Challenges and considerations when starting up Li ion battery research

- From a practical point of view

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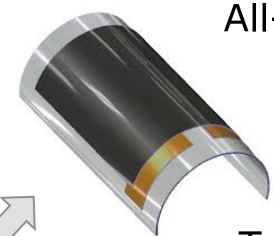
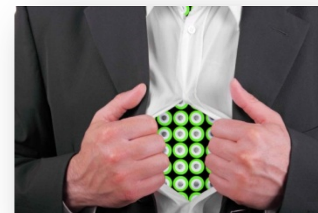
Li ion battery – which direction?

Organic batteries

All-solid-state battery

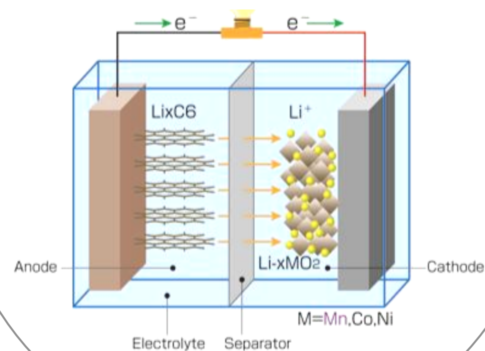


Textile/flexible batteries

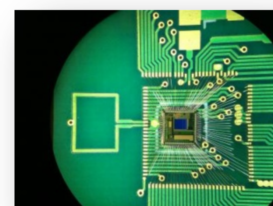


Grid storage

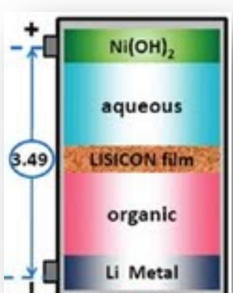
”Standard”
Li ion battery



Printable for circuit boards



Hybrid batteries



Capacitors

Na-intercalation batteries

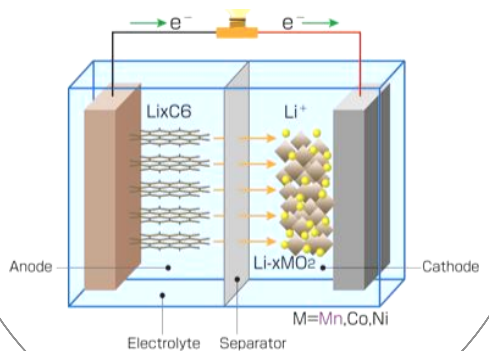
Research focus area?

New materials?
Anode
Cathode
Electrolyte

Degradation study?
Current collector/Casing
Electrolyte
Additives
Life time analysis

Modify materials?
Synthesis methods
Coatings

"Standard"
Li ion battery



Aim?
High power
High capacity
Life time
Safety
Price

Method?
Experimental
Modelling

New technique
Processing
Characterization technique
In situ/ex situ

Environmental issues?
Nontoxic transition metals
Nontoxic solvent/binder
Recyclability

Literature overview

Amount of ”hits” when searching in Scifinder:

Search name	Total	2013 (2 month!)
Lithium ion battery	70,000	1,500
Popular electrodes		
$LiFePO_4$	4,000	120
$LiCoO_2$	5,000	70
$Li_4Ti_5O_{12}$	2,300	90

+ electrolyte system, degradation studies, SEI formation, new techniques, reviews, etc.....

Its hard to get the full insight in the field! Both when you are new in the field... but also just to keep updated!

You need to find your own ”niche”

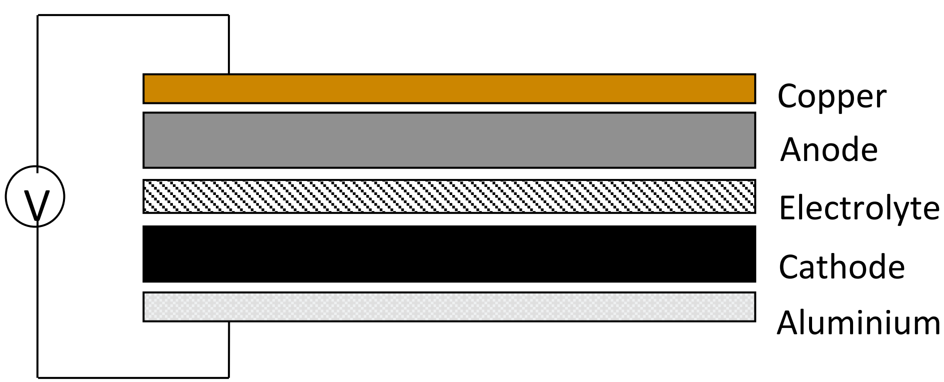
Research area: New cathode materials

1) **"Improve":** Modify the active particles or use surface coatings to improve performance

