Wir schaffen Wissen – heute für morgen

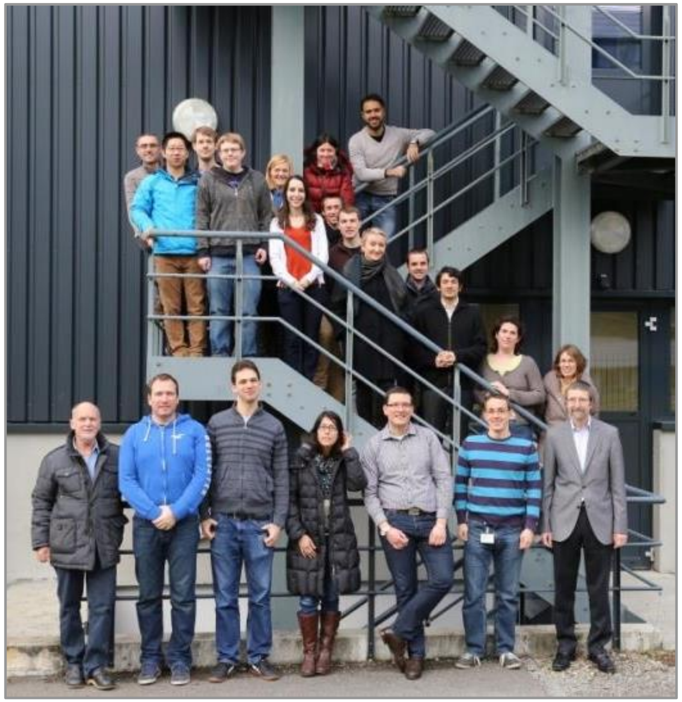
Paul Scherrer Institut

Petr Novák, Juliette Billaud, Cyril Marino, Rosa Robert,
Sébastien Sallard, Tsuyoshi Sasaki, Claire Villevieille

Development of Battery Materials:
Basics, Unknown Effects, and Beyond

Greetings from Switzerland

Battery Research in Switzerland



Storage

Swiss Competence Centers
for Energy Research

In cooperation with the CTI

Energy
Swiss Competence Centers for Energy Research

Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

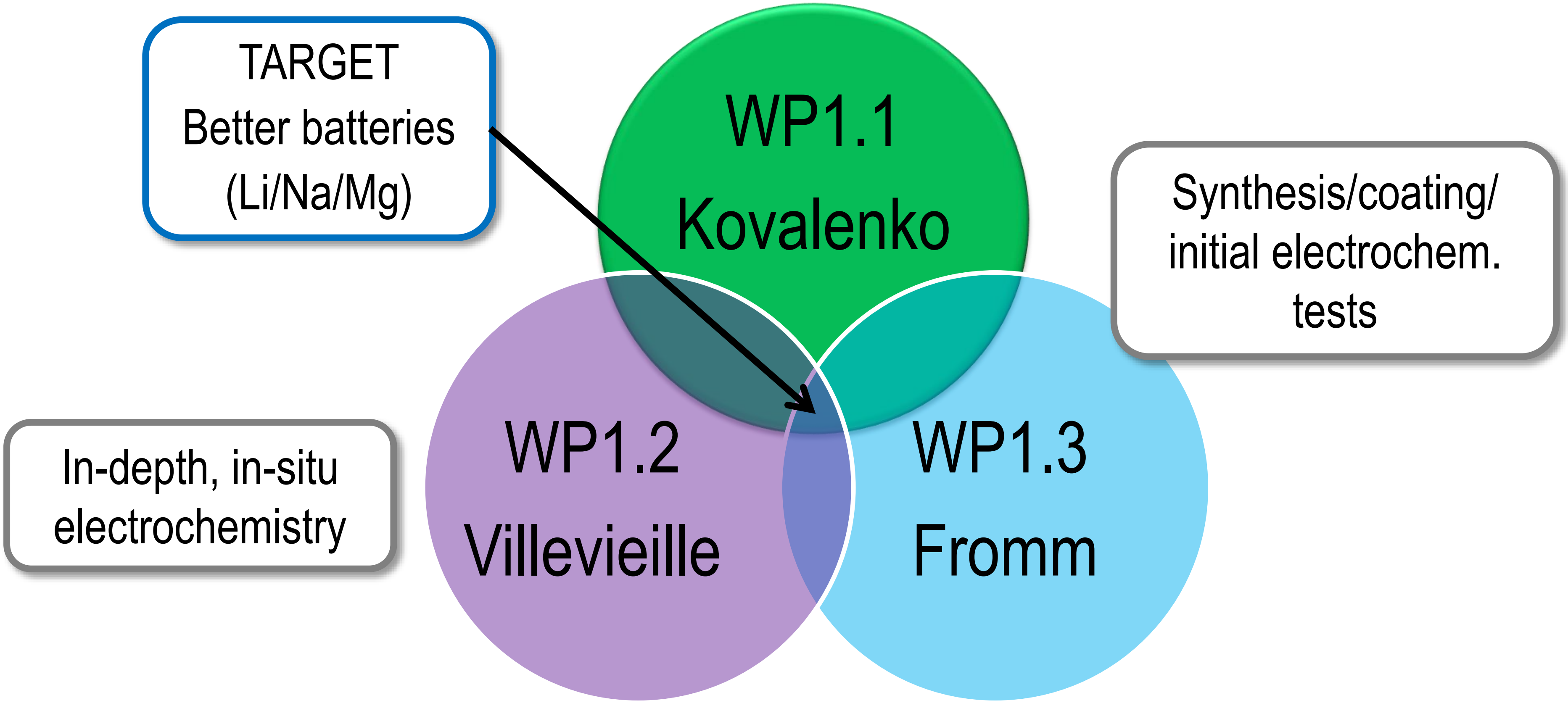
Swiss Confederation

Commission for Technology and Innovation CTI

Battery Research in Switzerland

Three different groups expert in:

- Synthesis of electroactive materials
- Characterizations of those new materials
- Electrochemical analysis of new type of electrodes
- Understanding of reaction mechanisms



TARGET
Better batteries
(Li/Na/Mg)

WP1.1
Kovalenko

Synthesis/coating/
initial electrochem.
tests

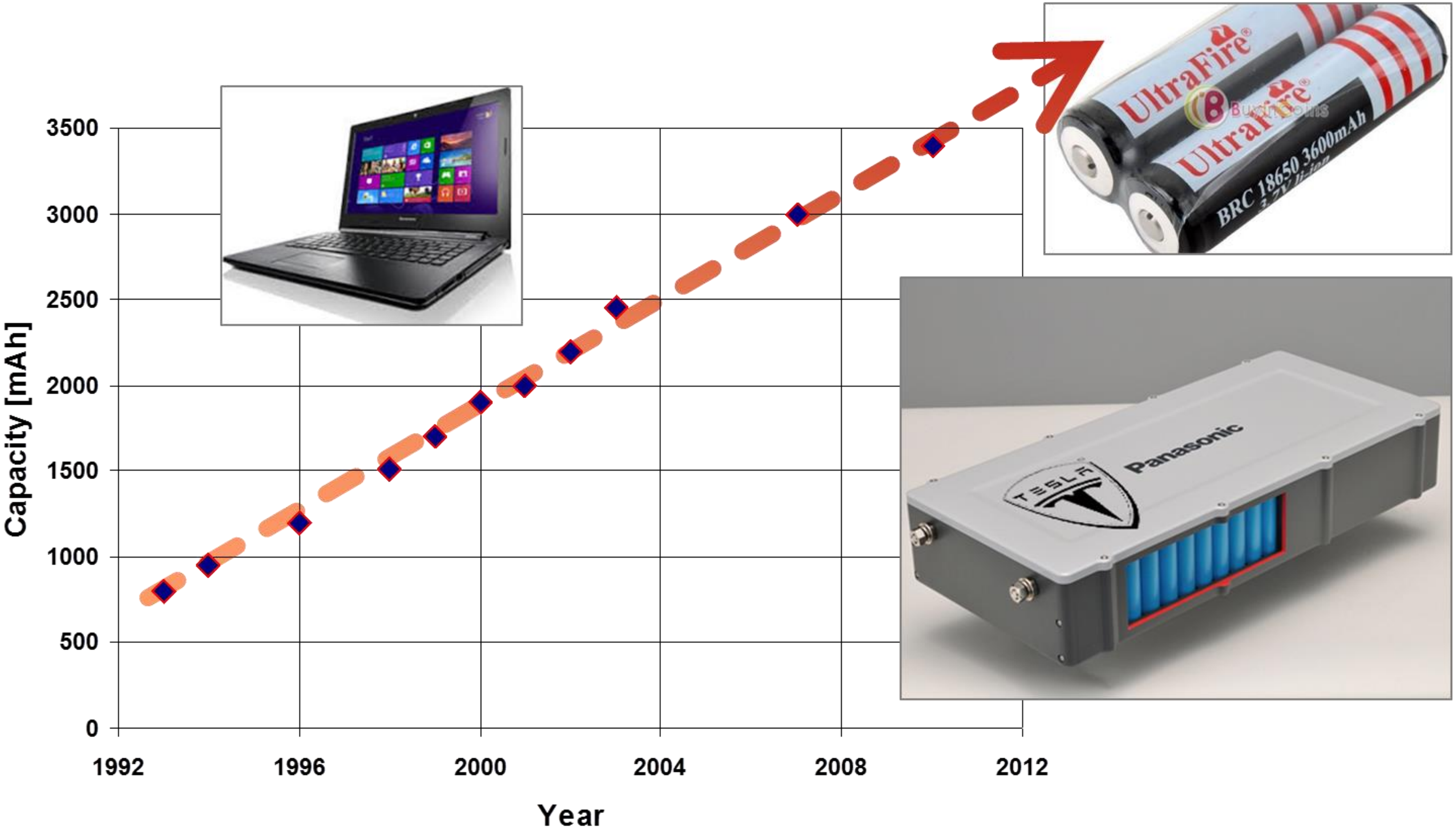
In-depth, in-situ
electrochemistry

WP1.2
Villevieille

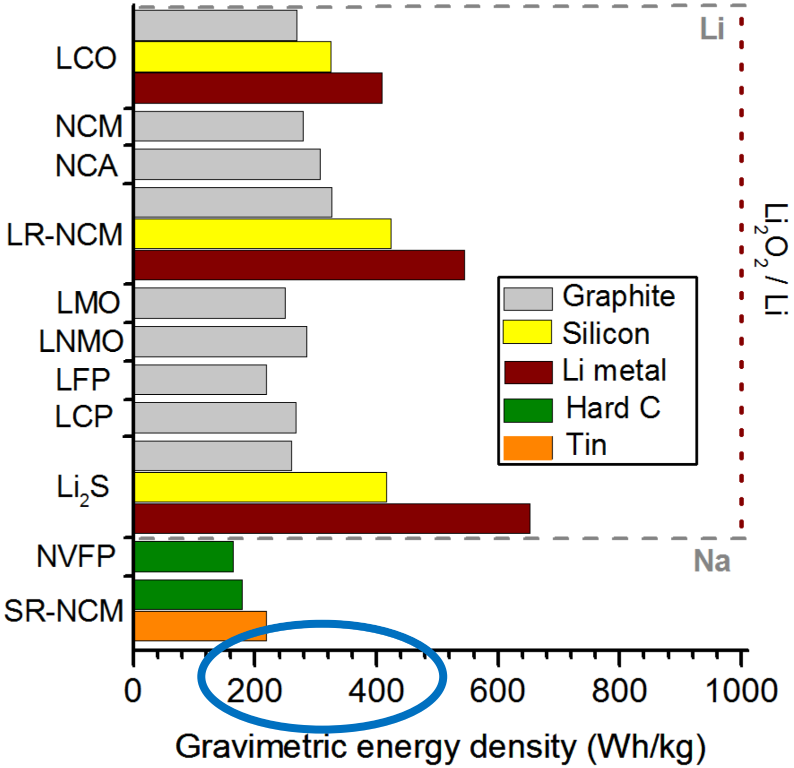
WP1.3
Fromm

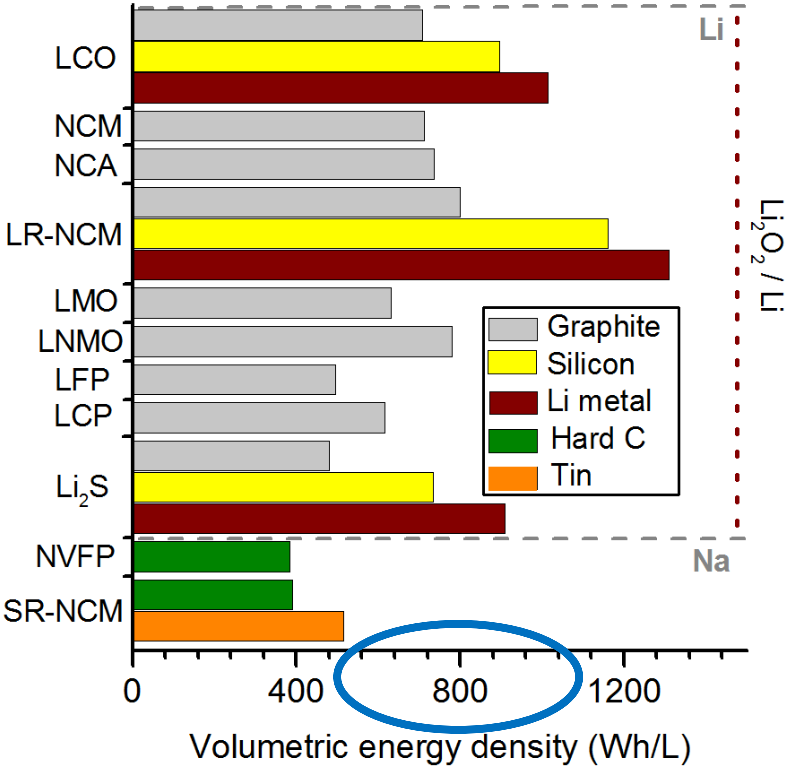
Batteries in Different Systems

Motivation: The “Battery Law”

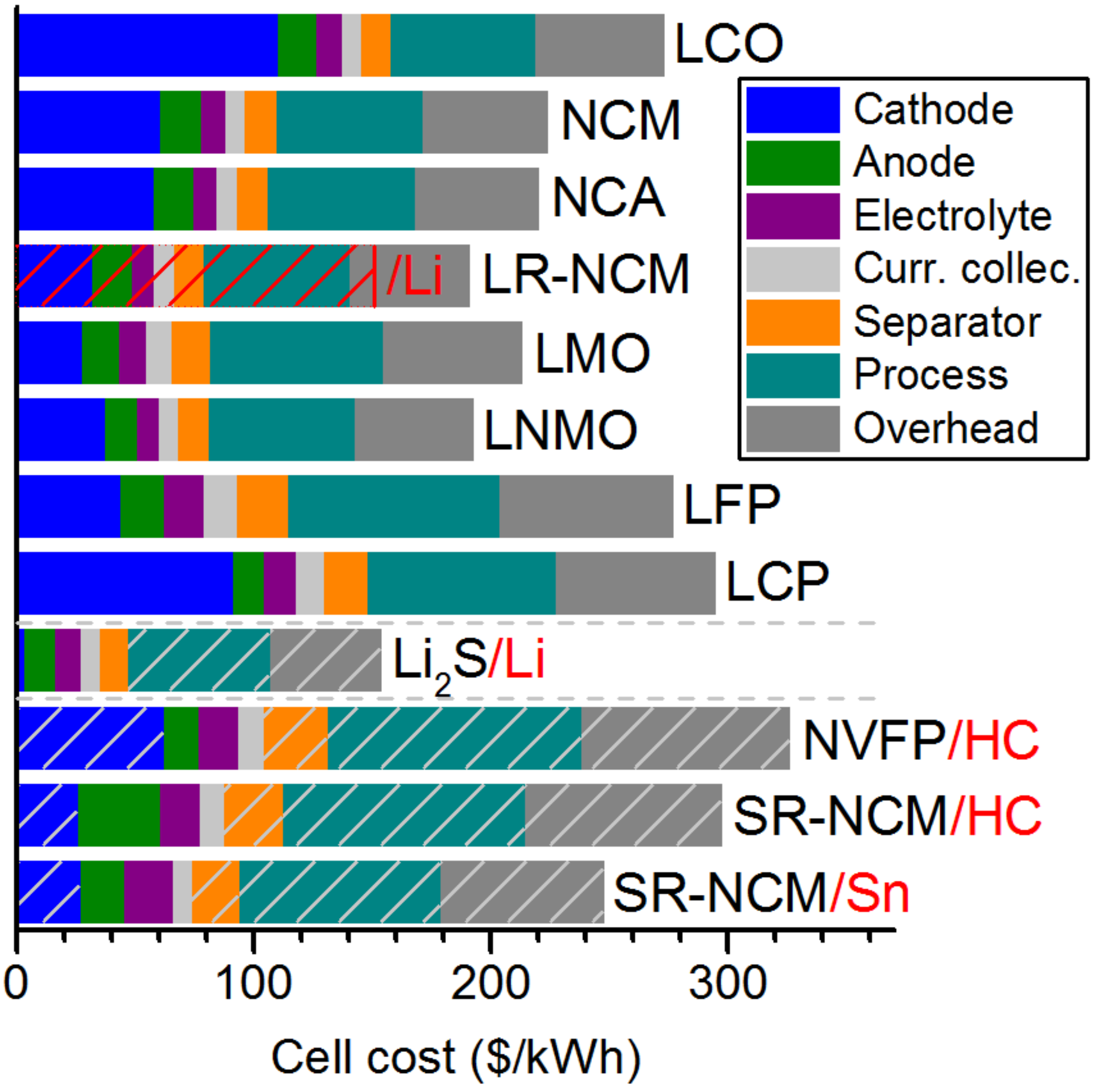


The Realistic Future



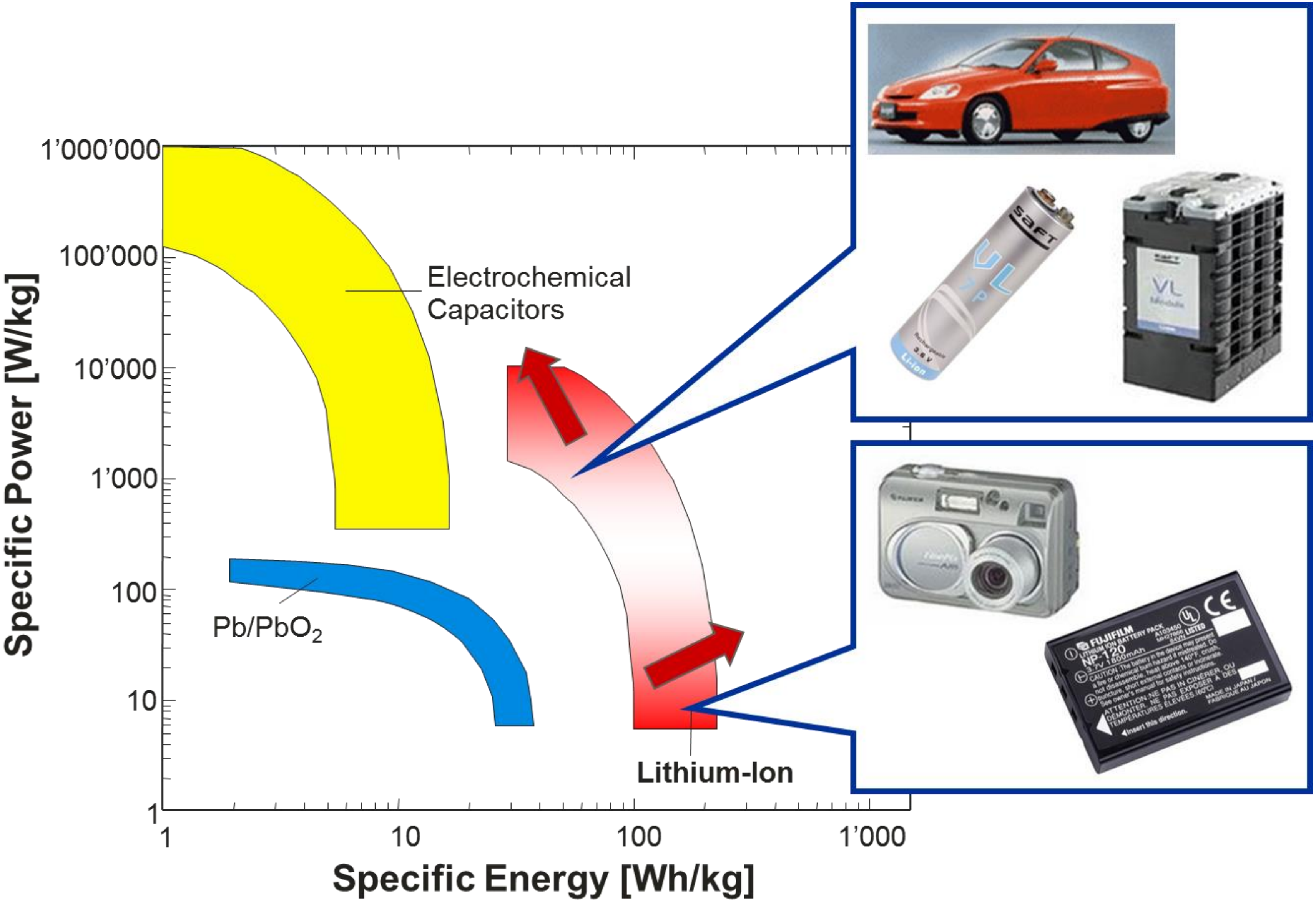


How Much Does It Cost?

