

9th Workshop
"Lithium-Sulfur Batteries"

November 28–29, 2022 | Online



HZB Helmholtz
Zentrum Berlin

MULTIDIMENSIONAL OPERANDO ANALYSIS OF LI/S BATTERIES WITH NEUTRONS AND PHOTONS

Sebastian Risse

Helmholtz-Zentrum Berlin

Department for Electrochemical Energy Storage

A live
View into Li/S
Batteries

ACKNOWLEDGMENT



Matthias Ballauff, Yan Lu, Joe Dzubiella, Stefano Angioletti-Uberti, Chanbum Park, Roland Steitz, Beatrix Seidlhofer, Günter Goerigk, Albrecht Petzold, Daniel Clemens

Ingo Manke, Nikolay Kardjilov, Henning Markötter, André Hilger, Tobias Arlt



Stefan Kaskel, Holger Althues, Susanne Dörfler, Thomas Abendroth, Tom Boenke

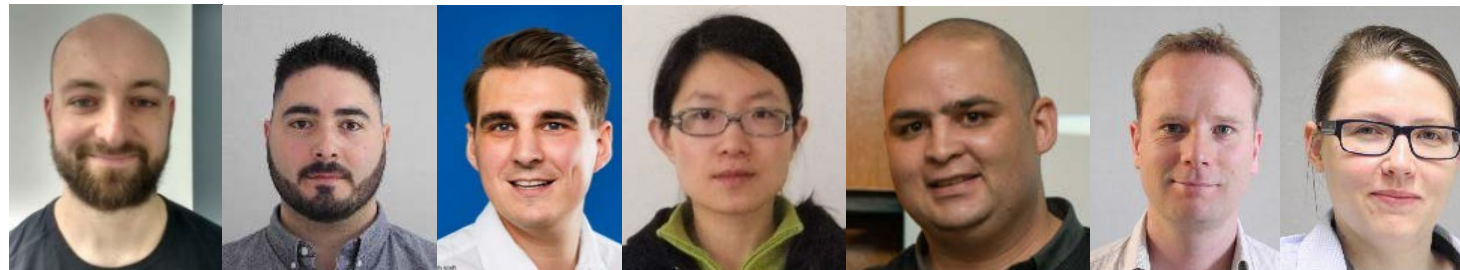
Electrochemistry Group @ HZB



S. Risse, Eneli Härk, Rafael Müller, Martin Schellenberger, Breno de Souza*, Piergiorgio Marziani*
* Visiting scientist



Bundesministerium
für Bildung
und Forschung



Former members: Arne Ronneburg, Luca Silvi, Marco Evertz, Yan Yang, Charl Jafta, Ben Kent, Karina Lemke



JOIN AS A POSTDOC

Operando Analysis of Batteries

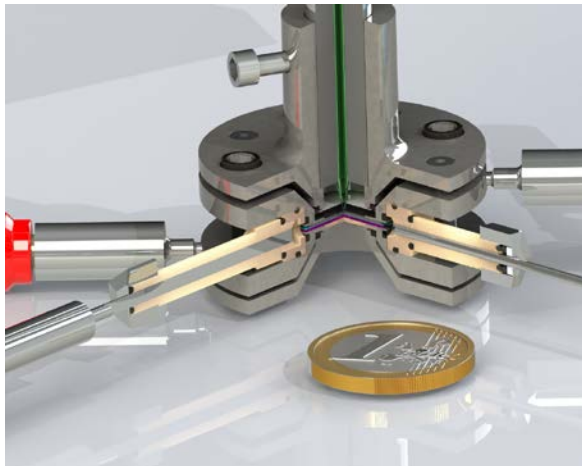
Contact: sebastian.risse@helmholtz-berlin.de

Postdoc-Position #1

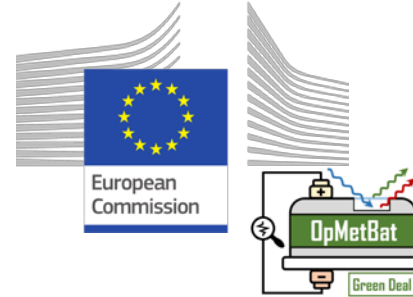
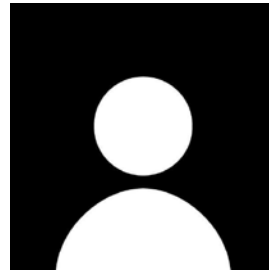


DFG Deutsche
Forschungsgemeinschaft
German Research Foundation

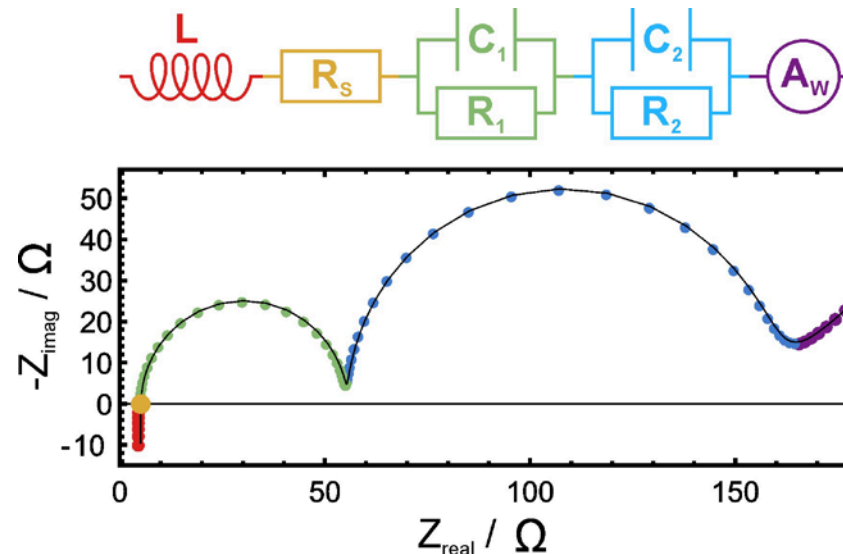
- 1 year from 01.01.2023
- Operando Li/S analysis
- Raman, EIS and UV/vis spectroscopy



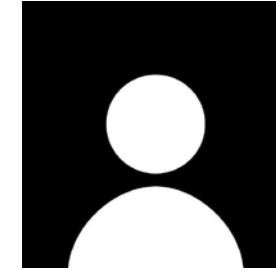
Postdoc-Position #2



- 2 years from 01.2.2023
- Operando EIS of LIBs & Li/S
- Metrology aspects

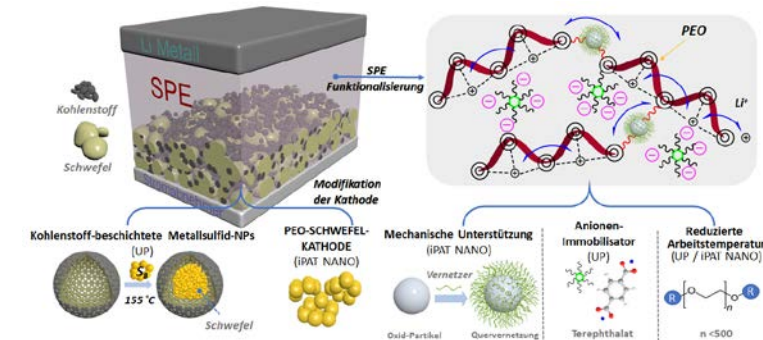


Postdoc-Position #3



Bundesministerium
für Bildung
und Forschung

- 3 year from 01.02.2023
- Operando Li/S analysis
- ASSB Li/S

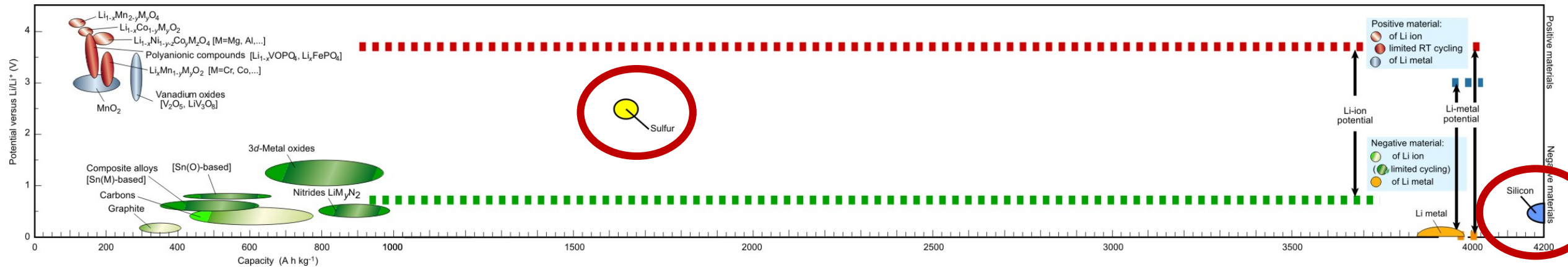


MOTIVATION – PROMISING HIGH CAPACITY ELECTRODES

Looking for Grand Challenges

Desired electrode properties:

- High energy density
- Low capacity fading
- Low cost
- Safety
- Environmental friendliness