2) **"Substitute":** Substitution of transition metals in known electrode materials (e.g. Ti, V, Fe, Mn, Ni...)

3) **"Na^+ ion conductor":** Li^+ ion exchange in Na^+ ion conducting materials (e.g. NASICON materials)

4) **"Li^+ ion conductor":** Substititute a metal ion from a good Li conductor with a redox active metal ion



Requirements

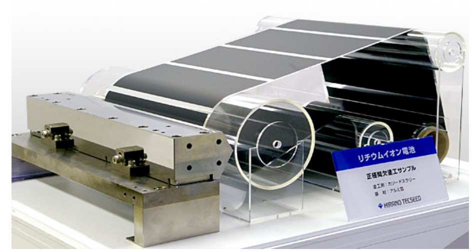
- High Li^+ conductivity
- High e^- conductivity
- High stability

Processing

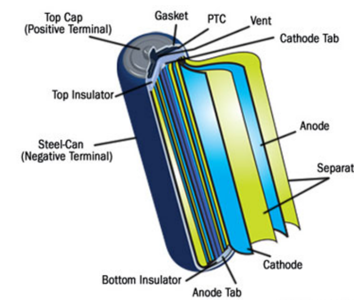
Raw materials

Mixing

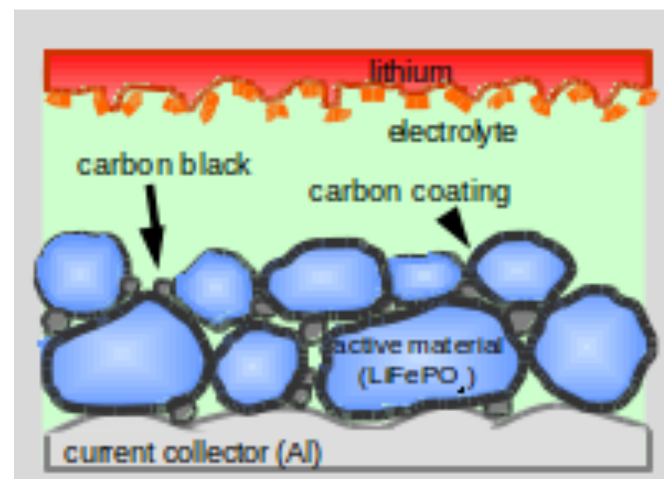
Casting



Cell assembly



Ingredients	Ratio
Active material	80-90 w%
Carbon black	5-10 w%
Binder	5-10 w%
Solvent	



www.iwe.kit.edu

Accept that the **process** from pure material to final electrode **can be long!** This is the KEY step for most battery producers!

Microstructure is VERY important!

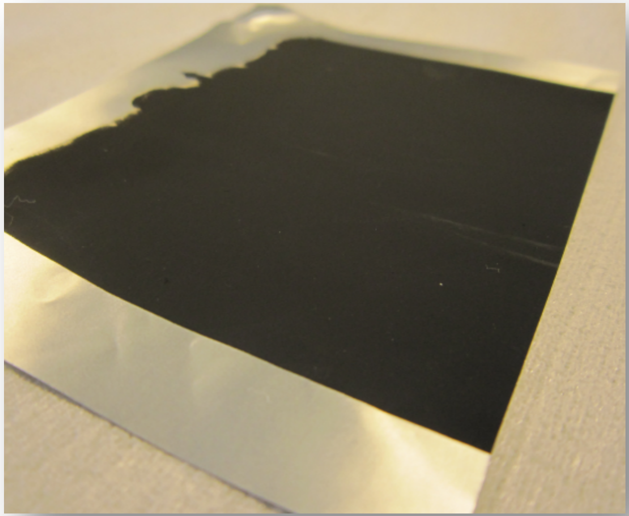
Electrode casting

Examples on challenges...