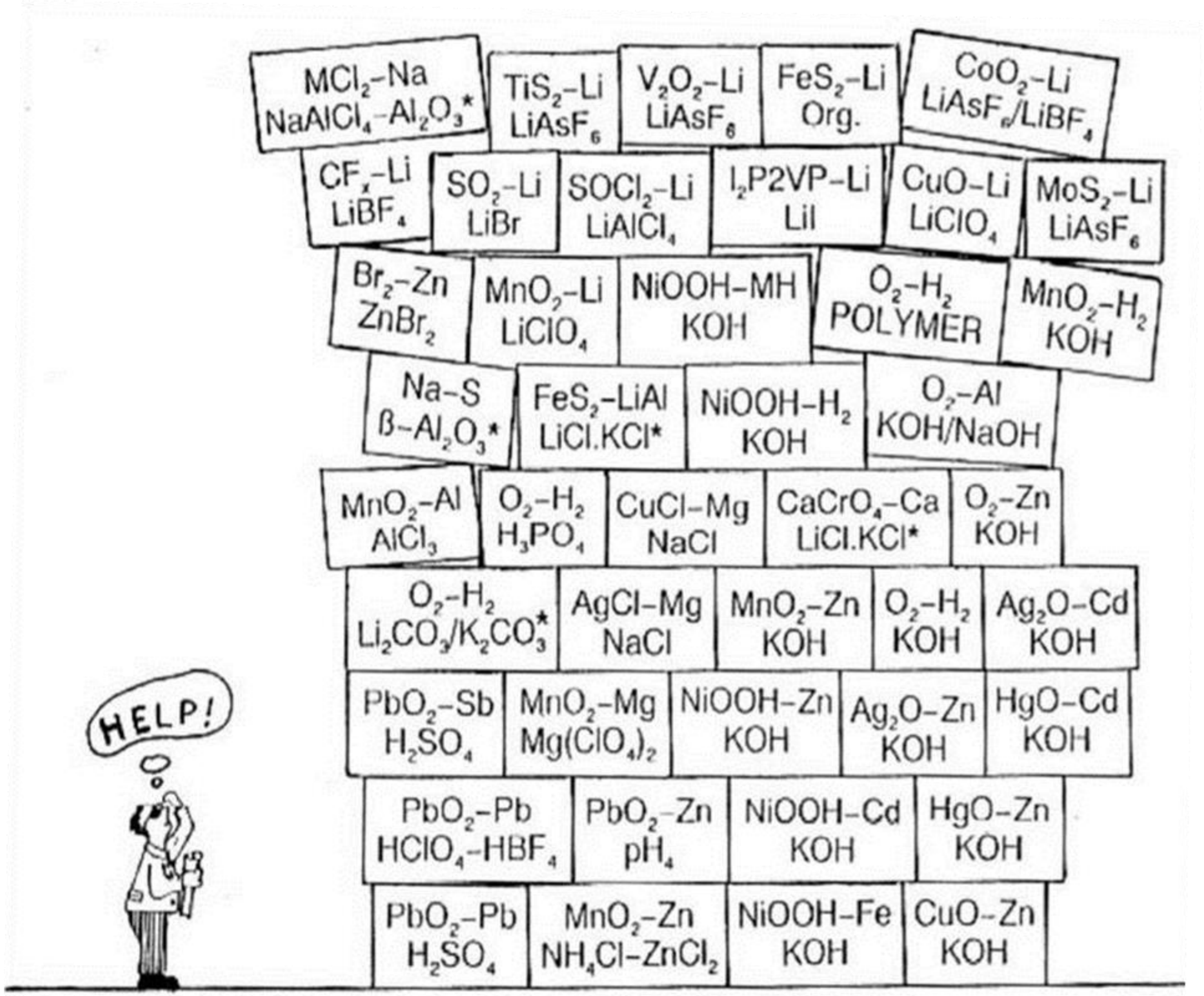


Material	Abbreviation
$LiCoO_2$	LCO
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	NMC
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	NCA
$xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Ni, Co, and Mn)	LR-NMC
$LiMn_2O_4$	LMO
$LiMn_{1.5}Ni_{0.5}O_4$	LNMO
$LiFePO_4$	LFP
$LiCoPO_4$	LCP
Li_2S	Li_2S
LiC_6	Graphite
$Li_{12}Si_7$	Silicon
Li	Li
$Na_{1.5}VPO_{4.8}F_{0.7}$	NVFP
$xNa_yMnO_3 \cdot (1-x)NaMO_2$ (M = Ni, Co, and Mn)	SR-NMC
Na_4C_{33}	HC
$Na_{3.1}Sn$	Sn

Ragone-Plot


1'000'000
100'000
10'000
1'000
100
10
1
1
10
100
1'000
Specific Power [W/kg]
Specific Energy [Wh/kg]
Electrochemical Capacitors
Pb/PbO_2
Lithium-Ion

Electrochemical Energy Storage in Batteries



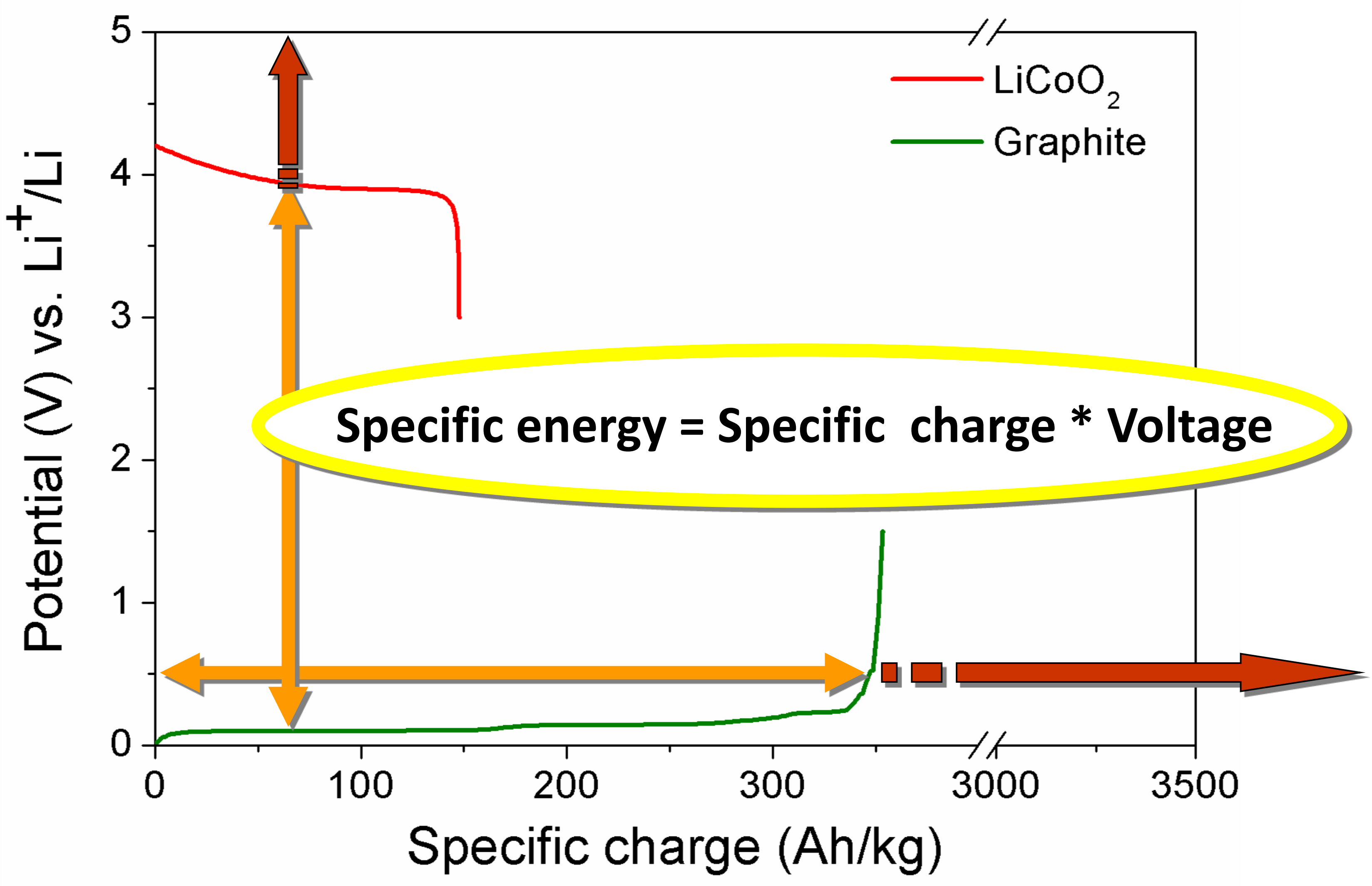
Faraday Law

$$Q = zF\frac{m}{M}$$

Specific Energy

$$W = UQ$$

Specific Energy

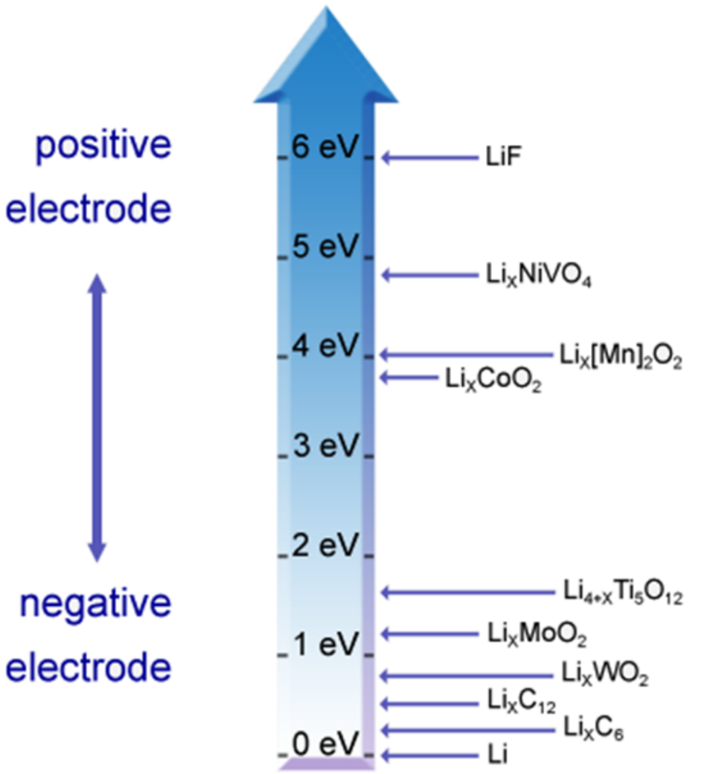


Specific energy = Specific charge * Voltage

⇒ Increase the voltage window and/or the specific charge

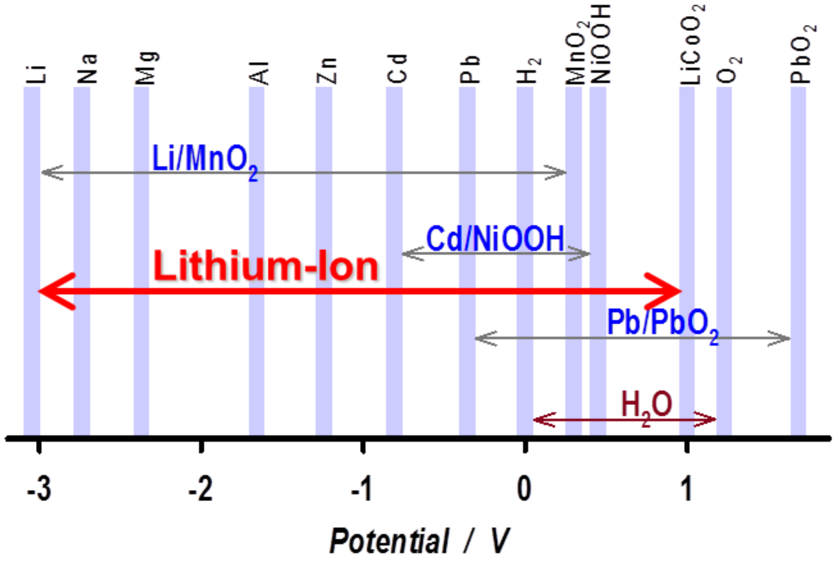
Electrochemistry: Nonaqueous Electrolytes

Potentials of Li-ion battery materials (vs. Li/Li^+)



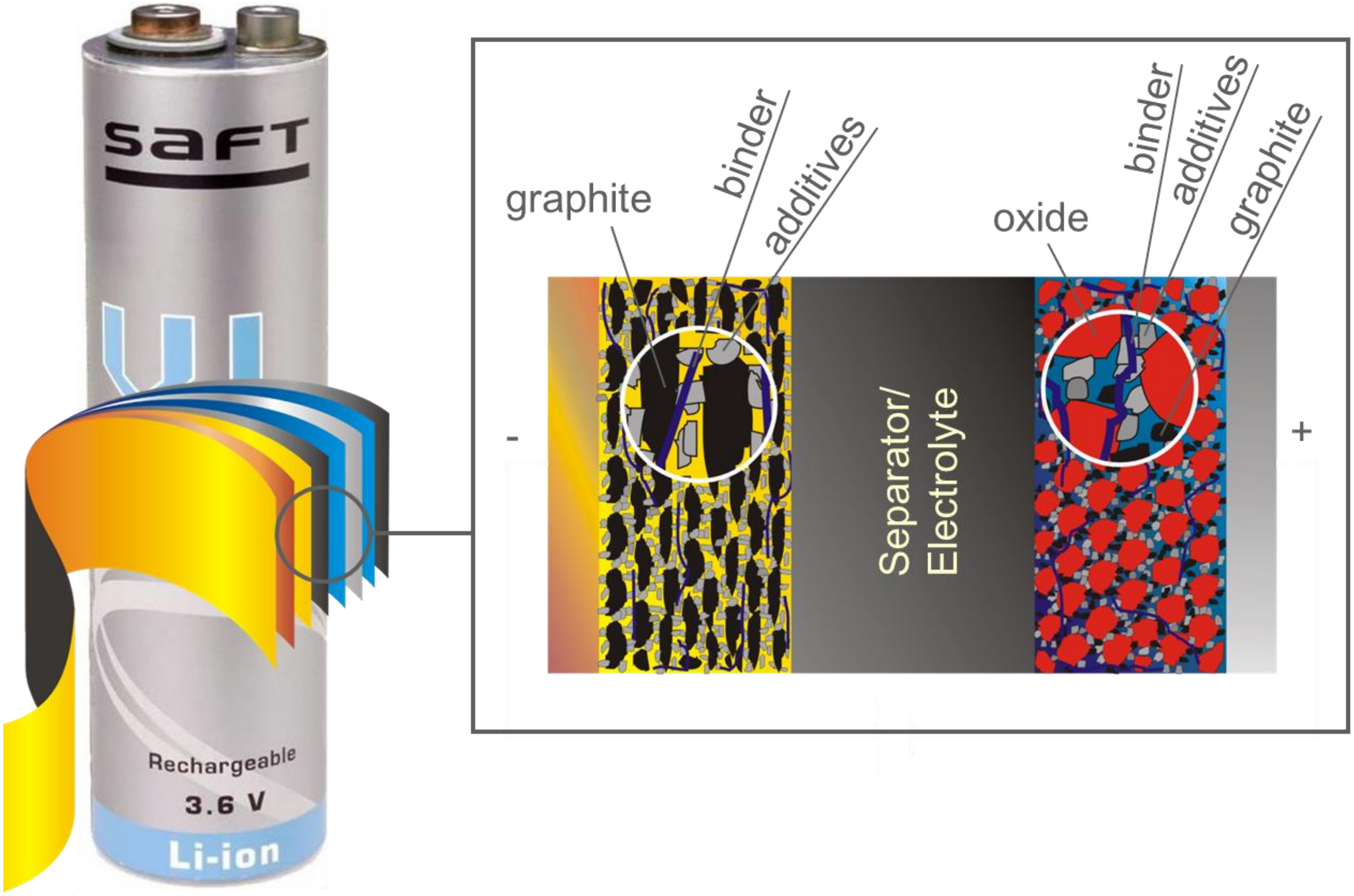
Source: Solid Energy GmbH, www.solid-energy.com

