DPG Frühjahrstagung Münster

Next Generation Batteries: Hopes and Problems

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Helmholtz Institute Ulm for Electrochemical Energy Storage

- Center of Excellence for research in electrochemical energy storage
- Founded in Jan. 2011
- New building on University Ulm campus for 80 scientists (now 103+20 at KIT)
- DLR battery modeling activities are integrated into HIU

Karlsruher Institut für Technologie

Universität Ulm

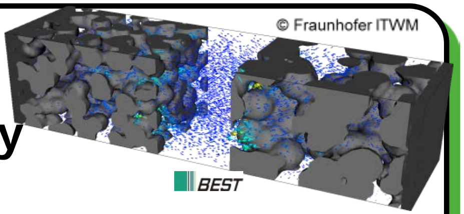
Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg

Deutsches Zentrum für Luft- und Raumfahrt

http://www.hiu-batteries.de/

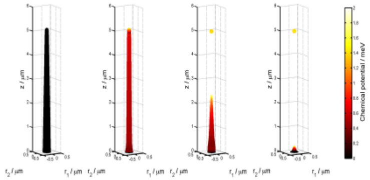
Battery modeling at HIU/DLR

Li batteries: Electrochemistry and transport



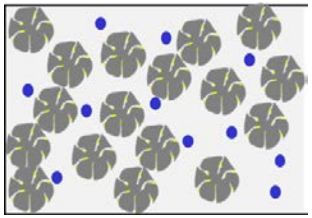
Understanding and optimization of influence of microstructure on function and life time

Battery safety



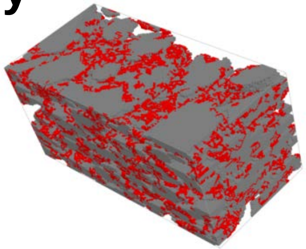
Understanding of degradation mechanisms. Theory for electrolytes

Metal-Sulfur cells: Redox-chemistry, Transport and nanostructures



Analysis of cycleability and reversibility

Metal-air cells: Multi-phase Chemistry and reversibility

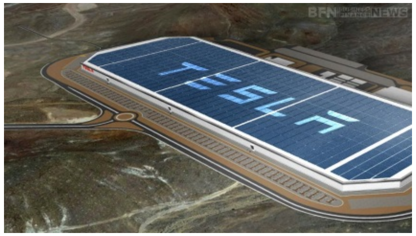


Improvement of bifunctional air oxygen electrode

Li resources / Cost:

~13.000 t/a Li are currently produced for world market of Li ion batteries

TESLA Gigafactory



Source: http://tesla.com

5.000 t/a Li for car batteries

8.000 t/a Li for PowerWall batteries

Estimated 10 more gigafactories are under consideration worldwide

United States Geological Survey 2017

	Mine production 2015	Mine production 2016[e]	Reserves[5]
United States	W	W	38,000
Argentina	3,600	5,700	2,000,000
Australia	14,100	14,300	1,600,000
Brazil	200	200	48,000
Chile	10,500	12,000	7,500,000
China	2,000	2,000	3,200,000
Portugal	200	200	60,000
Zimbabwe	900	900	23,000
World total (rounded)	[6]31,500	[6]35,000	14,000,000

Resources

About 49.000.000 t

Why alternatives to Li ion batteries?

The best performing cathodes are based on **N**ickel **M**angan **C**obalt (NMC) materials

	Mine production 2015	Mine production 2016[e]	Reserves[7]
United States	[e]760	690	21,000
Australia	6,000	5,100	[8]1,000,000
Canada	6,900	7,300	270,000
China	7,700	7,700	80,000
Congo (Kinshasa)	63,000	66,000	3,400,000
Cuba	4,300	4,200	500,000
Madagascar	3,700	3,300	130,000
New Caledonia[9]	3,680	3,300	64,000
Philippines	4,300	3,500	290,000
Russia	6,200	6,200	250,000
South Africa	3,000	3,000	29,000
Zambia	4,600	4,600	270,000
Other countries	11,600	8,300	690,000
World total (rounded)	126,000	123,000	7,000,000

Resources:
25.000.000
(Congo, Zambia)
+
120.000.000
on the floor of
Atlantic, Indian and
Pacific Oceans

Cobalt supply chain:

Byproduct of Ni or Cu mining
Co production is falling in 2016
Reserves sufficient to run 80.000.000 electric cars

Co is heavily associated with children labour (Estimated 40000 child miners Amnesty International 2016)

Systems Beyond Li

Cationic Shuttles

Sodium Ion Battery

Magnesium Battery

Zinc battery

Calcium Battery

Aluminum Battery

$\underbrace{\text{Magnesium, Zinc, Calcium, Aluminum}}_{\text{„multivalent shuttles“}}$