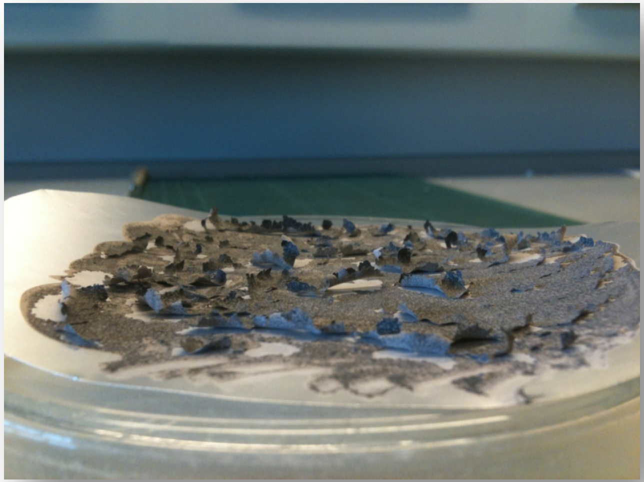
Each new material must be optimized seperately!

Highly dependent on particle size, agglomeration, surface properties, etc...

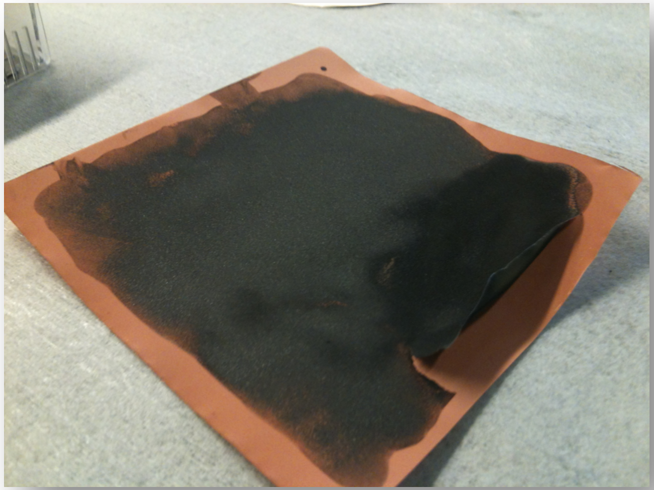
High quality coating



Too little binder (= too ”dry”)



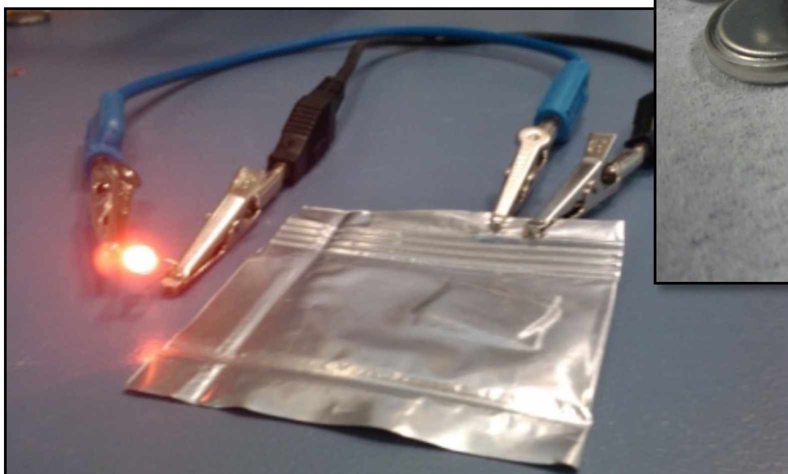
Too much binder (= too ”wet”)



