Helmholtz Institute Ulm
Electrochemical Energy Storage

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Electrochemical Energy Storage beyond Li Technology – Challenges and Perspectives

DPG Tagung, Bad Honnef, 2017

Content

- Introduction HIU
- Motivation for the topic
- New storage concept for Li ions
- Post-Li Systems
- Secondary Mg sulfur cells
- Organic cathodes
- Outlook

The Helmholtz Institute Ulm and its mission

HIU was founded on Jan 17, 2011 as a future

National Center of Excellence for Battery Research

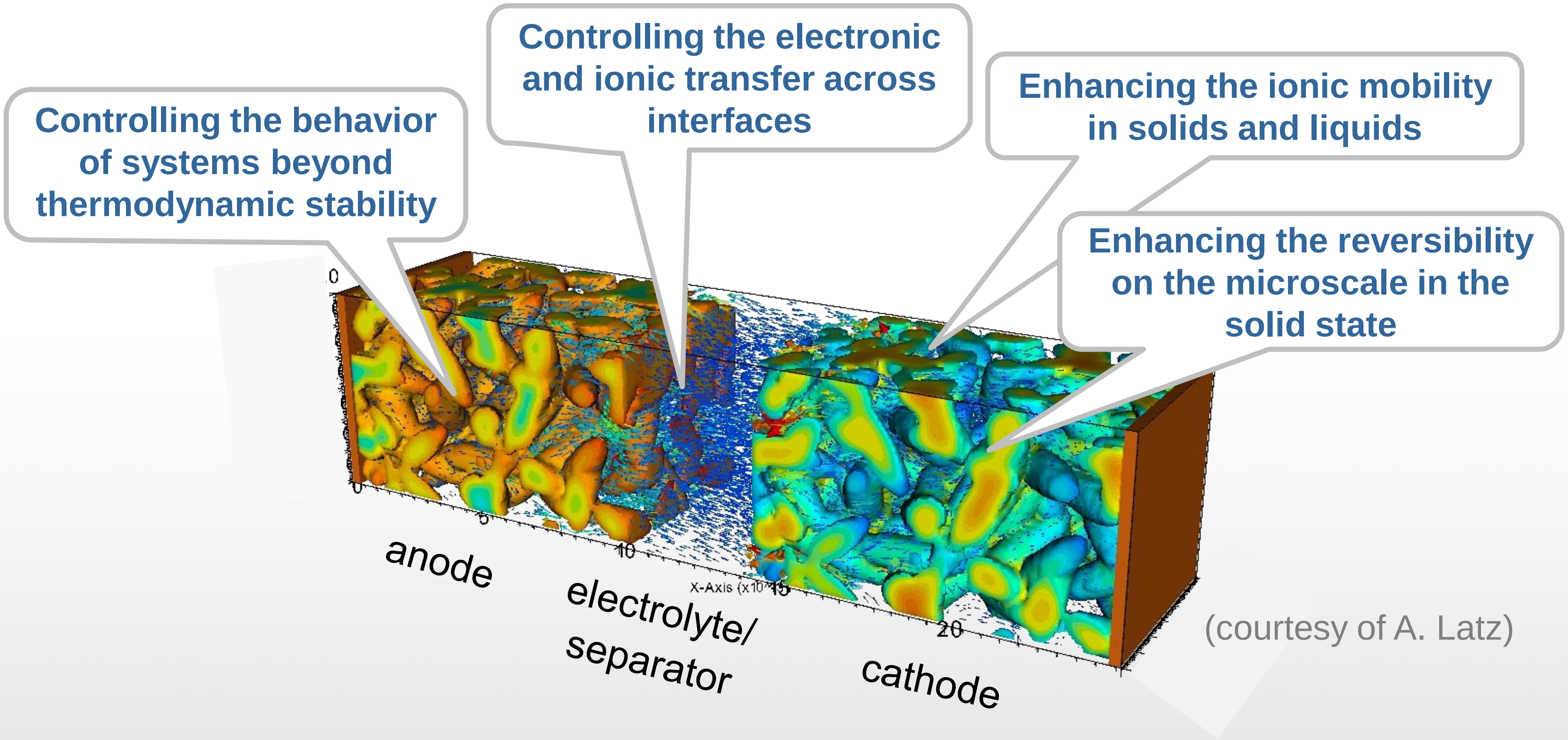
- Its mission is **application-oriented basic research on new materials and concepts for electrochemical energy storage**.
- Selected expertise is combined of all four partners, integrating research activities in the areas:

Electrochemistry – Materials – Theory – Methods – Systems

- research is integrated in the application-oriented programmatic research of the Helmholtz Association (Research Area ENERGY).

2016: 130 publications on Li (92) and post-Li (38) topics;
work was presented on 12 covers of international journals

- Scientific roadblocks / grand challenges are adressed
- Systematic, rational approach leading to knowledge base and model development



Research Topics at HIU

	Metal Deposition & Interfaces	Insertion Materials for Li	Li based conversion materials and alloys	Post-Li systems
Electrochemistry				
Materials				
Theory				
Methods				
Systems				

HIU New Building

Location:	Campus Ulm University
Labs & offices:	2.500 m^2
Staff:	about 110 employees (69 FTE) including 21 PIs
Inauguration:	31. Oktober 2014
Total cost:	13 Mill €

Battery research at Ulm

ca. 300 employees at Ulm

- Fundamental electrochemistry
- Surfaces/Interfaces
- theoret. modelling
- System modelling

- New Storage Concepts
- New Materials
- Modelling
- Systems

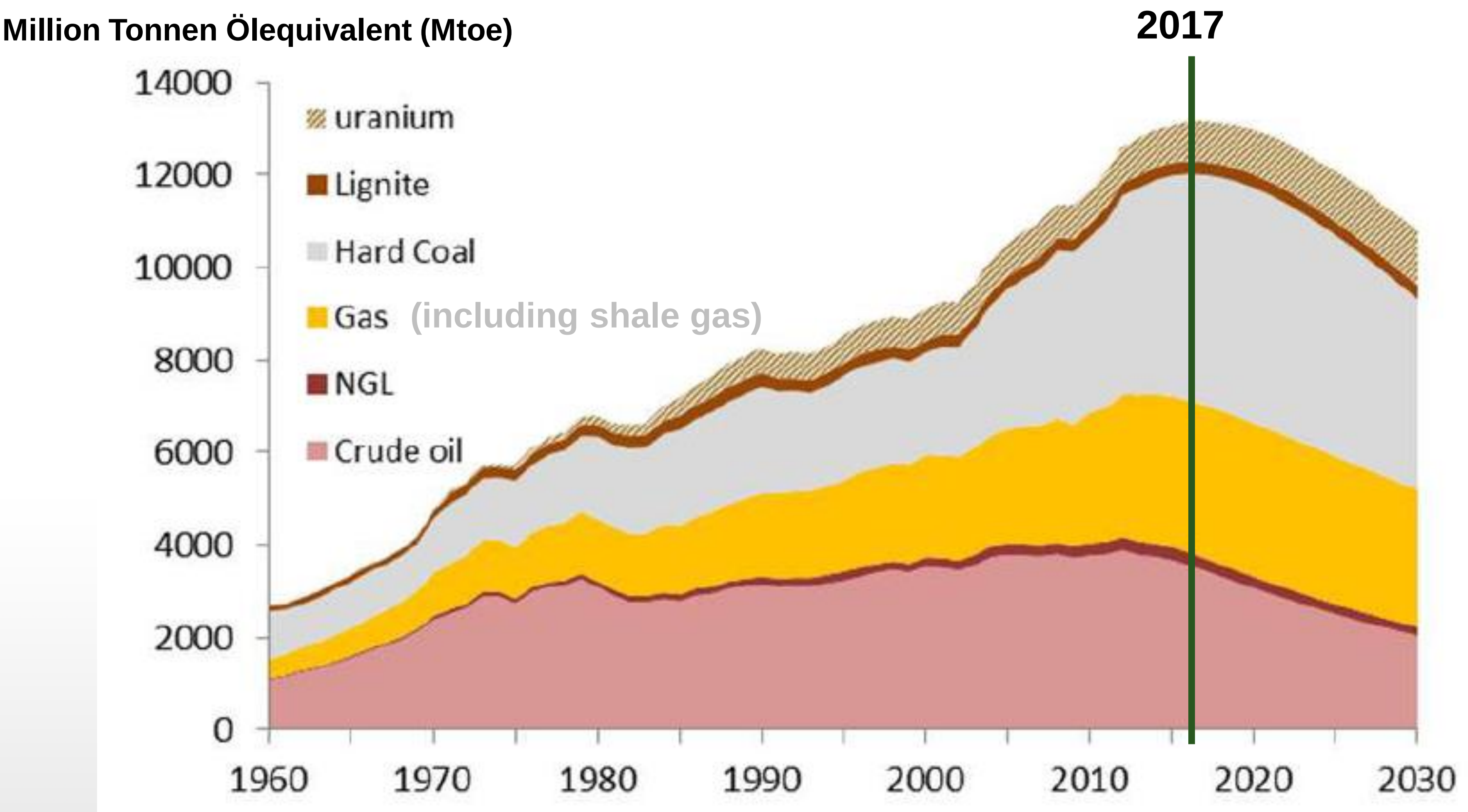
e-Lab Ulm

- Biggest experimental cell manufacturing line
- Materials upscale
- Safety

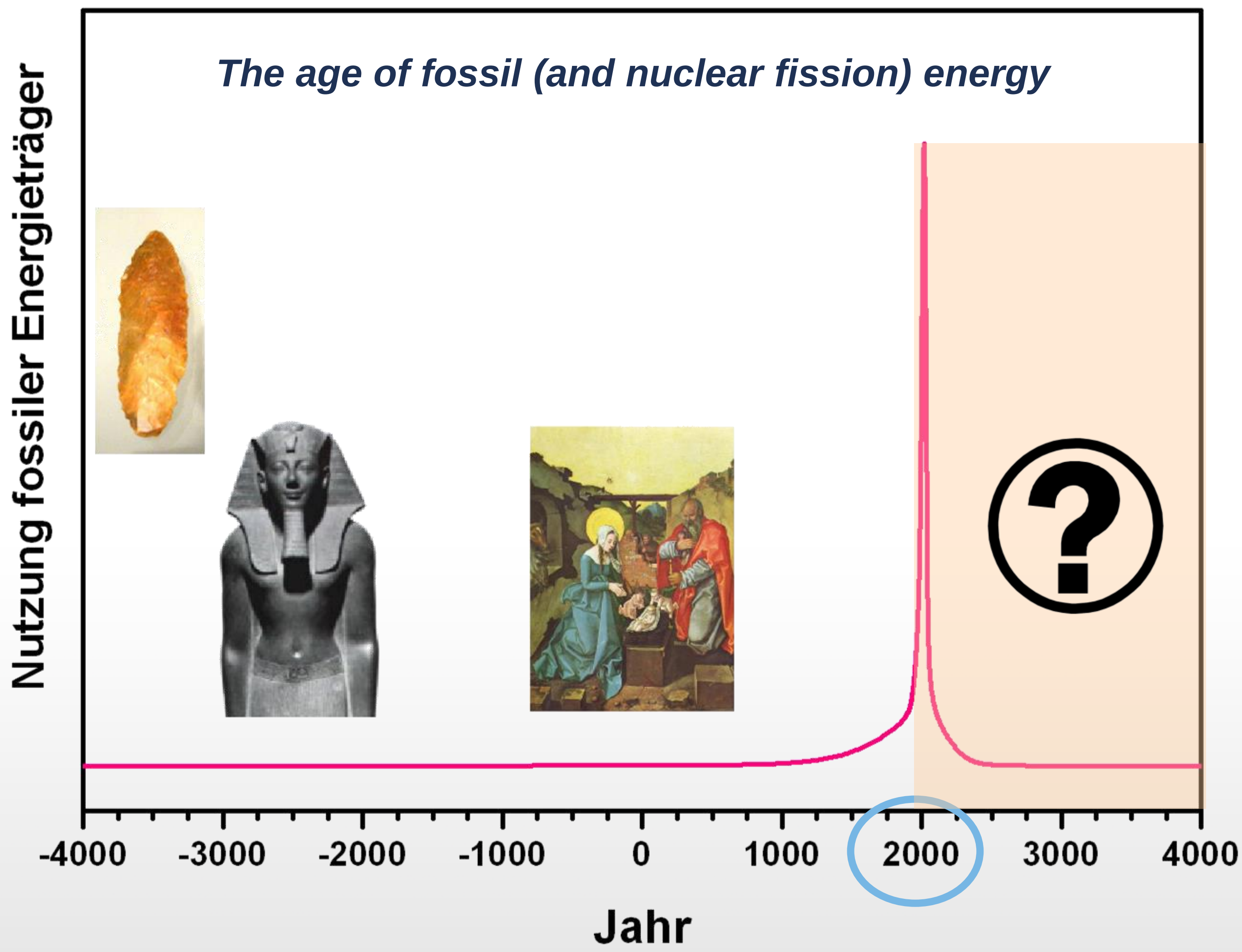
Ulm in 2016:
205 publications on batteries, including 116 on Li ion and 40 on post-Li systems

Energy Transition and Energy Storage

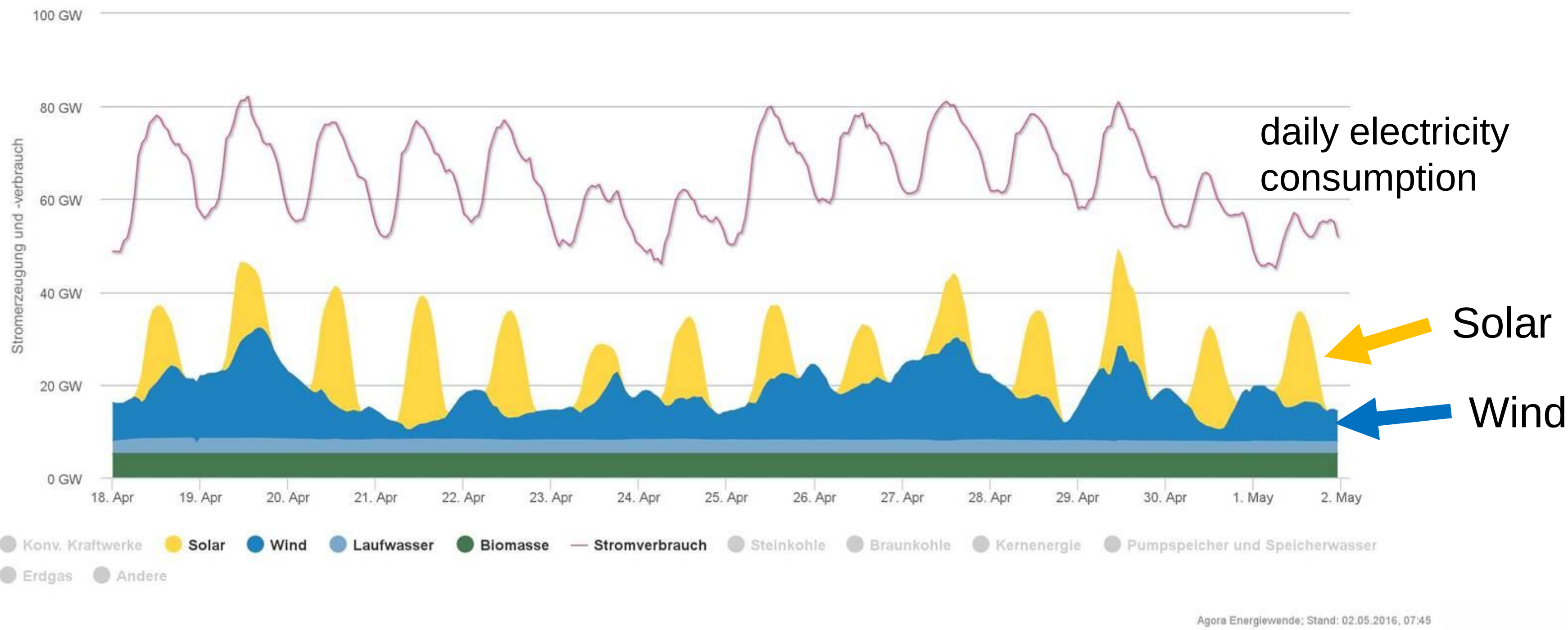
Weltweite Erzeugung von nicht-erneuerbaren Energieträgern



📖 **EWG, Fossil and Nuclear Fuels – the Supply Outlook (March 2013)**


The age of fossil (and nuclear fission) energy
Nutzung fossiler Energieträger
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000
Jahr
?