„multivalent shuttles“

Anionic Shuttles

Chloride Ion Battery

Fluoride Ion Battery

Partly great promises for improving sustainability, cost, safety, energy density

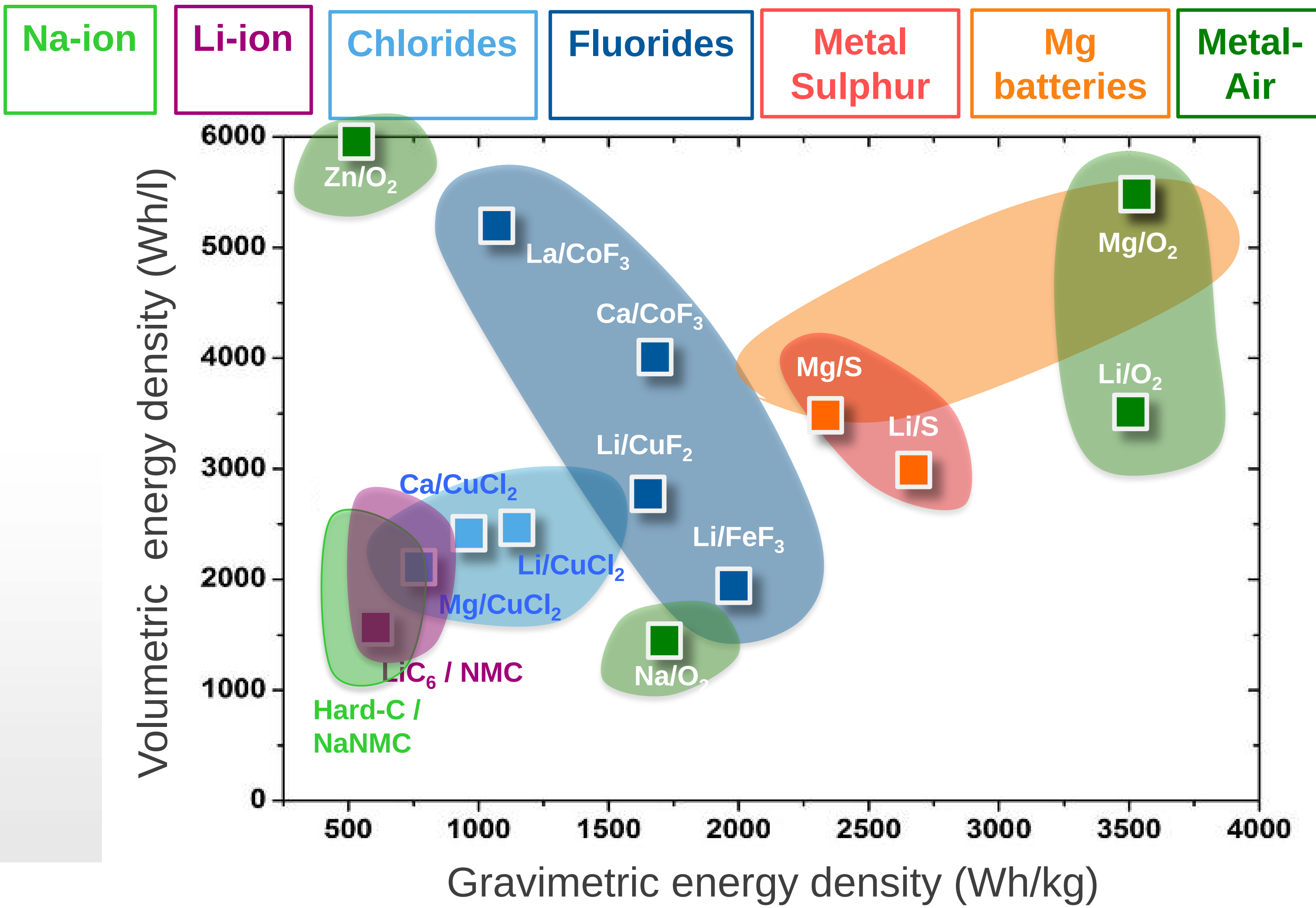
→ but no system commercialized, yet, due to novelty and scientific/technical obstacles

Facts about post Li systems

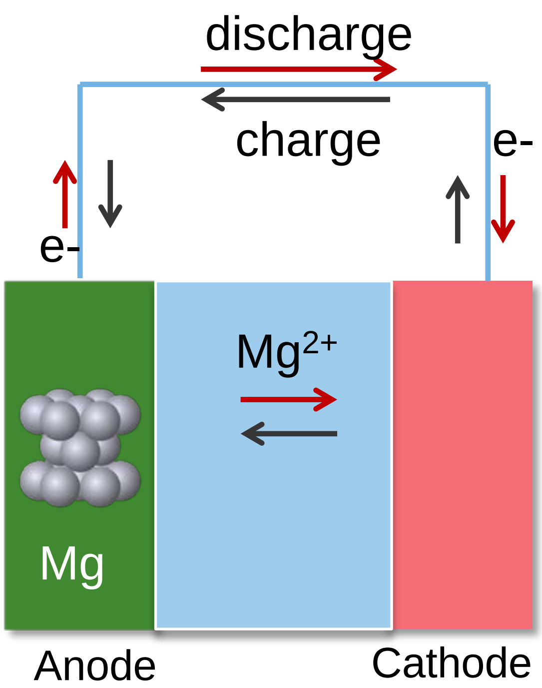
Element	Charge of ion	crystal ionic radii /pm[1]	Earth crustal abundance / ppm by weight[2]	Price (pure)[3] US$ per 100g	specific capacity		Potential vs. NHE/V
					$mA \cdot h \cdot g^{-1}$	$mA \cdot h \cdot cm^{-3}$	
Li	1	90	20	27	3862	2047	-3.04
Na	1	116	24000 + 10.8 g/L in seawater	25	1166	1130	-2.71
Mg	2	86	23300	3.7	2206	3840	-2.37
Ca	2	114	41500	20	1338	2006	-2.87
Zn	2	88	70	5.3	820	6845	-0.76
Al	3	68	82300	15.7	2980	8050	-1.66
Cl	-1	167	145 + 19.4 g/L in seawater	0.15	-	-	used only as shuttle

[1] *For coordination number 6, from R. D. Shannon "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". Acta Crystallogr A. 32 (1976) 751–767.*
[2] David R. Lide, ed., CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version 2009)
[3] www.chemicool.com

Theoret. storage capacities of electrochemical couples of Li Ion- and post-Li batteries (materials basis)