Anode: Silicon 4200 Ah/kg
Cathode: Sulfur 1675 Ah/kg

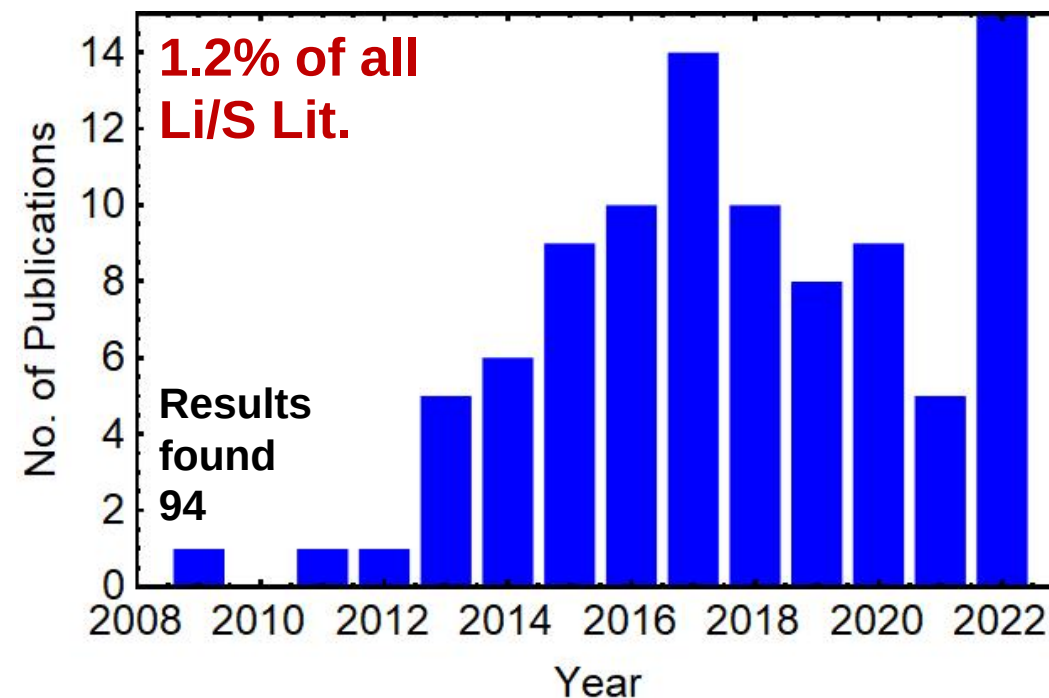
MOTIVATION – LITERATURE OF LI/S BATTERIES

A Web of Science Citation Report

Title=("lithium sulfur" OR "Li/S" OR "Lithium Sulphur")



Title=("lithium sulfur" OR "Li/S" OR "Lithium Sulphur")
+ operando, situ



MOTIVATION – OPERANDO ANALYSIS

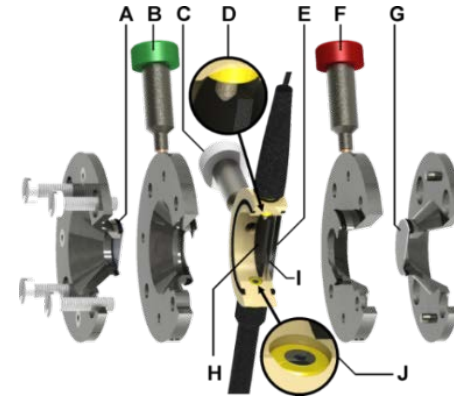
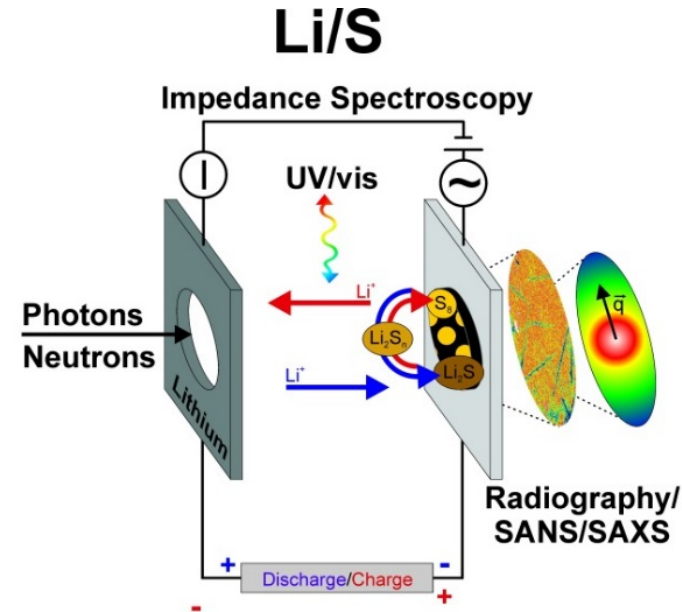
Following performance determining processes in energy storage systems in real-time

Advantages:

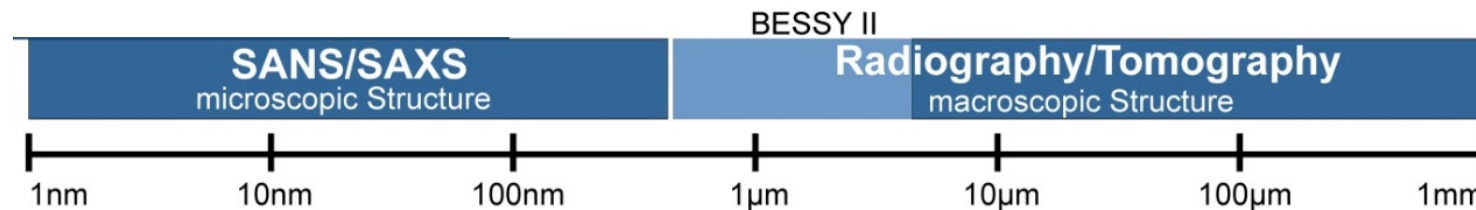
- Sustainability
- High Energy Density of 2500 Wh/kg (<500 for Li-ion cells)

Challenges:

- Strong Capacity Fading
- Low Rate Capability



Pertinent Length Scales

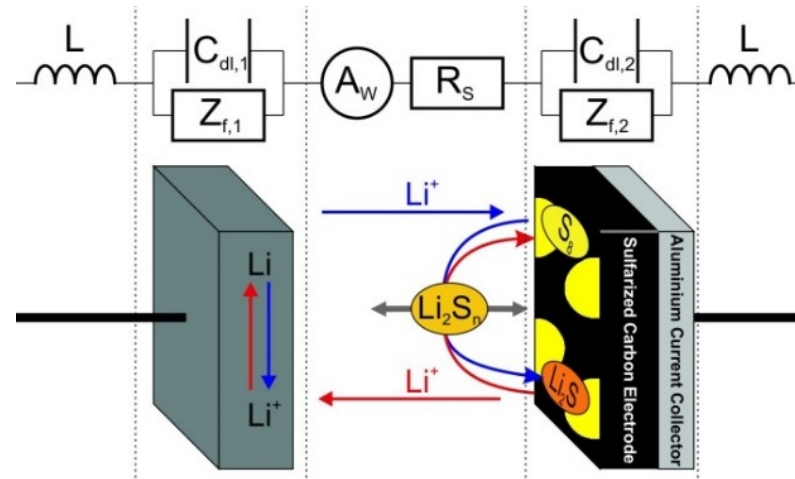
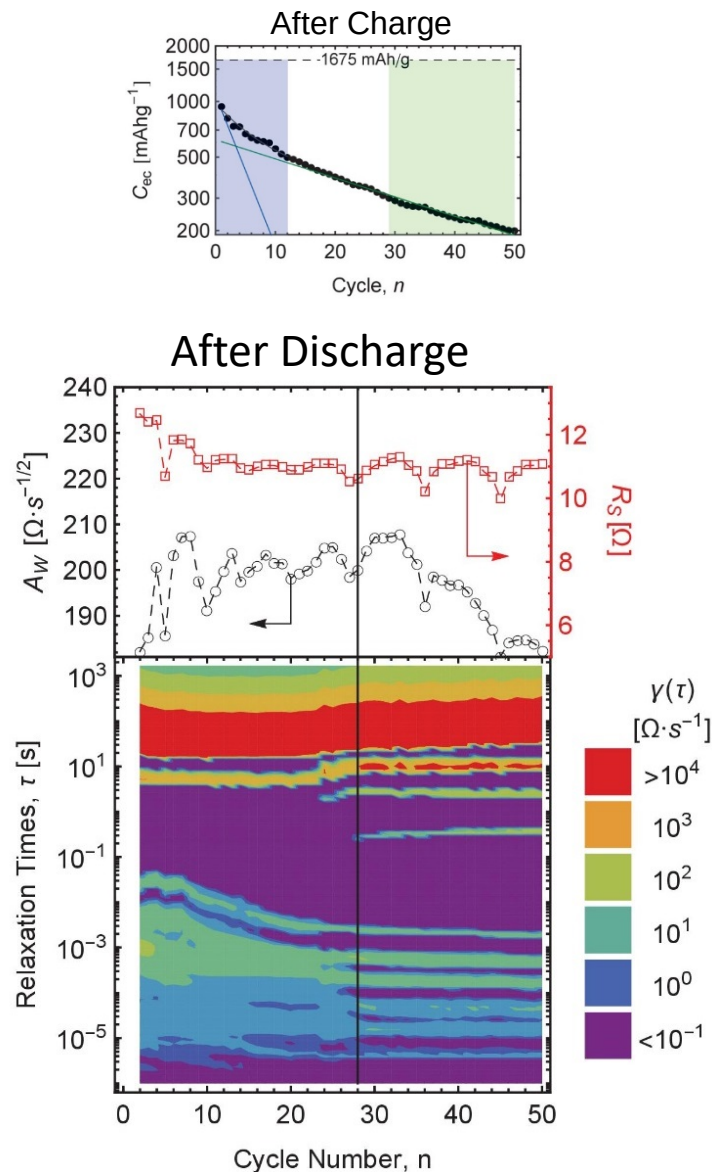


Our Approach

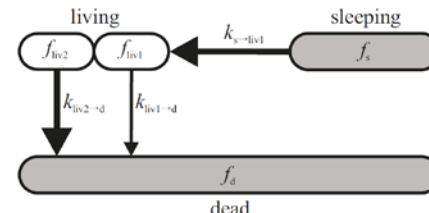
Mechanistic understanding of degradation process through multidimensional *operando* analysis of many cycles