Why storage and which type?



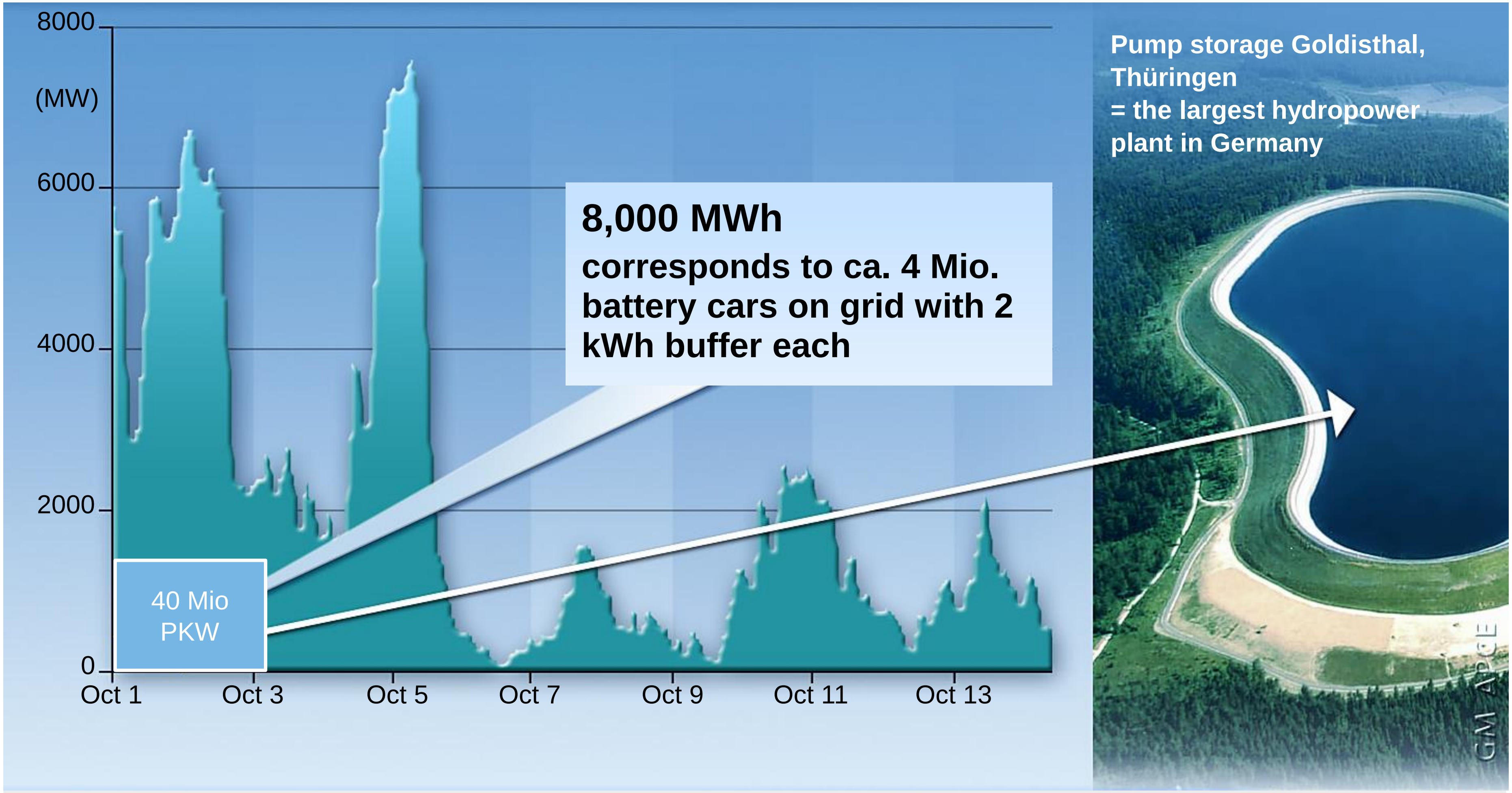
- **short-term** storage → grid stabilization (fly wheels, capacitors)
- **hourly** storage → distriution of peaks over the day (pump storage, Batteries)
- **daily-/weekly** storage→ seasonal storage (H_2 in caverns, „power-to-gas“)

- Number (2015): 26.772 turbines[1)]
- Power: 45 GW[1)]
  (> 27% of conventionalpower plant capacity)
- Electricity production 2015: 86 TWh[2)]
  (13,3% of annual consumption)

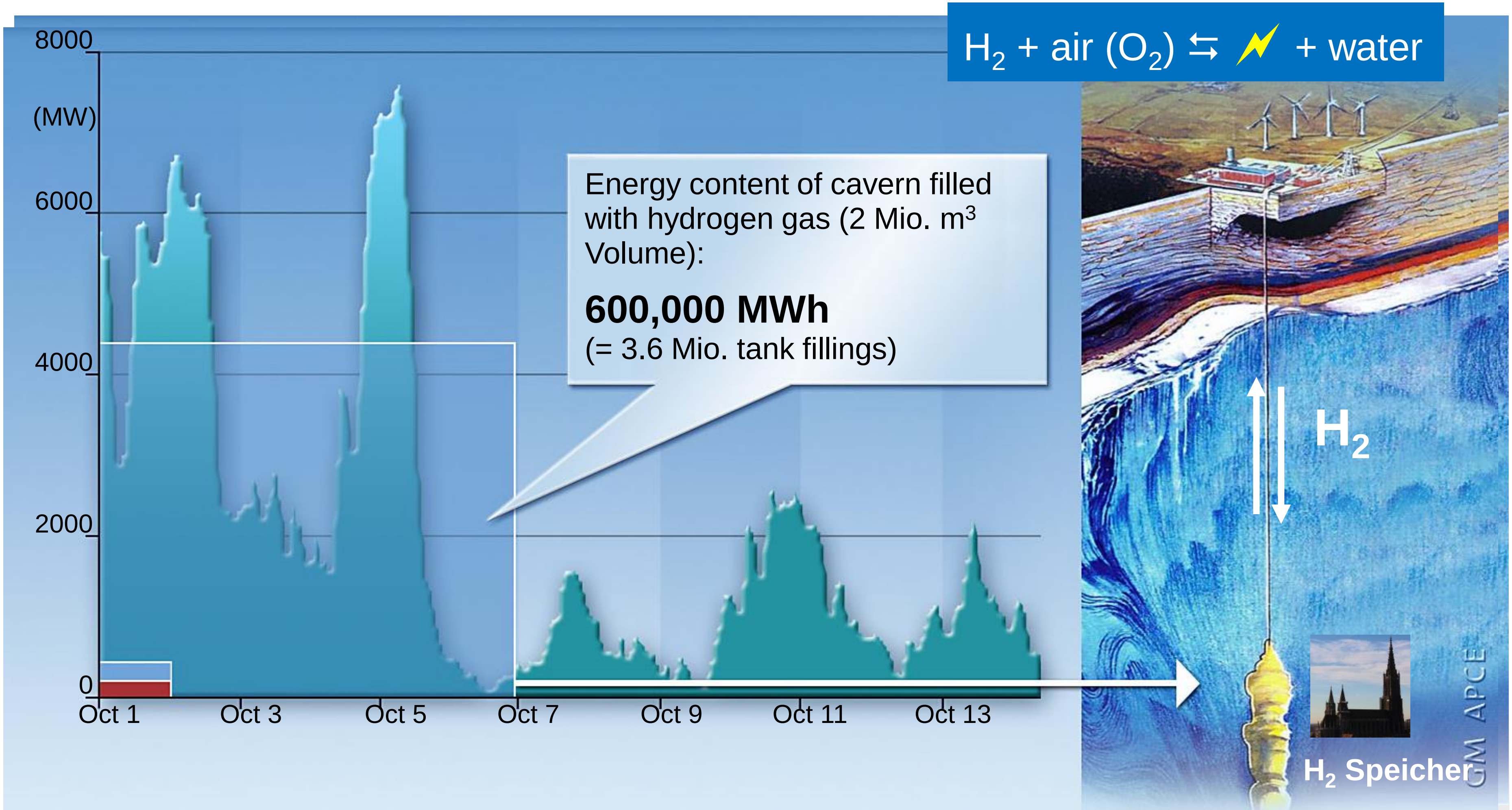
TenneT Netz:
40% of installed wind energy in Germany

1) Bundesverb. Windenergie, 2016
2) Strom-Report.de, 2016

Pumped hydro



→ **Buffer for some minutes to hours**



→ Only H_2 allows efficient storage with supply over weeks.

General situation in battery development

Speicherung Erneuerbarer Energie mit Batterien

stationär

portabel

mobil

Motivation for building “better” batteries

Helmholtz Institute Ulm
Electrochemical Energy Storage

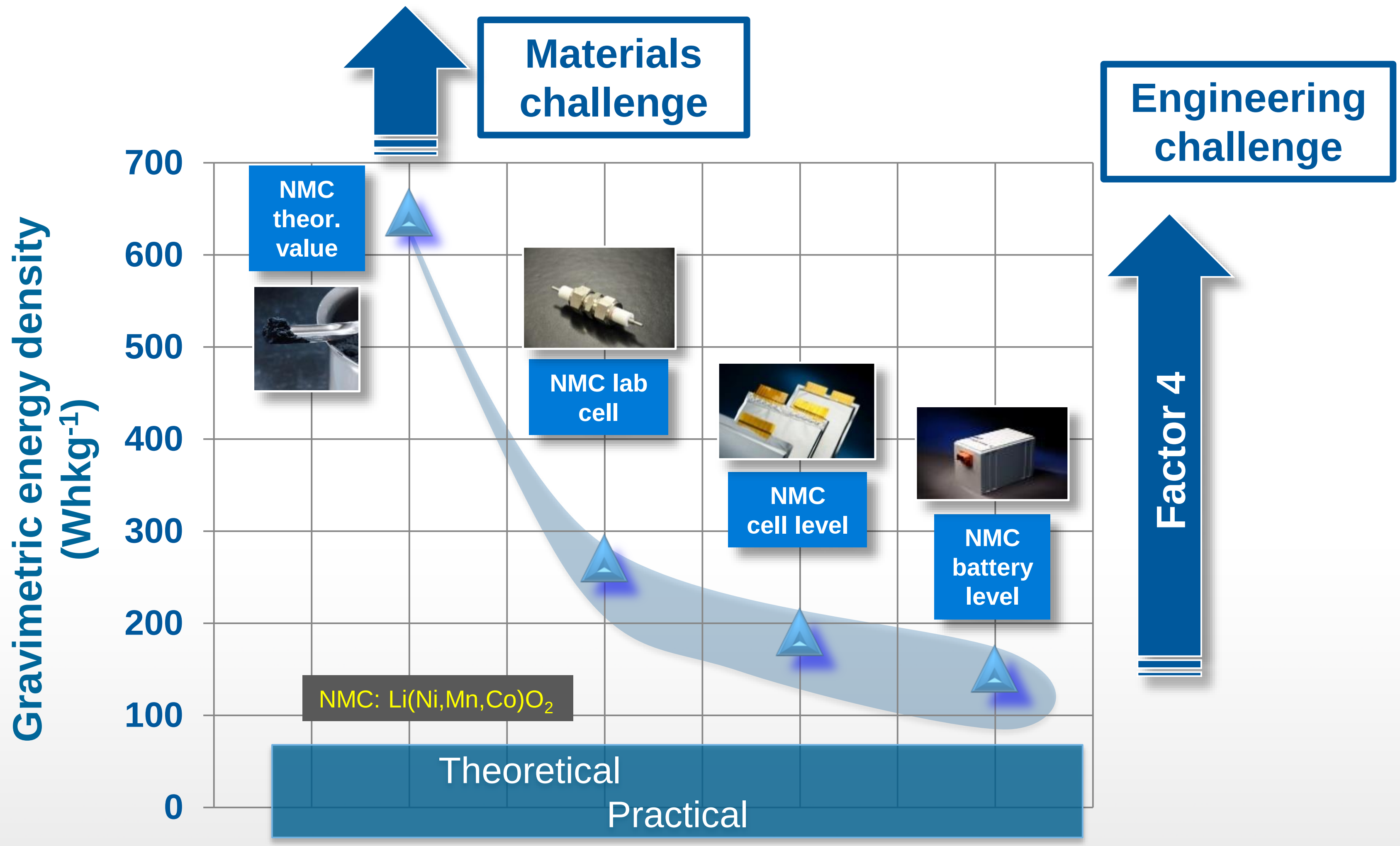
Better Batteries

- cost
- energy density
- power
- safety

Sustainability

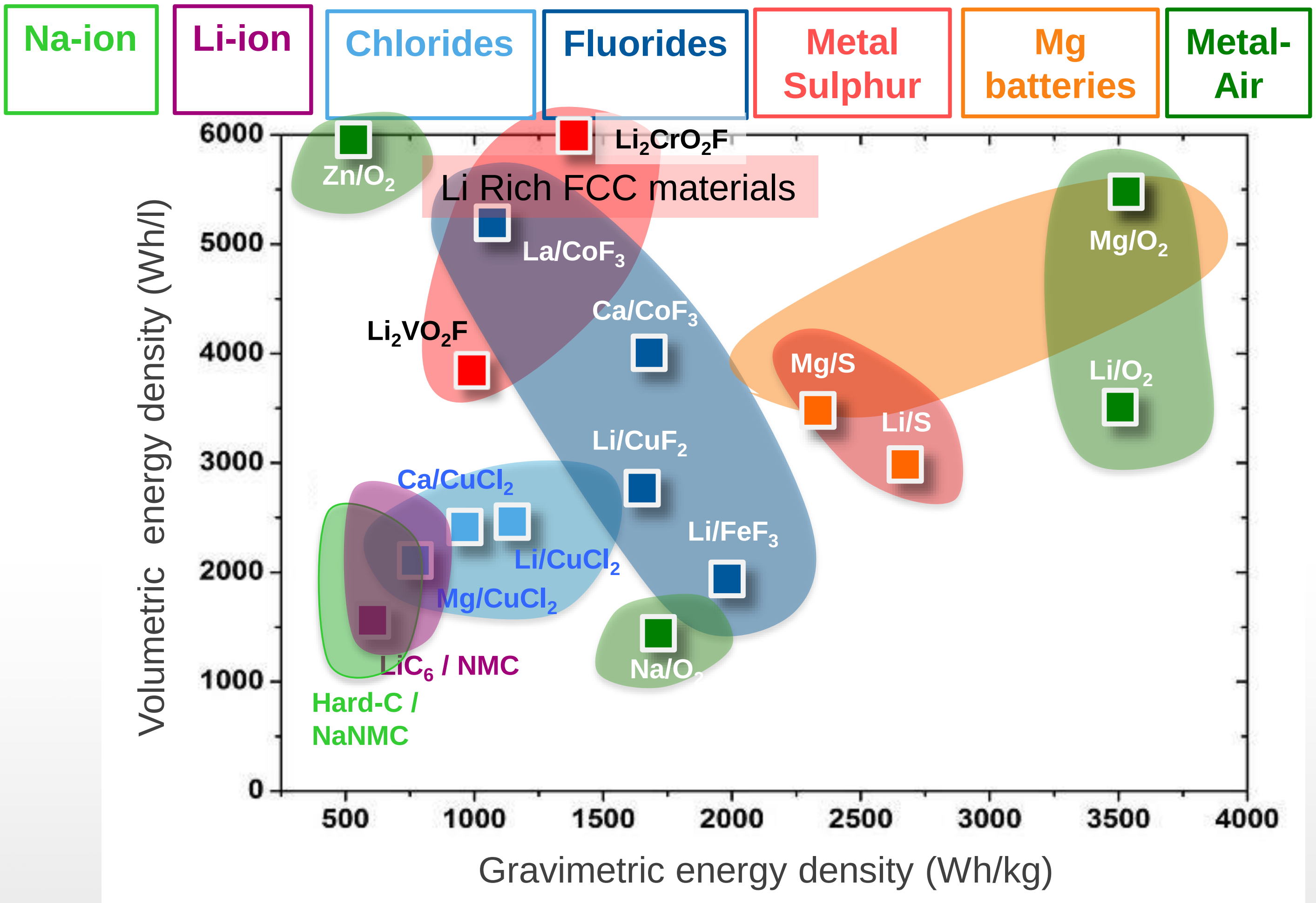
- elemental abundance
- recyclability
- ecological footprint
- toxicity