Standard potentials of battery electrodes

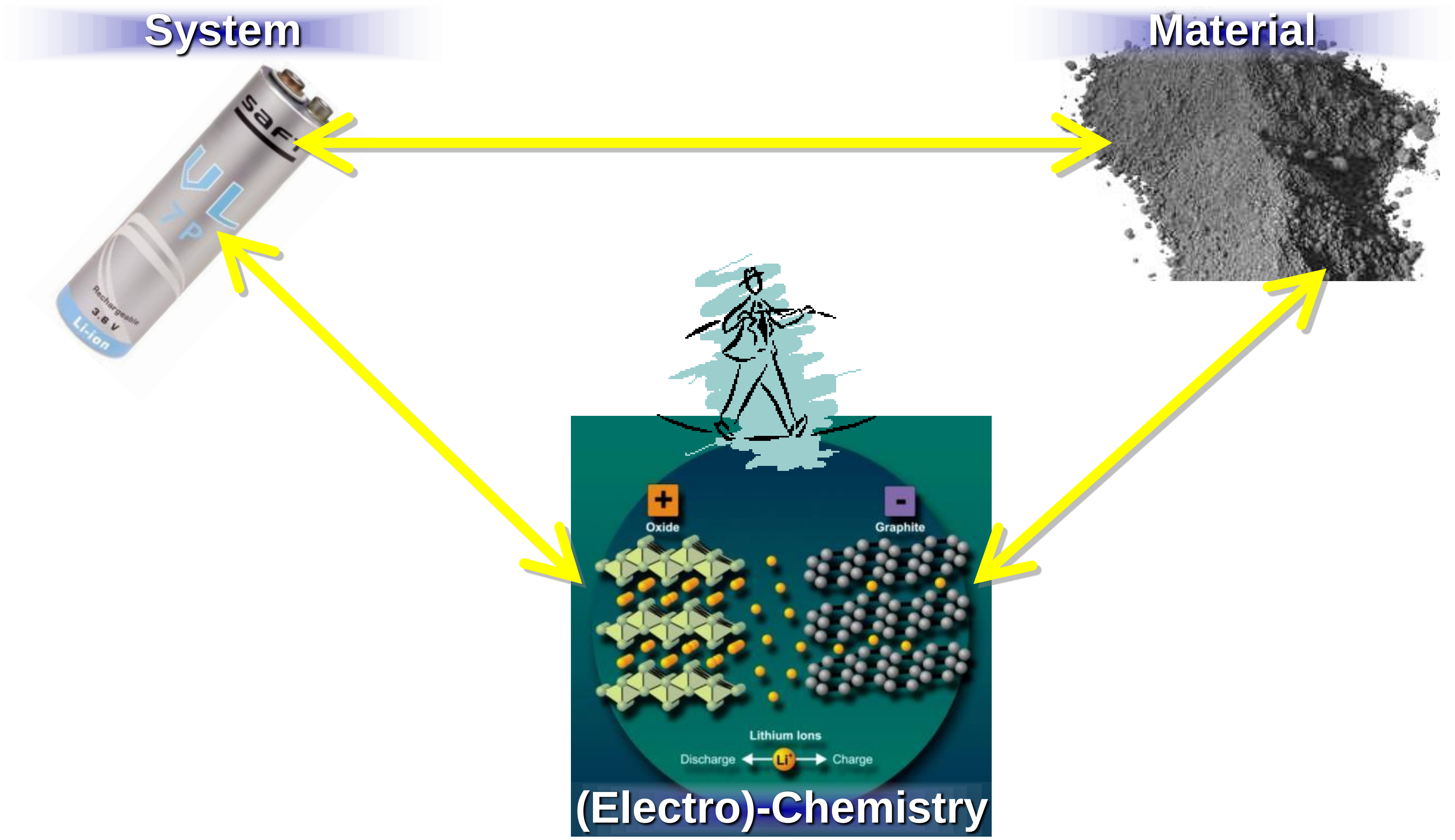


- *Wide potential window*
- *Very negative potential at the anode (reductive conditions)*
- *High potential at the cathode (oxidative conditions)*

What Is Inside a Battery?



The Battery Research

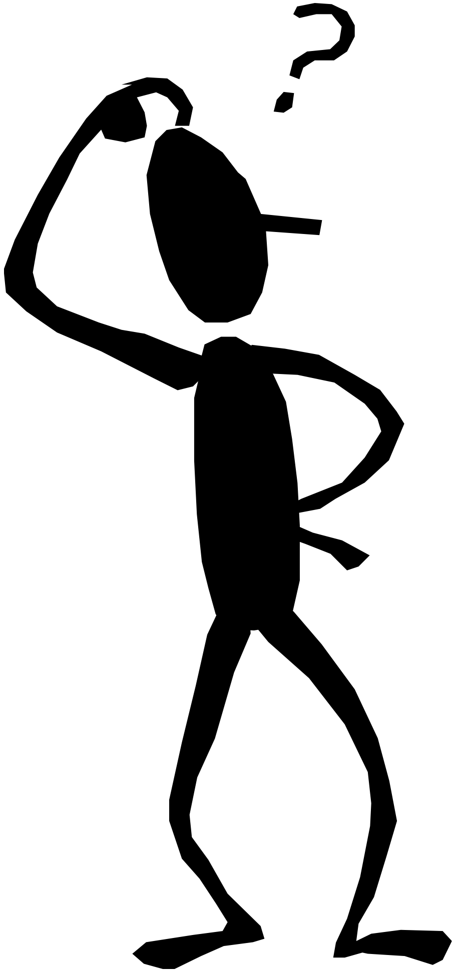


System

Material

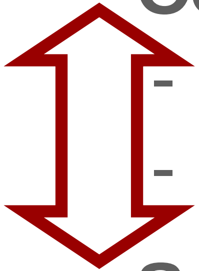
(Electro)-Chemistry

The Challenges



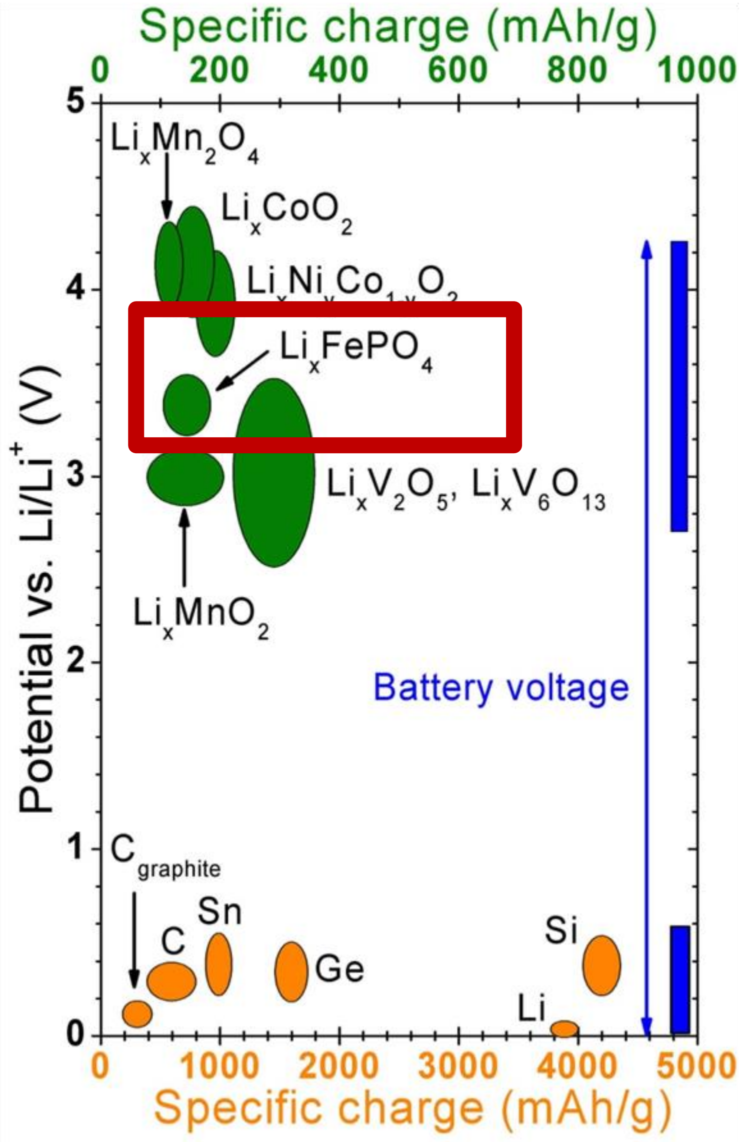
- **Environment:** ~~Hg~~, ~~Cd~~, ... ; recycling

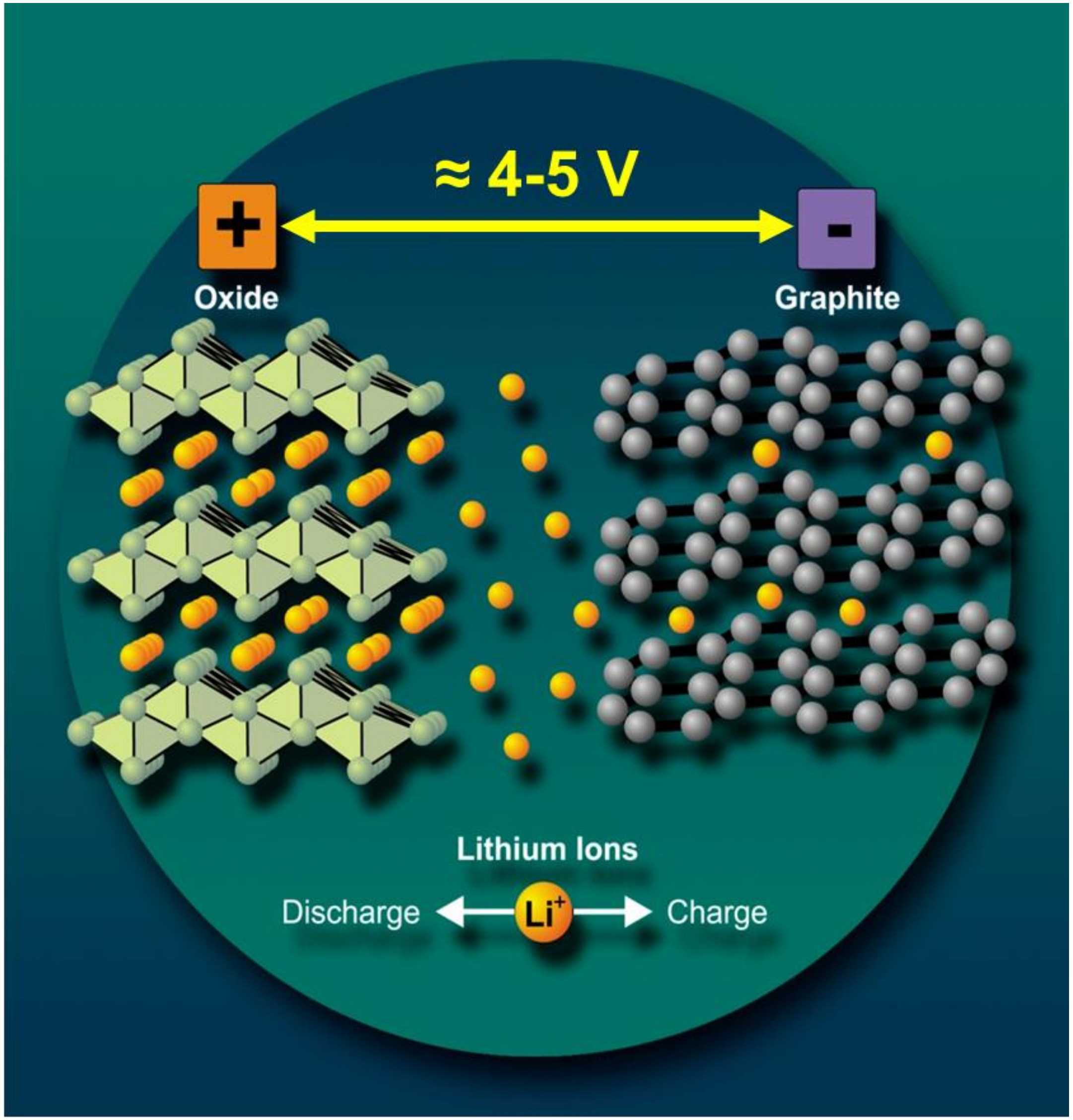
- **Cost:**
  - cheap raw materials
  - cheap technology



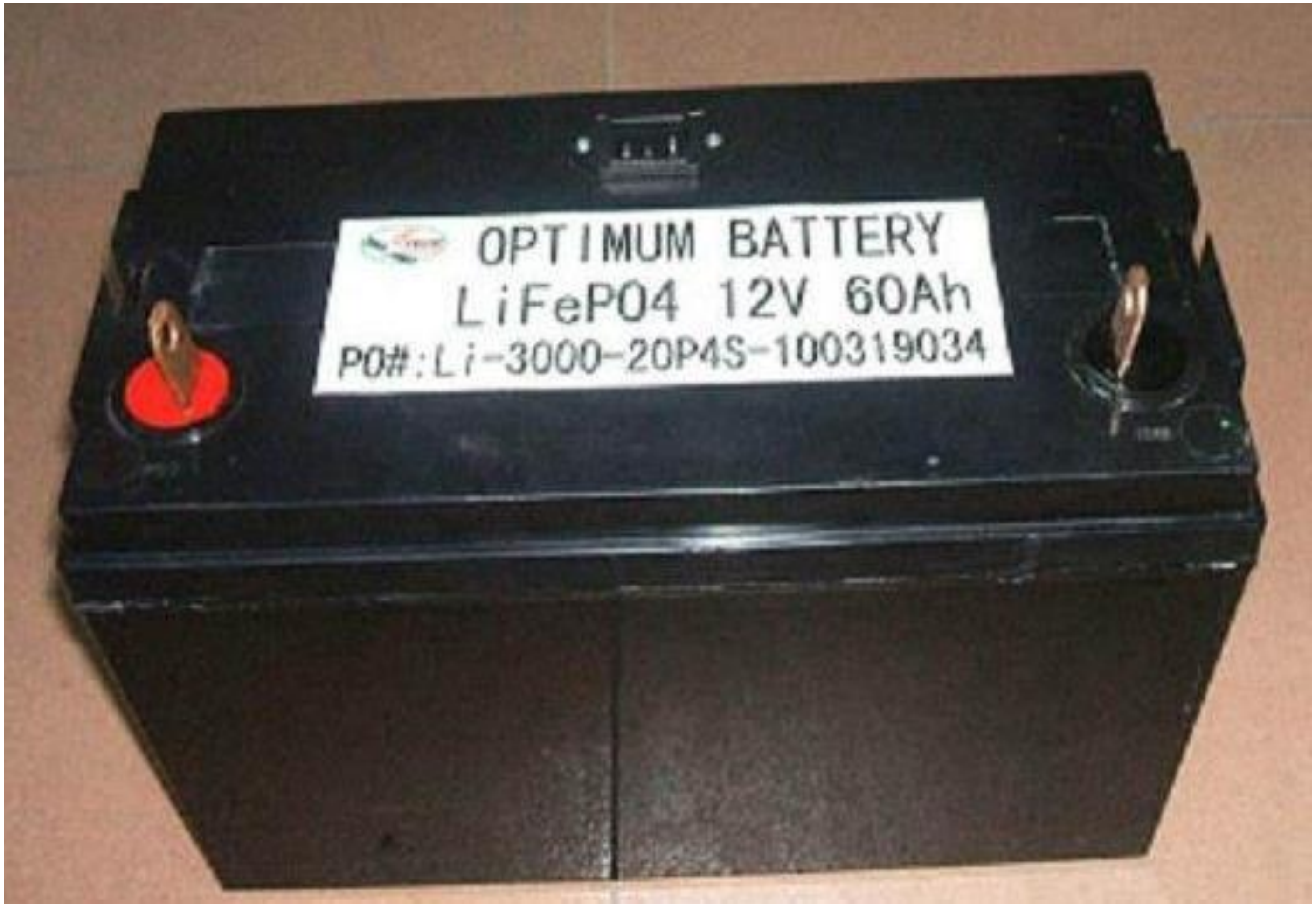
- **Safety:**

Materials in Lithium-Ion Batteries





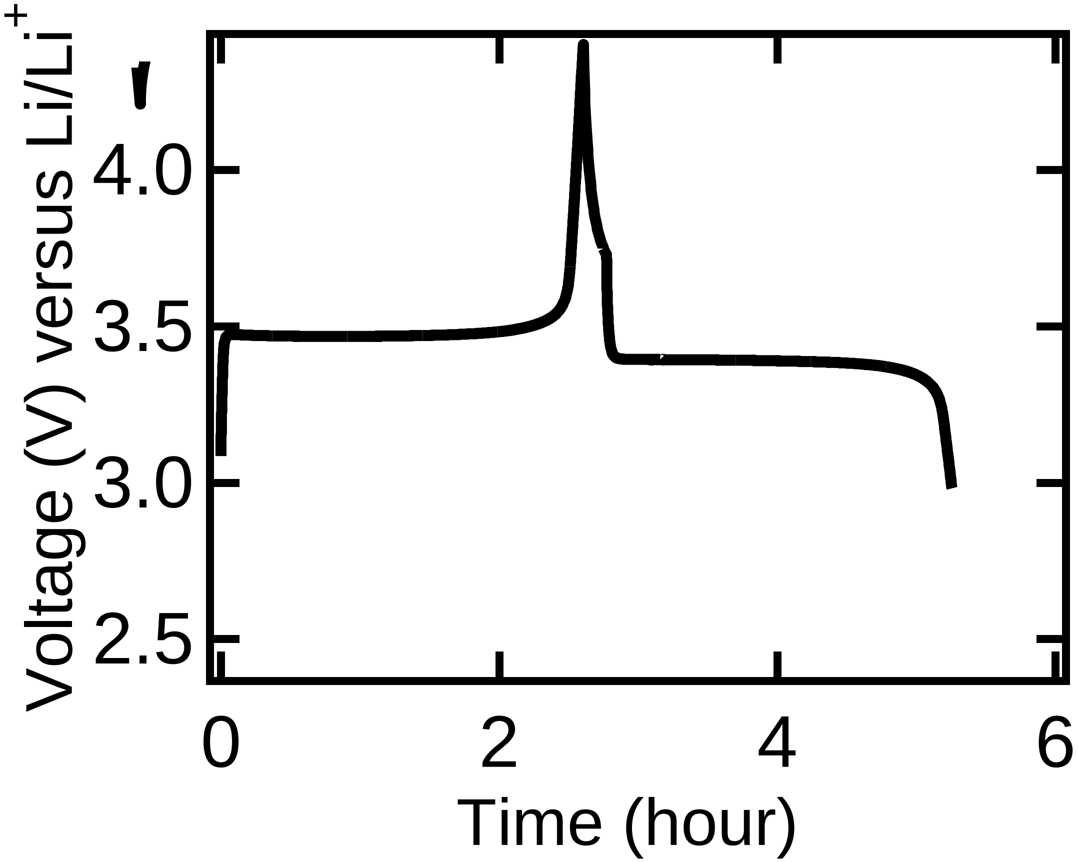
Batteries Based on $LiFePO_4$



They are on the market. They are considered to be safe.

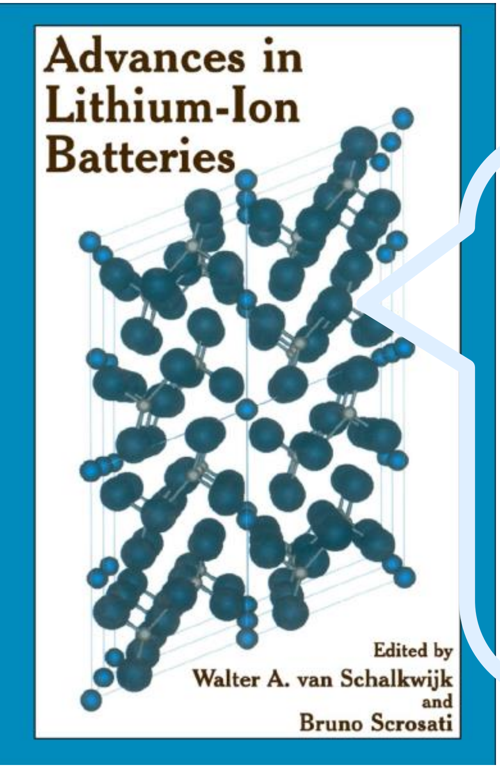
But do we understand them???