CAPACITY FADING AND IMPEDANCE

Correlation of EIS and fast/slow fading processes

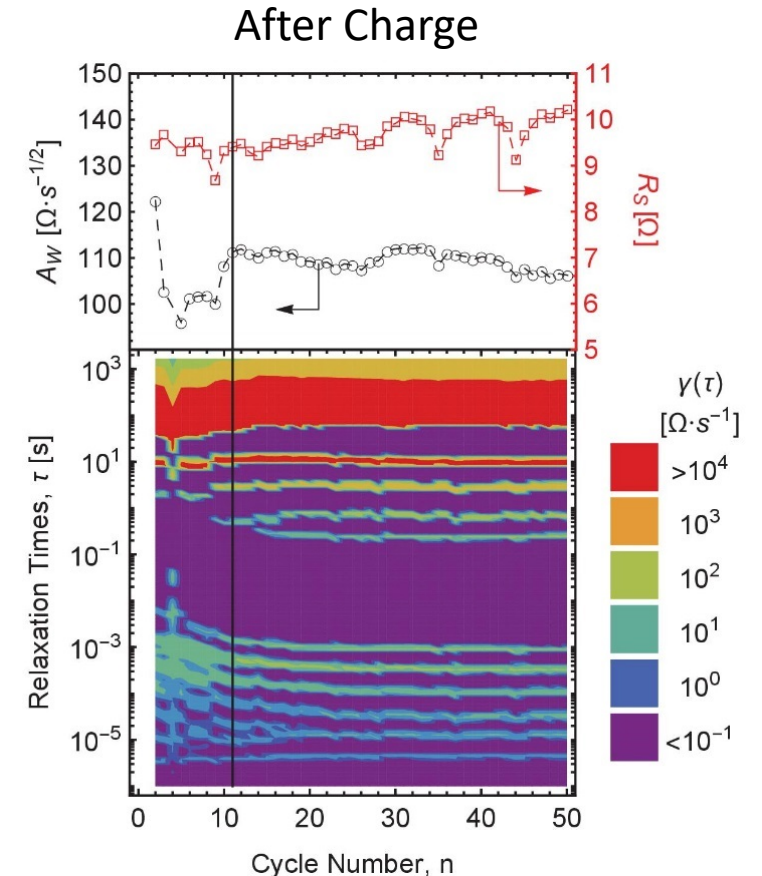
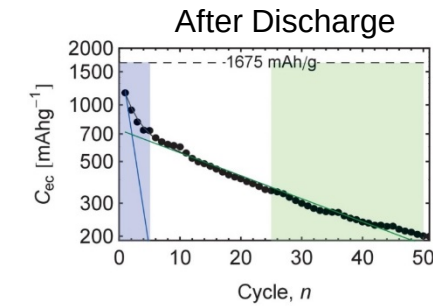


Markov chain process to model capacity fading



S Risse*, S Angioletti-Uberti, J Dzubiella, M Ballauff, *Journal of Power Sources* 267 (2014) 648-654

Corrosion of lithium metal anode leads to a fast capacity fading process during the first cycles



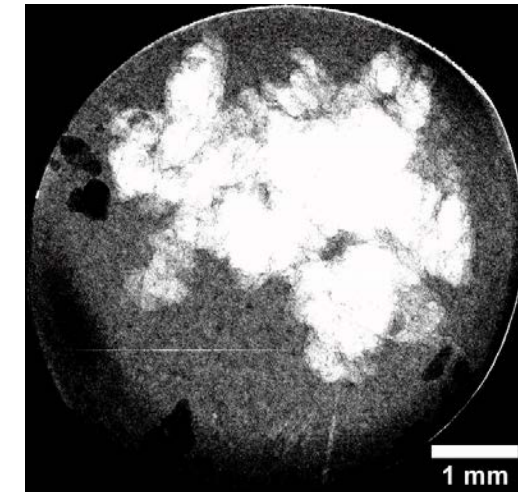
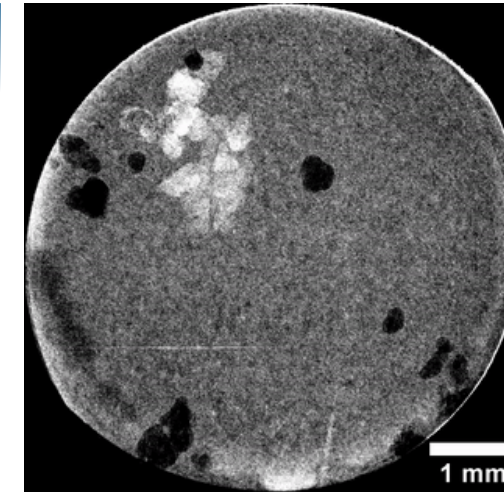
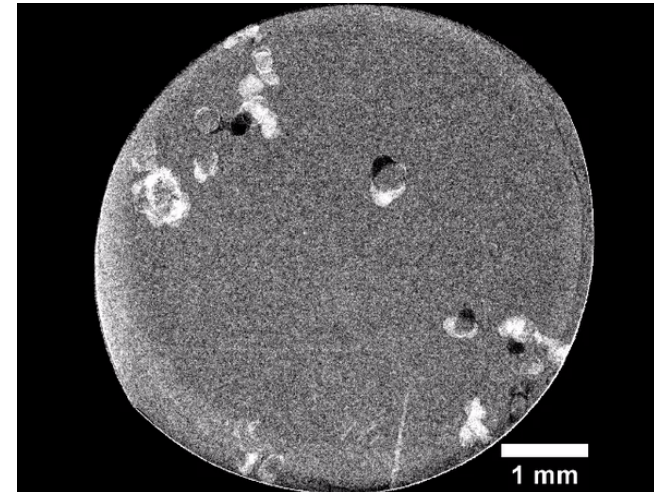
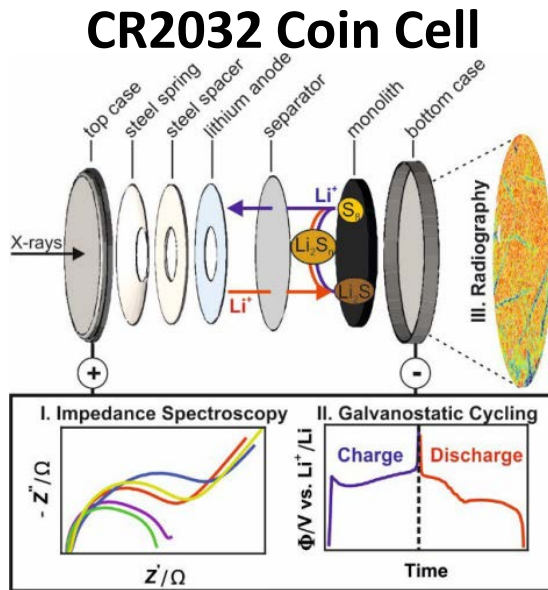
FIRST OPERANDO X-RAY RADIOGRAPHY OF LI/S CELL

Morphology and capacity fading

2nd Cycle (0.1C)

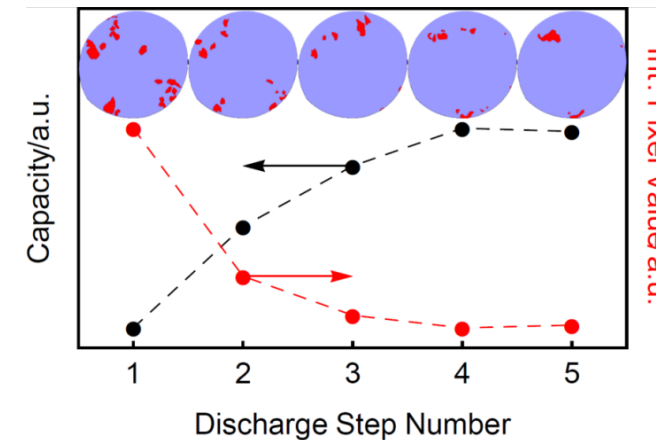
5 Cycles @ 0.5C

1 Cycle @ 0.1C



- DOL/DME (1/1 w/w)
- 8_{wt%} LiTFSI
- 4_{wt%} LiNO₃
- **0.1M Li₂S₈**
- S/C = 17_{wt%}
- C_A = 2.24 mg/cm²
- E/S = 36 μL/mg_{Sulfur}

- Formation/Dissolution of β-sulfur dendrites
- Appearance and disappearance of white stains
- No direct observation of Li₂S
- Circular front of high transmission at the end of discharge
- Reproduced by S.-H. Yu *et al.*, *Energy Environ. Sci.* 11 (2018) 202-210

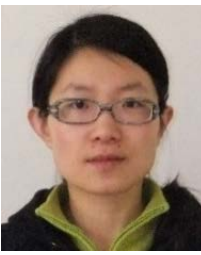


Areas of high transmission show inverse proportionality to discharge capacity

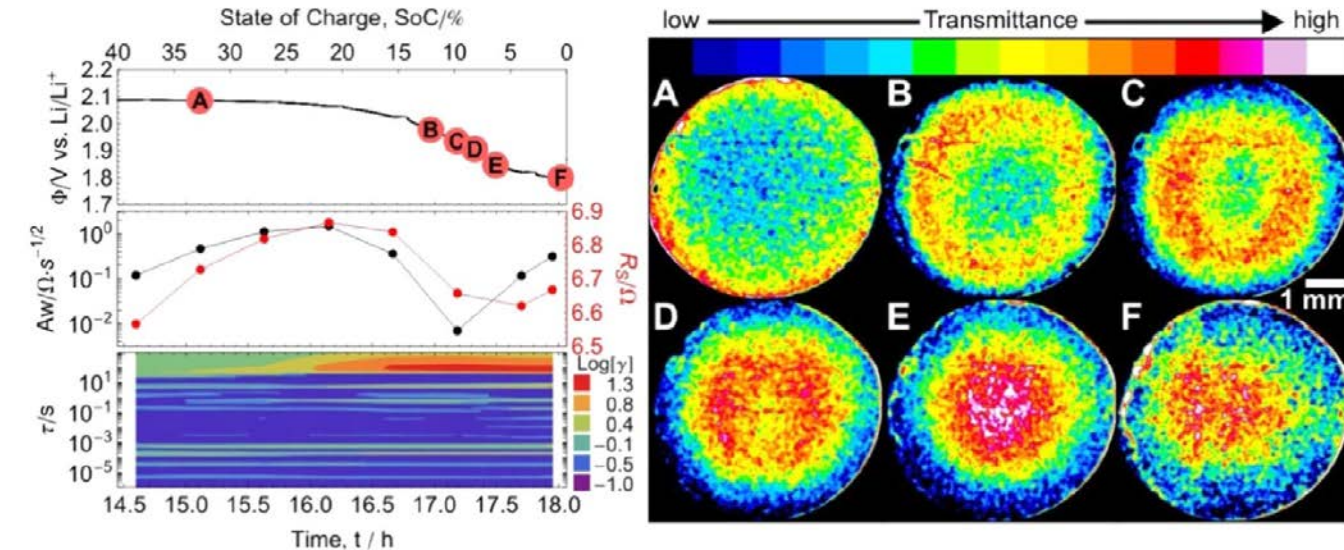
Dry out of cathode material during discharge with high C-rates (decrease of capacity) and its recovery at lo C-rates