Theoretical and practical energy density



Values for NMC from: http://msdssearch.dow.com

Theoretical numbers of electrochemical couples

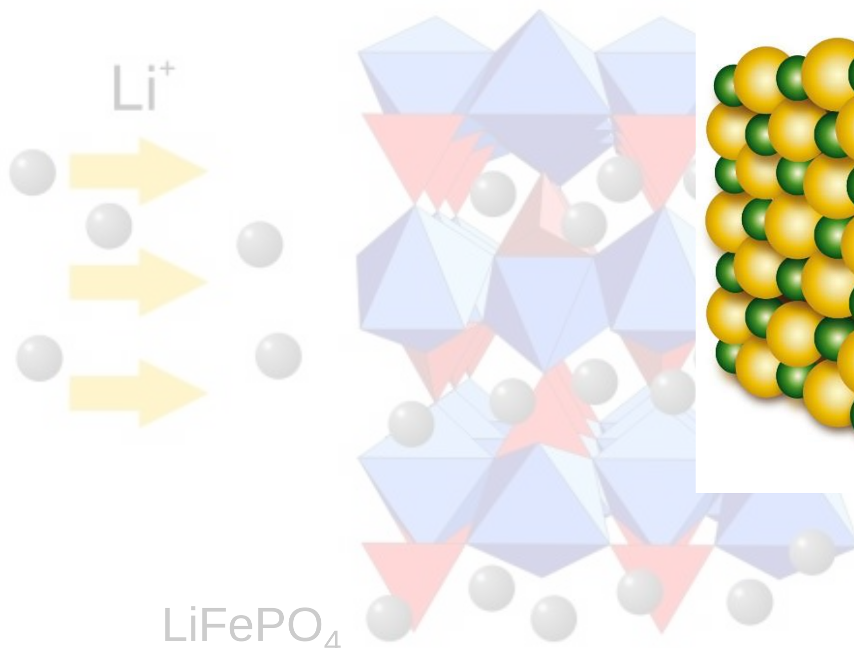


A new way for storing lithium ions

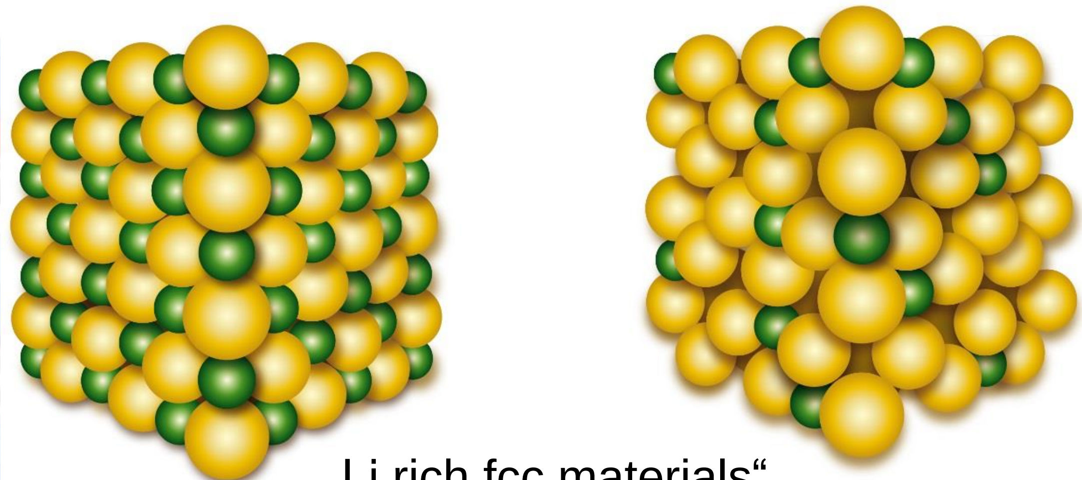
Storage on site rather than interstitial storage

Not by classical intercalation, and not by conversion, but by
storage <u>on lattice sites</u> of a cubic cation disordered material.

→ Paradigm change in storing Li



Ref. J. Molenda (2011)

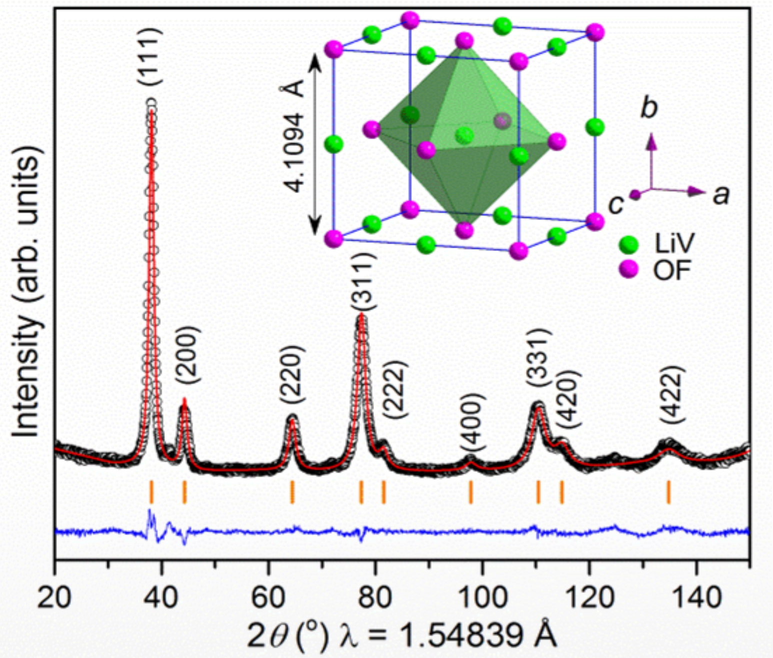


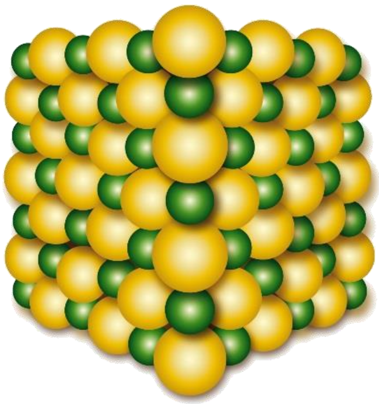
„Li rich fcc materials“

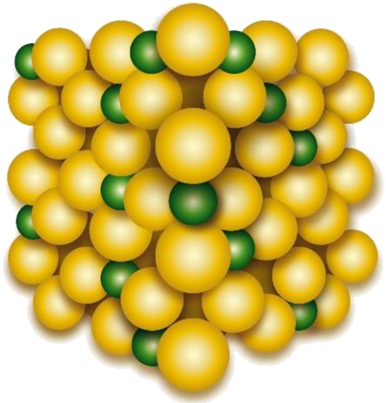
📖 R. Chen, M. Fichtner *et al.*, Adv. Energy Mater. (2015)

Neutron diffraction pattern (FRM-II, Garching)

Li sensitive

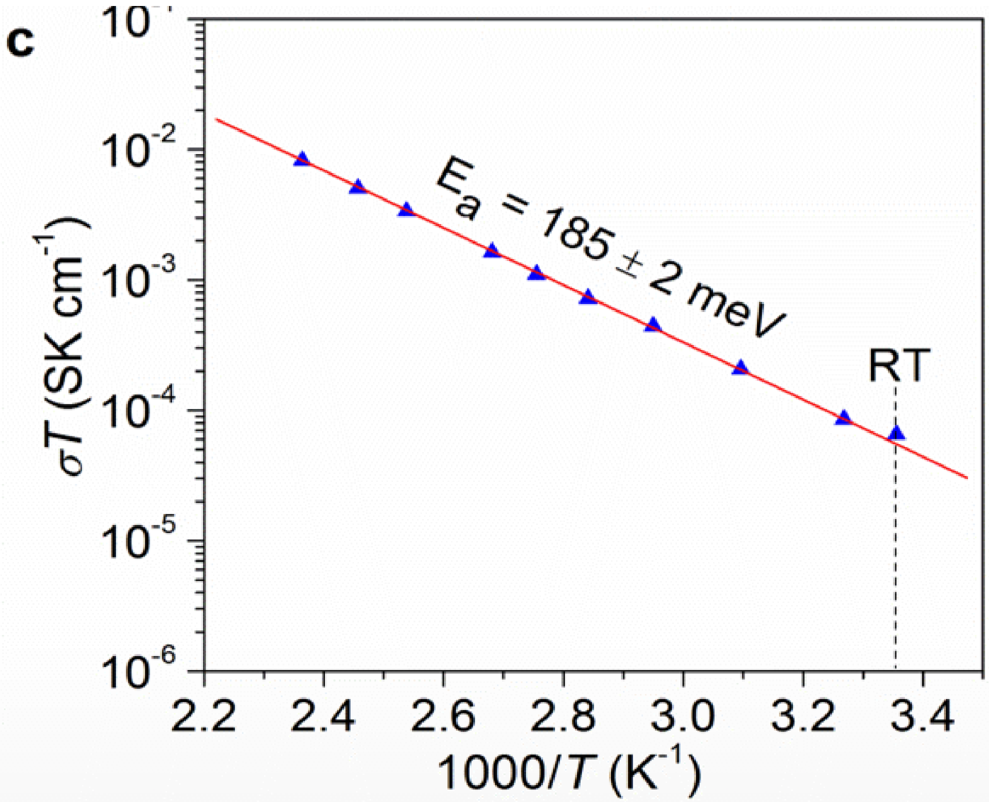






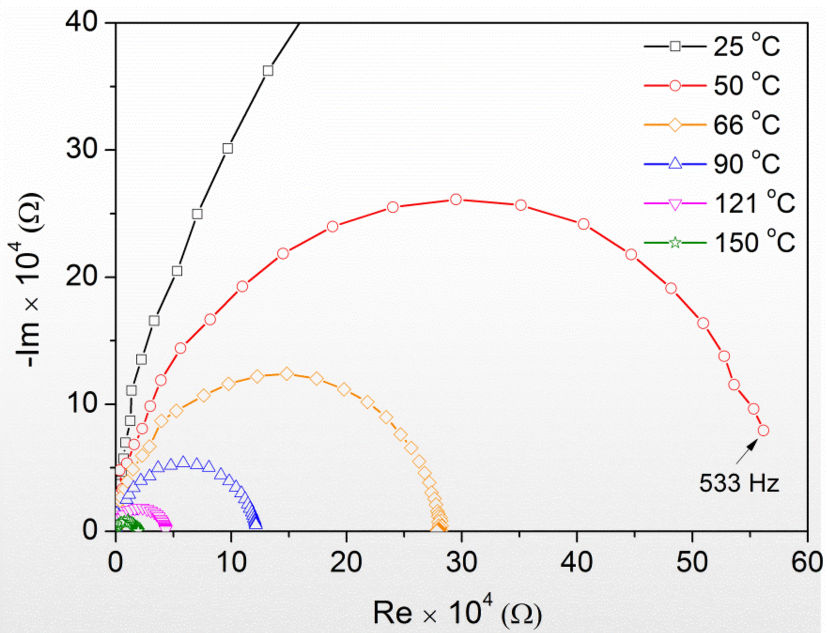
Li_2VO_2F
→ 66% of cation sites occupied by Li

When Li^+ ions are extracted from the lattice, a Li-vacancy reordering may occur to relieve the electrostatic repulsion, and to minimize the delithiation-induced lattice strain and volume change.

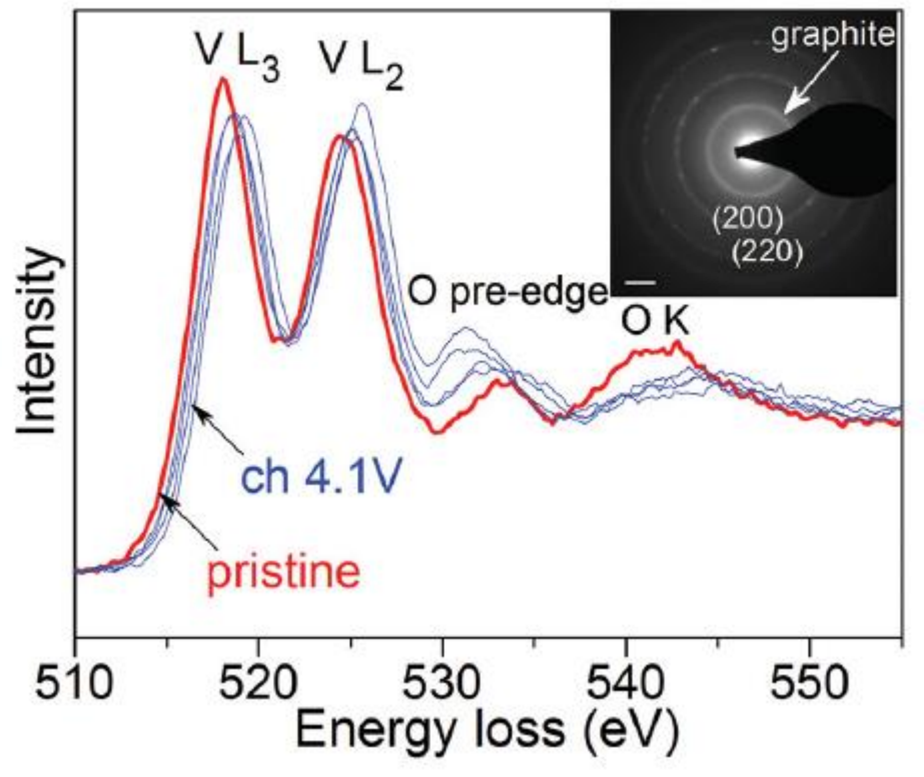


Arrhenius plot of bulk ac electrical conductivity of a Li_2VO_2F pellet at various temperatures.

E_a at 25 °C
Li_2VO_2F: 185 meV
$LiFePO_4$: 600 meV



ELNES of V L $_{2,3}$ and O K-edges of pristine Li_2VO_2F and sample **charged to 4.1 V**.