Charge/Discharge curve of LiFePO$_4$:

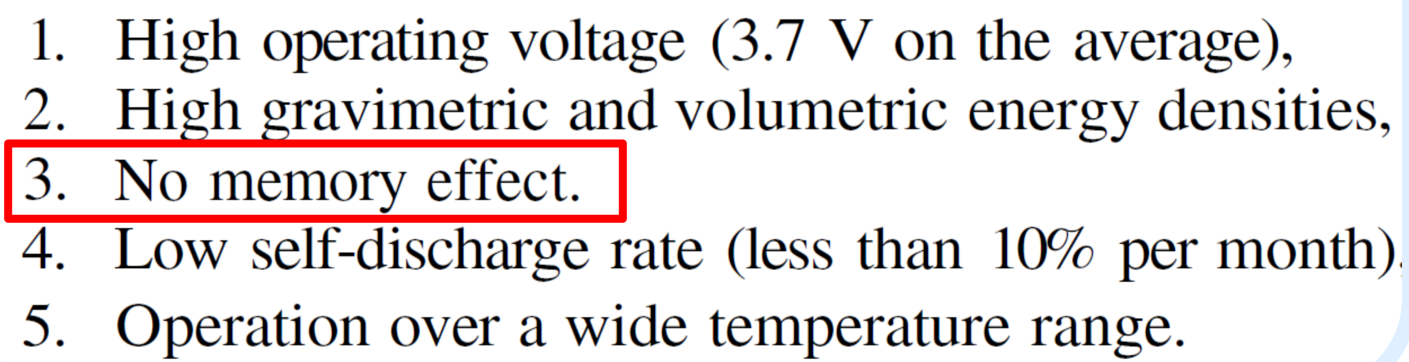


The charge/discharge voltage curves of LiFePO$_4$ are very flat, because they undergo a two-phase reaction

Li-Ion Batteries



The features of Li-ion batteries are as follows:



1. High operating voltage (3.7 V on the average),
2. High gravimetric and volumetric energy densities,
3. No memory effect.
4. Low self-discharge rate (less than 10% per month).
5. Operation over a wide temperature range.

Advances in Lithium-Ion Batteries
Edited by Walter A. van Schalkwijk,
Bruno Scrosati

Really?
Revisit this classical question!

What Is a ‘Memory Effect’?

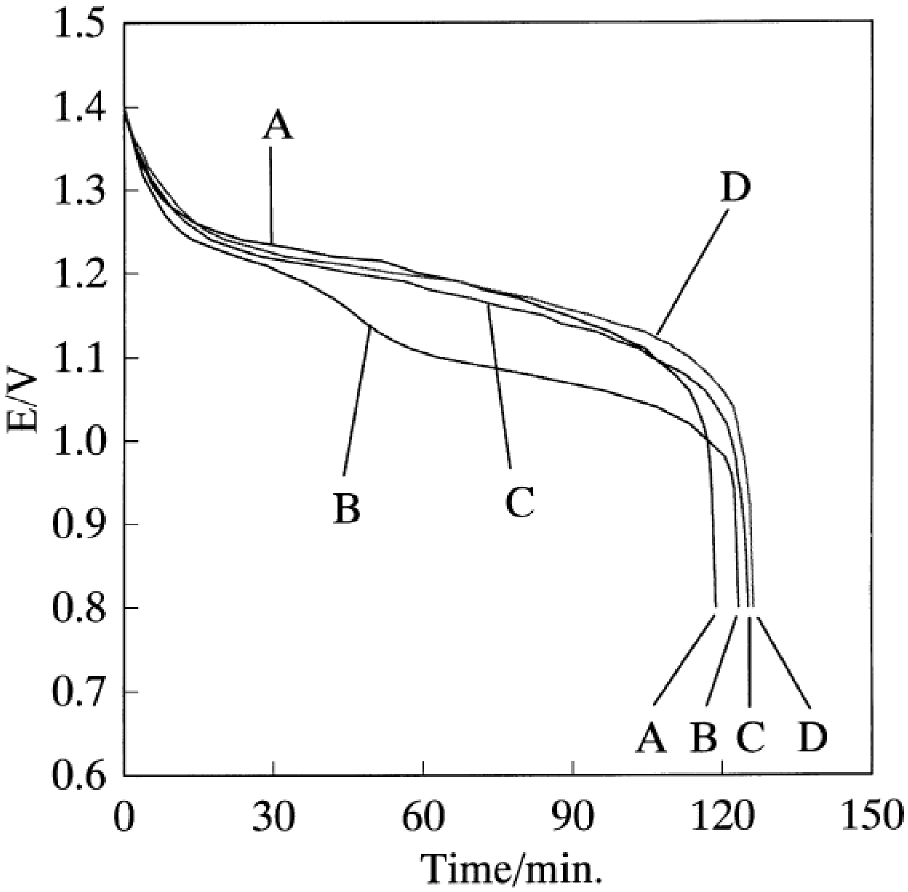
Memory effect:

Observed in Ni-Cd and Ni-MH batteries

Example:
Ni-MH AAA-size

(B) After 300 shallow discharge cycles

The battery recalls the depth of previous cycles



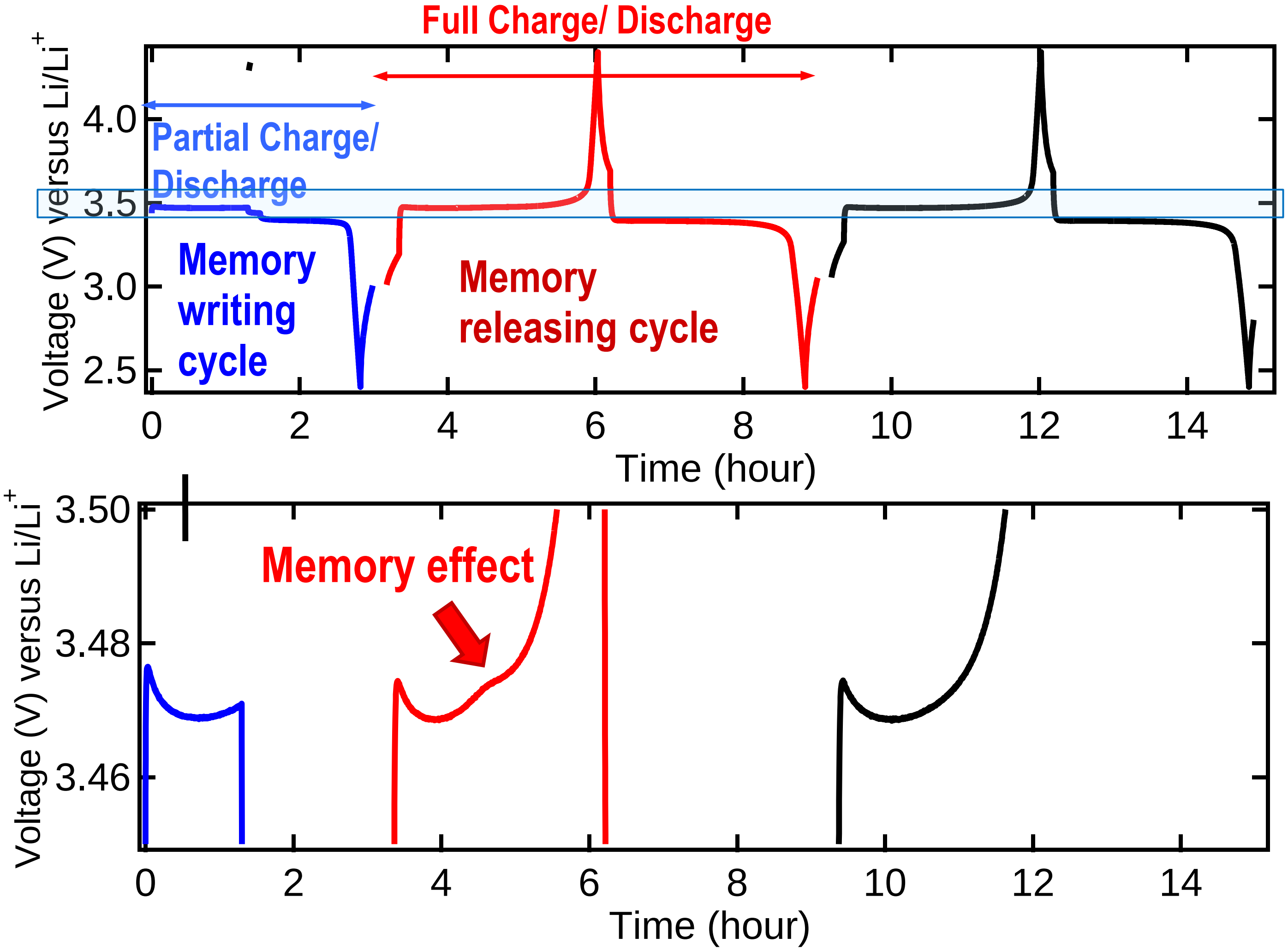
Sato, Y., Takeuchi, S. & Kobayakawa K. “Cause of the memory effect observed in alkaline secondary batteries using nickel electrode” *J. Power Sources* **93,** 20-24 (2001).

Experiment: A Memory Effect

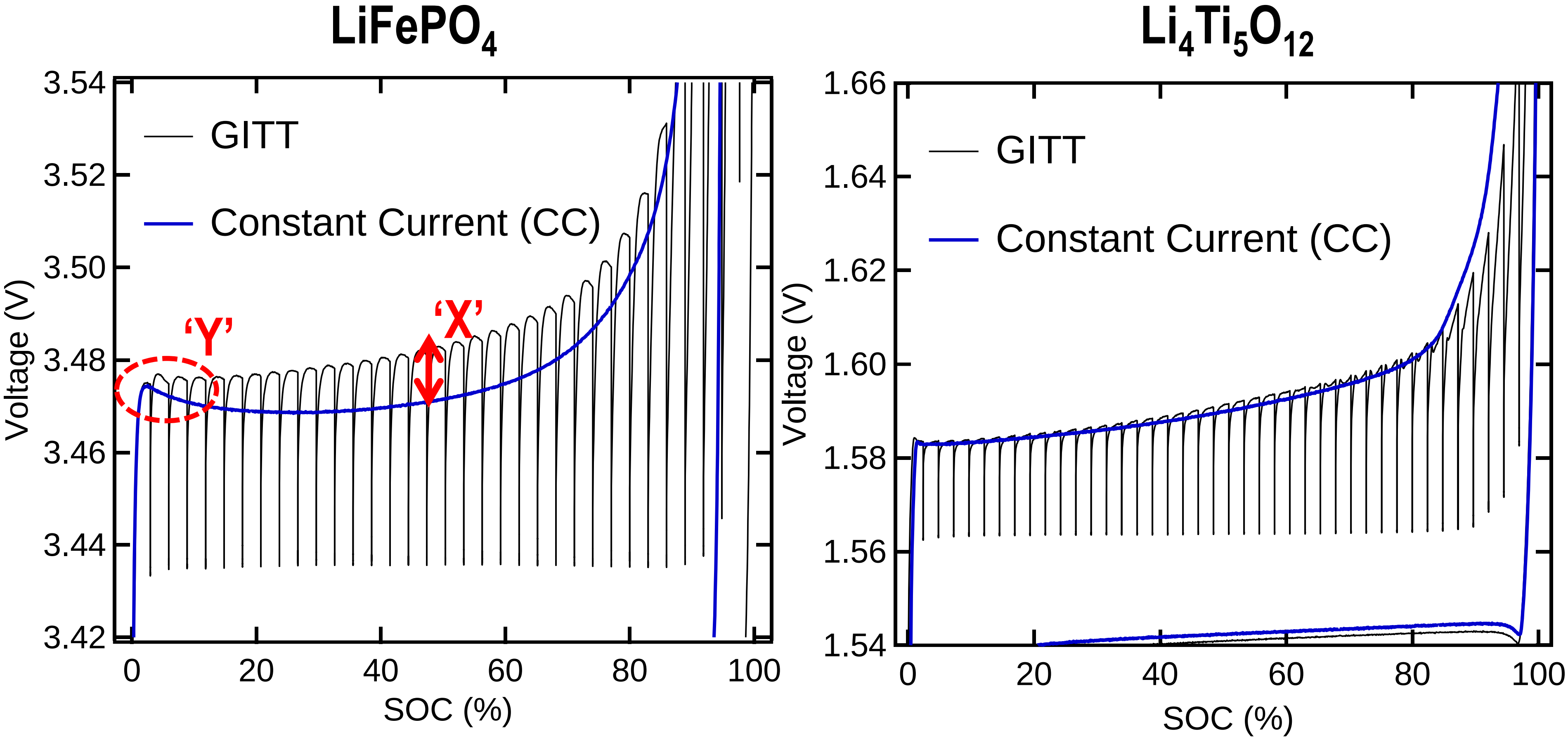
To our surprise, we found a slight but clear memory effect in the charge curve of $LiFePO_4$

Zoom

Expanded figure



GITT Measurements of $LiFePO_4$ and $Li_4Ti_5O_{12}$

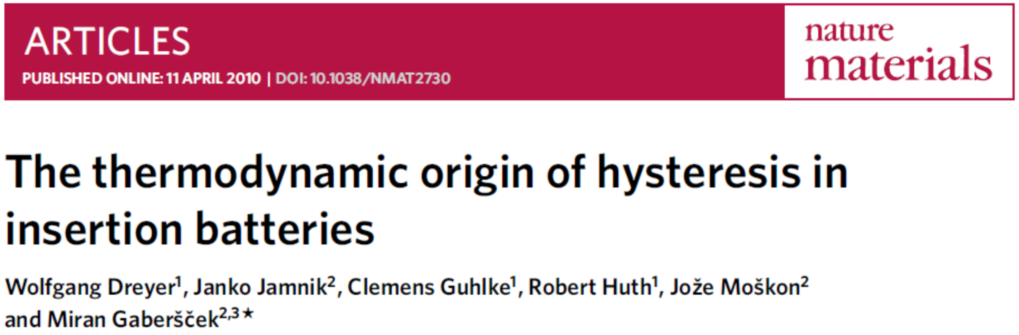


Each pulse current in GITT and CC current are identical (C/4)

X: Polarization increasing after relaxation, Y: Overshoot at the beginning
X and Y are the keys to understanding the mechanism of the memory effect.

Many-Particle Model

In 2010 by
W. Dreyer et al.

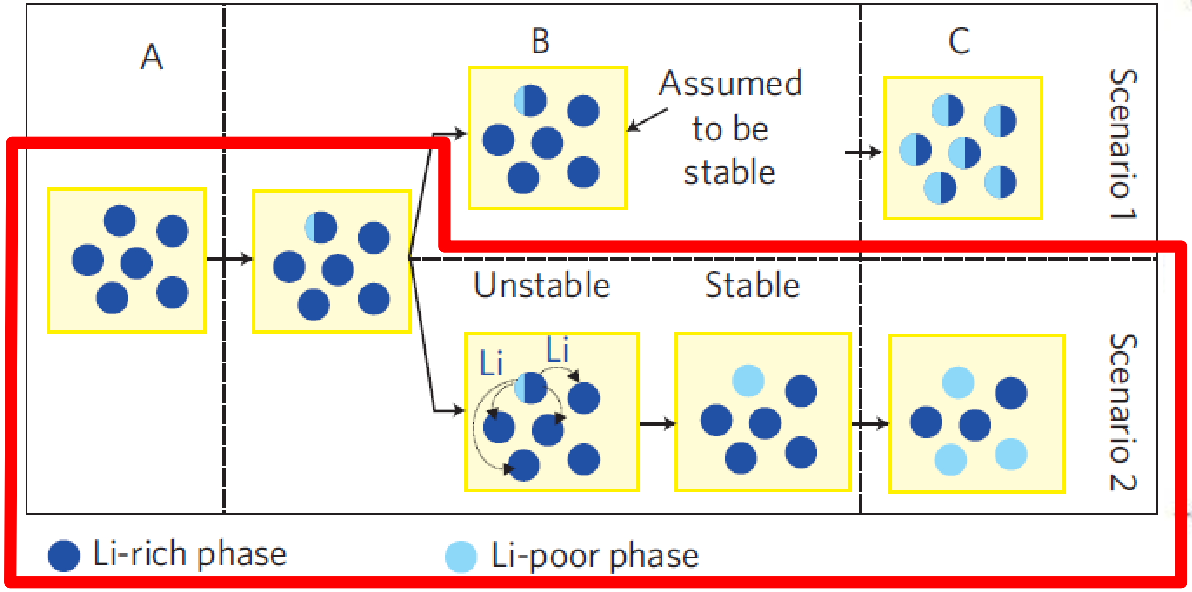


ARTICLES
PUBLISHED ONLINE: 11 APRIL 2010 | DOI: 10.1038/NMAT2730

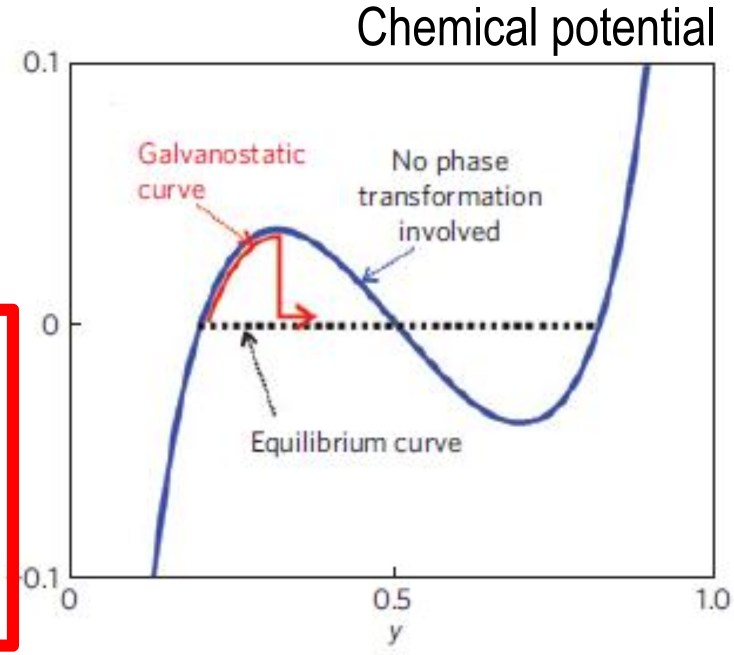
nature materials

The thermodynamic origin of hysteresis in insertion batteries

Wolfgang Dreyer[1], Janko Jamnik[2], Clemens Guhlke[1], Robert Huth[1], Jože Moškon[2] and Miran Gaberšček[2,3]*