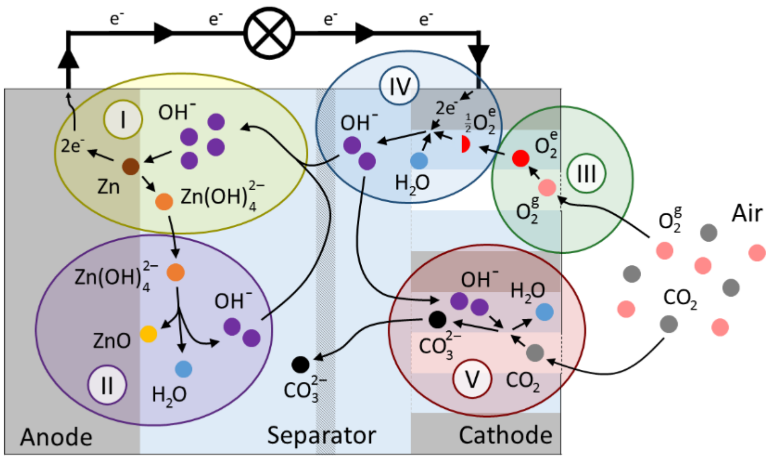
Properties of Magnesium and Lithium



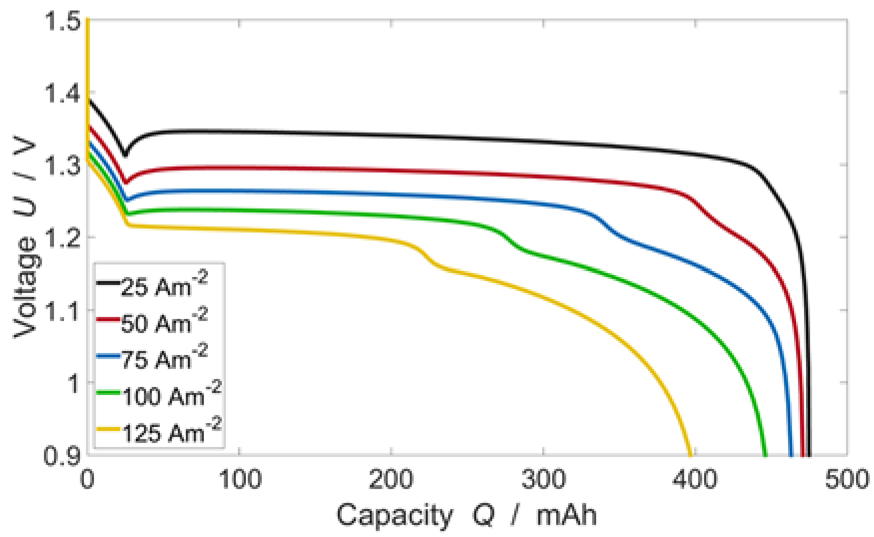
	Li	Mg
Atomic weight	6.9	24.3
Ionic radius	90 pm	86 pm
Ionic charge	+ 1	+ 2
Reduction potential	- 3.04 V	- 2.37 V
Density	0.53 g/cm³	1.74 g/cm³
Gravimetric capacity	3861 mAh/g (Li) **372 mAh/g (LiC_6)**	2205 mAh/g
Volumetric capacity	**2061 mAh/cm³**	**3832 mAh/cm³**

- 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 special electrolyte for Mg!**
- **Mg anode is easily passivated with most of the known electrolytes**

- **Chemical Reactions**
  - I. $Zn + 4OH^{-} \rightleftharpoons Zn(OH)_4^{2-} + 2e^{-}$
  - II. $Zn(OH)_4^{2-} \rightleftharpoons ZnO + 2OH^{-} + H_2O$
  - *III.* $O_2^{g} \rightleftharpoons O_2^{e}$
  - *IV.* $\frac{1}{2}O_2^{e} + H_2O + 2e^{-} \rightleftharpoons 2OH^{-}$

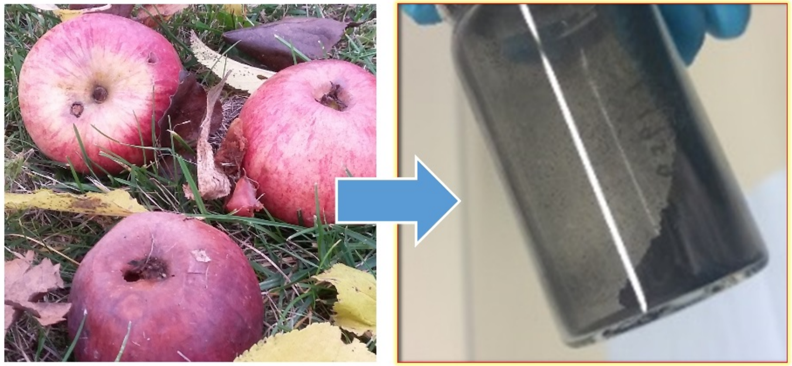


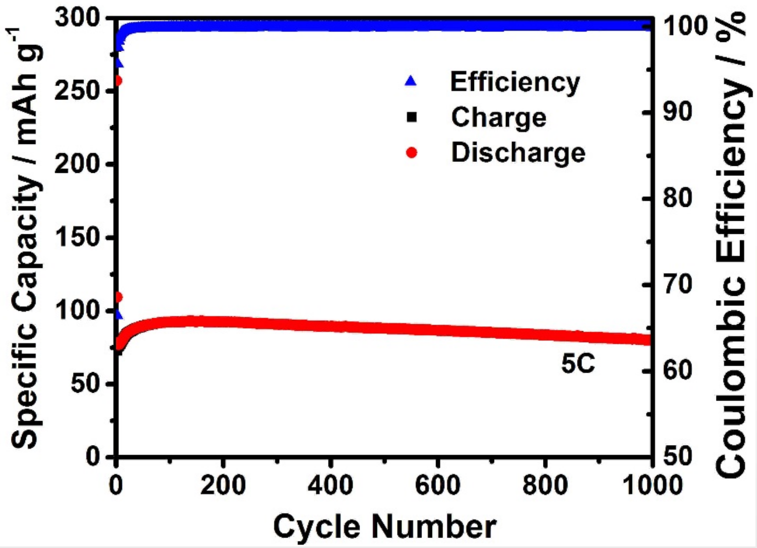
- **Specific energy:** 1086 Wh·kg^{-1}
  Energy density: 6090 Wh·l^{-1}
  Low cost and **safe**



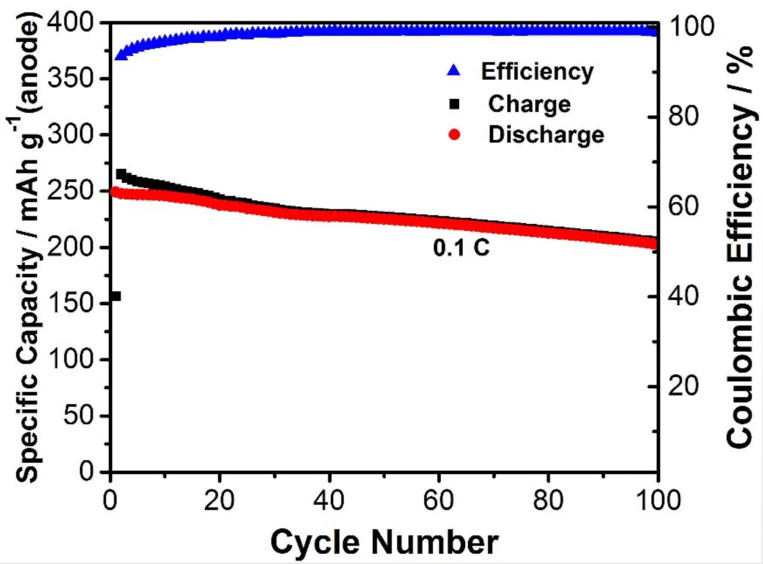
- Challenges include: Zn **dendrites**, electrolyte **carbonation**, Zn **passivation**
- **Alternative electrolytes needed (ionic liquids, neutral electrolytes)**