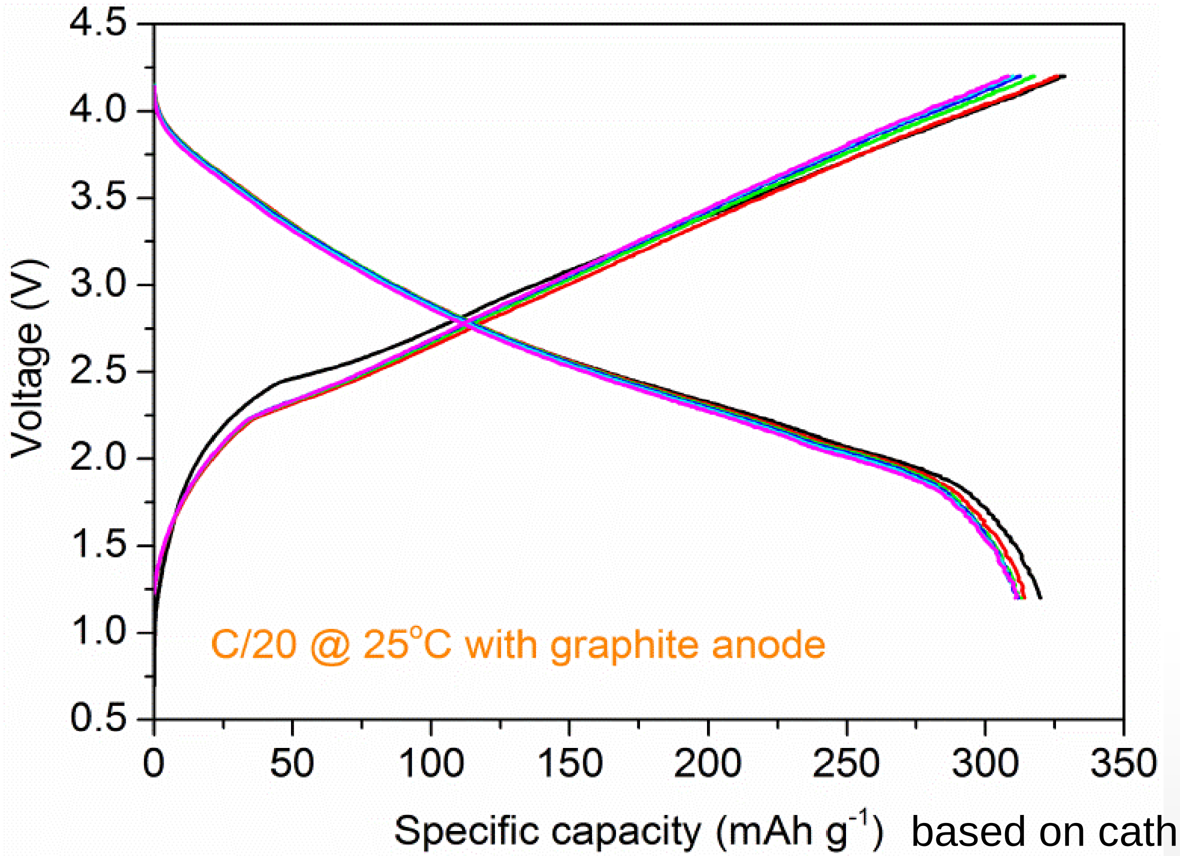


Well separated V L_3 (518 eV) and L_2 -edges (524.2 eV) owing to the V 2p–3d dipole transition.

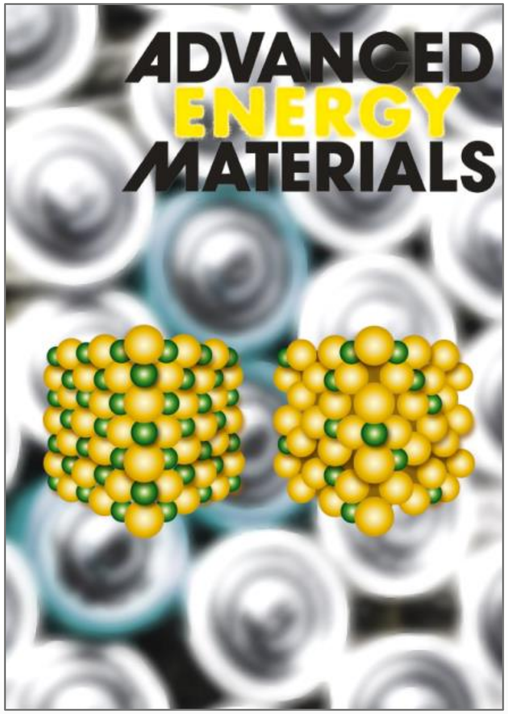
Upon charging to 4.1 V:
V L-edges shift by about 1 eV to higher energy loss (with a maximum of 519 eV for the V L_3 -edge, **typical for V^{5+}**.

(ref.: J. G. Chen et al., *Surf. Sci.* **1994** , *321* , 145)

V^{3+} ⇔ V^{5+}



based on cathode weight

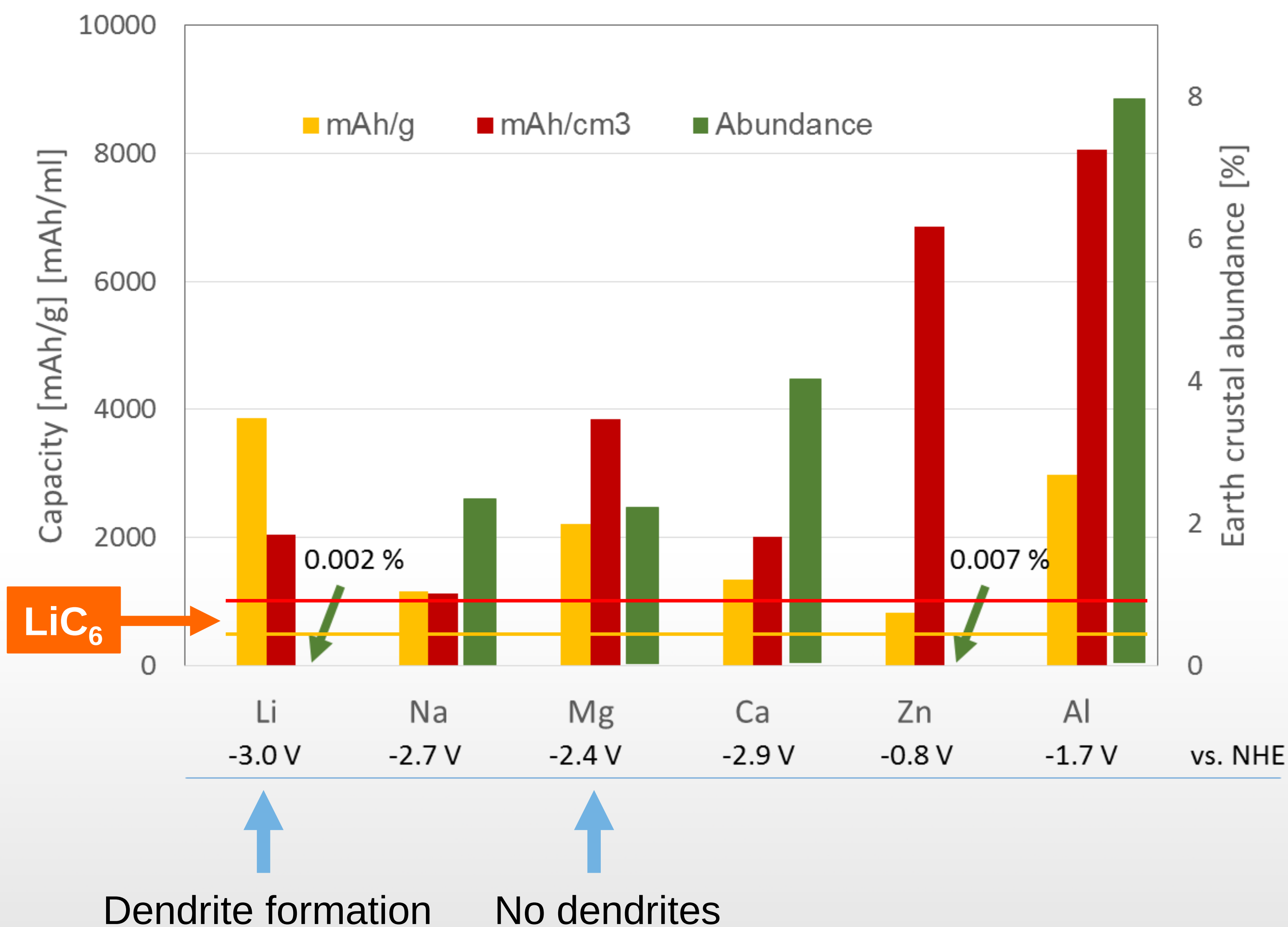


Stable slope; no voltage fading

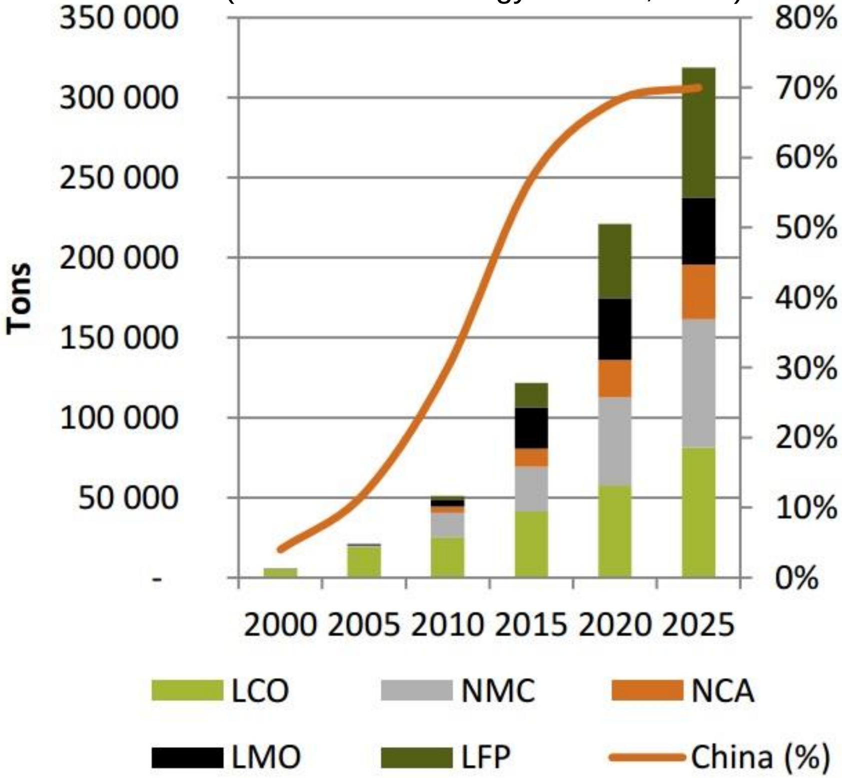
R. Chen *et al.*, Adv. Energy Mater. (2015)

Post Li ion and post-Li systems

Motivation / Energy Density, Abundance



(ref. Avicenne Energy Studies, 2016)



Active materials in cathodes, worldwide market

Strong increase in LIB production expected

Reality overhauls predictions

Cathode (currently NMC: $Ni_xMn_yCo_zO_2$)

→ Cobalt

- expensive
- co-mined with Ni
- children labour
- Co resources+reserves last for 85 Mio. battery cars

Anode:

Cell needs 100 – **160 g** Li / kWh

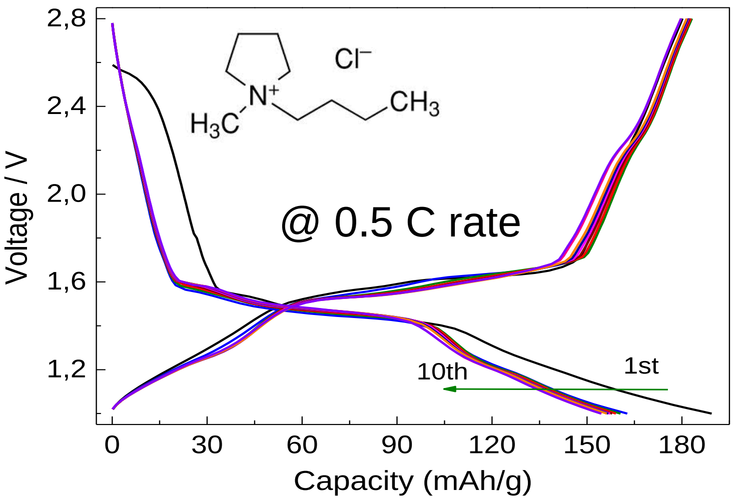
Germany: 40 Mio cars running on LIB will consume 15 x the current worldwide Li production. On the long run: will there be a cost-effective recycling?

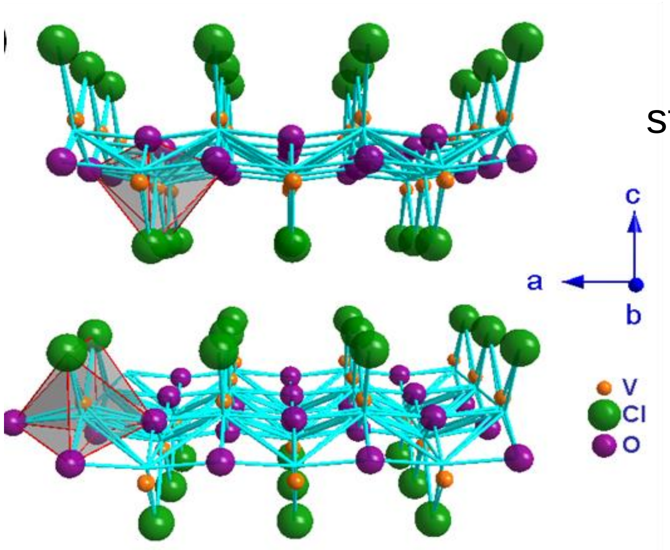
Replace cathode and anode:

Mg sulfur batteries

VOCl as cathode

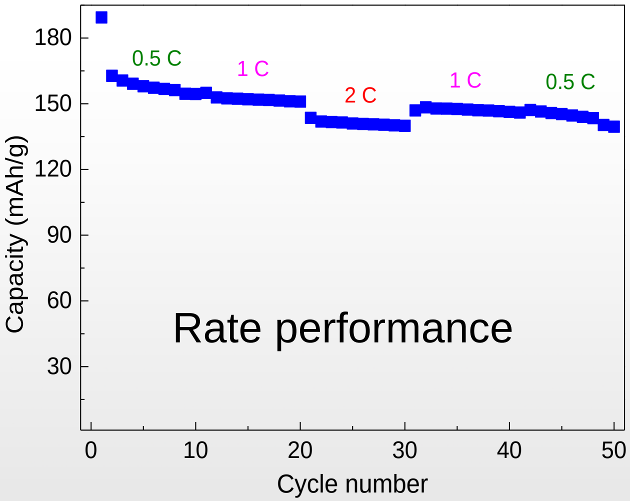
0.5 mol $PP_{14}Cl$ in PC as electrolyte





stable in air

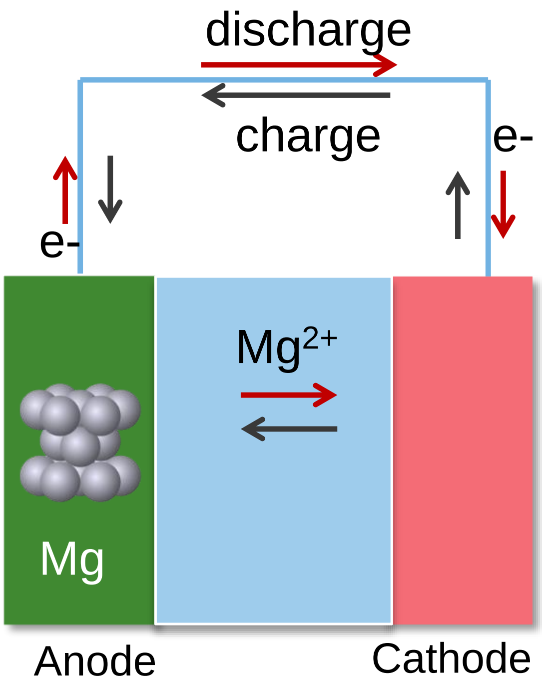
The theoretical capacity is 261 mAh g^{-1} based on 1 mol e^- transfer;
< 0.7 e^- should be kept in practice to avoid structural collapse



Mixed intercalation and conversion mechanism

P. Gao, M. Fichtner *et al.*, Angew. Chemie Int. Ed. 53 (2016) 4285

Properties of Magnesium and Lithium



	Li	Mg
Atomic weight	6.9	24.3
Ionic radius	90 pm	86 pm
Ionic charge	+ 1	+ 2
Reduction potential	- 3.04 V	- 2.37 V
Density	0.53 g/cm³	1.74 g/cm³
Gravimetric capacity	3861 mAh/g (Li) **372 mAh/g (LiC_6)**	2205 mAh/g
Volumetric capacity	**2061 mAh/cm³**	**3832 mAh/cm³**

- Mg offers good handling and operational safety.
- **No dendrite formation** with Mg metal as anode → major safety issue with Li metal batteries.
- Mg is naturally 1000x more abundant on earth than Li.
- **Mg/S offers theoretical 3200 Wh/L compared to theoretical 2800 Wh/L for Li/S**
- **But: Sulfur cathode needs non-nucleophilic electrolyte for Mg!**

Electrolyte development is key

First Electrolytes, Grignard-based

Gregory, 1988

Electrolytes:
Lewis acid-base complexes
$Mg_2Cl_3^+ [A]^-$
nucleophilic !