X-RAY IMAGING OF MONOLITHIC CATHODE

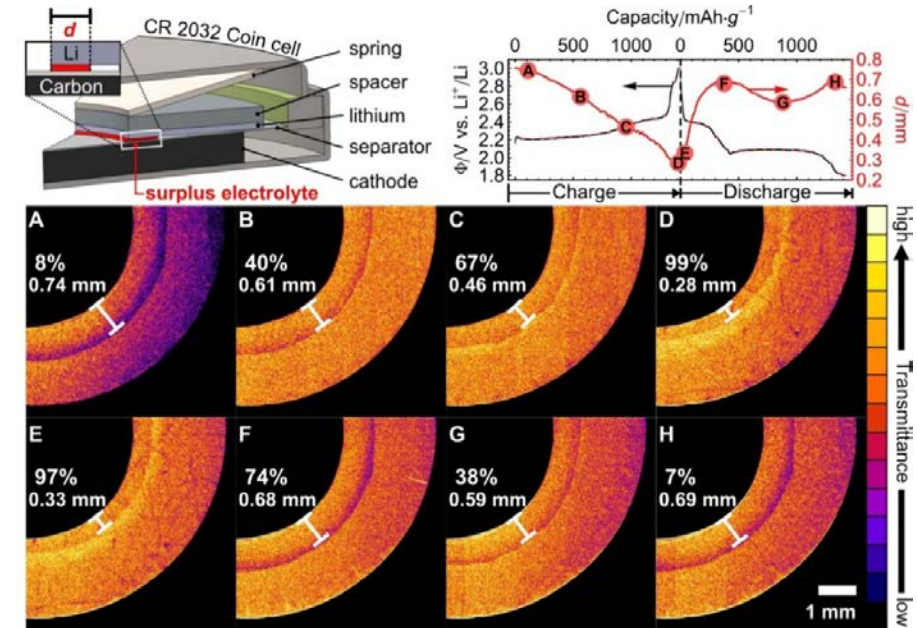
Correlation of EIS and fast/slow fading processes



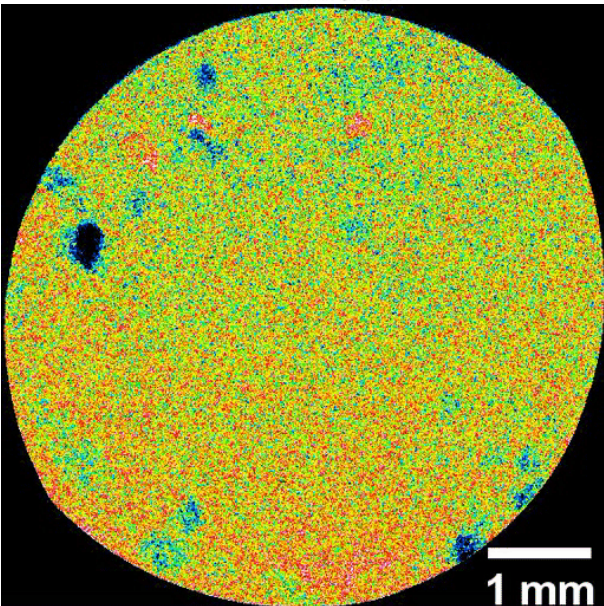
Yan Yang



- Circular reaction front that migrates from the edge of the lithium anode hole to the center
- Mainly controlled by Li^+ ions diffusion

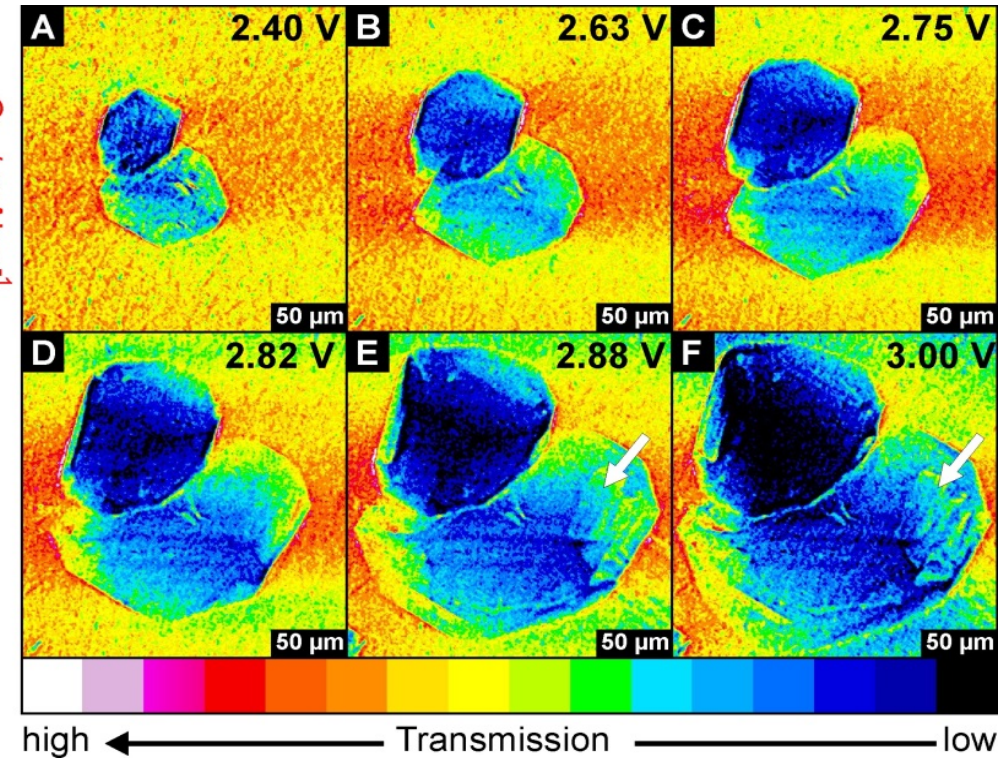
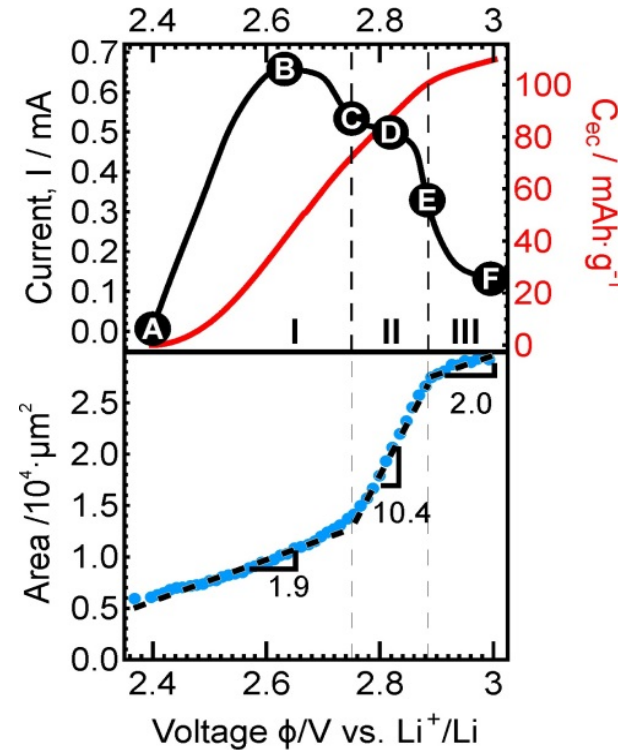
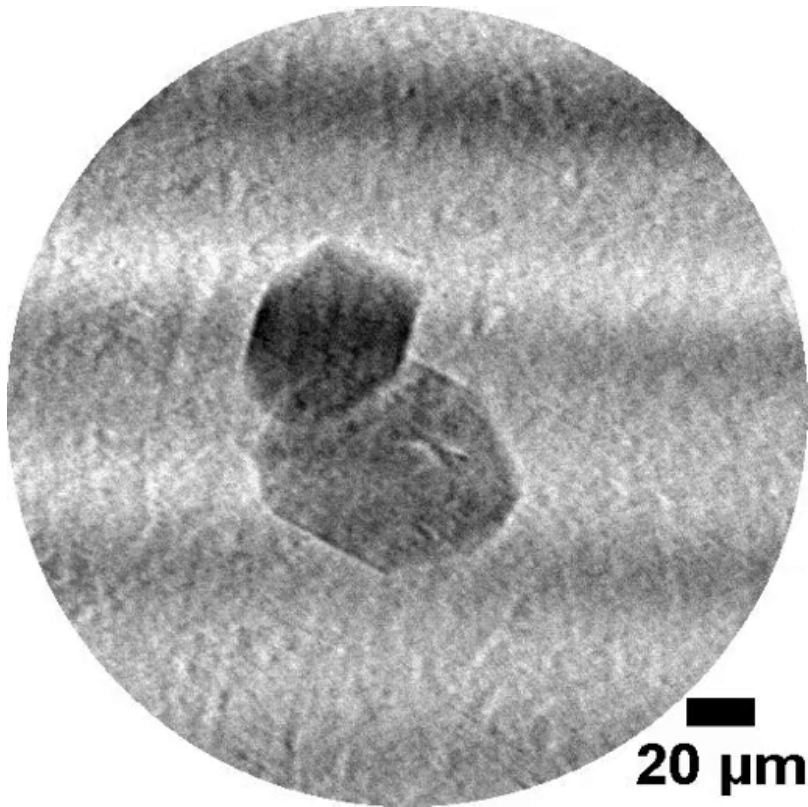


- Surplus electrolyte ring between separator and lithium anode hole
- Possible origins: concentration gradient, volume change of polysulfides, viscosity change, change of transport properties of polysulfides