Na-ion cell with hard carbon anode made of apple biowaste



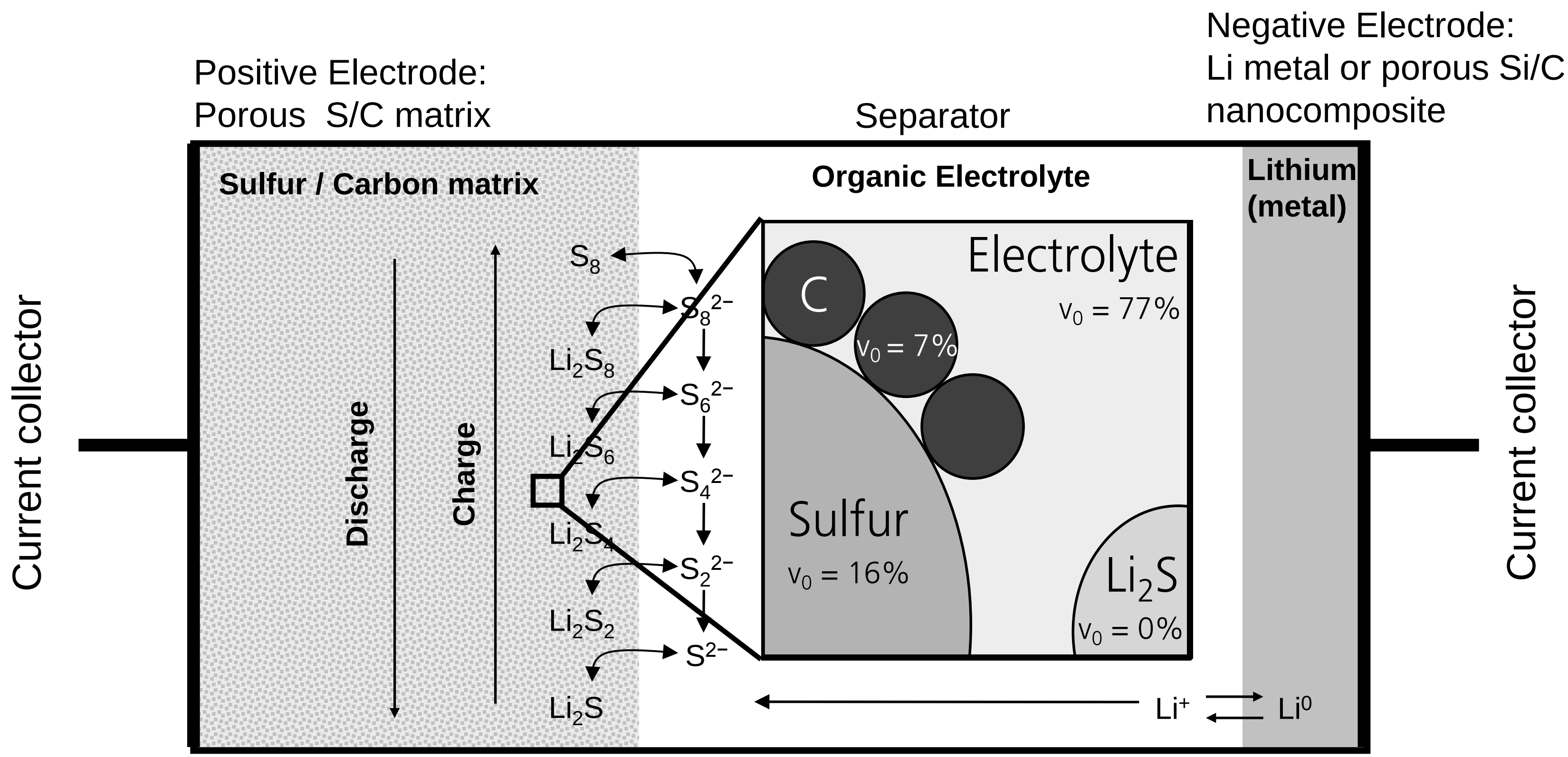


NaNMC – Apple Hard Carbon



📖 L. Wu et al., ChemElectroChem (2015) doi: 10.1002/celc.201500437
📖 http://www.swr.de, Landesschau aktuell: „Forschung am Ulmer Helmholtz-Institut: Batterien aus Apfelresten“

Example: Metal-sulfur battery (Cobalt free)



Global reaction: $S_8 + 16\ Li \rightleftarrows 8\ Li_2S + 3400\ kJ/mol$

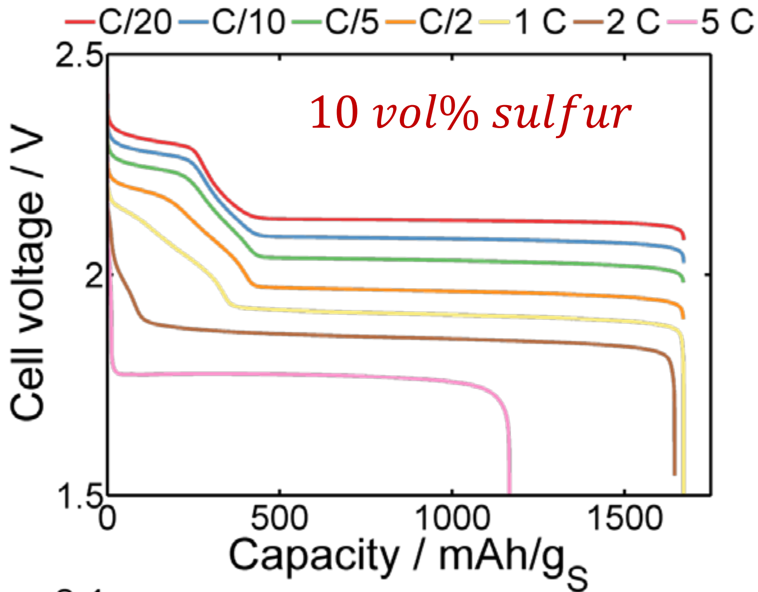
Complex chemistry, complex multi-phase behavior, Redox shuttle