2000

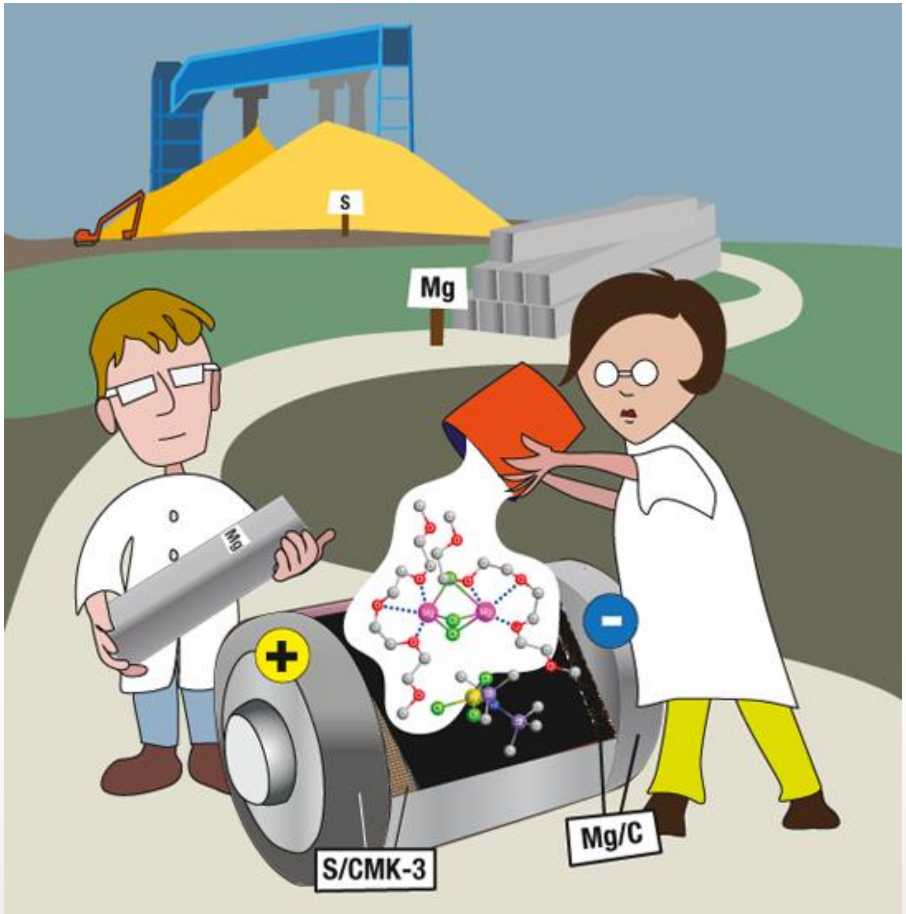
Electrolytes:
Lewis acid-base complexes
$Mg_2Cl_3^+ [A]^-$
non-nucleophilic !

2011

Electrolytes:
Mg-salts with big anions
$Mg^{2+} [A]-$
non-nucleophilic
Cl-free

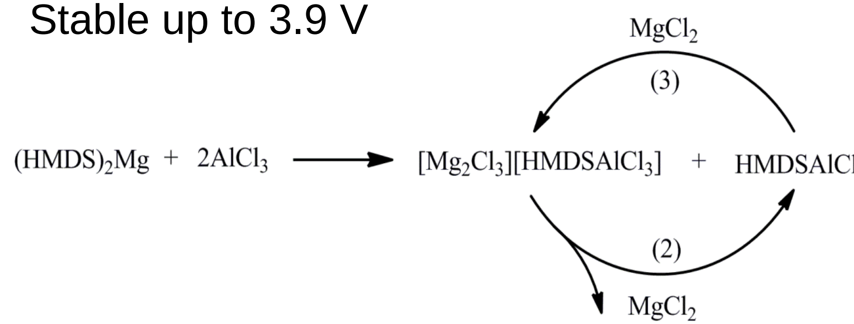
2016

Sulfur can be easily reduced and needs <u>non-nucleophilic electrolyte</u>



Adv. Energy Mater. (2015)

New non-nucleophilic and powerful electrolyte.
Simple to make from standard materials in various solvents.
Stable up to 3.9 V



- M. Fichtner *et al.*, EP 2824751A1 (2013)
- Zh. Zhao-Karger *et al.*, RSC Advances 3 (2013)
- Zh. Zhao-Karger *et al.*, RSC Advances 4 (2014)
- Zh. Zhao-Karger *et al.*, Adv. Energy Mater. 5 (2015) 1401155
- B.P. Vinayan *et al.*, Nanoscale 8 (2016) 3295

$(HMDS)_2Mg + 2AlCl_3$

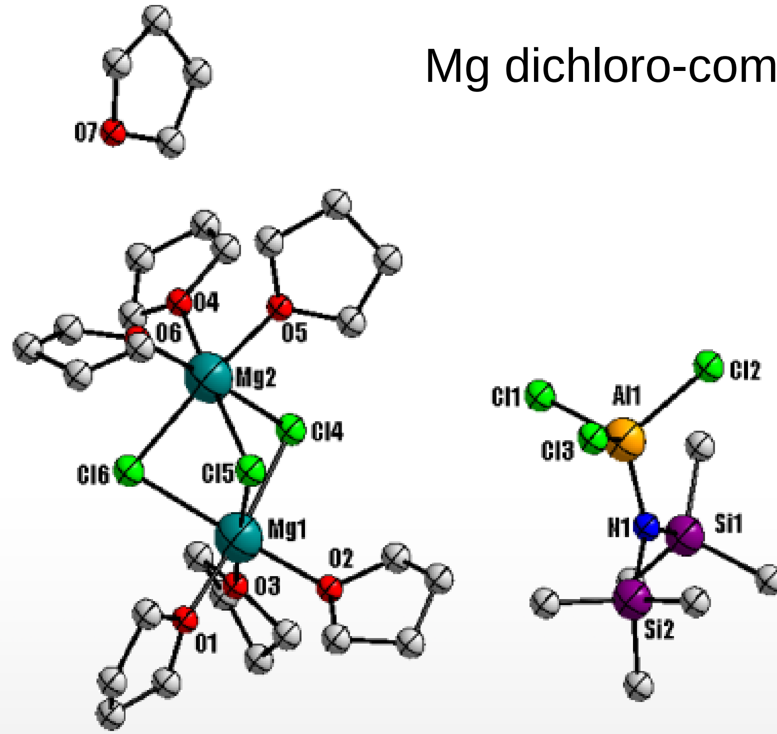
glymes, THF, IL, DME,…. →

½ $[Mg_2Cl_3][(HMDS)AlCl_3]$ + 3/2 $(HMDS)AlCl_2$

Single crystal XRD

ORTEP plot of
$[Mg_2(\mu\text{-}Cl)_3 \cdot 6THF]$ $[HMDS \cdot AlCl_3] \cdot THF$
(H atoms are omitted for clarity)

Mg dichloro-complex

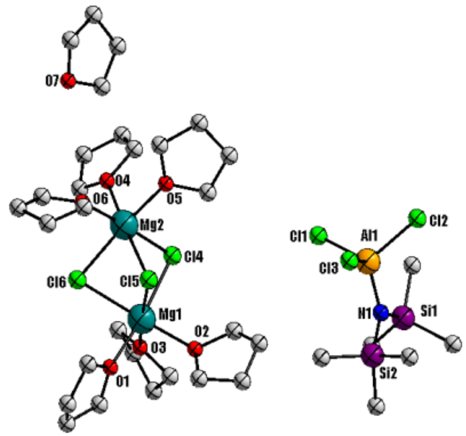


$Mg_2(\mu\text{-}Cl)_3 \cdot 6THF]^+ \cdot THF$ $[HMDS\ AlCl_3]^-$

<u>Features</u>

- **non-nucleophilic**
- **versatility w. solvents**
- **up to 2 M Mg^{2+} solutions**
- **99% electrolyte efficiency**
- **stability up to 3.9 V**
- **used *in-situ***

📖 Zh. Zhao-Karger, M. Fichtner, *et al.* RSC Adv. (2013)
📖 Zh. Zhao-Karger, M. Fichtner, *et al.*, Adv. Energy Mater. (2015)



Mg$_2$(μ-Cl)$_3$·6THF]$^+$·THF   [HMDS $AlCl_3$]$^-$

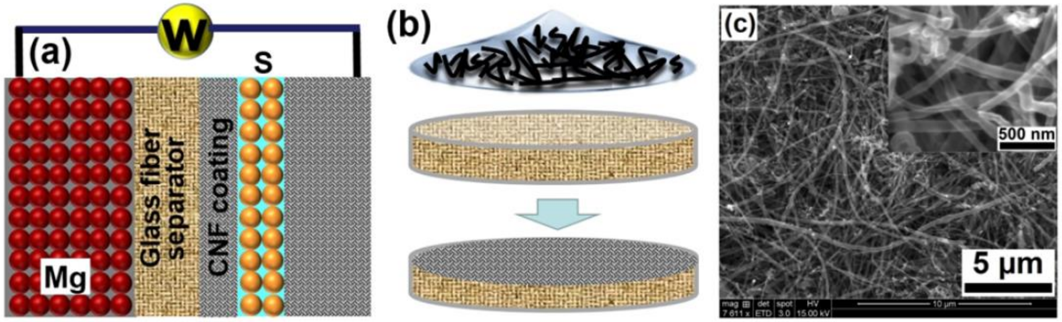
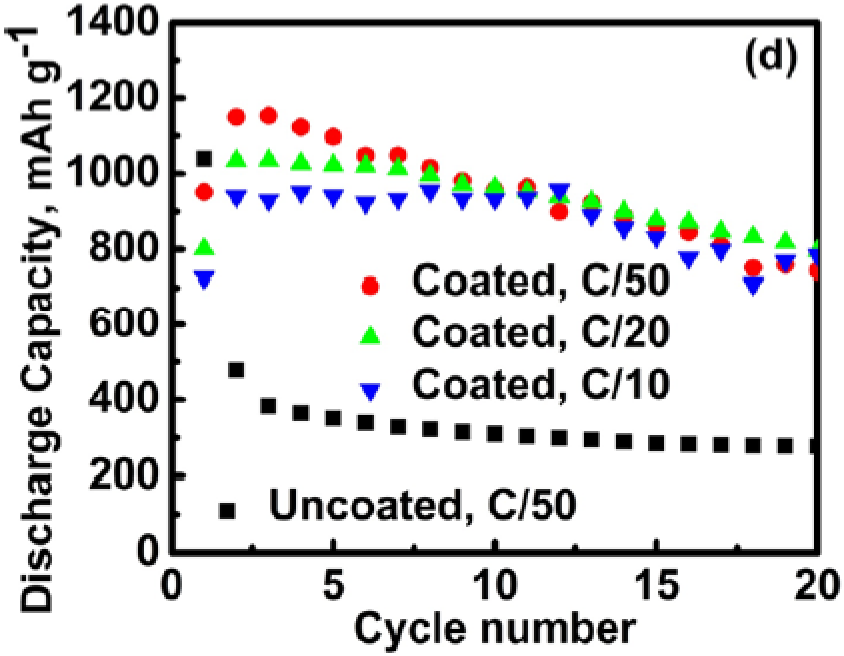


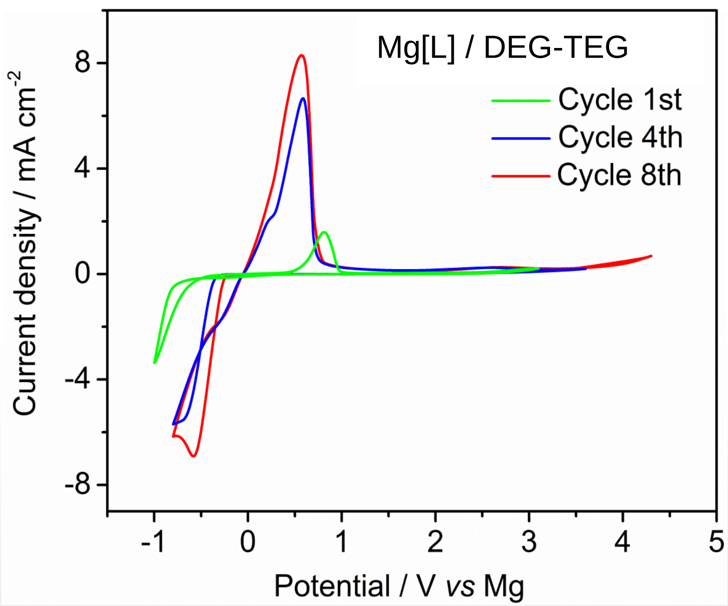
Figure 1. (a) Schematic of a Mg–S cell with an activated-CNF-coated separator. (b) Schematic of the formation of the CNF-coated separator. (c) Scanning electron microscopy image of the CNF coating (inset is a magnified image).