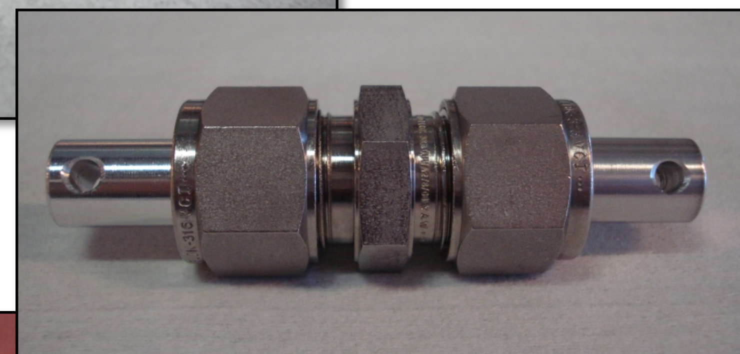
Test cells

Coin cells

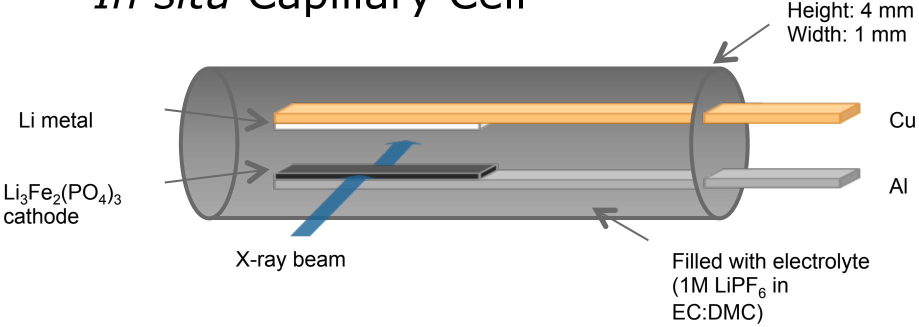
Pouch cell

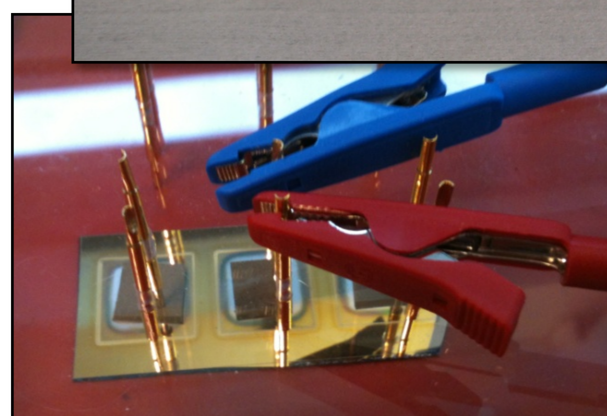


Swagelok cell



In situ Capillary Cell





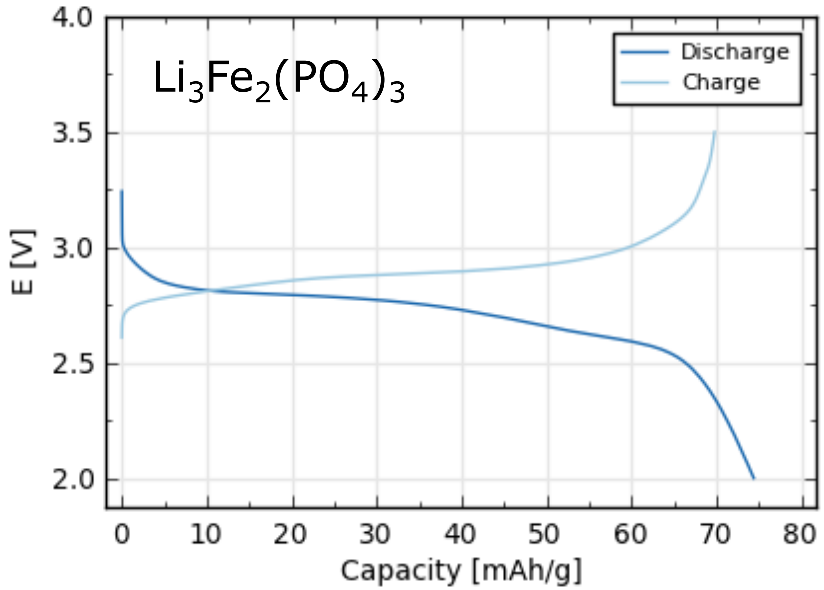
Thin films

Reproducibility

It's ”easy” to make the first battery!

But then it gets difficult...