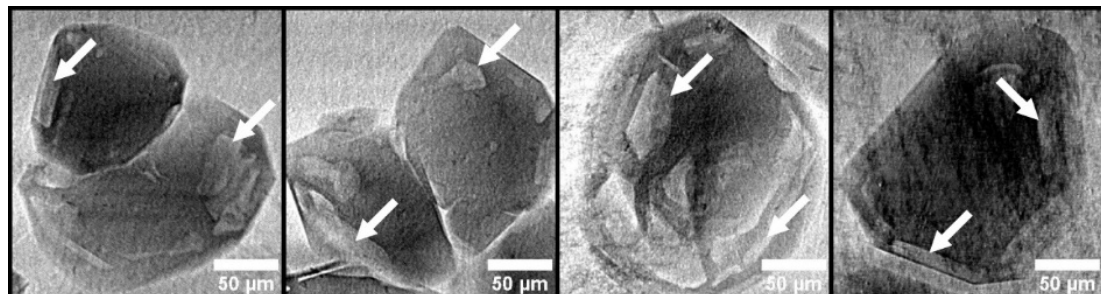


SYNCHROTRON X-RAY IMAGING

From crystal formation to reaction kinetics

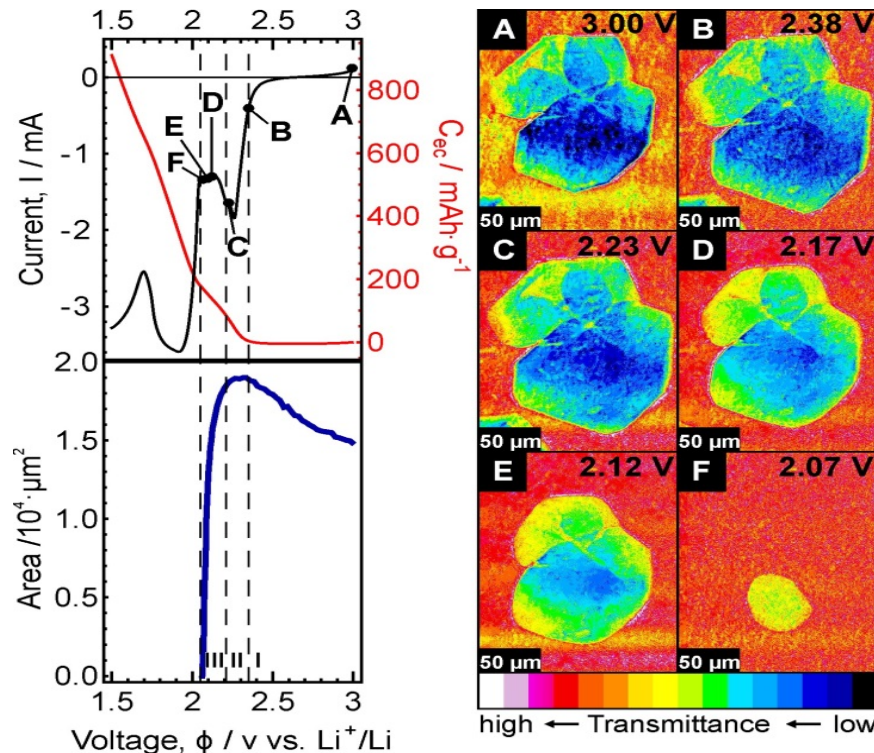
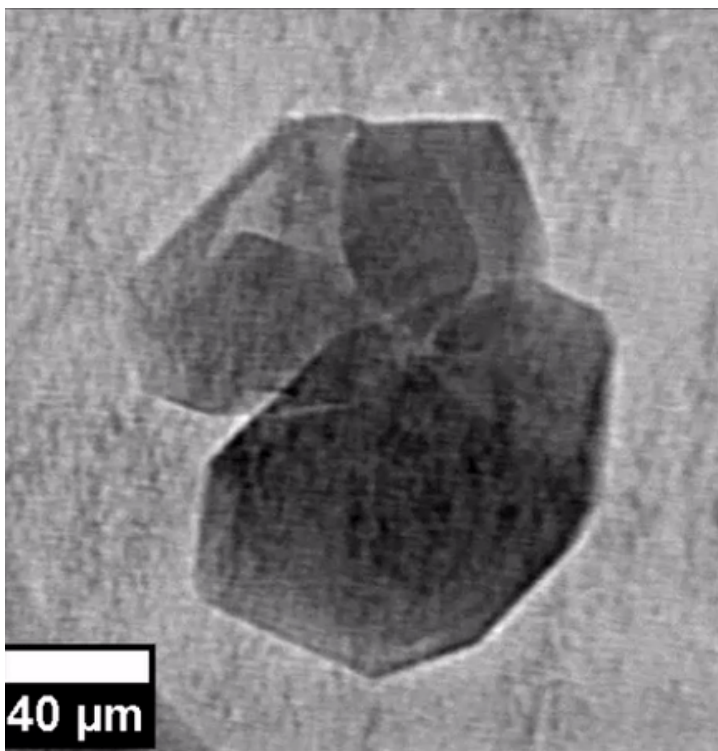


- Three growth regimes (fastest from 2.75V – 2.88 V **just after** cathodic peak)
- Crystal defects during fast growth aligned to crystal edges
→ recrystallization or liquid inclusions(?)

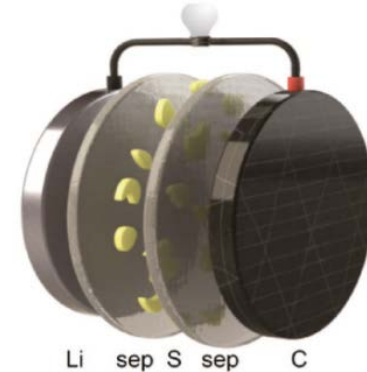


SYNCHROTRON X-RAY IMAGING

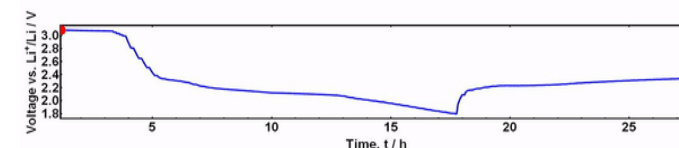
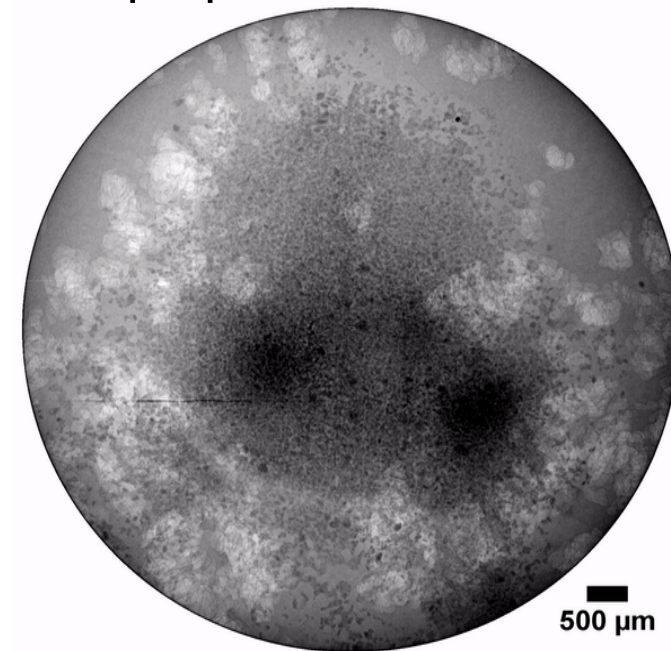
From crystal formation to reaction kinetics



Harks *et al.*, *Adv. Energy Mater.* 7 (2017) 1601635



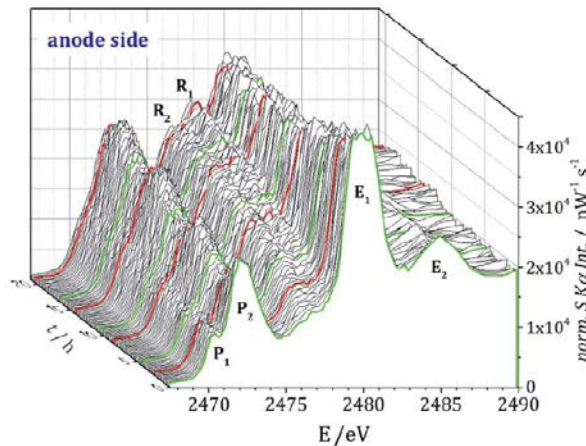
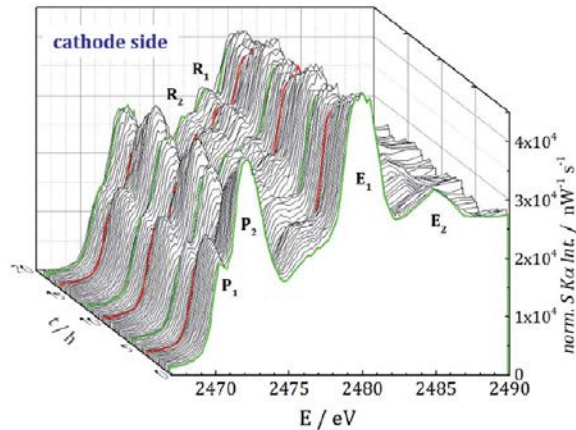
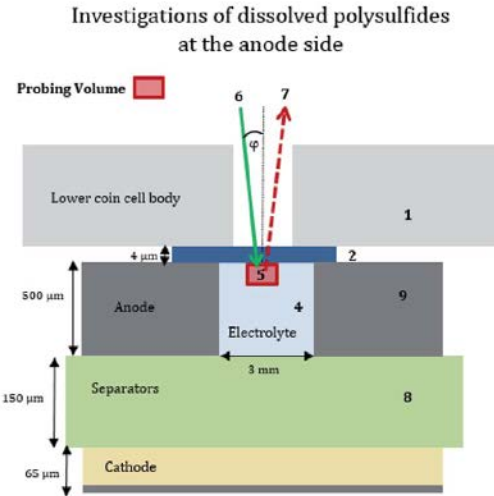
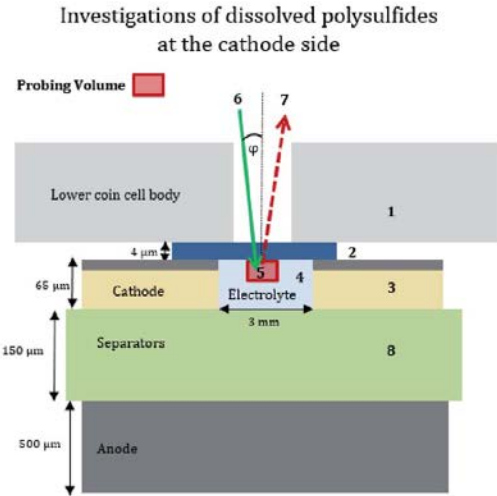
Fast sulfur dissolution by polysulfide mediated comproportionation



- Rapid dissolution of α -sulfur during first discharge step **just after** first anodic peak
- Strong indication for short-chain polysulfide mediated sulfur dissolution process
- Sulfur must not be electrically connected to the conductive host matrix