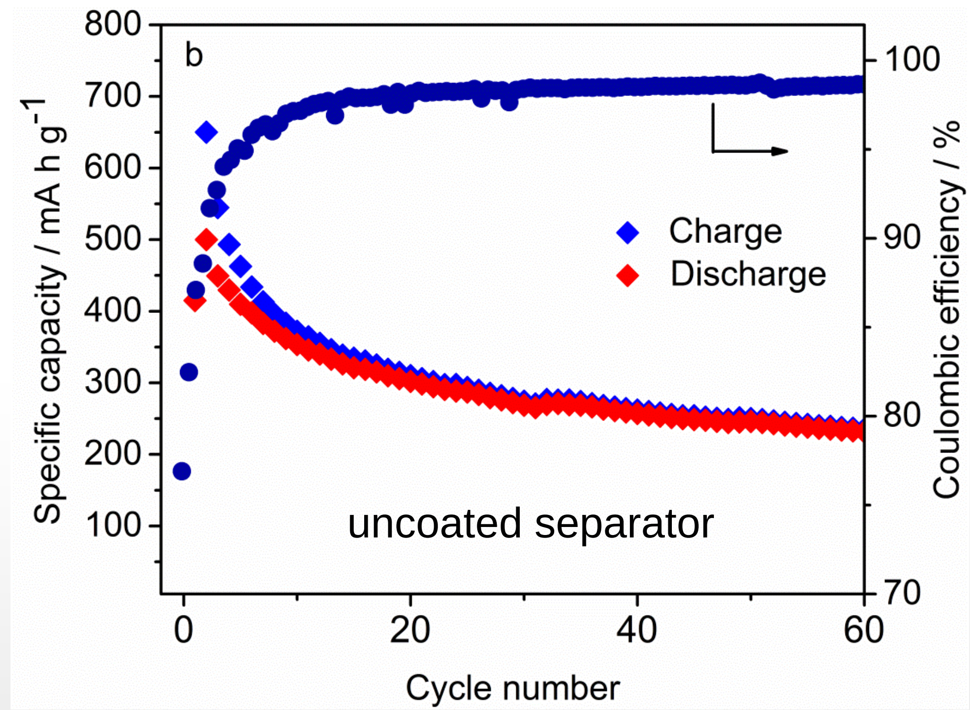


📖 A. Manthiram *et al.*, ACS Energy Lett. (2016)

📖 Zh. Zhao-Karger, M. Fichtner, *et al.*, Adv. Energy Mater. (2015)

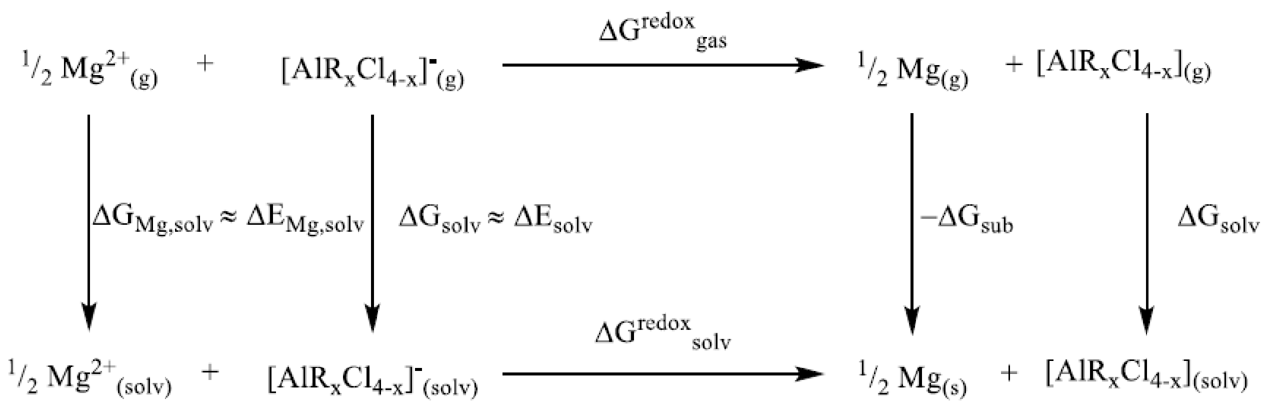
- Mg [L] with big boron-based anion, easy to synthesize
- Cl-free salt
- soluble in ethers
- non-nucleophilic
- 3.8 V stability limit
- > 98% efficiency





Zh. Zhao-Karger, E.G. Bardaji M. Fichtner, J. Mater. Chem. A (2017) online

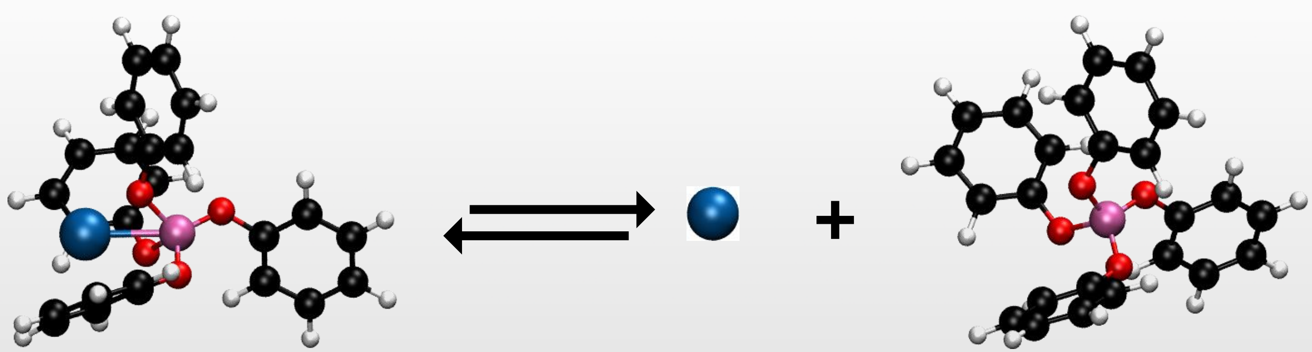
- Improved strategy for calculating redox potentials



📖 Z. Zhao-Karger, J. E. Mueller, X. Zhao, O. Fuhr, T. Jacob, M. Fichtner, *RSC Adv*., 2014, 4, 26924

Study association energies of Mg-ions with candidate anions in solvents

→ screening for anion-solvent interactions (avoid stronger interaction → reduced kinetics)



Major issues to be solved

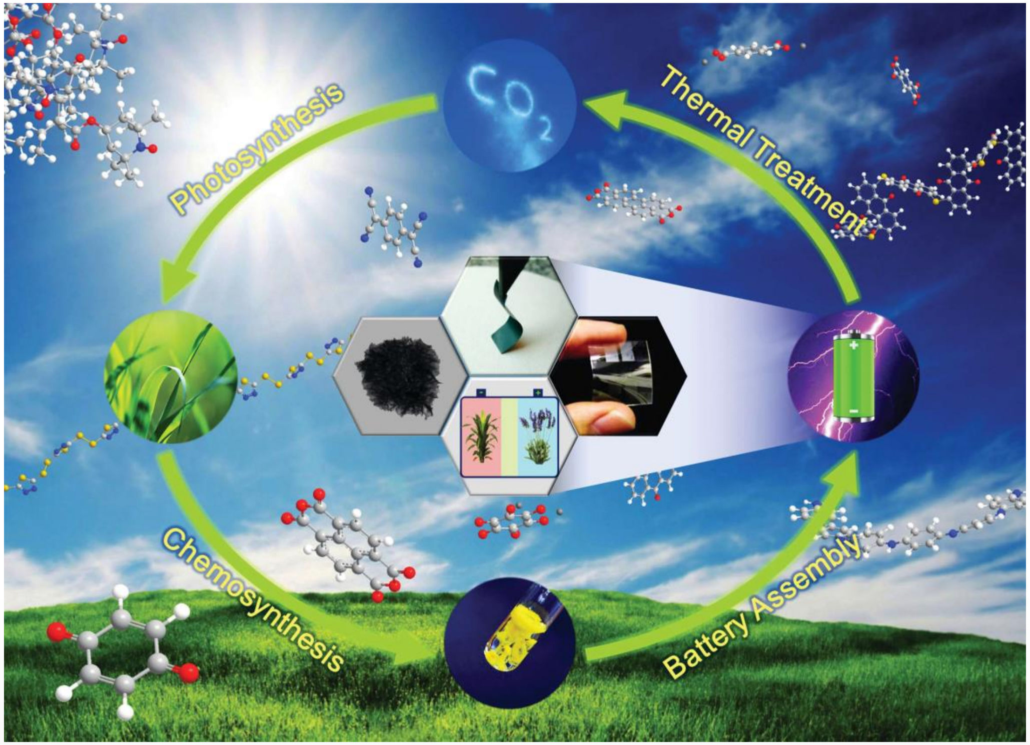
- Kinetic barriers / overpotentials are still too high
- Role of surface layers on Mg?

- Reversibility
- Fate of the sulfur in the system

Organic electrodes

Organic electrodes

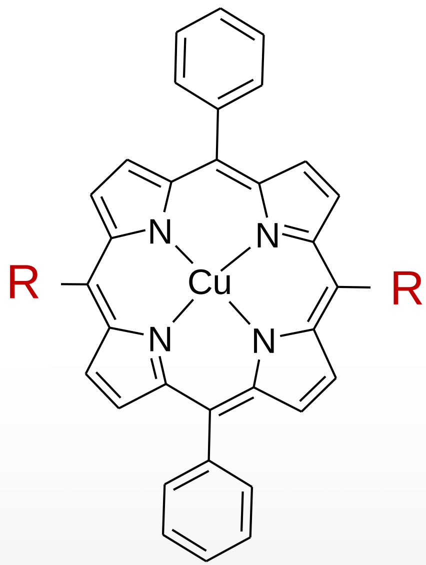
- Good theoretical capacity
- Structural diversity and flexibility
- Tunable properties
- Good safety
- Low cost
- Easy processing
- Sustainability and environmental friendliness
- Broad field of applications:
  - Li, Na and Mg based batteries
  - supercapacitors
  - redox flow batteries
  - all-organic batteries



Z. Song & H. Zhou, *Energy Environ. Sci.*, 2013, 6, 2280.

Porphyrins

A new class of highly conjugated porphyrin complex enabling high performance of rechargeable batteries



1

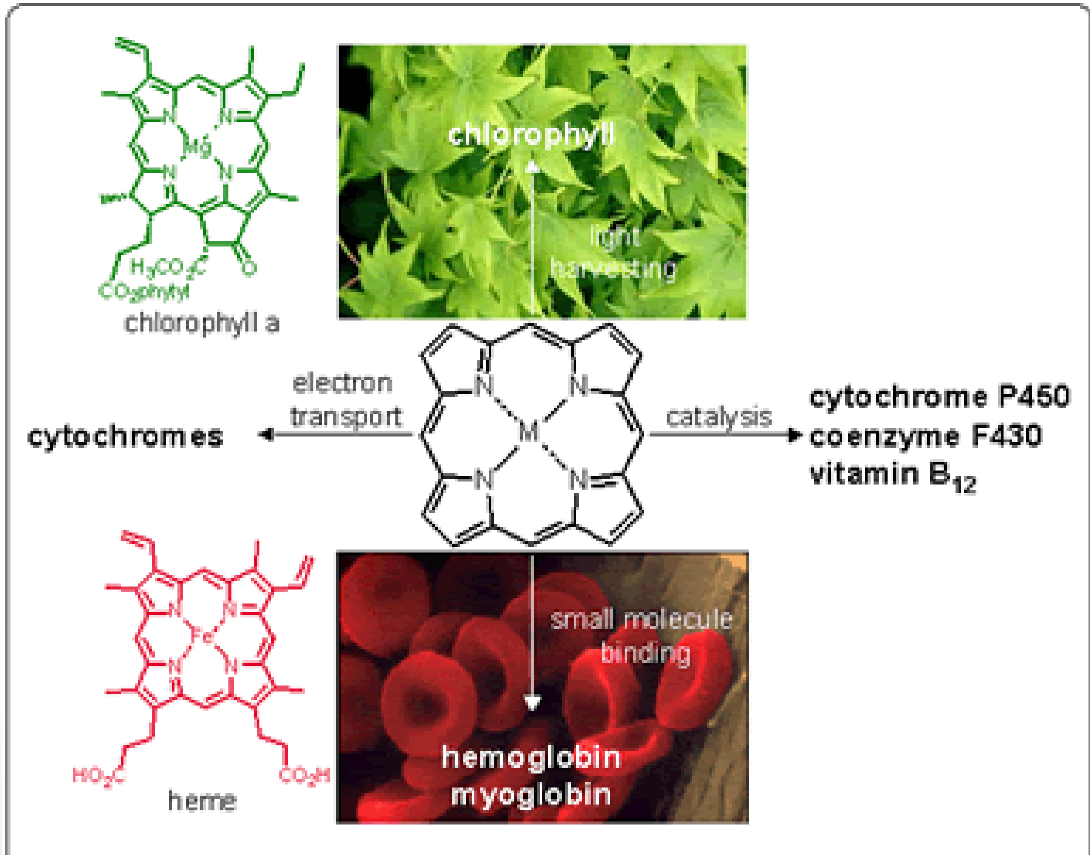
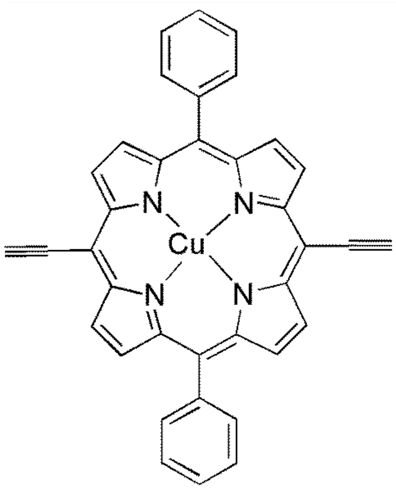
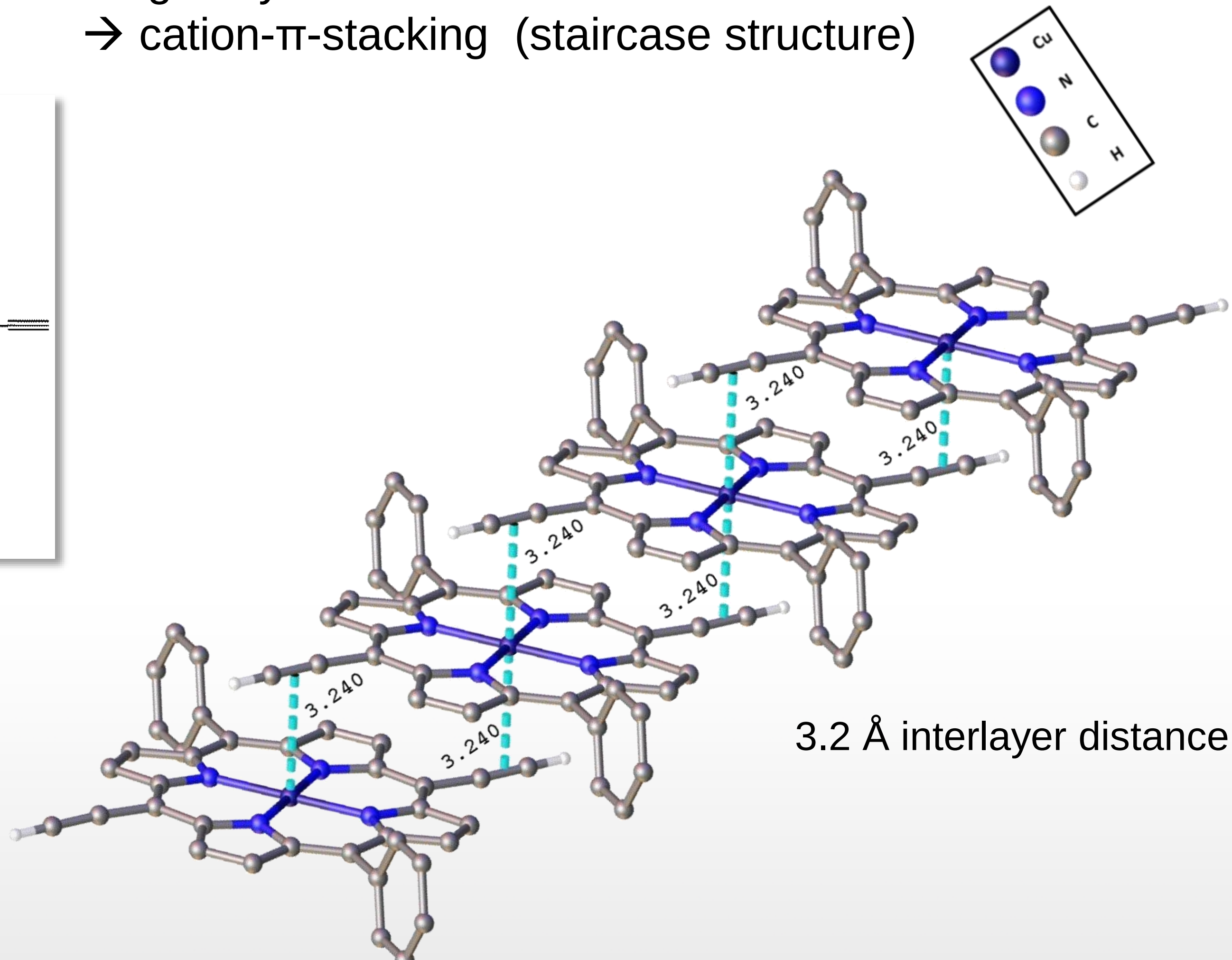