1. How reproducible is it?
2. How large are the uncertainties?
3. How can you optimize the performance? (reduce binder + carbon content)



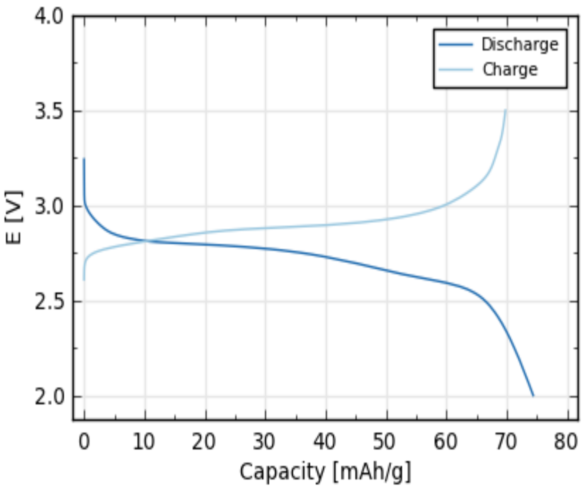
OBS: The results are highly dependent on the mass of active materials (and the uncertainty of this!).

Collaboration! Visit other laboratories – much of the important information has to be tried ”hands on”.

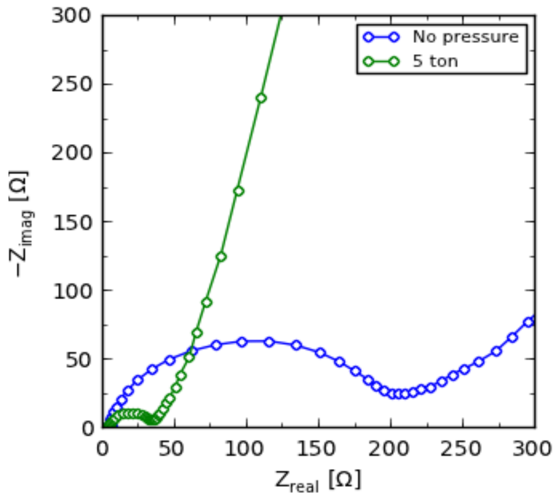
Characterization techniques

Possible characterization techniques for standard ”fingerprint” tests, e.g.:

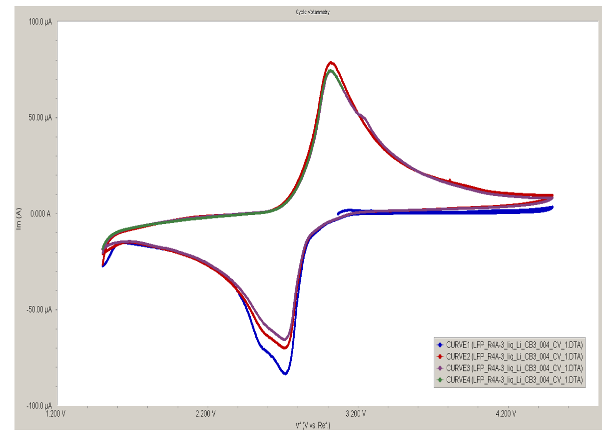
Charge/discharge cycling



Impedance spectroscopy



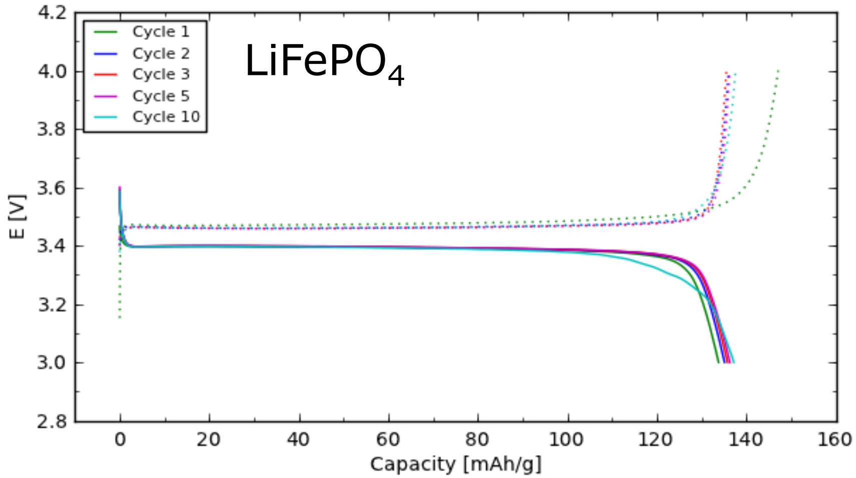
Cyclic voltammetry

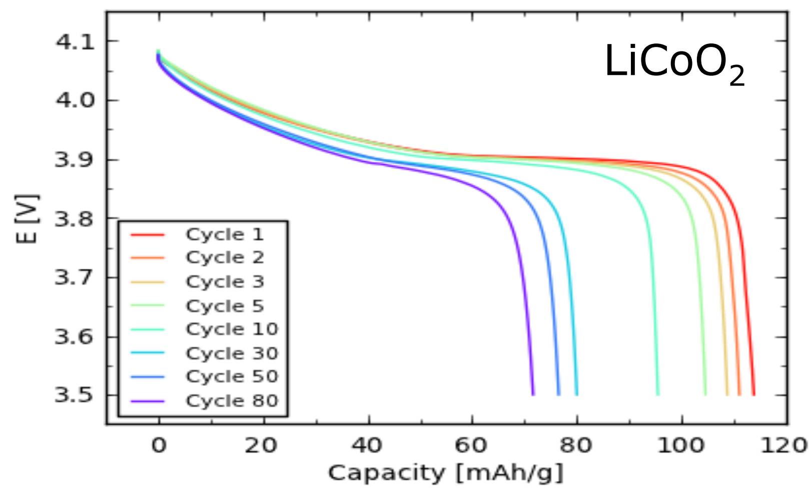


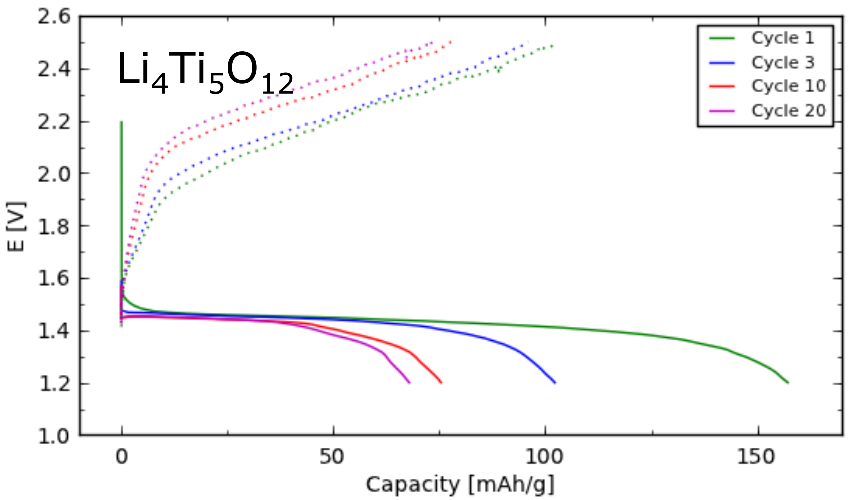
Material characterization techniques: XRD, SEM, etc.

Air-sensitive samples complicates this significantly!

Reproducing literature….







NDA with Phostech/Süchemie

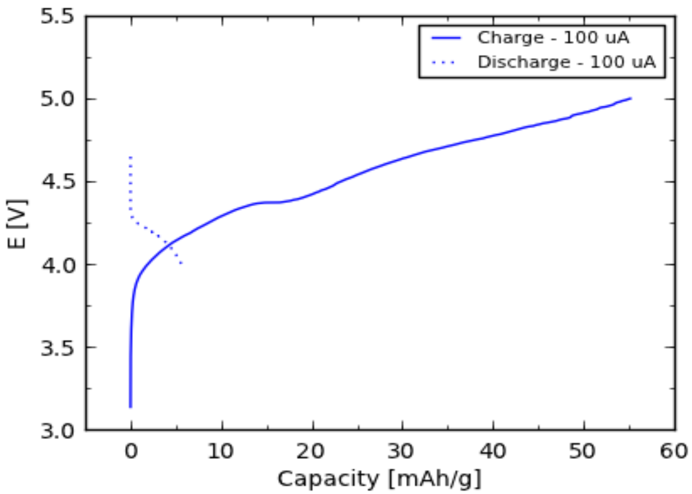
” However, the slurry preparation requires for experience….”