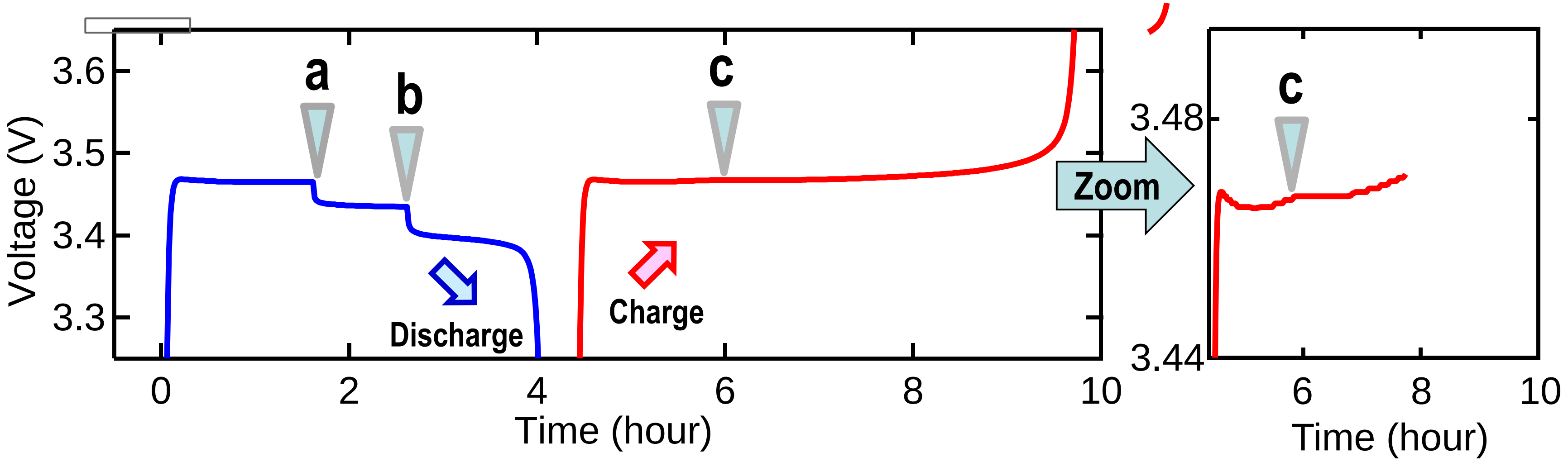


Particle-by-particle charging process

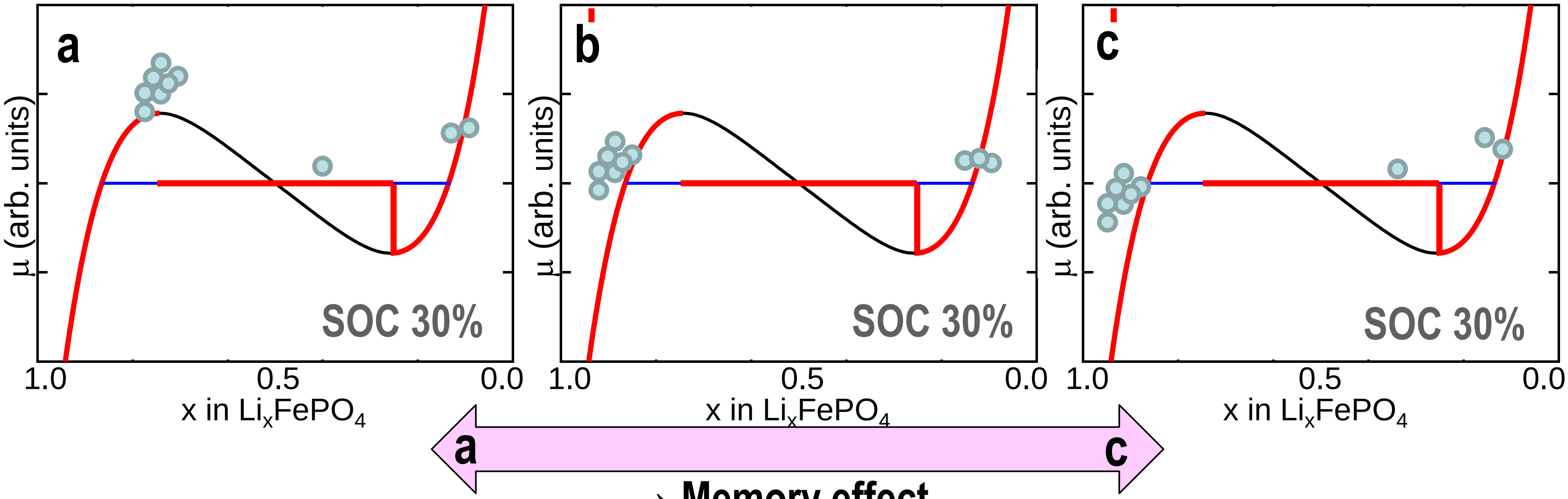

Chemical potential

based on a non-monotone single-particle chemical potential

The Mechanism of the Memory Effect



Chemical potential



→ **Memory effect**

Thus, the Memory Effect Is…

The memory effect is **the “delayed” overshooting**, which normally appears at the beginning of the charge curve, due to the division of the Li-mole fraction into two groups.

$LiFePO_4$ (LFP)

Another “strange behavior” of $LiFePO_4$…

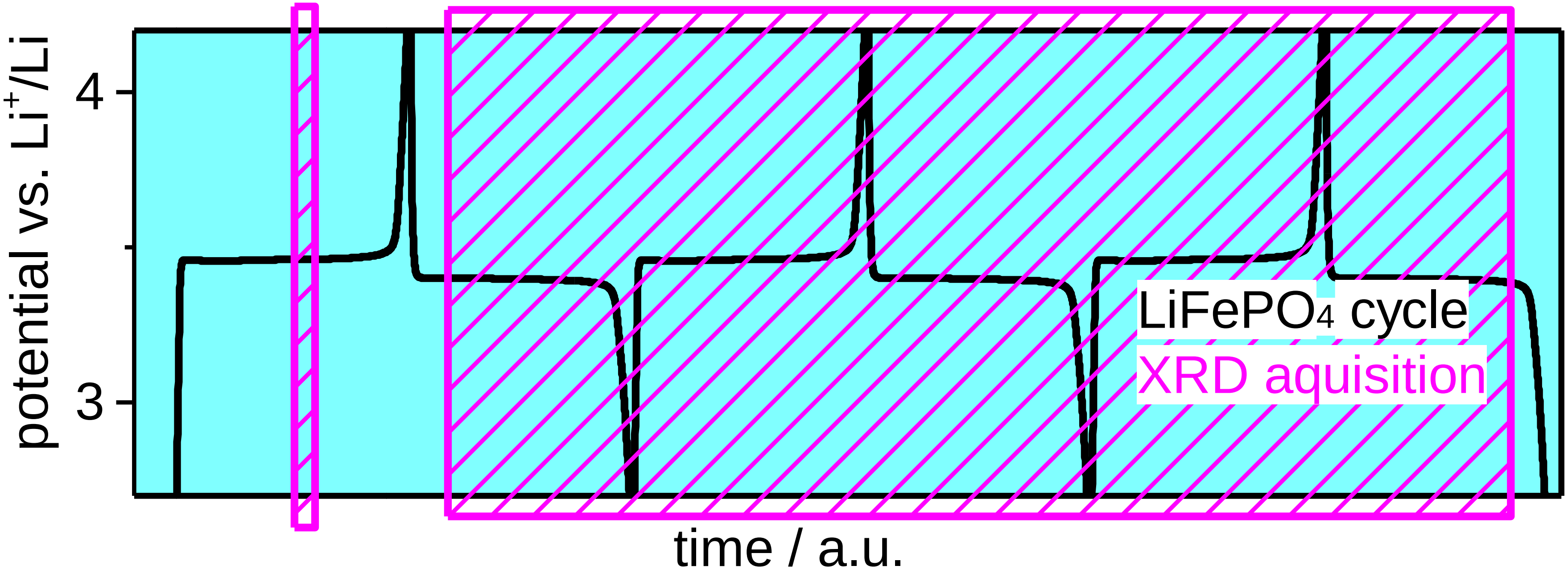
In situ XRD during electrochemical impedance spectroscopy

1) snapshot

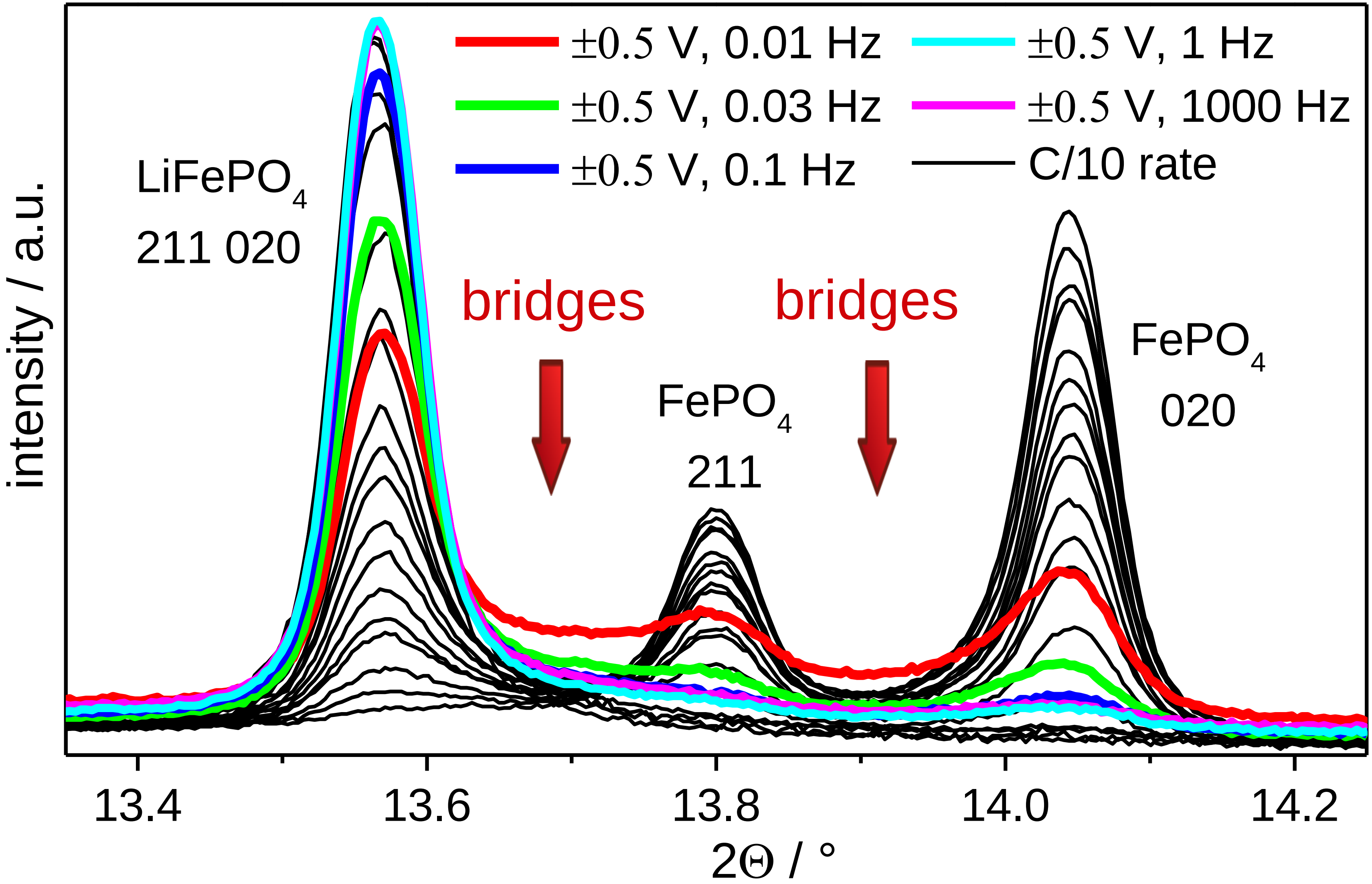
→ $t_{XRD} << t_{cycle}$

2) bulb exposure

→ $t_{XRD} >> t_{cycle}$

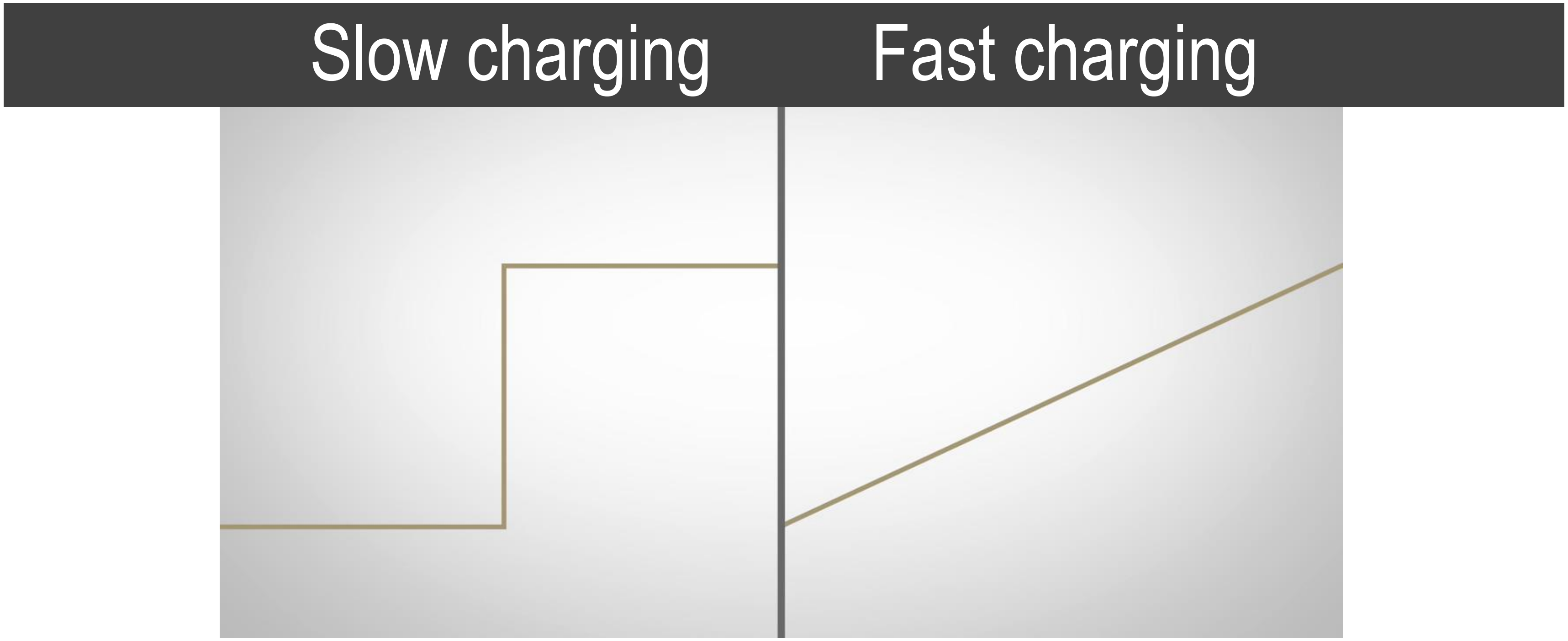


In situ XRD during EIS



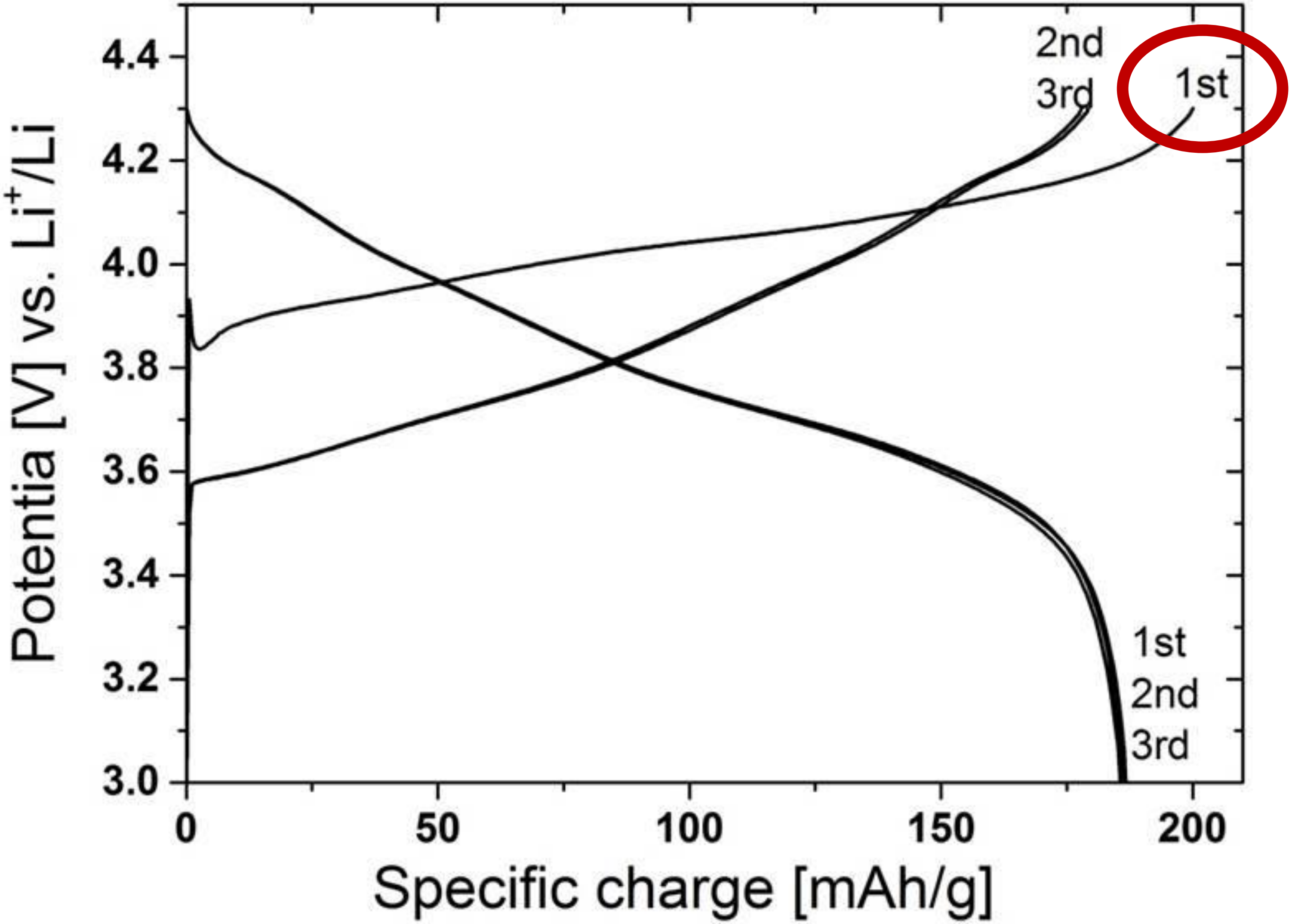
$LiFePO_4$

There is a **continuous solid-solution reaction** for $LiFePO_4$ at high rate conditions, with consequences on the charging process.