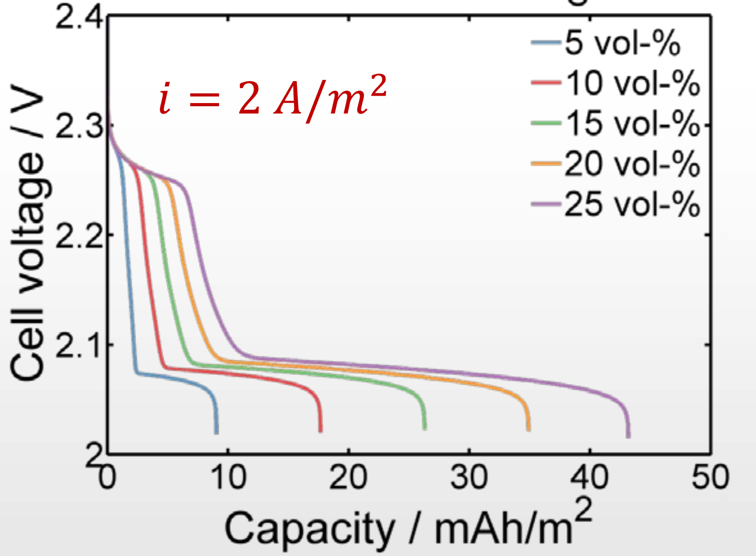
Base model (without degradation)

- S/C composite electrode
- Variation of current amplitude (C-rate)
  - Influence on
    - Transport
    - Kinetics
- Variation of sulfur content
  - Increase in capacity
  - No pore clogging included

➔

Validated with experiments of Canas et. al (2014) at the DLR in Stuttgart



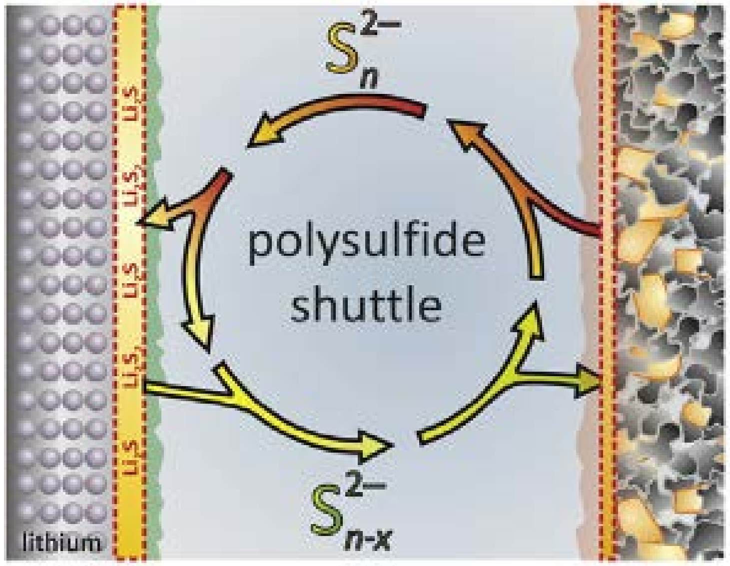


Loss mechanism: Shuttle effect

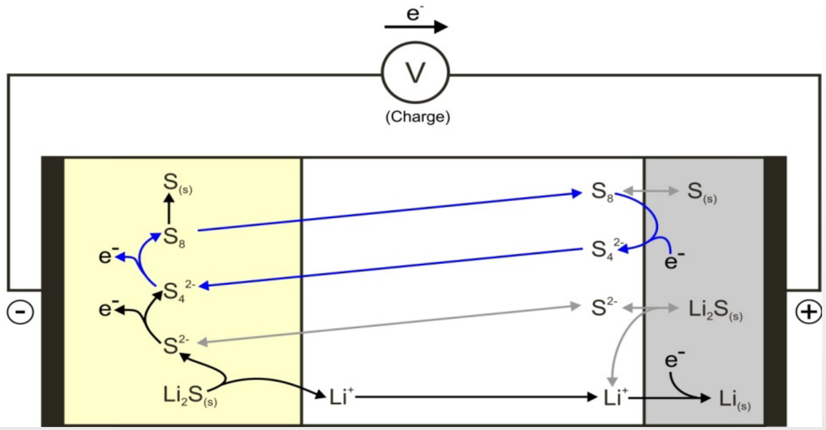
- Partial reduction of dissolved polysulfides at negative electrode during charge
- Precipitation of Li_2S

➔ Columbic efficiency ↓

Capacity decay

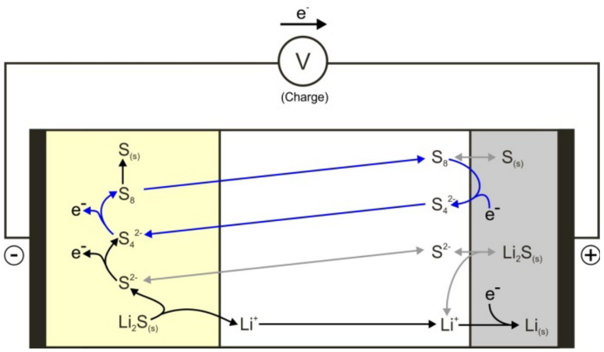


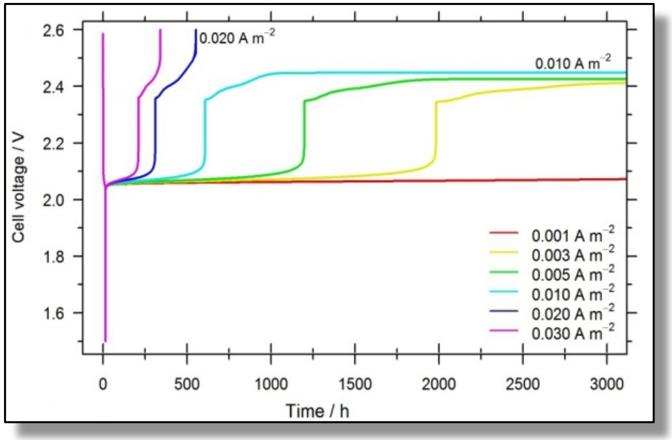
Busche, Martin Rolf, et al. *Journal of Power Sources* 259 (2014): 289-299.