Sales Manager, Süd-chemie AG

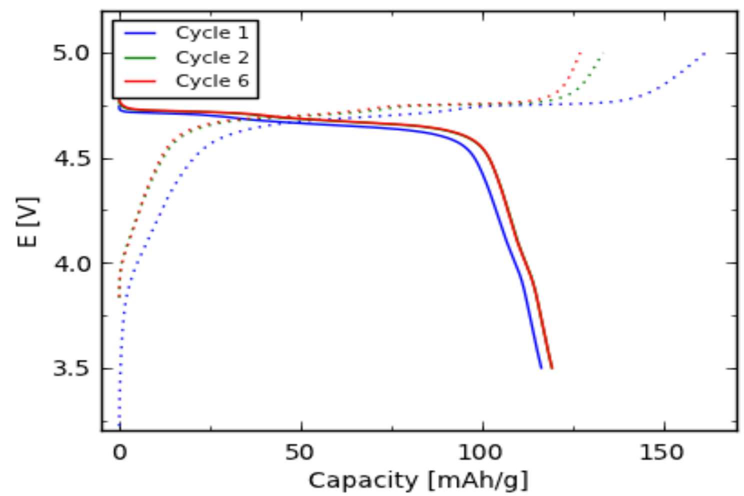
High voltage cathodes

$LiMn_{1.5}Ni_{0.5}O_4$

First try...



After optimization...

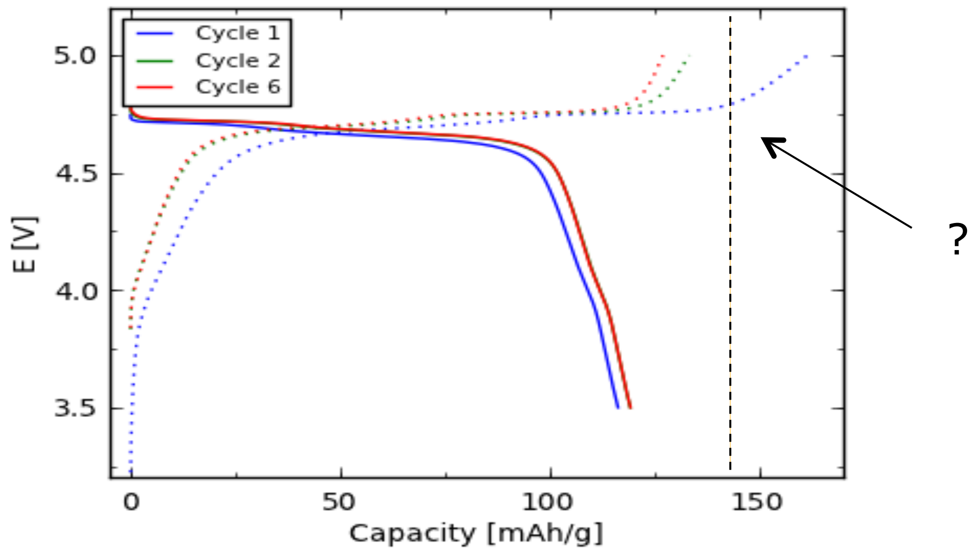


Matrix based on 10 publications on $LiMn_{1.5}Ni_{0.5}O_4$

Raw materials	Mixing	Processing	Cell assembly	Testing
Synthesis method	Ratio of ingredients	Thickness	Electrolyte solvent	Charge rate
Particle size	Method for mixing	Method	Salt	Potential window
Carbon source	Mixing time	Drying time	Separator	Relaxation time
Binder type		Drying temp	Additives	
		Mass load	Cell type	
		Pressing	Absorption time	

High voltage cathodes – difficulties....

Theoretical capacity: 146 mAh/g



Decomposition of electrolyte > 4.5 V!

- On cathode particles
- On carbon black
- On current collectors

Stability of the electrolyte is highly important!

Additional challenges...

1. Dissolution of metal ions from the cathode in the electrolyte
2. Oxygen evolution from cathode
3. Formation of surface-electrolyte-interfaces (SEI)
4. Corrosion of current collectors

Reduce the uncertainties

- Keep things simpel – only change one parameter at a time
  (use standard electrolyte, carbon black, binder etc.)