OPERANDO XAS OF LI/S CELL

Quantitative measurement of mass deposition of polysulfides in the electrolyte (*PTB-work*)



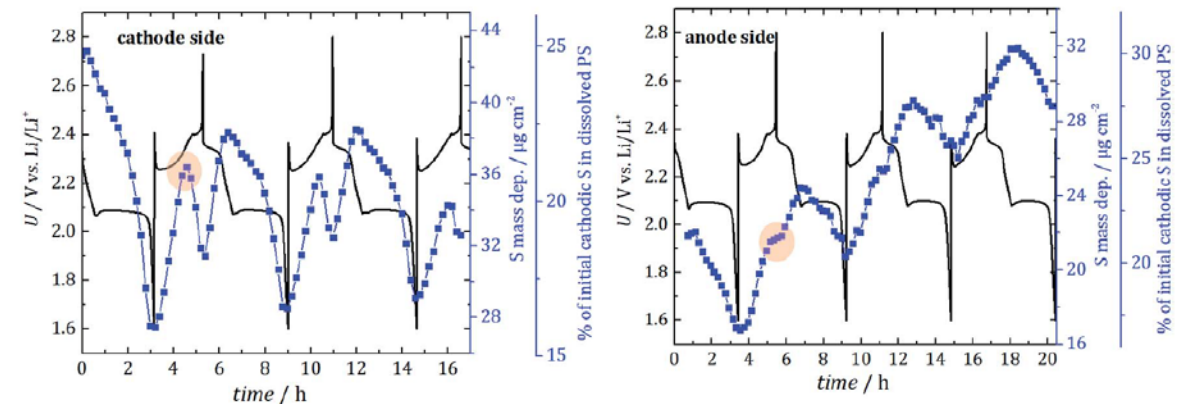
- Quantitative measurement of sulfur mass deposition
- Measurement of long and short chain polysulfides in the vicinity of the anode and cathode
- Elucidation of state-of-charge dependent diffusion processes in Li/S cells
- Data could serve as benchmark for subsequent simulations
- **Electrolyte properties are decisive!**



Claudia Zech

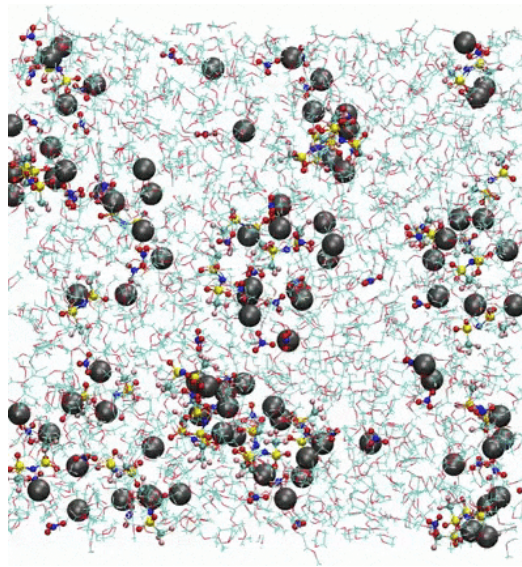
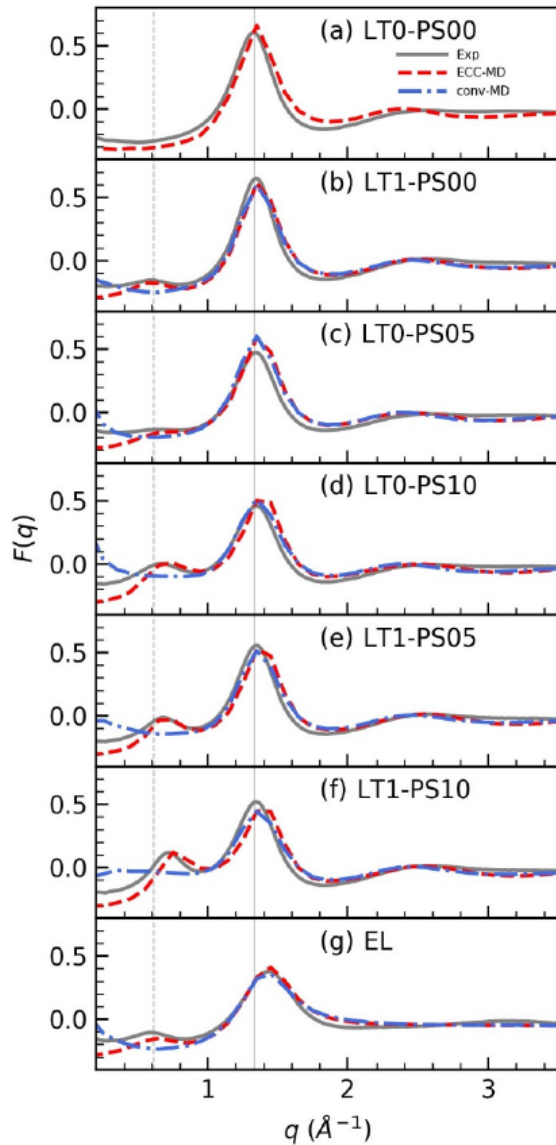


Burkhard Beckhoff

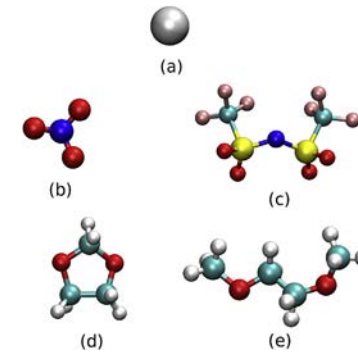


MD SIMULATION OF ELECTROLYTE IN LI/S BATTERIES

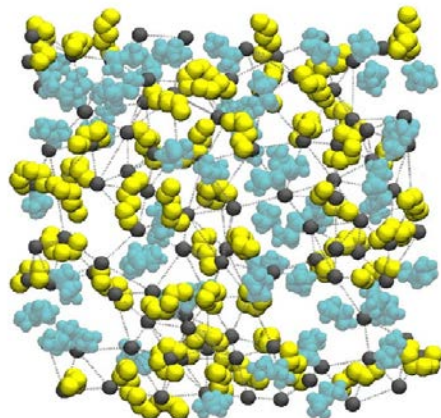
Elucidation of complex ion interactions in the Li/S electrolyte



C. Park, M Kanduč, R Chudoba, A Ronneburg, S. Risse, M Ballauff, J Dzubiella*, *J. Power Sources* 373 (2018) 70

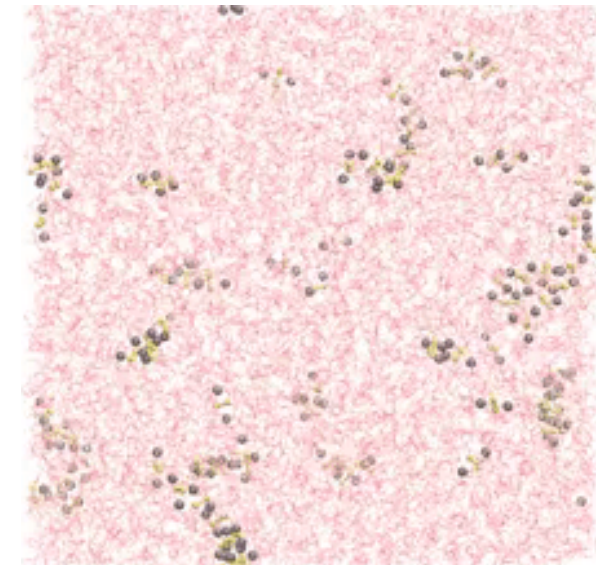


- Ion diffusion in Li/S electrolyte
- Pair distribution function



- Assessment of MD simulations with structure factor from neutron total scattering (NTS)

C. Park, M Kanduč, TF Headen, TGA Youngs, J Dzubiella S. Risse*, *Energy Storage Materials* 52 (2022) 85-93



- Short chain polysulfide clustering



Chanbum Park

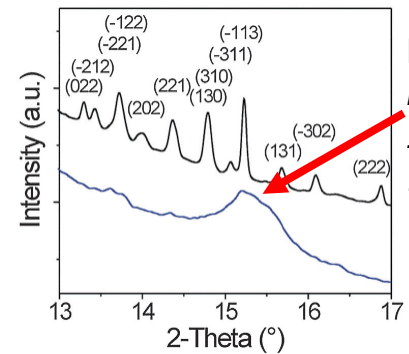
C. Park, A Ronneburg, S. Risse, M Ballauff, M Kanduč, J Dzubiella* *J. Phys. Chem. C* 123 (2019) 10167

Next Step:

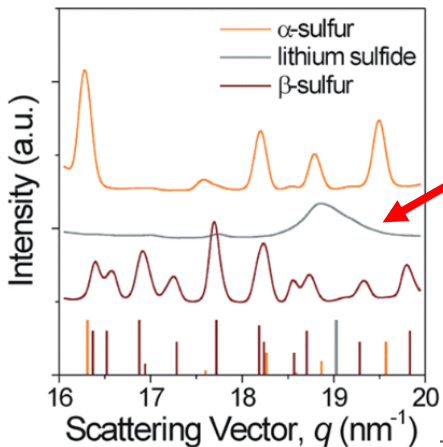
QENS + NTS + MD
Simulation study of new electrolyte by **TU Dresden**

XRD AND SANS OF LI2S

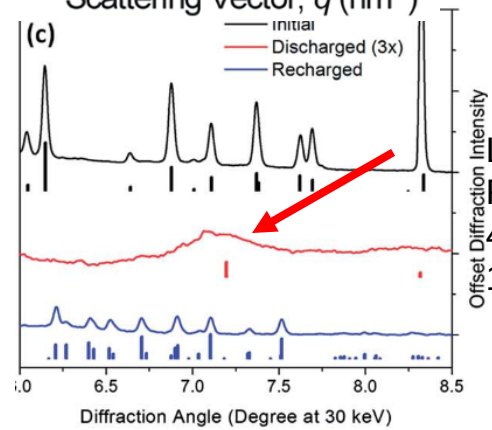
Following the microscopic discharge product