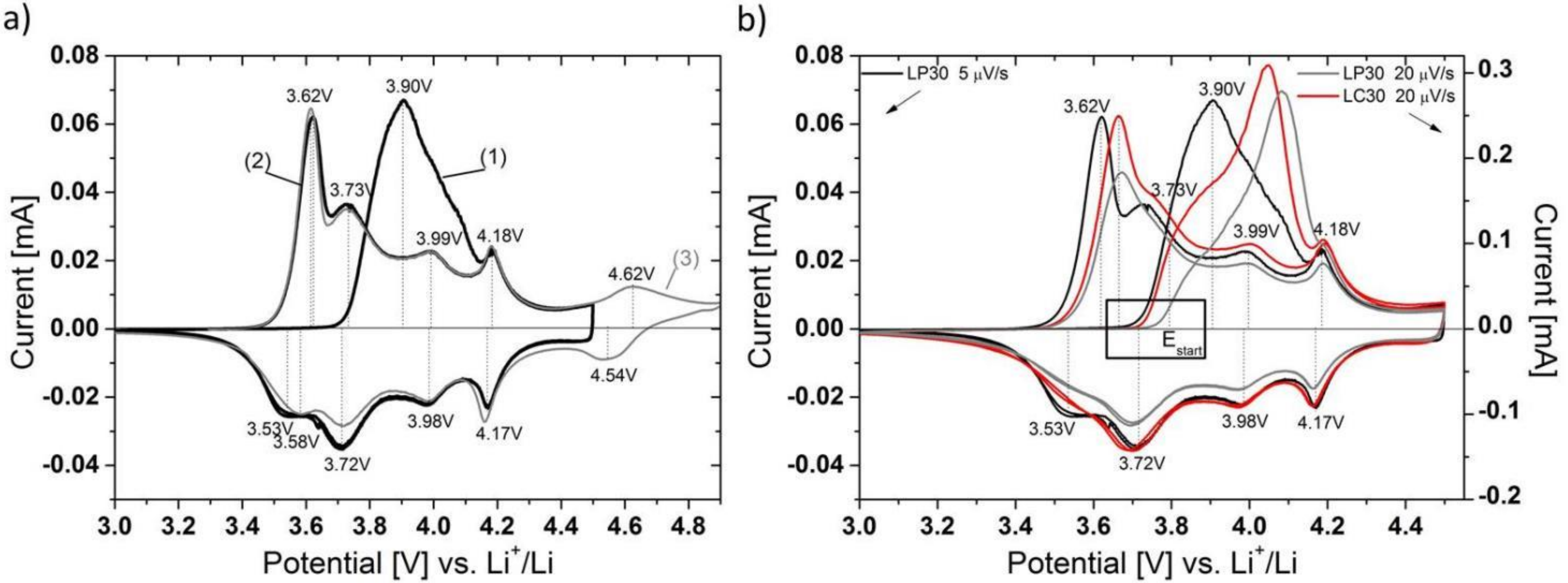


The lithium (de)-insertion mechanism of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – Galvanostatic Curves

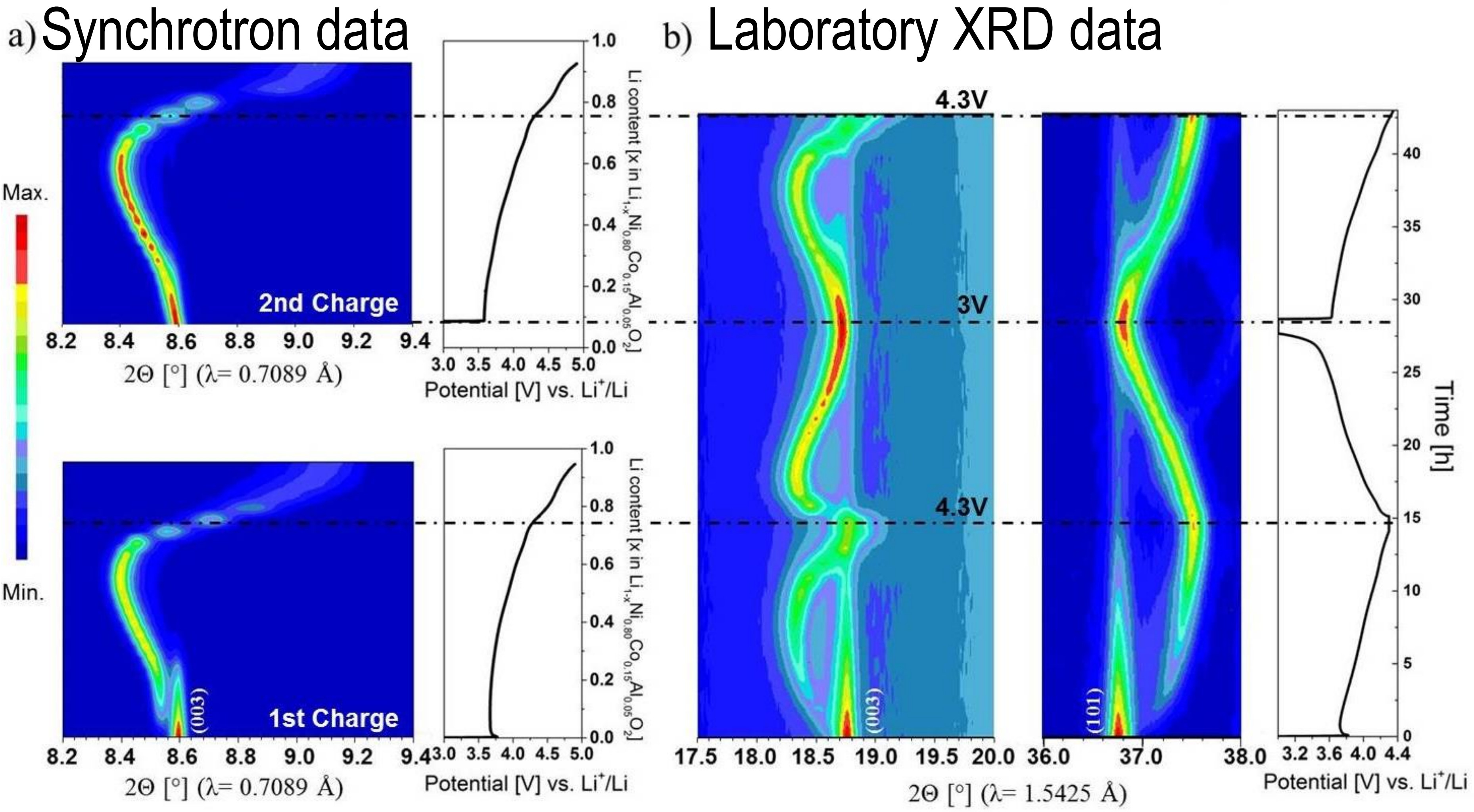


$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – Cyclic Voltammetry



After the activation during the first cycle, there is a sequential rearrangement of the lattice

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – *Operando* XRD

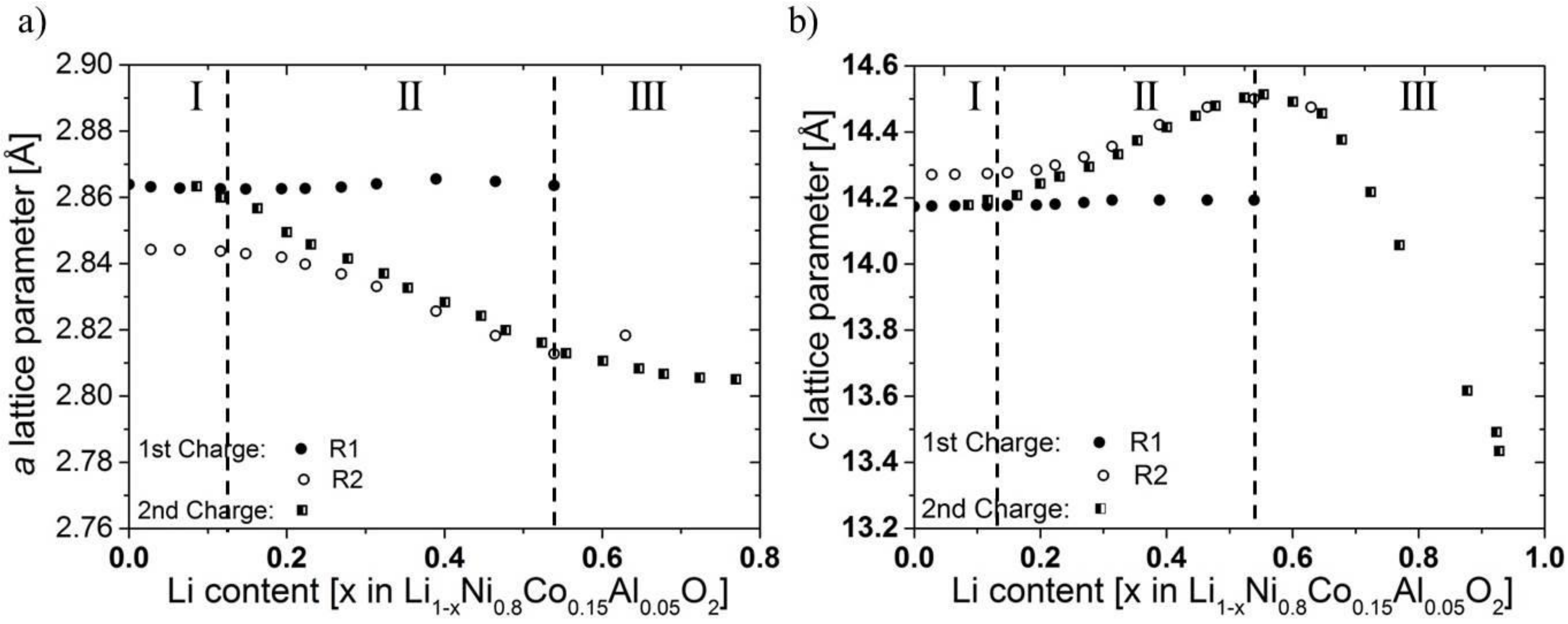

a) Synchrotron data

b) Laboratory XRD data

Clear differences in the reaction pathways of the 1st and 2nd cycle

PAUL SCHERRER INSTITUT PSI

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – *Operando* XRD



R1: pristine phase

R2: second rhombohedral phase

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ – Conclusions

- For the first charge, the poor Li^+ ion mobility of the fully lithiated NCA electrode causes a large overpotential needed to form a second phase

- This phase has faster lithium-ion mobility and increased electrical conductivity compared to R1

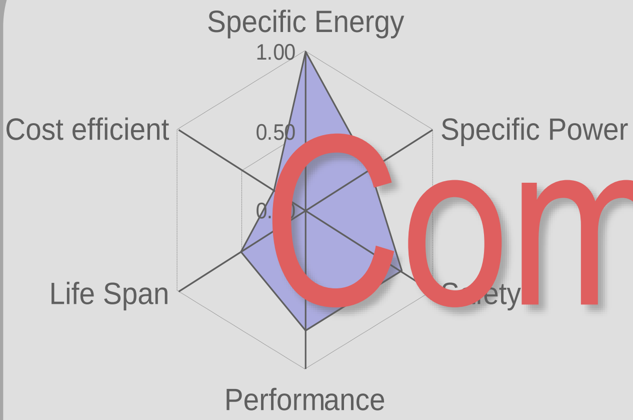
- De-insertion of Li from the R2 phase proceeds via a solid solution mechanism and a fully lithiated phase at the end of the discharge to 3.0 V is not achieved => Li content between $0 < 1-x < 0.03$

- The second charge starts with an NCA with some lithium deficiency and larger electrical conductivity compared to the R1 phase that allows the reaction to proceed in a solid solution manner, as for the following cycles

HE-NCM materials (“5 Volt”)

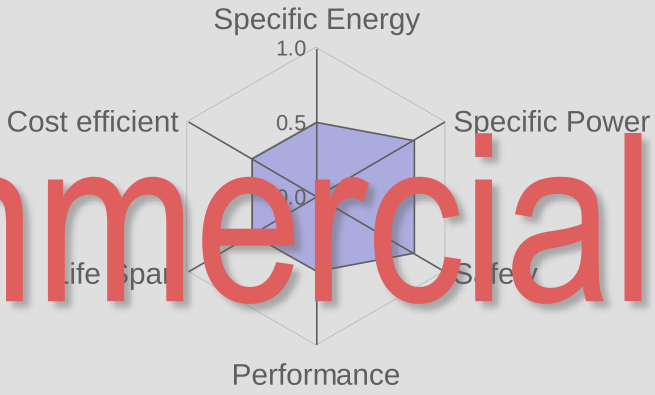
Overview of Materials for the Positive Electrode

$LiCoO_2$



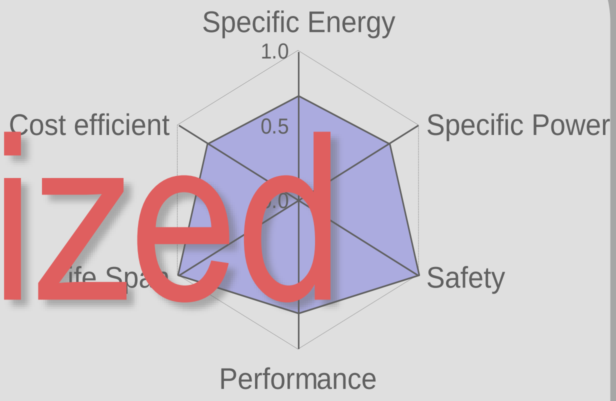
Pot. 3.9 V
Theor. Cap. 140 mAh/g

$LiMn_2O_4$



Pot. 4 V
Theor. Cap. 150 mAh/g

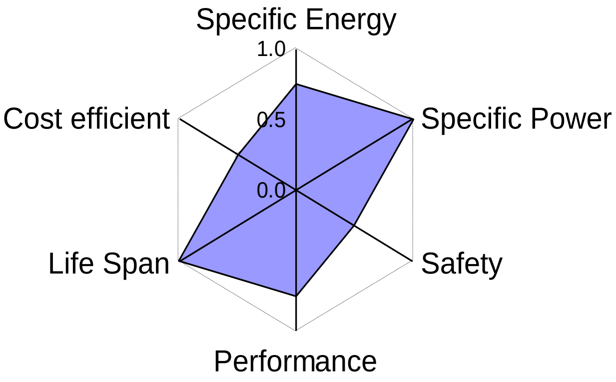
$LiFePO_4$



Pot. 3.5 V
Theor. Cap. 170 mAh/g

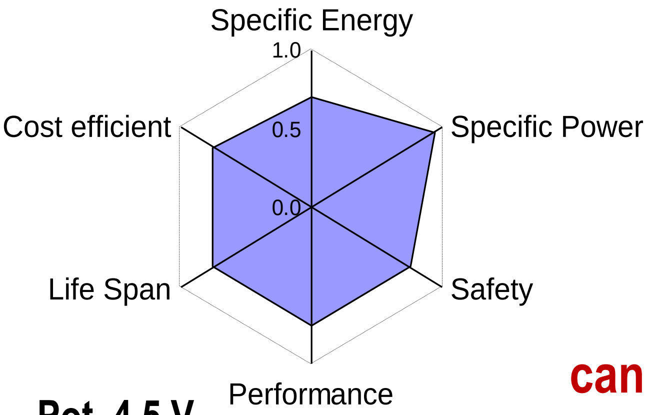
Commercialized

NCA (Ni, Co, Al)



Pot. 4 V
Theor. Cap. 180 mAh/g

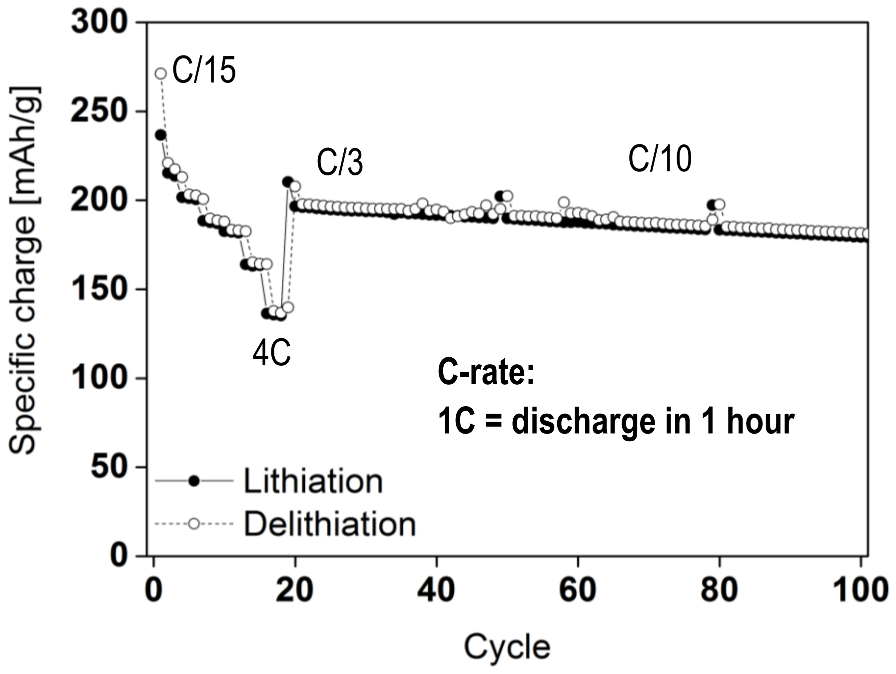
HE-NCM (Ni, Co, Mn)



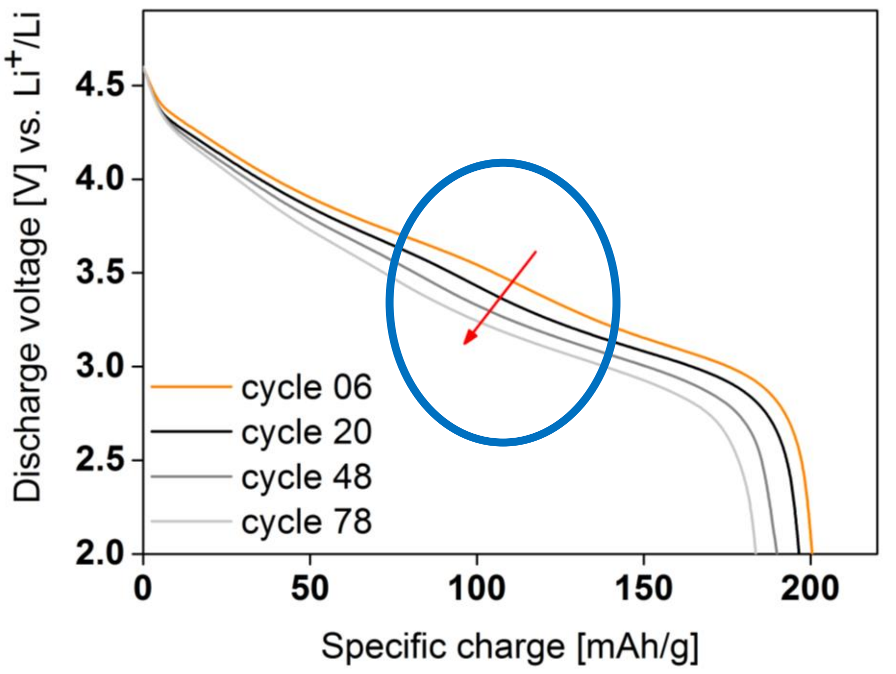
Pot. 4.5 V
Theor. Cap. 240 mAh/g

At high potentials
NCA and NCM materials
can offer higher specific energy

Cycling Properties of HE-NCM (Ni, Co, Mn)



C-rate:
1C = discharge in 1 hour



Very high specific charge compared to other cathodes ☺ but…

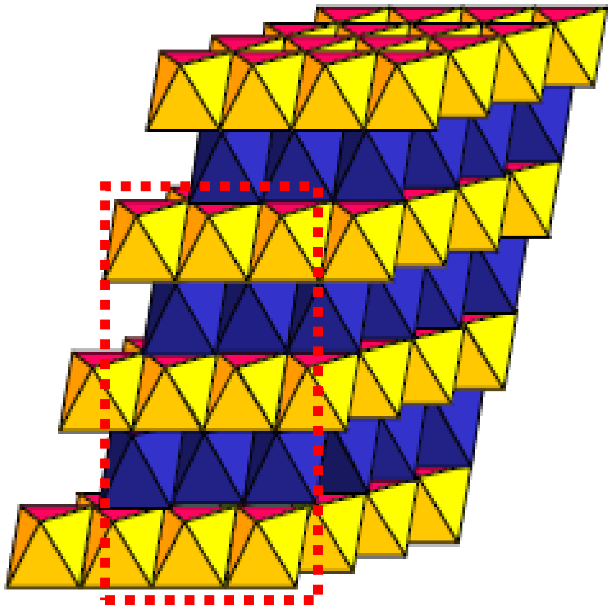
- Strong fading during cycling ☹
- Drop of potential during cycling (leaching, structure) ☹

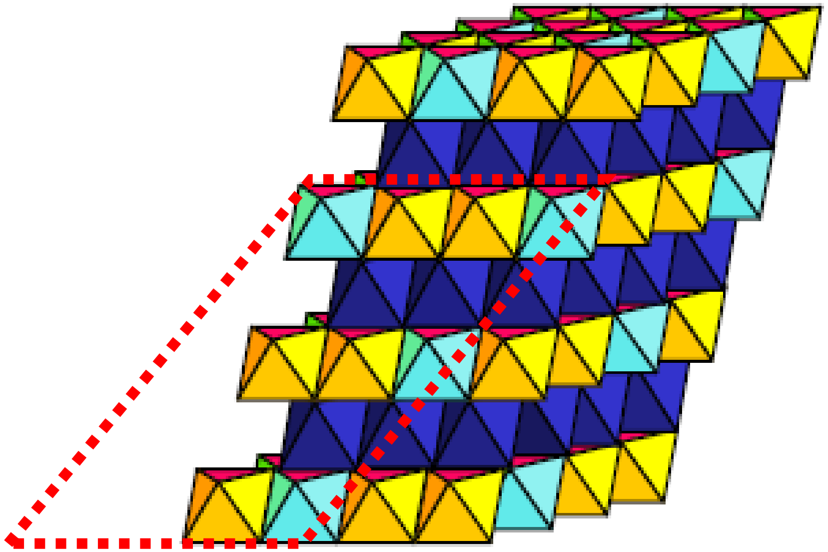
⇒ How to stabilize the potential and buffer the fading?