Figure 1. Diverse functions of metalloporphyrins in Nature

Hemocyanin-derived
(Molluscs, Arthropoda)
4 electron transfer from 16 to 20 π electrons; OCV vs. Li: 3.0 V

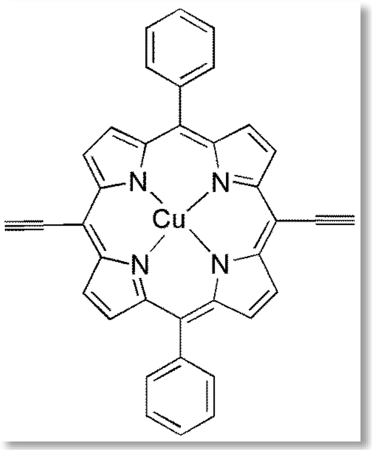
Single crystal data
→ cation-π-stacking (staircase structure)





3.2 Å interlayer distance

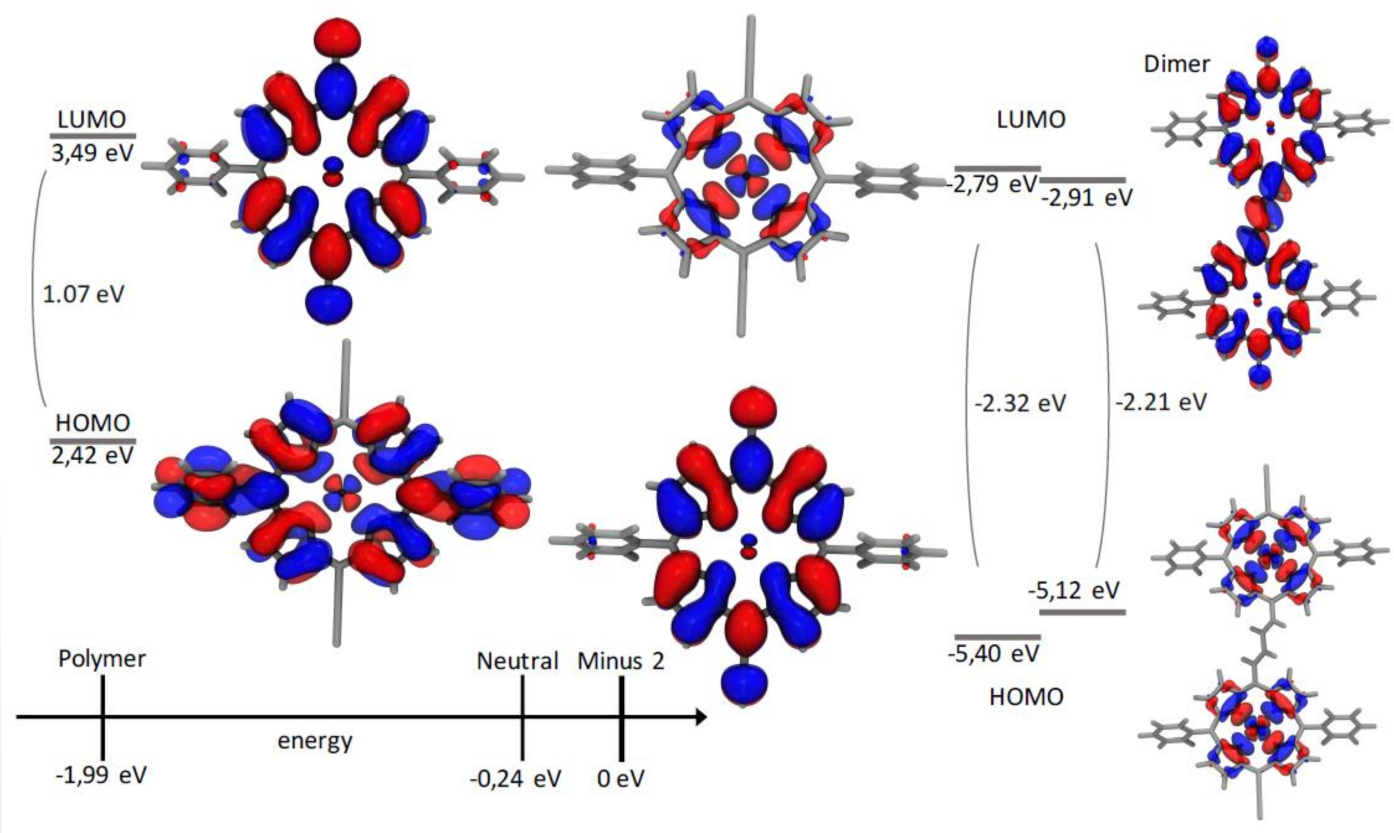
📖 P.Gao, M. Fichtner *et al.*, submitted (2017)



CuDEPP

[5,15-Bis(ethynyl)-10,20-diphenylporphinato]copper(II)

- 18 π aromatic compound
- Small HOMO-LUMO gap allows facile electrons exchange

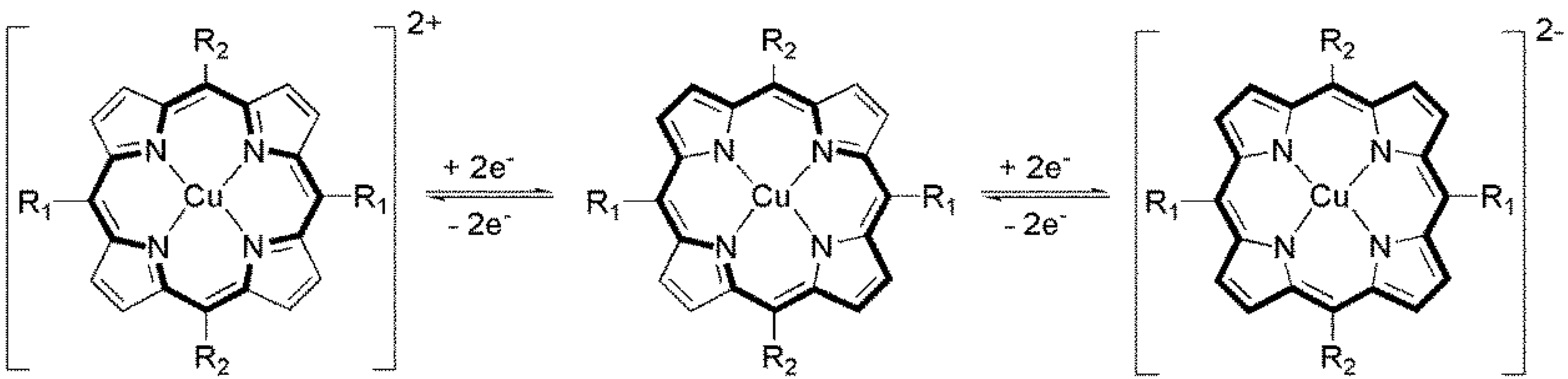


CuDEPP^{2-} **CuDEPP** **dimer**

DFT-B3LYP by J. Muller, Ch. Jung

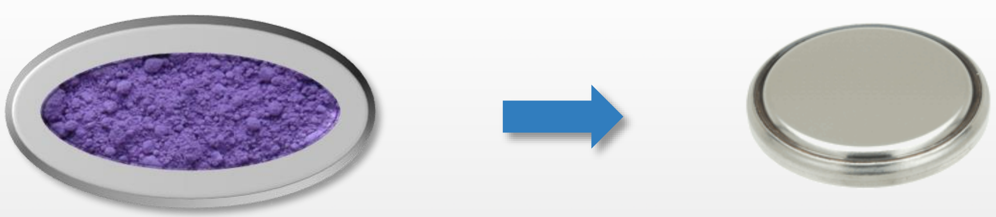
Porphyrin works as both electron donor and acceptor

Cu^{2+} center does not participate



16 π 18 π 20 π

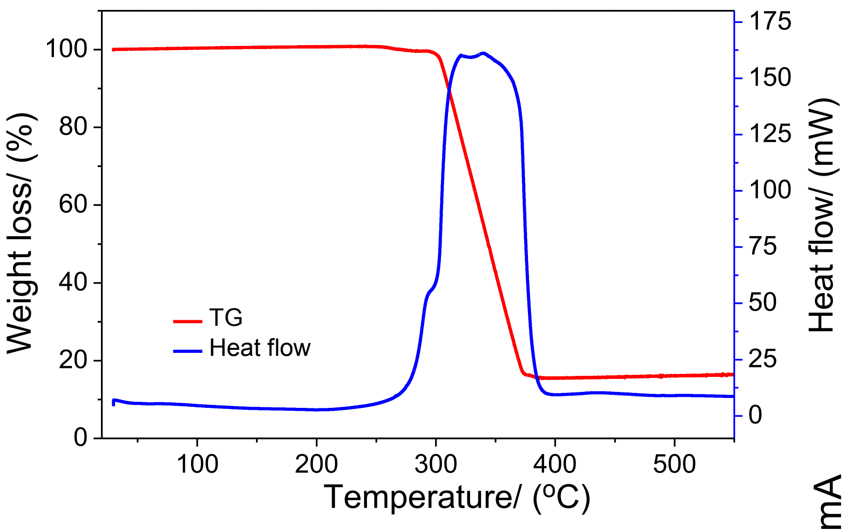
CuDEPP



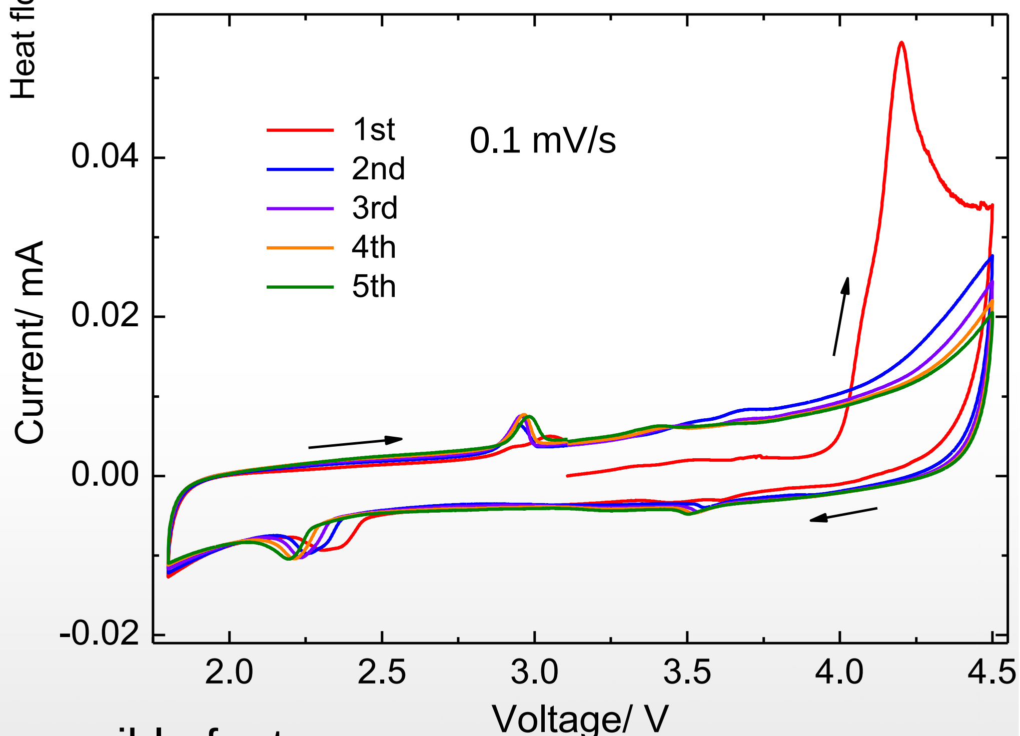
Theoret. capacity: 187 mA h g^{-1} (four electrons)

Thermal stability, electrochemistry

TGA-DSC in air



CV of the first 5 cycles

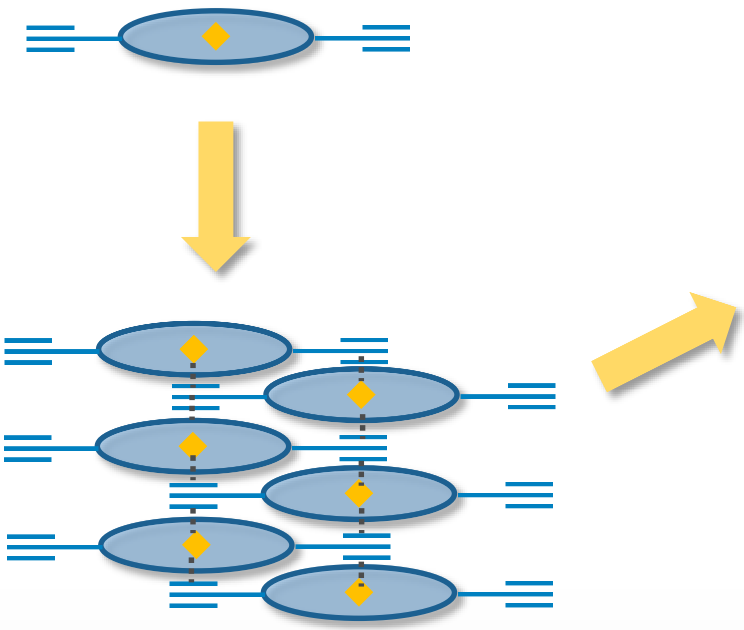


2 reversible features

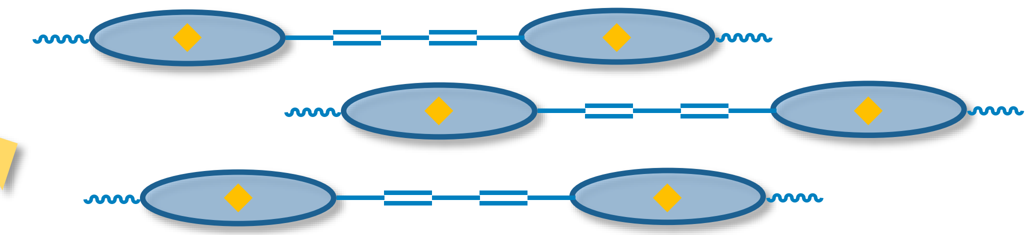
$CuDEPP^{2+} \leftrightarrows CuDEPP \leftrightarrows CuDEPP^{2-}$