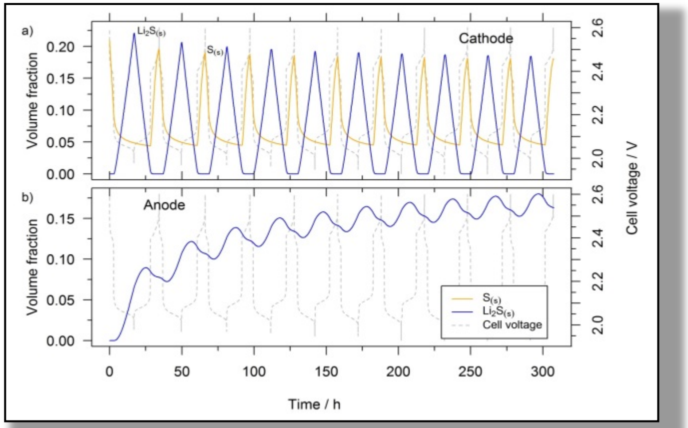
Consequences of Polysulfide shuttle at HIU

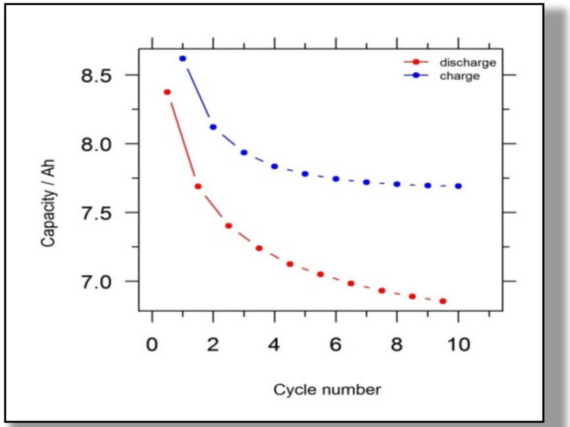
Infinite charging at small currents





Capacity decay during cycling

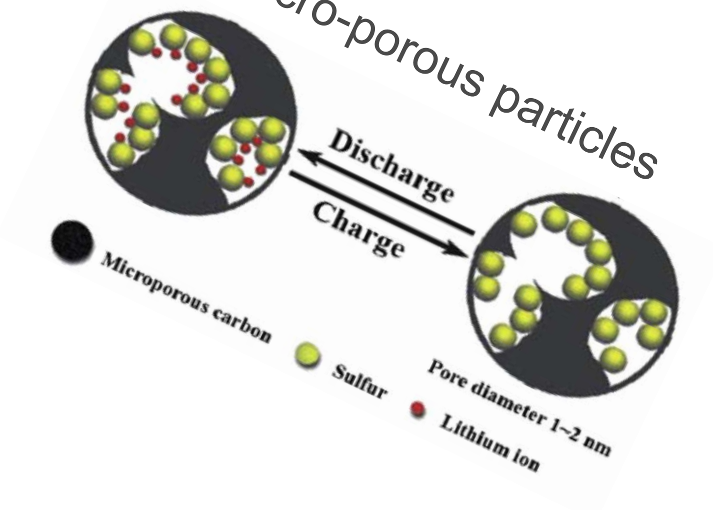




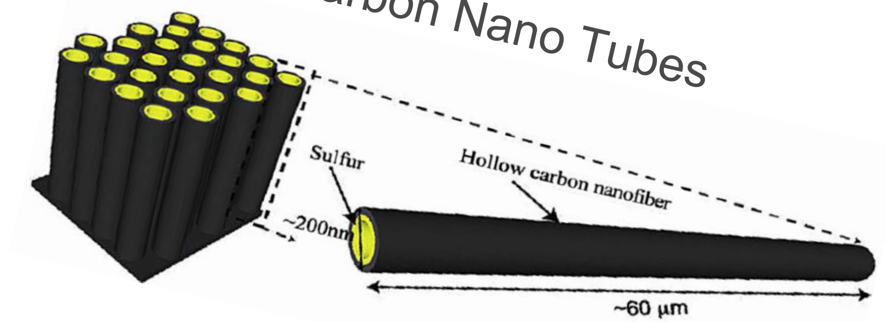
Hofmann, A.F. et.al. *J. Power Sources*, 259 (2014) 300–310