Kulisch J *et al.*,
PCCP.
16 (2014)
18765

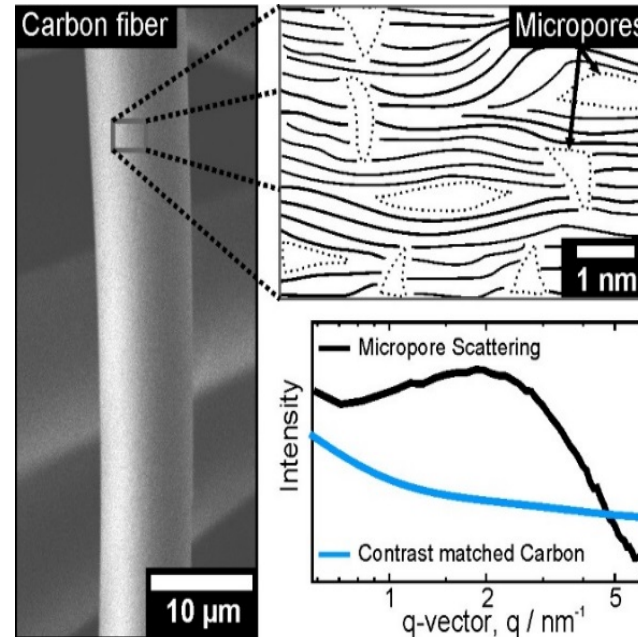


Schneider A *et al.*,
Chem. Mater.
27 (2015)
1674

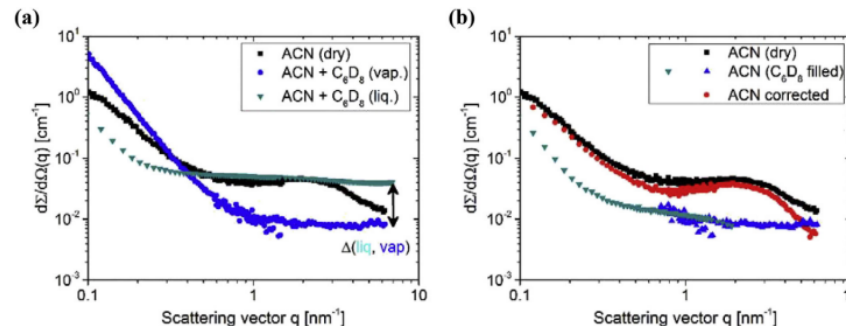


Lowe MA *et al.*,
RSC Adv.
4 (2014)
18347

Small angle Neutron Scattering (SANS)

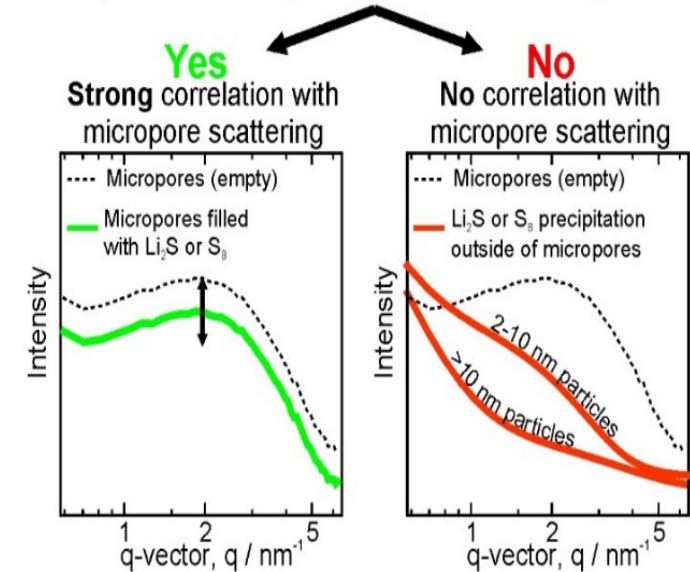


Full characterization of electrode
material ACN-157-15



CJ Jafta, A Petzold, S Risse, D Clemens, D Walalcher,
G Goerigk, M Ballauff, *Carbon* 123 (2017) 440

Precipitation of S_8 or Li_2S in the micropores?



- + 25 meV interaction energy
- + Probe of bulk electrode
- + Crystallinity is not needed
- + Very high contrast to deuterated electrolyte
- + **Locus of precipitation site!**



Eneli Härk



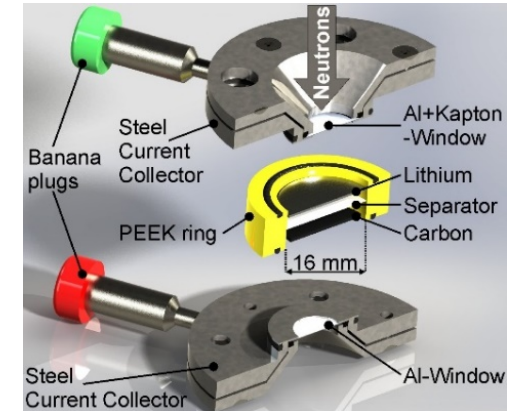
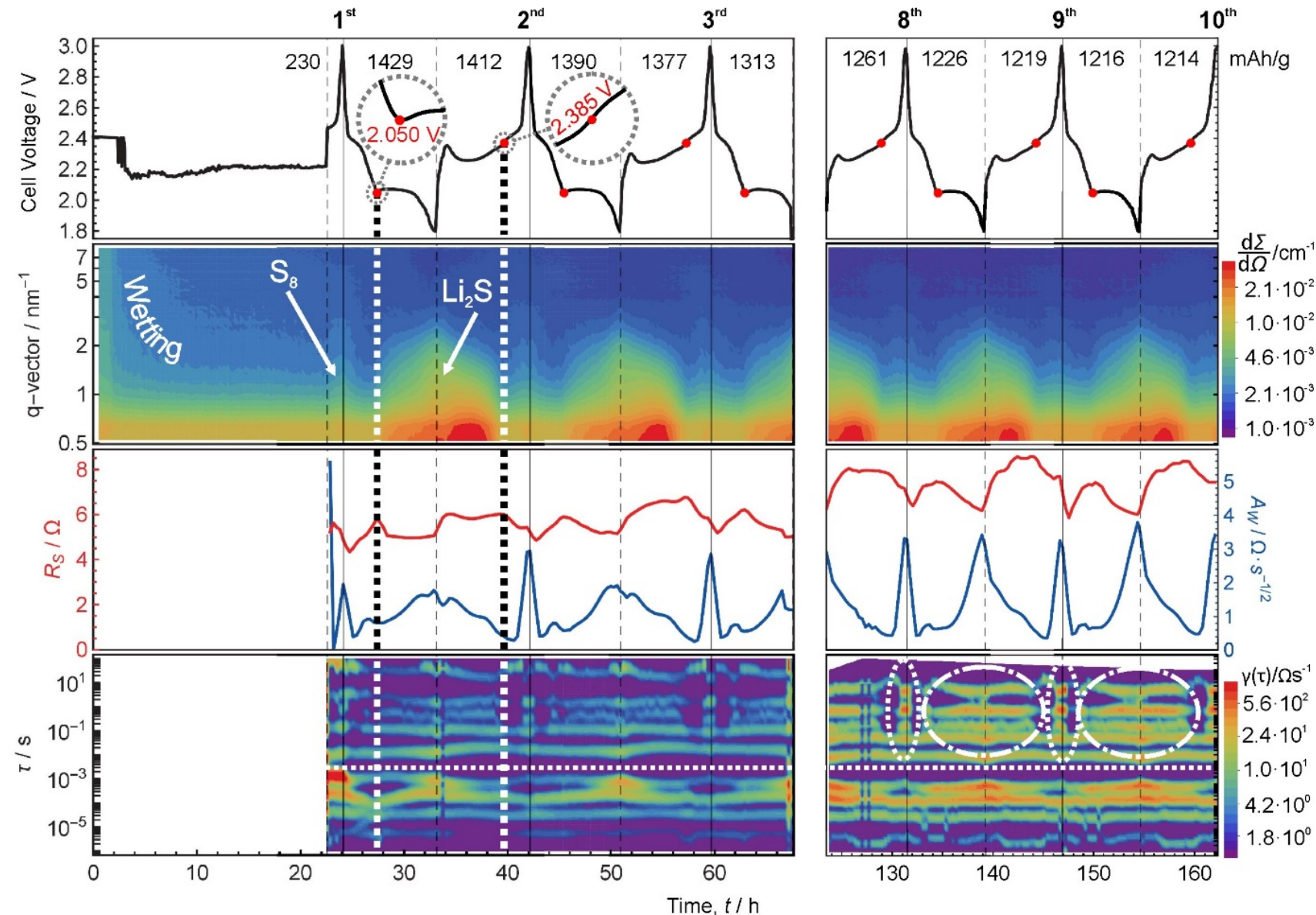
Charl Jafta



Ben Kent

OPERANDO SANS EXPERIMENT OF A LI/S CELL

Following the microscopic discharge product



Eneli Härk



Ben Kent

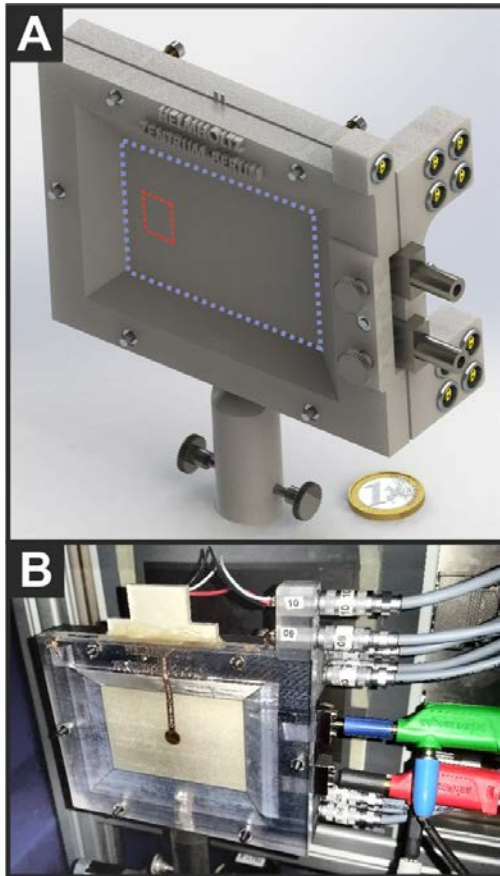
- Stable cycling over 10 cycles
- Unique access to Li_2S precipitation due to contrast matching
- Neither Li_2S nor S_8 precipitate in micropores
- Correlation between phase precipitation and *in-situ* EIS