HE-NCM: Li_2MnO_3 Stabilized NCM

$Li(Ni, Co, Mn)O_2$

$Li_2MnO_3 = Li(Li_{1/3}Mn_{2/3})O_2$





$r_{Li^+}=0.72$ Å, $r_{Mn^{4+}}=0.53$ Å, $r_{Ni^{2+}}=0.69$ Å, $r_{Co^{3+}}=0.54$ Å → Layered structure

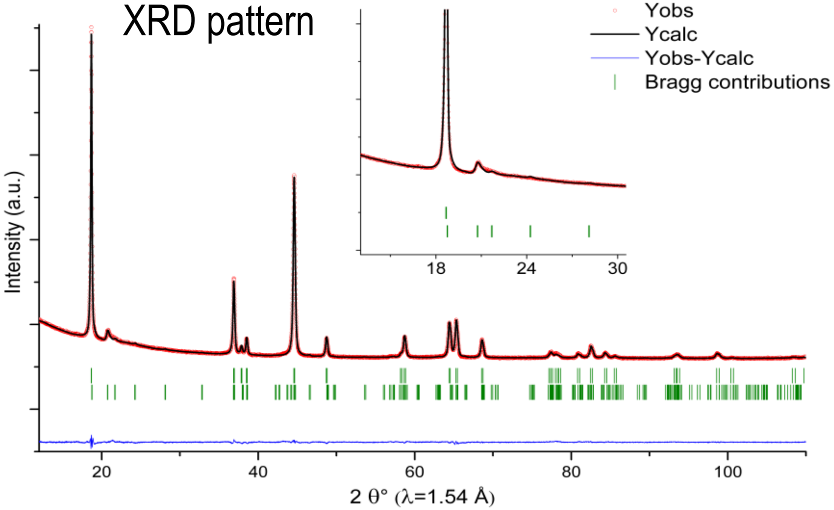
- 3 [M] slabs
- Hexagonal structure (R-3m)

- 3 $[Li_{1/3}Mn_{2/3}]$ slabs
- Monoclinic structure (C2/m)

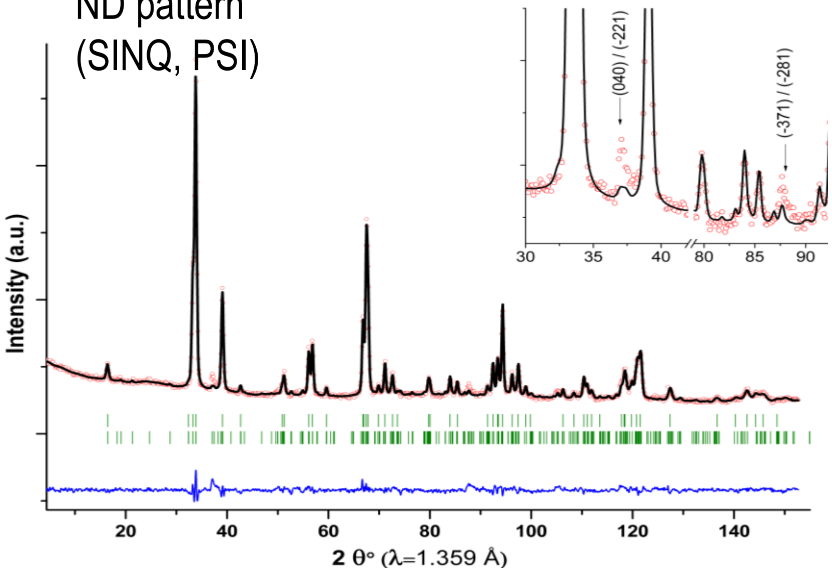
HE-NCM: Phase Coexistence

XRD & Neutron Diffraction

XRD pattern



ND pattern
(SINQ, PSI)



Li_2MnO_3 is accommodated in the NCM host lattice

Monoclinic distortions → Li_2MnO_3

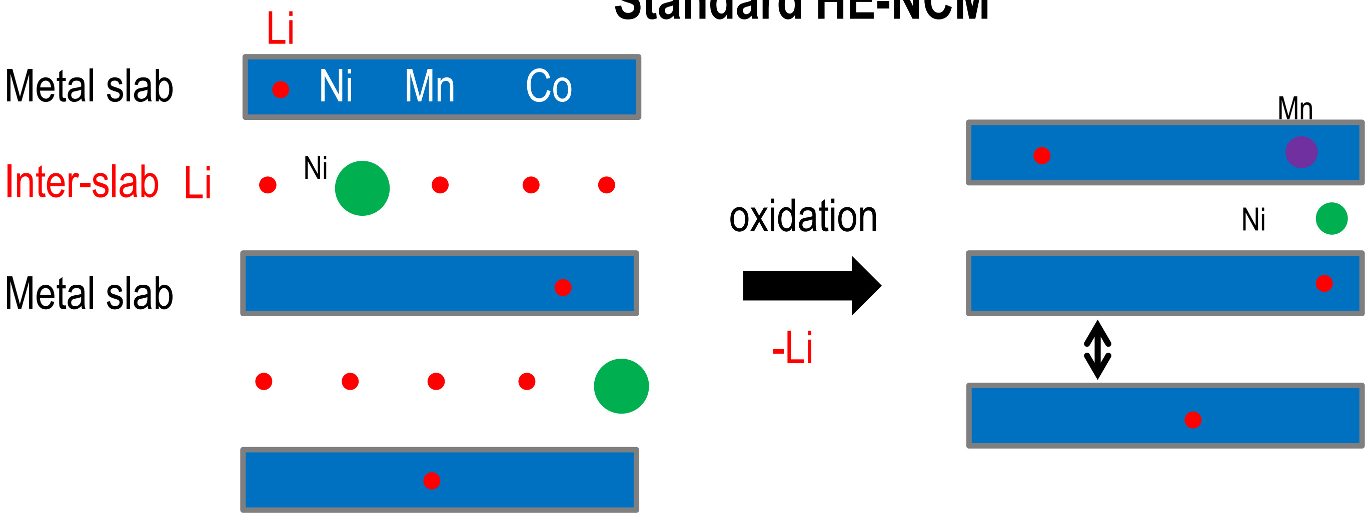
➔ **Li/Ni exchange ca. 5%**

Stacking faults

➔ **Apparent Li^+/Mn^{2+} exchange ca. 20%**

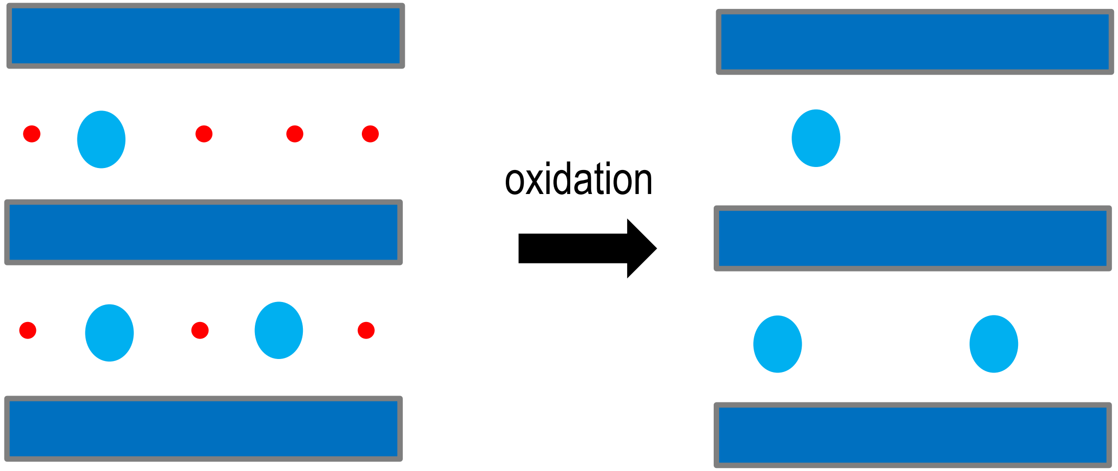
Concept to Stabilize HE-NCM

Standard HE-NCM



Transit to the anode

Modified HE-NCM



Strategy: insert “inactive” element:
- to avoid structural transition
- to avoid layer shrinkage
- to reduce anode “pollution”

Syntheses

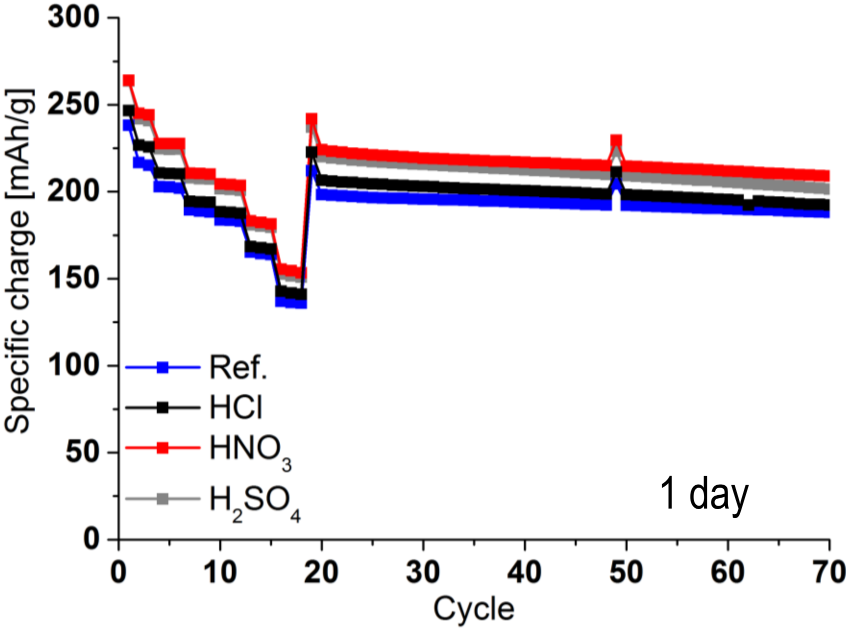
Post-treatment (acid treatment of HE-NCM)

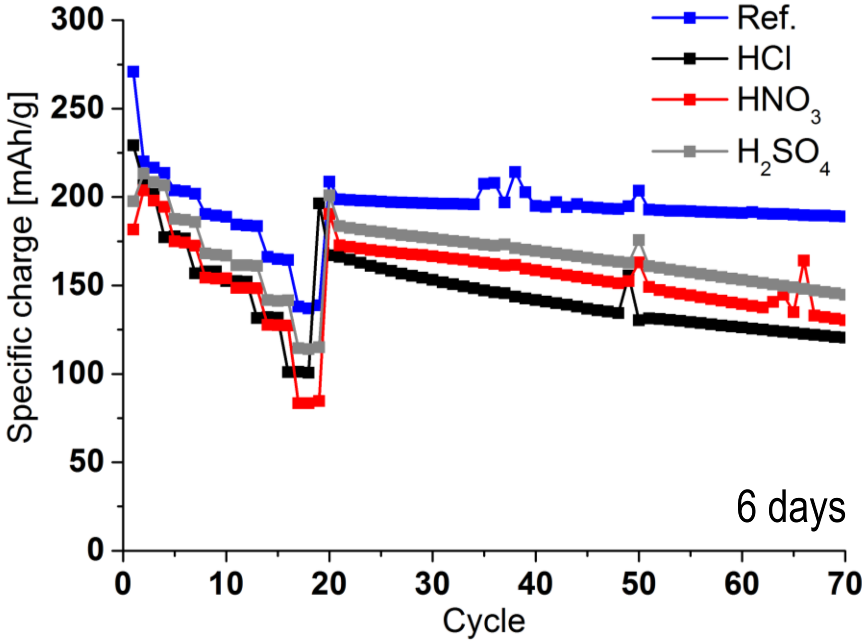
- Choice of the cation difficult (due to size and steric effects) ☹
- Control of the position of the cation ☺
- Porosity and morphology kept ☺

Home-made synthesis (sol-gel method)

- No control of the position of the cation ☹
- Wide variety of cations ☺
- Possibility of cation mixing ☺
- Flexibility of the synthesis ☺

1st Step Post-Treatment → Acid 'Washing' to Remove Li

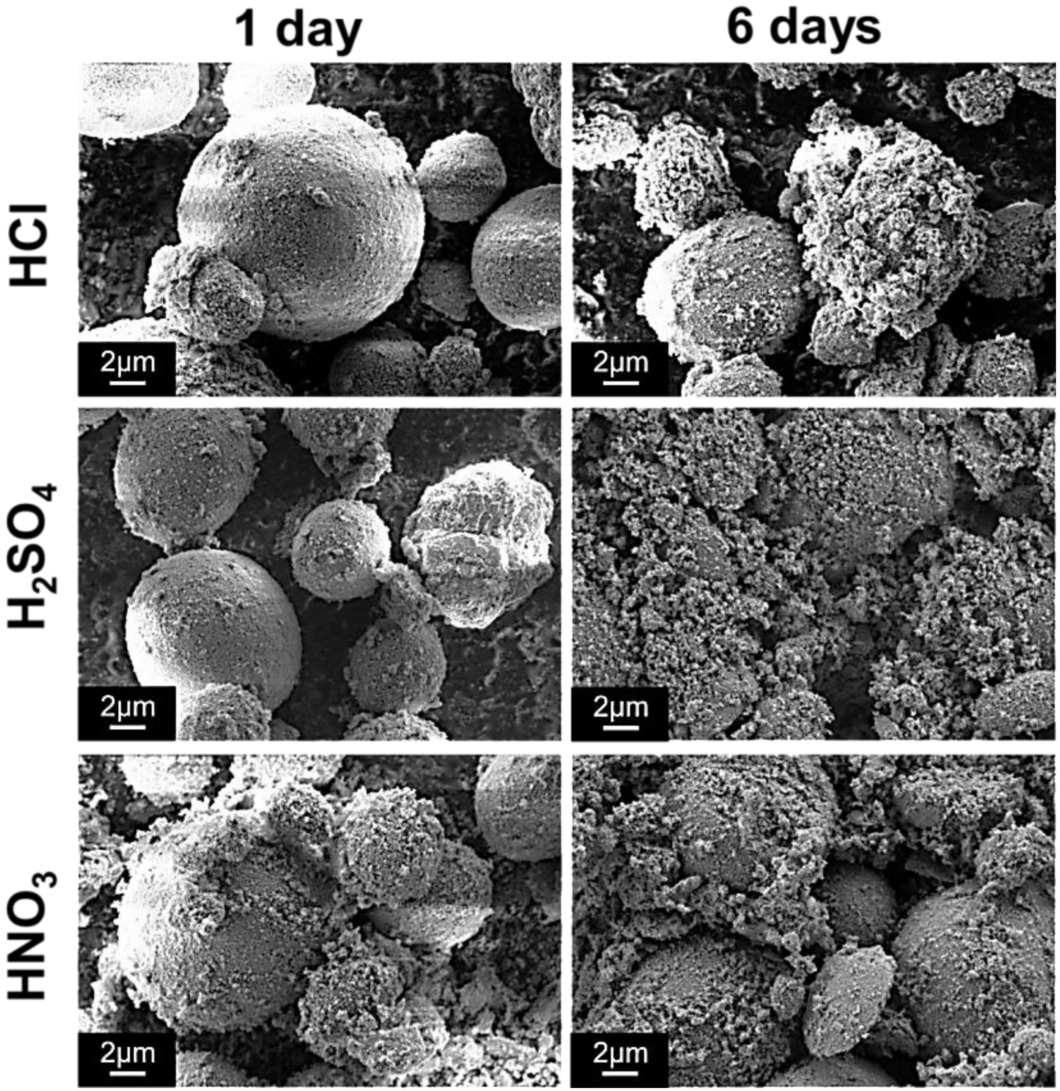




Acid-treated samples: higher specific charge (with less Li)

Reference sample: the best one (too much Li removed?)

