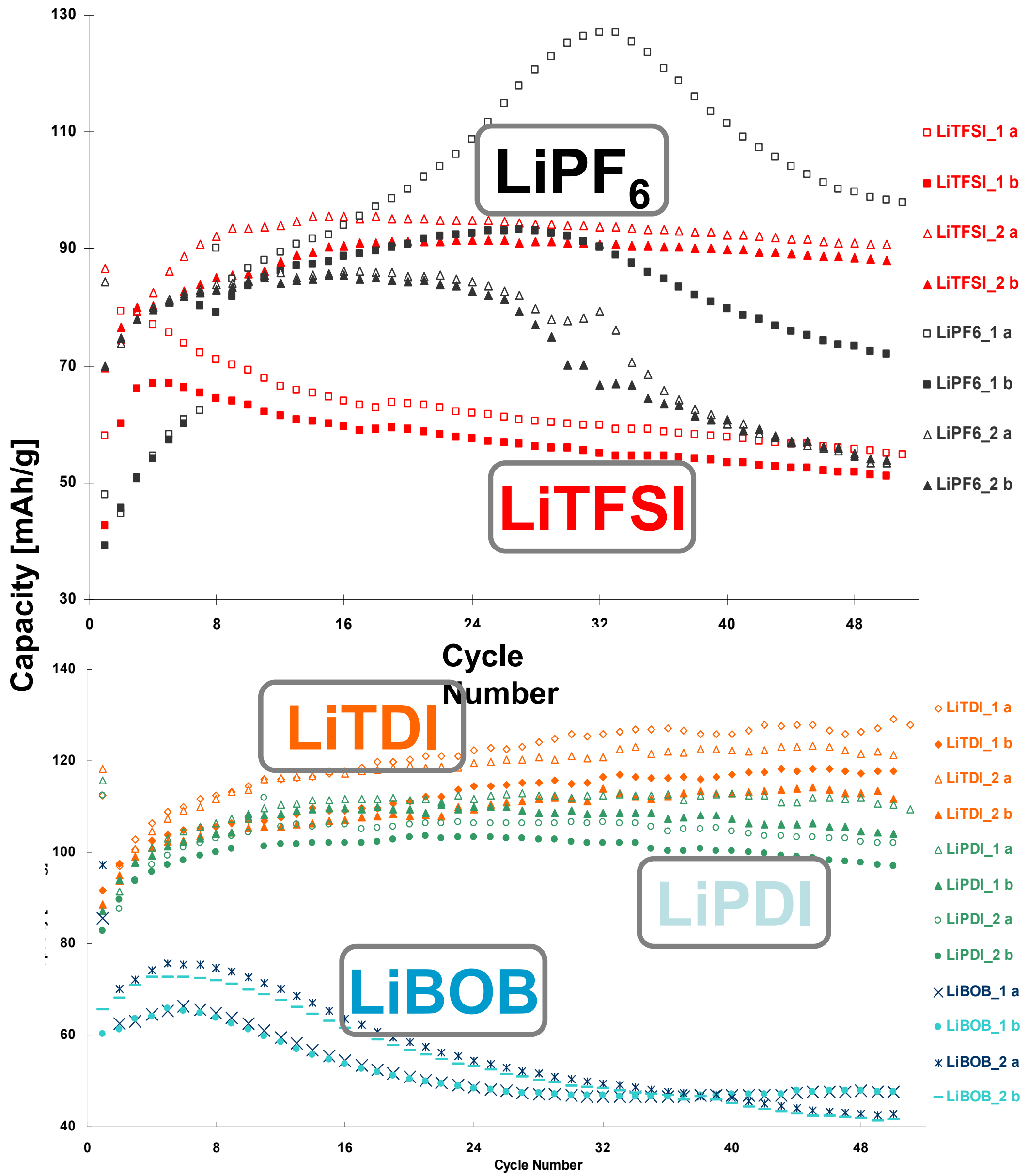
Electrolyte systems studied . . .

	Structure	Cut-off voltage [V]	Conc.	Name
LiTFSI		2.0 – 3.7	Corrosion on Al current collector	
$LiPF_6$		2.0 – 3.7	Sensitive to H_2O	
LiTDI		2.0 – 4.0	New !	
LiPDI		2.0 – 4.0		
LiBOB		2.0– 4.2	Studied on the anode side	

Solvents: EC : DEC 2:1

Electrochemical performance . . .