Different approaches to retain sulfur species…

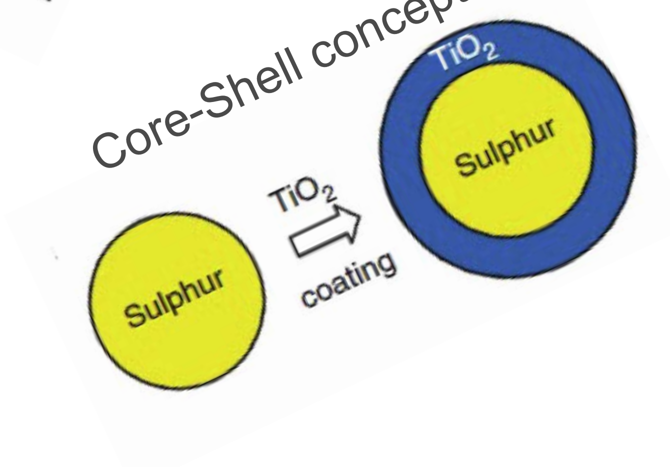
Micro-porous particles



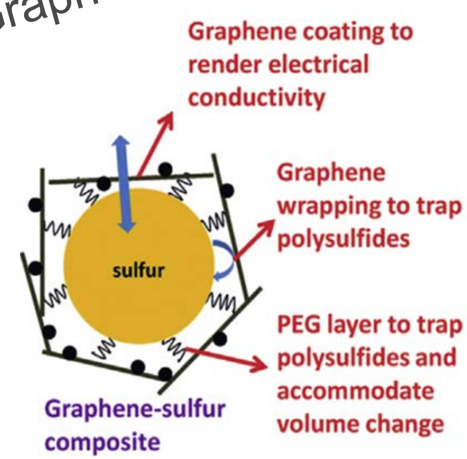
Carbon Nano Tubes



Core-Shell concept



Graphene Wrapping



L. Chen et al, *J. Power Sources*, 267 (2014) 770–783.

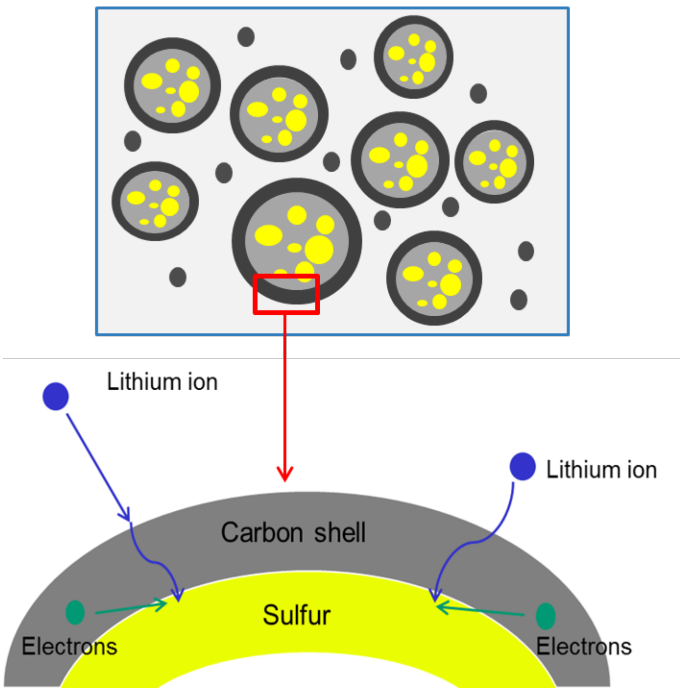
Modeling of nanostructured electrodes

Goal: Investigation of fundamental limiting effects

Single particle model

- Model 1

➔Solid carbon shell



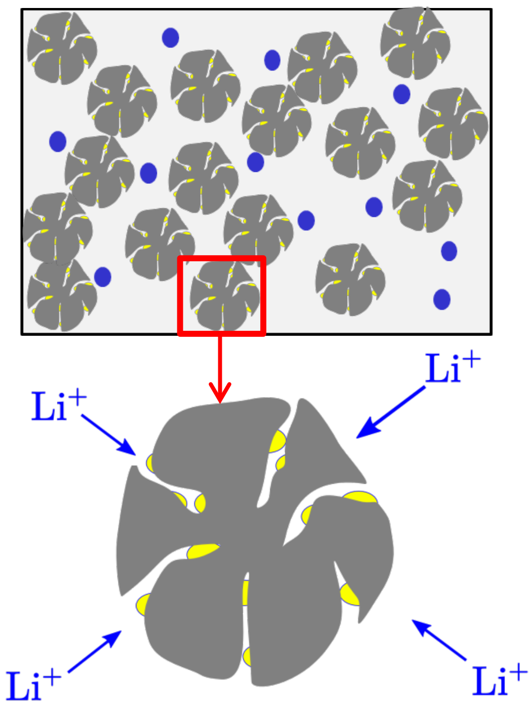
Particle surface:

- $\phi^{\mathrm{ref}} = const.$
- $c_{Li^+} = const.$

➔ Only Li enters particle

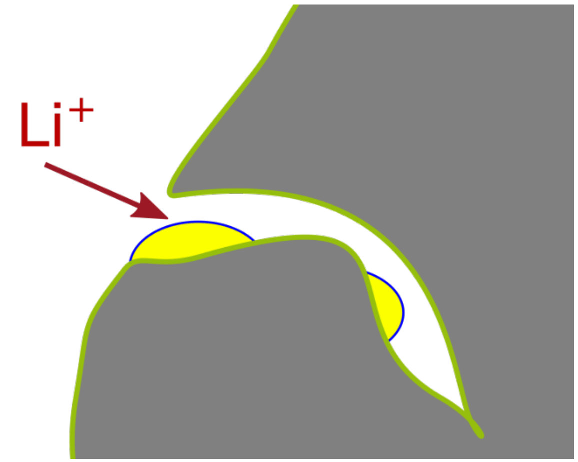
- Model 2

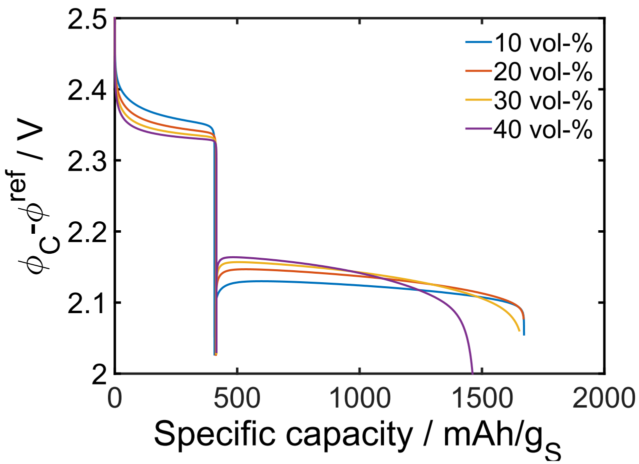
➔Microporous sphere



Structural effects

- Nucleation of S_8 / Li_2S
  - Pore space is reduced
  - Li_2S needs much more volume
- Effective transport + pore clogging
  - Hindered diffusion in porous media
    - $D_i^{eff} = D_i^0 \varepsilon_{elyte}^{1.5}$
- Passivation of active surface area by S_8 / Li_2S
  - Solid reaction products are electronically non-conducting