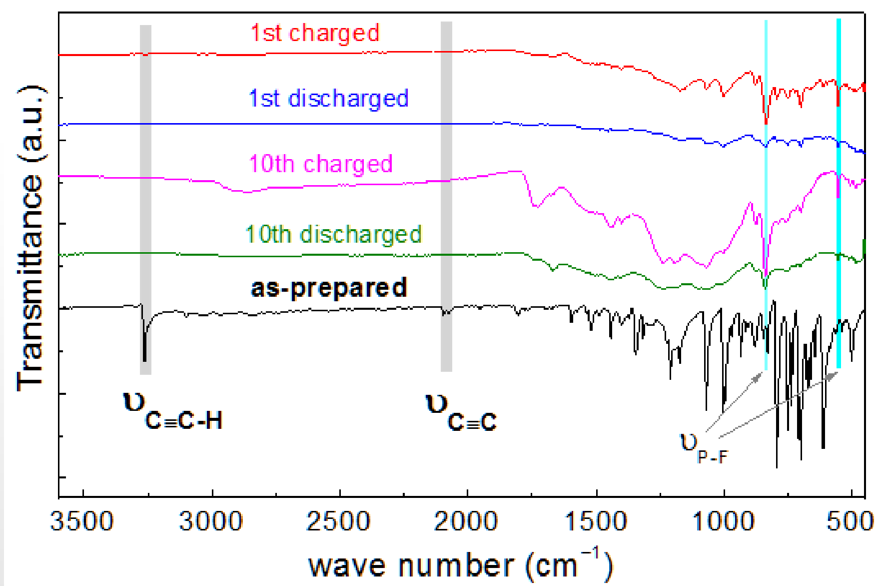
as-prepared electrode

after initial cycle



Electropolymerization

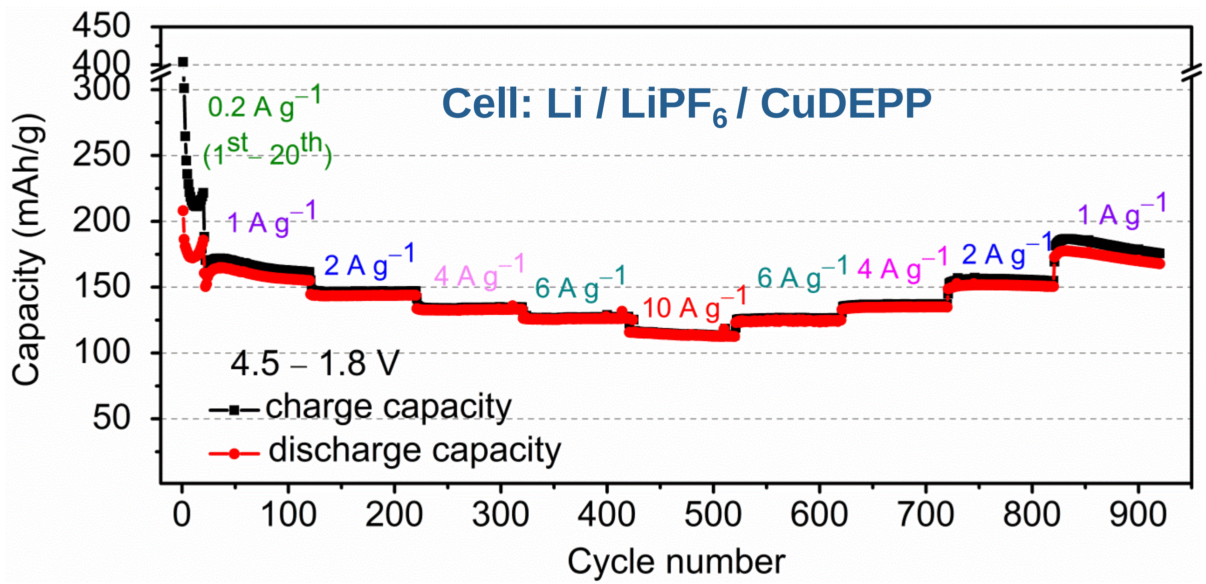


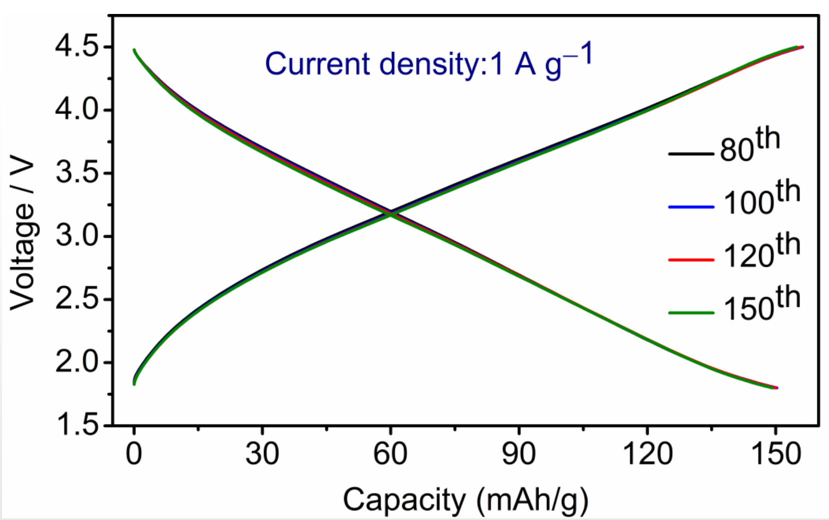


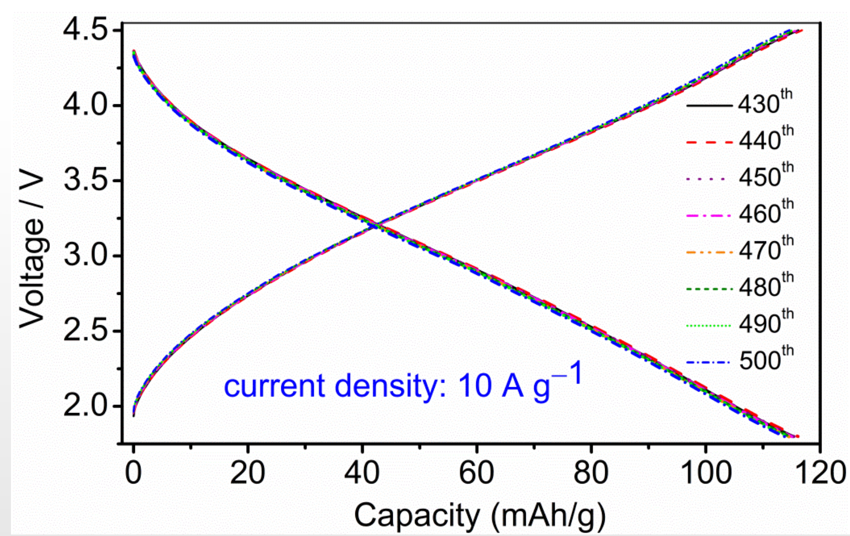
IR data

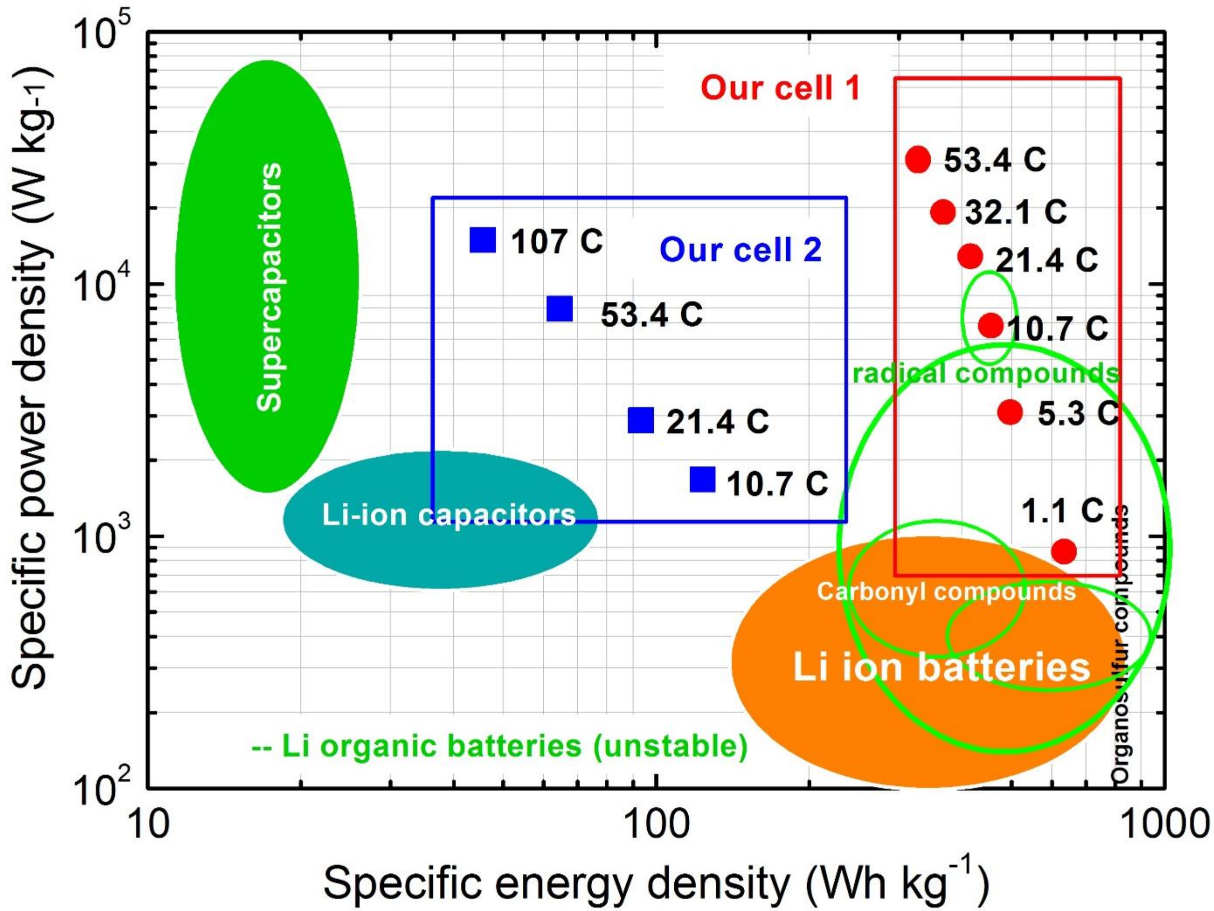
- P.Gao, M. Fichtner *et al.*, submitted (2017)
- Bedioui, F. *et al.*, Acc. Chem. Res. (1995)

Rate performance and cycling









Power density measured up to 30 kW/kg

Cell 1: Li/$LiPF_6$/**CuDEPP** (as cathode)

Cell 2: **CuDEPP**/PP_{14}TFSI/Graphite (as anode)

P. Gao, Z. Zhao-Karger, M. Fichtner et al., WO Application and paper submitted (2017)

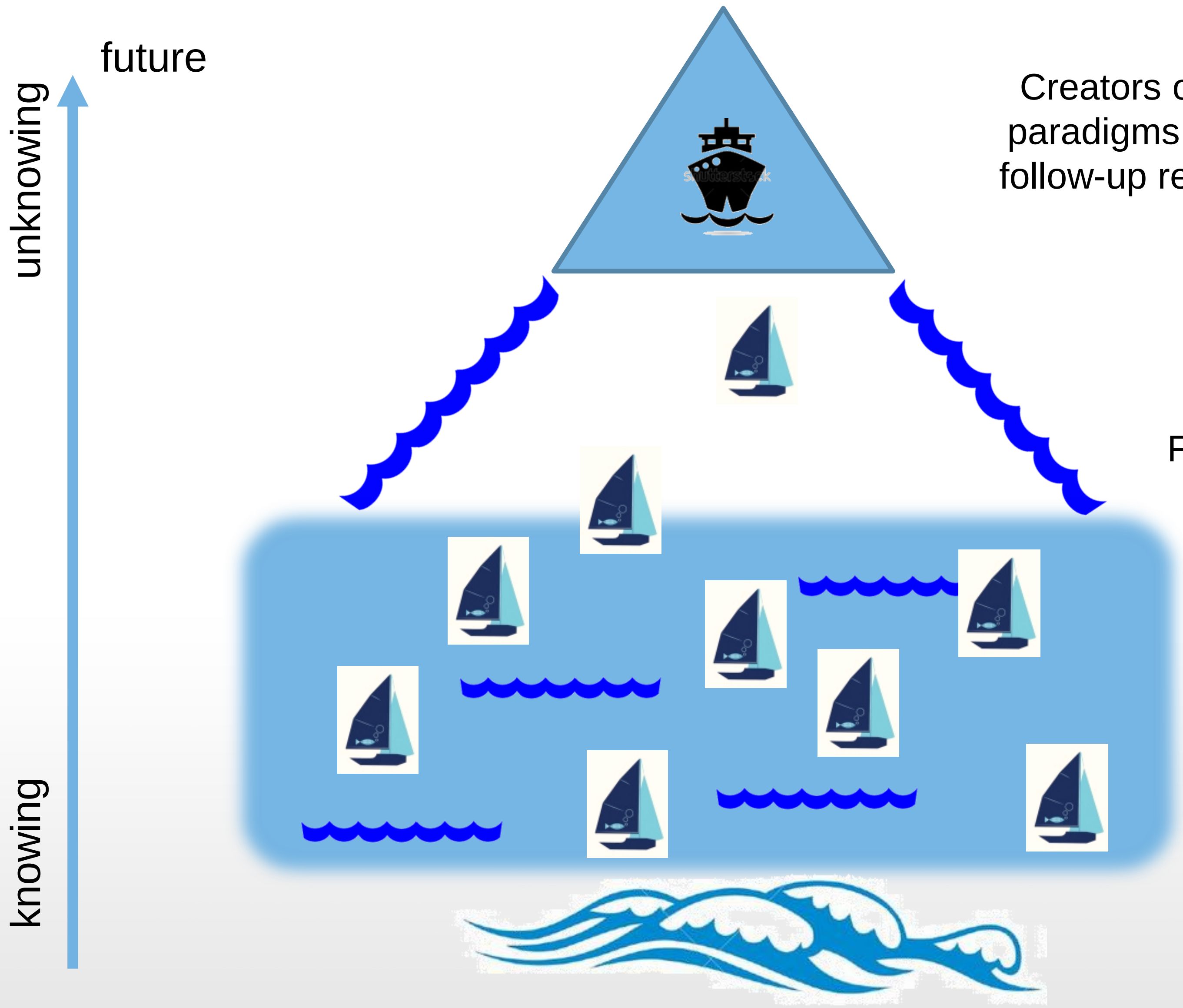
Physicists ?

Yes, the development of new storage materials is governed by synthetic and physical chemists

but phycisists can be experts for …

- theoretical modeling on all levels:
  - atomistic level: prediction of materials structure, thermodynamics and kinetics
  - interfaces under electrochemical working conditions
  - transport combined with reaction kinetics on a mesoscale up to micron range
- Structure-property relationships of new materials
- Processes at interfaces (very crucial…)
- Elucidating mechanistic and structural details while the material is operating.
- ….

The „Sea of Battery Research“



Creators of new paradigms and of follow-up research

Few frontrunners

Big sea of paradigmatic research

Paradigms in:

- Storage principle
- Materials classes
- Analytics
- Modelling
- …

The Group

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Johann Chable
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Zhirong Zhao-Karger

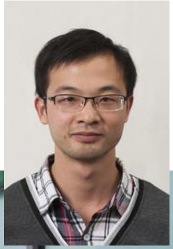
Maximilian Fichtner

modelling:
J. Mueller

from KIT:

M. Ruben

Z. Chen



Helmholtz Institute Ulm
Electrochemical Energy Storage

Thank you !