a - charge capacity
b - discharge capacity

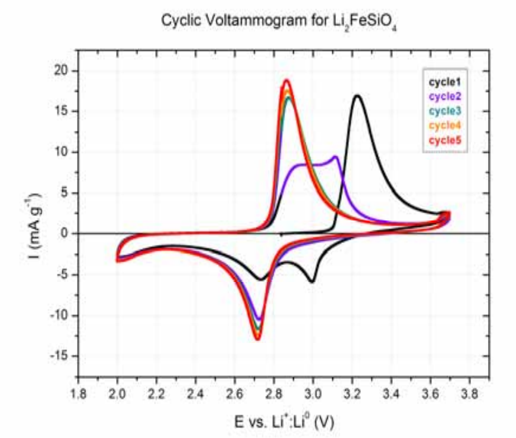


Comparative study: LiTFSI *vs.* $LiPF_6$

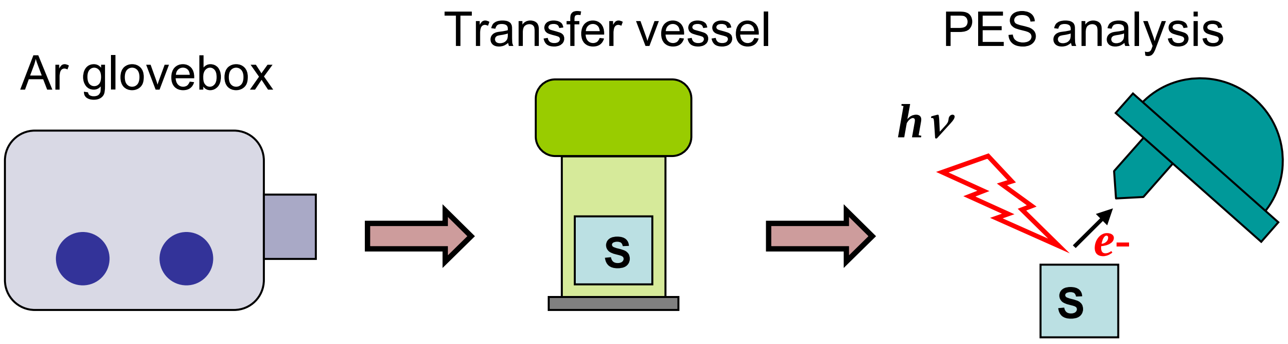
Li_2FeSiO_4/C cycled with two electrolytes:

(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.



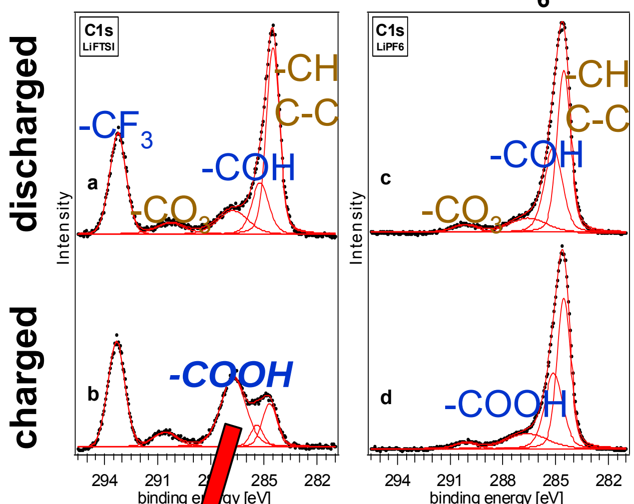
Safe transfer from cell to XPS analysis:



Comparative study: LiTFSI *vs.* $LiPF_6$

C 1s

LiTFSI | $LiPF_6$

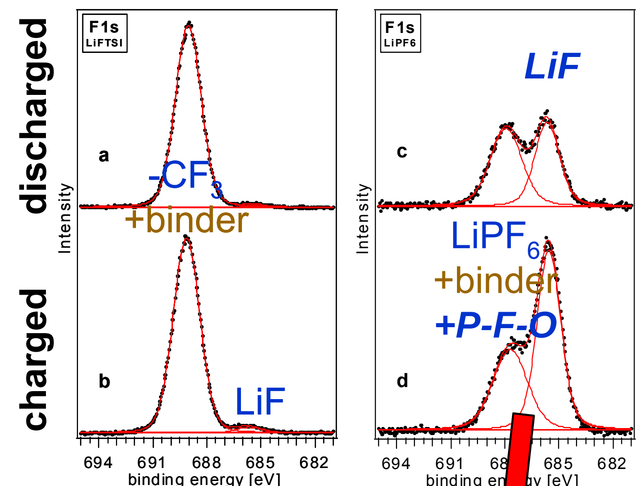


Solvent reaction:

EC ⟶ polymer

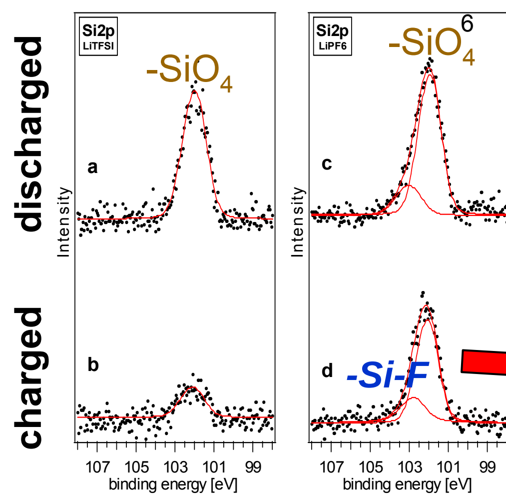
F 1s

LiTFSI | $LiPF_6$



Si 2p

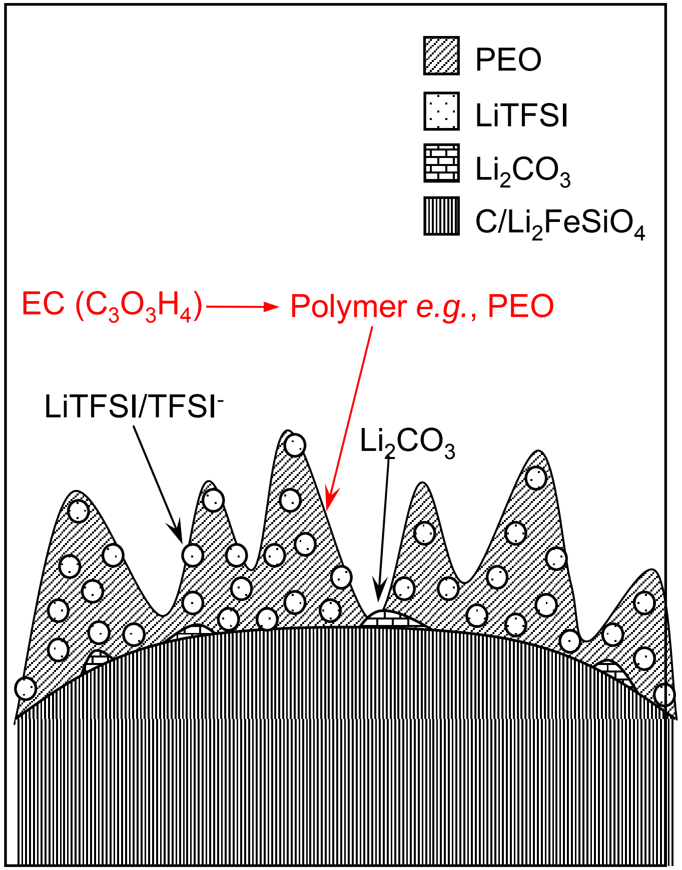
LiTFSI | $LiPF_6$

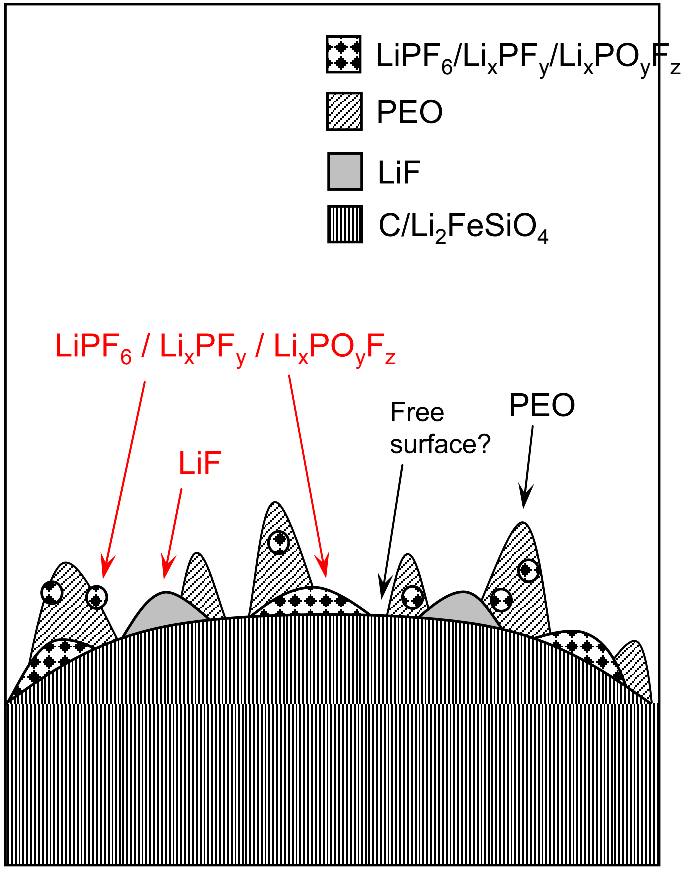


- **Salt degradation: PF_6 ⟶ P-F-O**
- **LiF formation**

- **Corrosion of electrode: Si-F bonds**

SEI models deduced (schematic)





LiTFSI electrolyte

- Decomposition of the solvent

$LiPF_6$ 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_2FeSiO_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!