Morphology of the Particles after Washing



Analysis:

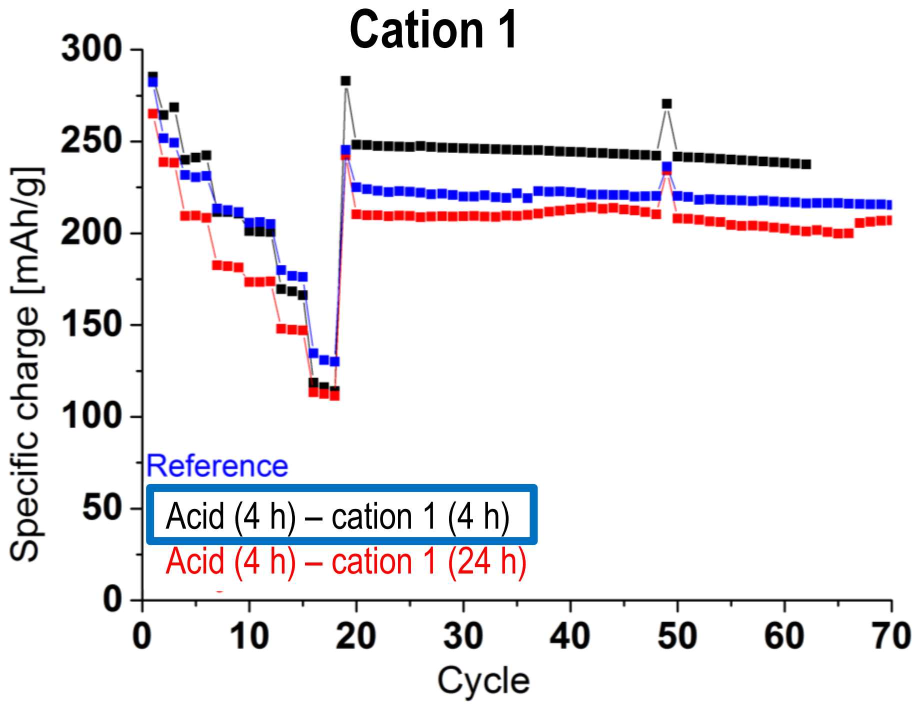
- Loss of the original morphology after 6 days
- Insignificant damage with HNO_3 after 1 day
- BET doubled in 1 day

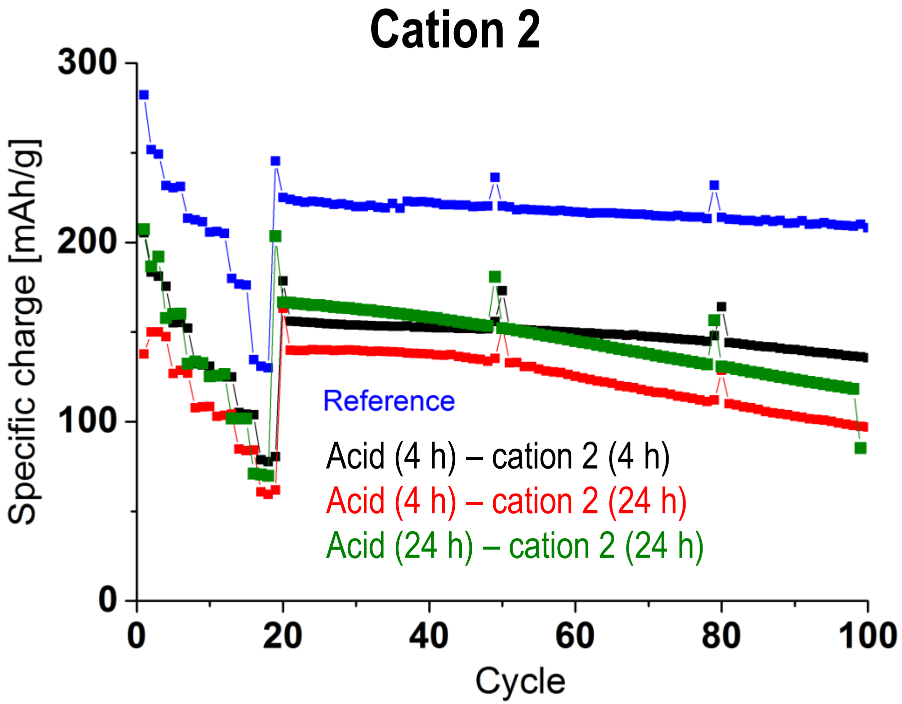
⇩

Conclusion:

- 1 day treatment selected for the exchange

2nd Step Post-Treatment → Cation Exchange


Cation 1

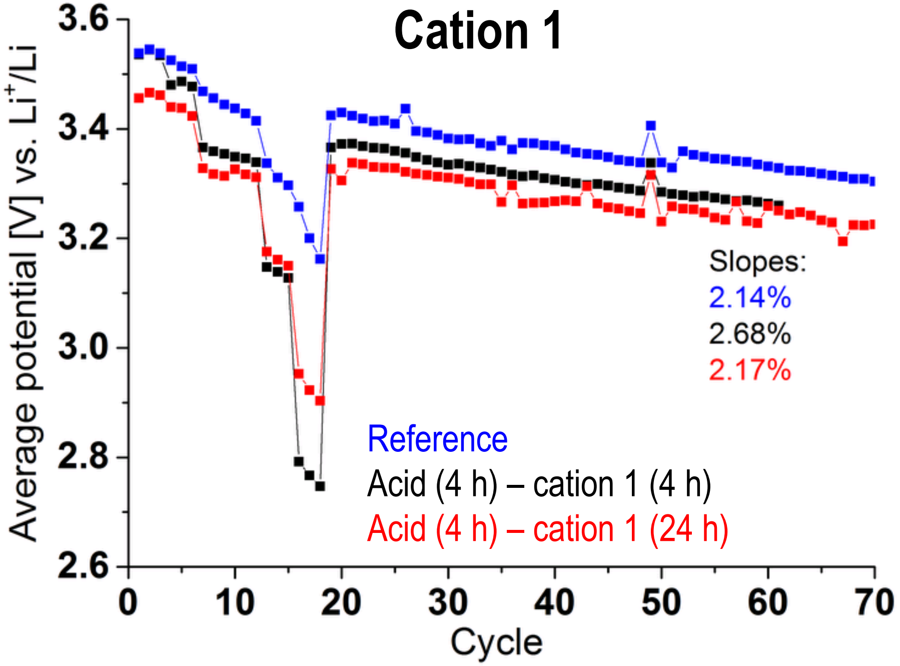

Cation 2

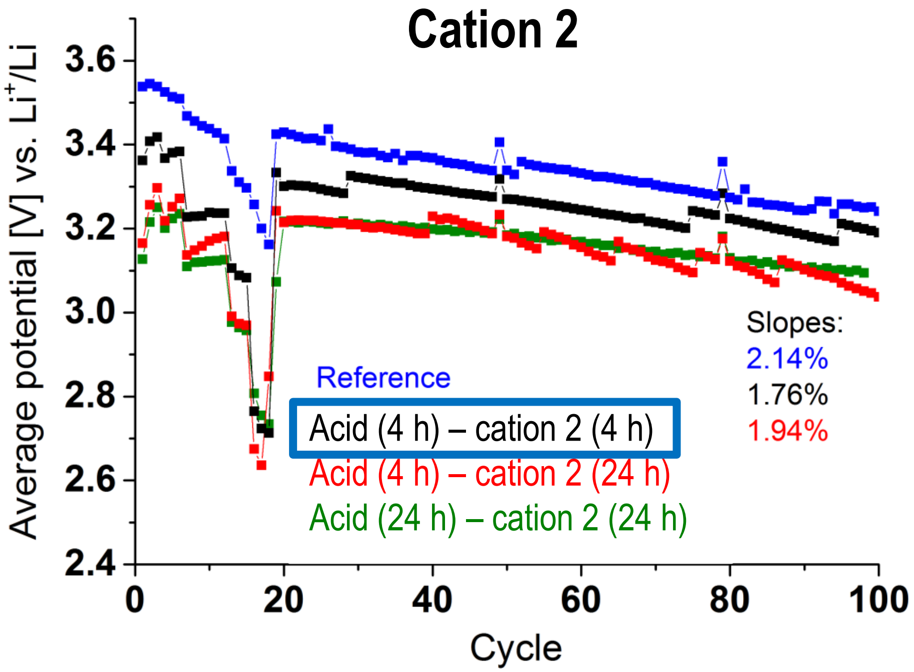
- Fading less pronounced ☺
- Specific charge higher for the 4 h acid/exchange ☺

- More fading regardless of the treatment ☹
- Very low specific charge ☹

Do we have a clear winner ???

Evolution of the Potential during Cycling





Remember

- Specific charge higher and more stable for 4 h/4 h ☺
- Higher potential fading than reference ☹

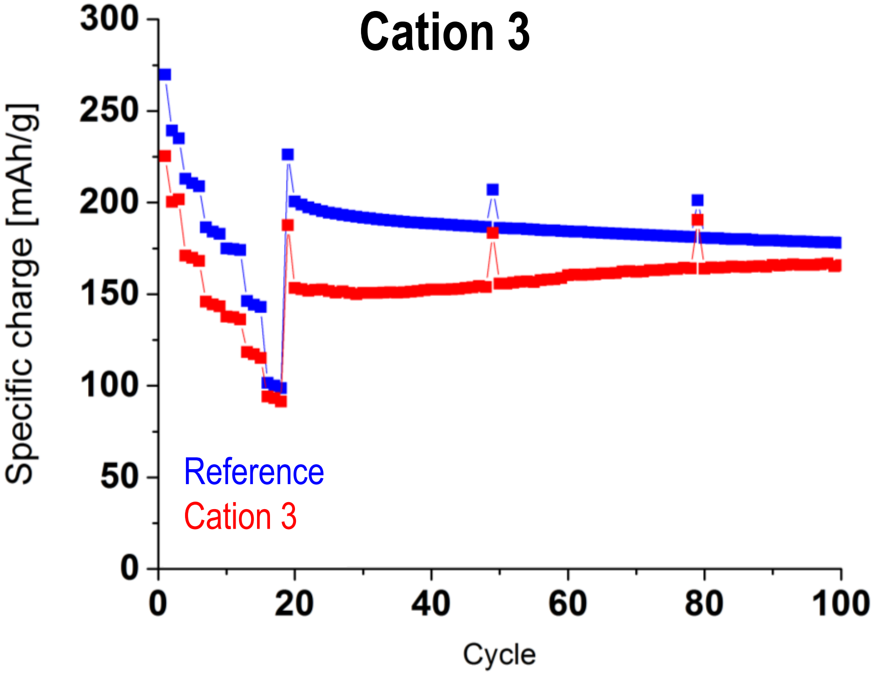
We improved specific charge with less Li…

Remember

- Specific charge lower than reference ☹
- Mitigation of potential fading ☺

We improved the voltage fading…

Home-Made Synthesis



- Lower specific charge ☹
- More stable specific charge ☺

So we found some winners ☺. BUT, why are they winners?
=> More next year

Na-ion batteries

Li- and Na-Ion Facts

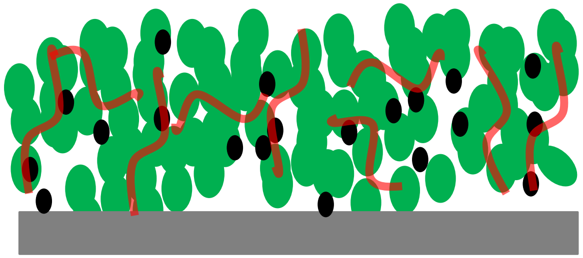
Property	Lithium	Sodium
Ionic radius (Å)	0.69	0.98
Molar mass (g mol^{-1})	6.94	22.99
Voltage vs. S.H.E. (V)	-3.045	-2.714
Theor. capacity (mAh g^{-1})	3861	1165
Crustal abundance (ppm)	20	23600
Cost (USD/t)	24000	500
Anode current collector	Cu	Al
BGS Supply risk index* (1 = very low; 10 = very high)	6.7	-

*British Geological Society Supply Risk Index:
Factors considered include scarcity, production concentration, reserve distribution, recyclability, substitutability, political stability

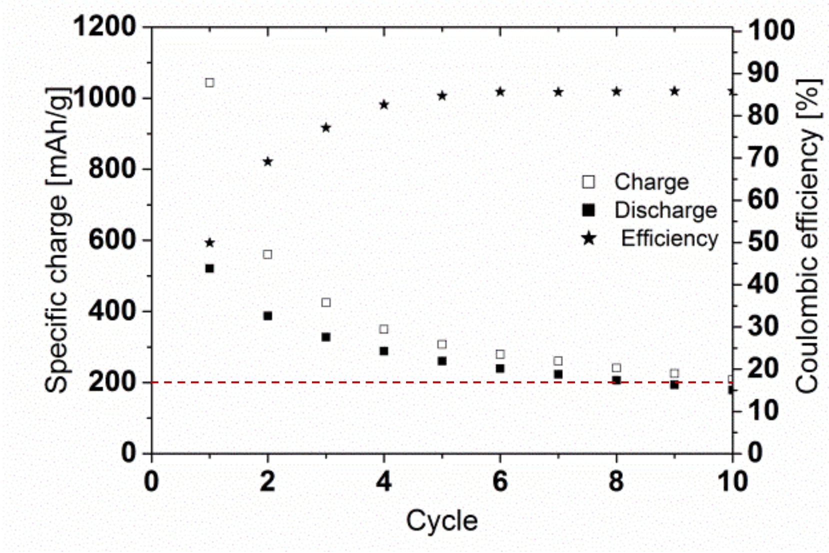
Differences Li-Ion/Na-Ion Batteries

Standard electrode formulation

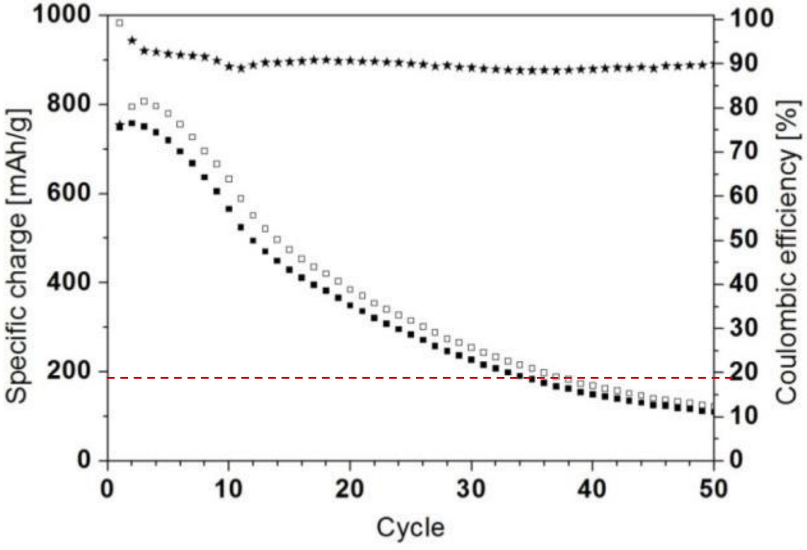
- ● 80% active material
- • 10% conductive additive (Super P)
- ∿ 10% **poly(vinylidene) difluoride (PVDF) binder**



Sn electrode (PVDF binder)



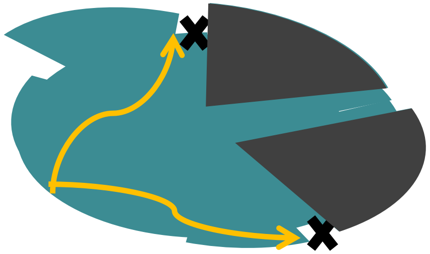
Sn electrode (CMC binder)



Know-how of LIBs cannot be applied to NIBs ☹

Alloys: Volume Expansion Challenge

Underlying Problem:



Huge Volume Expansion

↓

Pulverization of Electrode

Loss of electronic contact

Dead weight material

Alternative → Alloy materials such as MSn_2

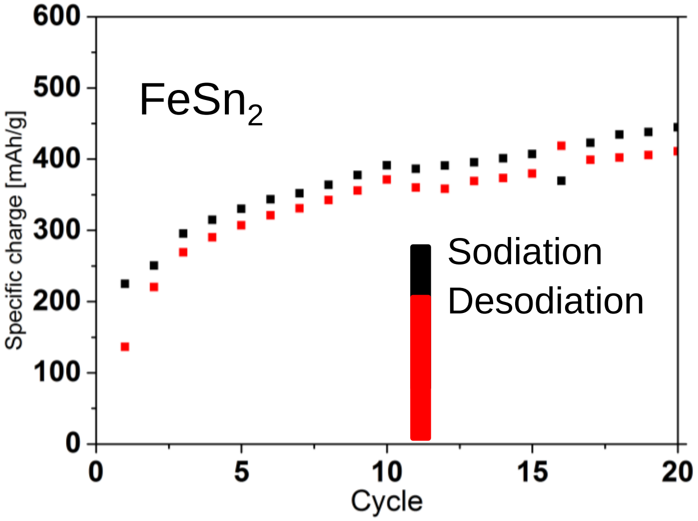
Buffer volume changes by alloying <u>active metal</u> with <u>inactive metal</u>

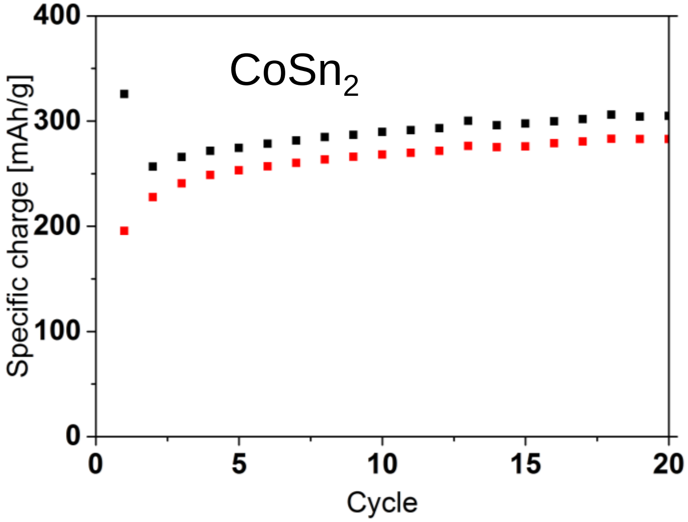
(Sn) (M = Co, Fe, Mn)

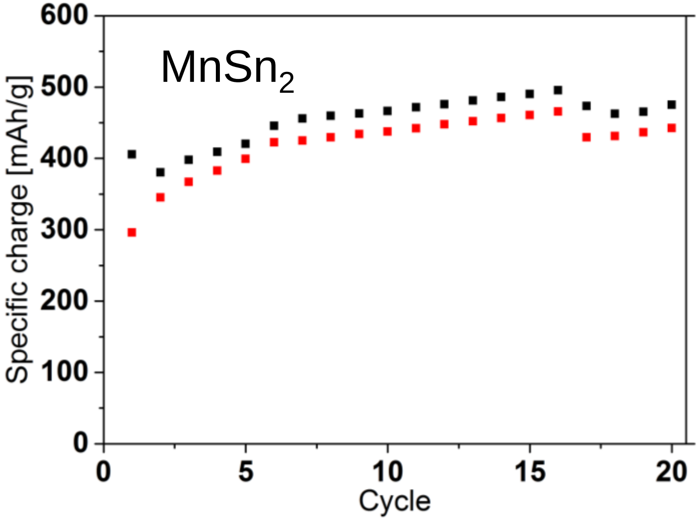
$Na_{15}Sn_4$ alloy

Don't alloy with Na

Electrochemistry of MSn_2

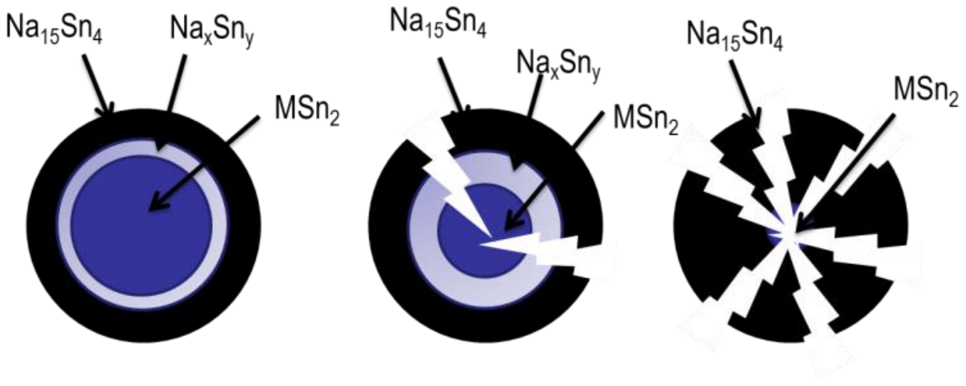






Constant increase of the specific charge

→Possible “activation” mechanism?



Conclusion

There is lot of fun when doing research on batteries!

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http://www.psi.ch/lec/electrochemical-energy-storage