Results: Surface Defects

Transport overpotential

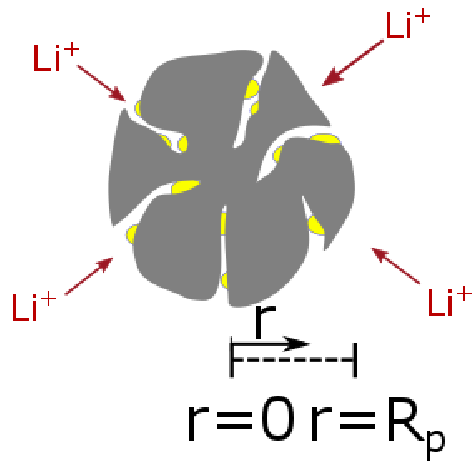
- Li^+ transport into particle

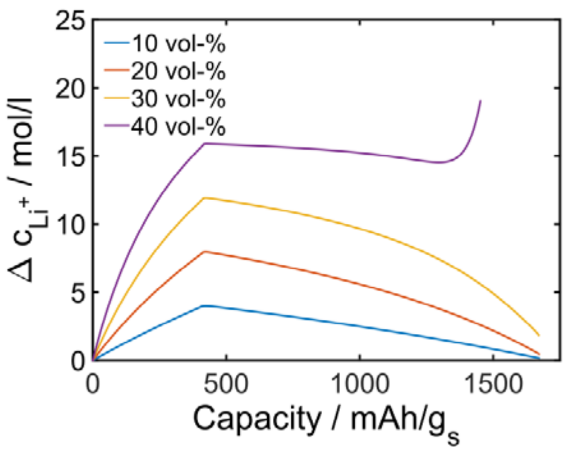
$$\dot{N}_{Li^+}\Big|_{r=R_p} = -D^{eff}_{\mathrm{Li}^+}\frac{\partial c_{\mathrm{Li}^+}}{\partial r}\Big|_{r=R_p} - D^{eff}_{\mathrm{Li}^+}\, c_{\mathrm{Li}^+}\frac{z_{\mathrm{Li}^+}F}{RT}\frac{\partial \phi_{elyte}}{\partial r}\Big|_{r=R_p}$$

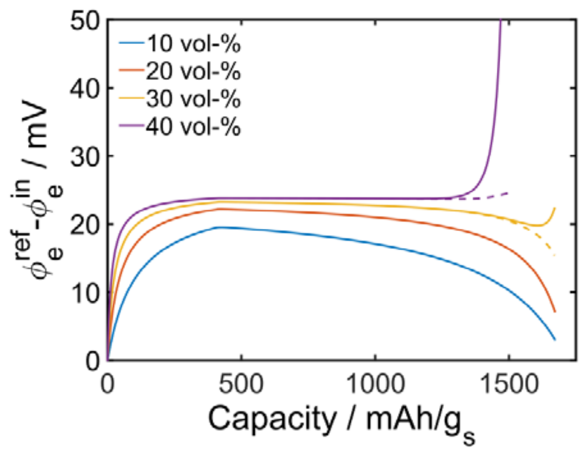
- Transport against gradient in c_{Li^+}

➔ Additional transport resistance

➔ Additional driving force for polysulfide loss





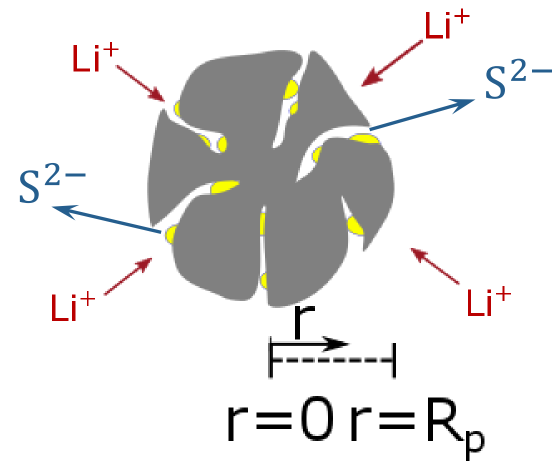


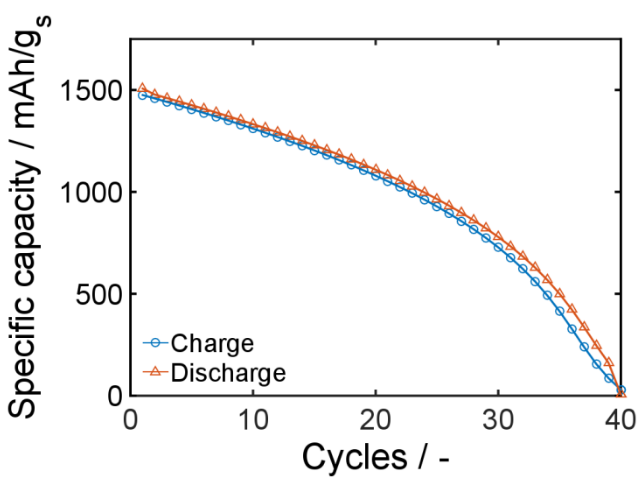
Results: Cycling properties

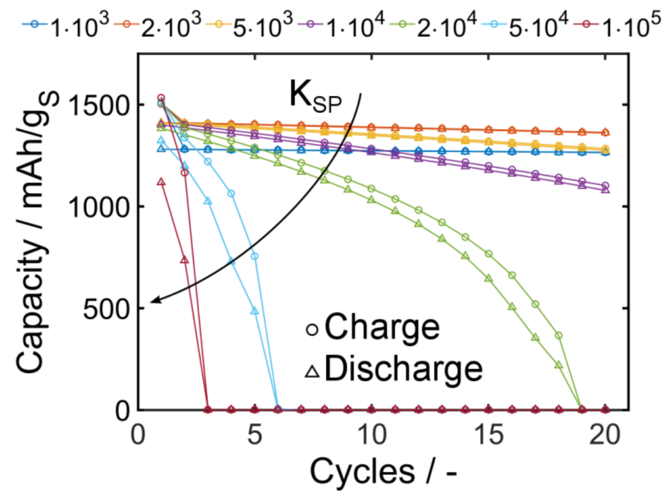
Cycling & degradation

- Loss of S^{2-}
  - ➔ Capacity fade
- Influence of Li_2S solubility
  - ➔ Low solubility = long cycle life

➔ Suitable choice of electrolyte system







Encapsulation is good idea, but creates additional problems

Summary

- In the long run alternatives for Li ion batteries are necessary
- There are many theoretical alternatives for Li – ion batteries
- Each alternative, so far, I plagued with many problems
- Working cells do exist only on Lab scale
- Counter measures for existing problems very often create additional (interesting) research problems
- Theory and simulation helps to improve the understanding of the nonlinear interplay of transport and reactions

Thank you for your attention!

Opportunity

PhD positions available

http://www.hiu-batteries.de

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