- Make 3-electrode cells for testing!
  (you will always encounter problems that cannot be understood otherwise)

- New interesting technique:
  Redox shuttle technique [1] – To determine the full capacity of active particle (without microstructure effects from mixing)

- Be critical to literature....! MANY papers are being published all the time. Many with the goal of quantity instead of quality!

  - Example: Capacities larger than theoretical! – uncritical publishing

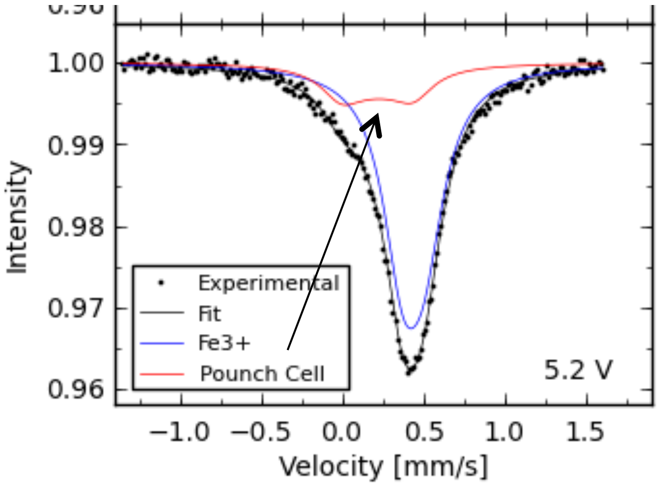
[1]: *A rapid solution method to determine the charge capacity of $LiFePO_4$*,
Trinh, Schougaard *et al*., j. power sources, 200, 92, 2012.

Example: Error in Fe^{4+}/Fe^{3+} activity in published work!

In situ Mössbauer Spectroscopy – Identification of $Fe^{2+/3+/4+}$ oxidation state

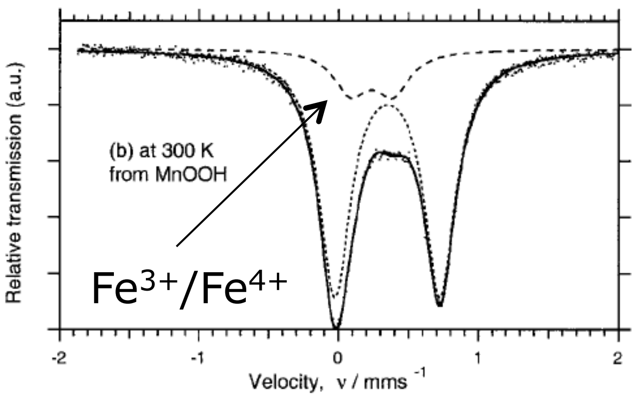
My results

$Li_3Fe_2(PO_4)_3$

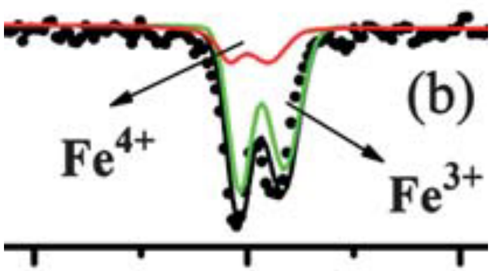


Published results

$LiFe_xMn_{2-x}O_4$



Li_2FeSiO_4



1. *Shigemura et al, J. Electrochem. Soc.* ***2001****, Volume 148, A730*
2. *Lv et al,* J. Mater. Chem., **2011**, 21, 9506

Uncritical publishing!

Other pitfalls to be aware off...

1) Carbon coating is not possible at Fe^{3+} materials (will form Fe^{2+} during reduction)

2) Possible exhaustion of electrolyte after vacuum sealing in pouch cell bags

3) Watch out for impurities in the current collectors, casing, etc. (Cu plating occurs at 3.5 V vs. Li^{+}/Li)

4) Li metal forms an alloy with Aluminium (dont use this at the anode side)

5) Weigh the carbon black in Al foil to avoid static electricity!

Be optimistic!
You only learn when things do NOT work as you expected... ;)

Thank you for your attention!