FIRST OPERANDO IMAGING OF LI/S POUCH CELL

Investigation of industrially relevant cell formats



Rafael Müller

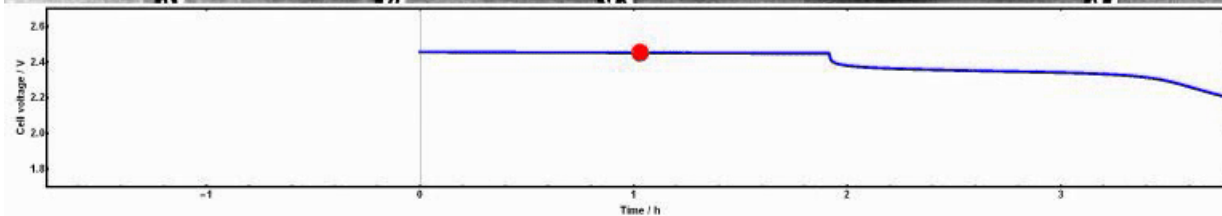
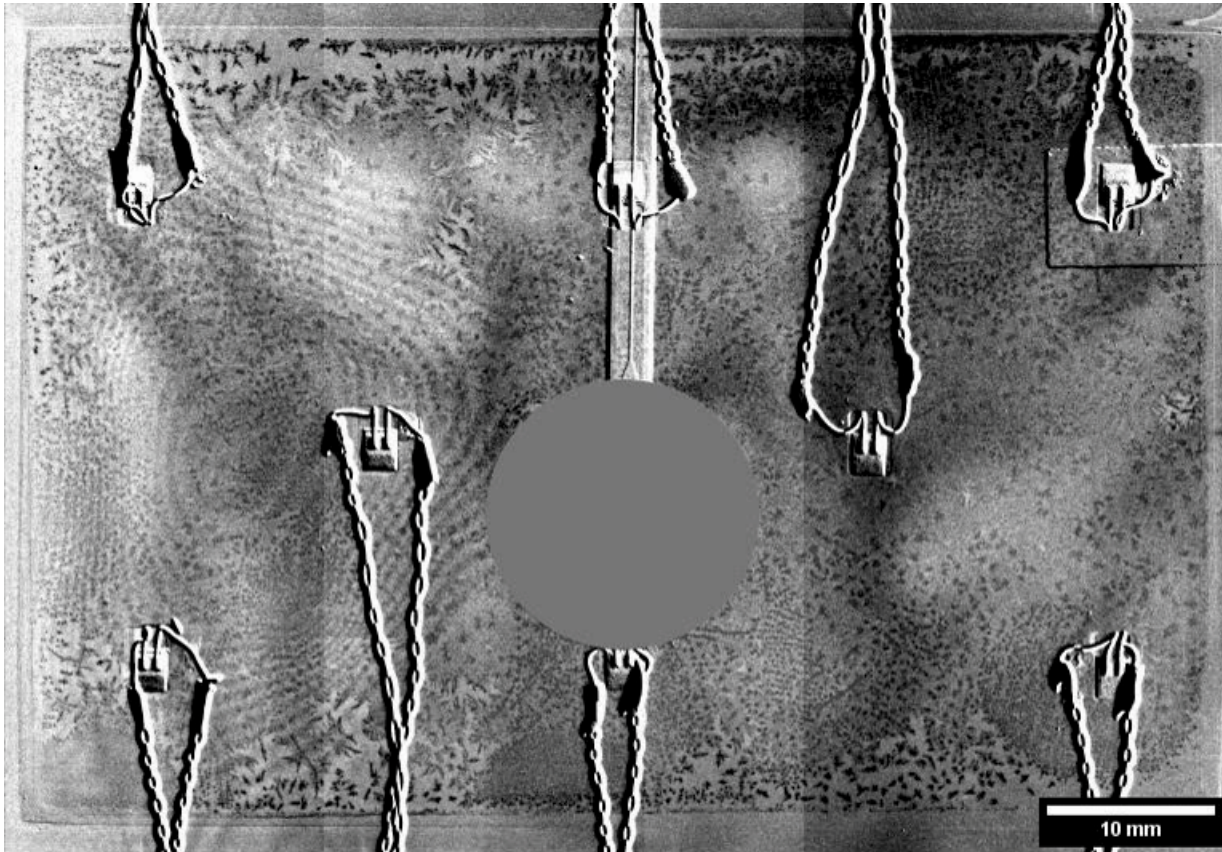


B: Assembled and connected holder
in the HZB μ CT experiment

C: Pouch cell of Fraunhofer IWS with Radiography overlay

FIRST OPERANDO IMAGING OF LI/S POUCH CELL

Full Cell View



Full cell view video (DD30)

Video available online (see SI of R Müller *et al.*)

Static features:

- pressure sensor (masked)
- 8 temperature sensors connected by twisted cables



Rafael Müller

Operando features:

- Initial sulfur distribution
- Dissolution upon discharge
- Li_2S formation and dissolution
- Attenuation domains
 - Cell thickness, wrinkles
 - Electrolyte migration
 - Polysulfide concentration
- (initial beam equilibration fringes)

DD30 Cell details:

Cell dimensions: $71 \times 46 \text{ mm}^2$

Positive electrode: CNT buckypaper with 30 wt% sulfur

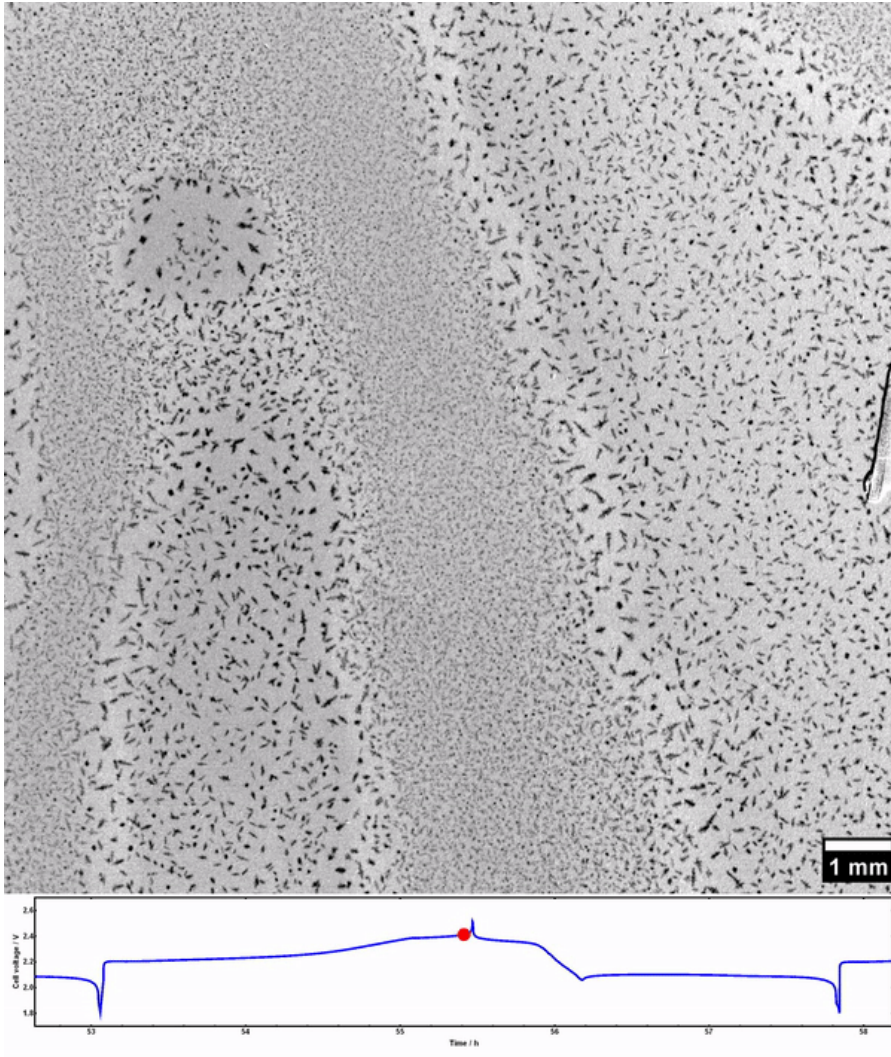
Electrolyte: DME/DOL (1/1), 1.0 M LiTFSI, 0.5 M LiNO_3

Charge rate: 0.1 C

E/S ratio: $\sim 35 \mu\text{L mg}_\text{S}^{-1}$

FIRST OPERANDO IMAGING OF LI/S POUCH CELL

Zoom Study

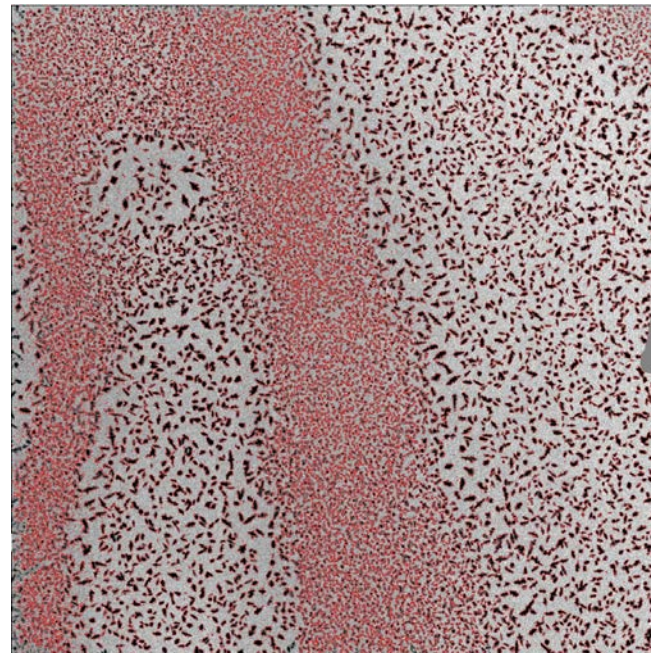


Zoom view video (DD30)

Video available online (see SI of R Müller *et al.*)

Operando features

- Concentric kinetics of sulfur particle growth / dissolution
- S-particle contrast high enough for automatic analysis
- Li_2S domains exhibit gradual edges
 - quantitative separation difficult
- Pseudo-flatfield and contrast enhancement were applied



- Particle mapping in ImageJ
- Time dependent formation analysis interesting for validation of precipitation models in Li/S batteries (e.g., Lattice-Boltzmann-Model)



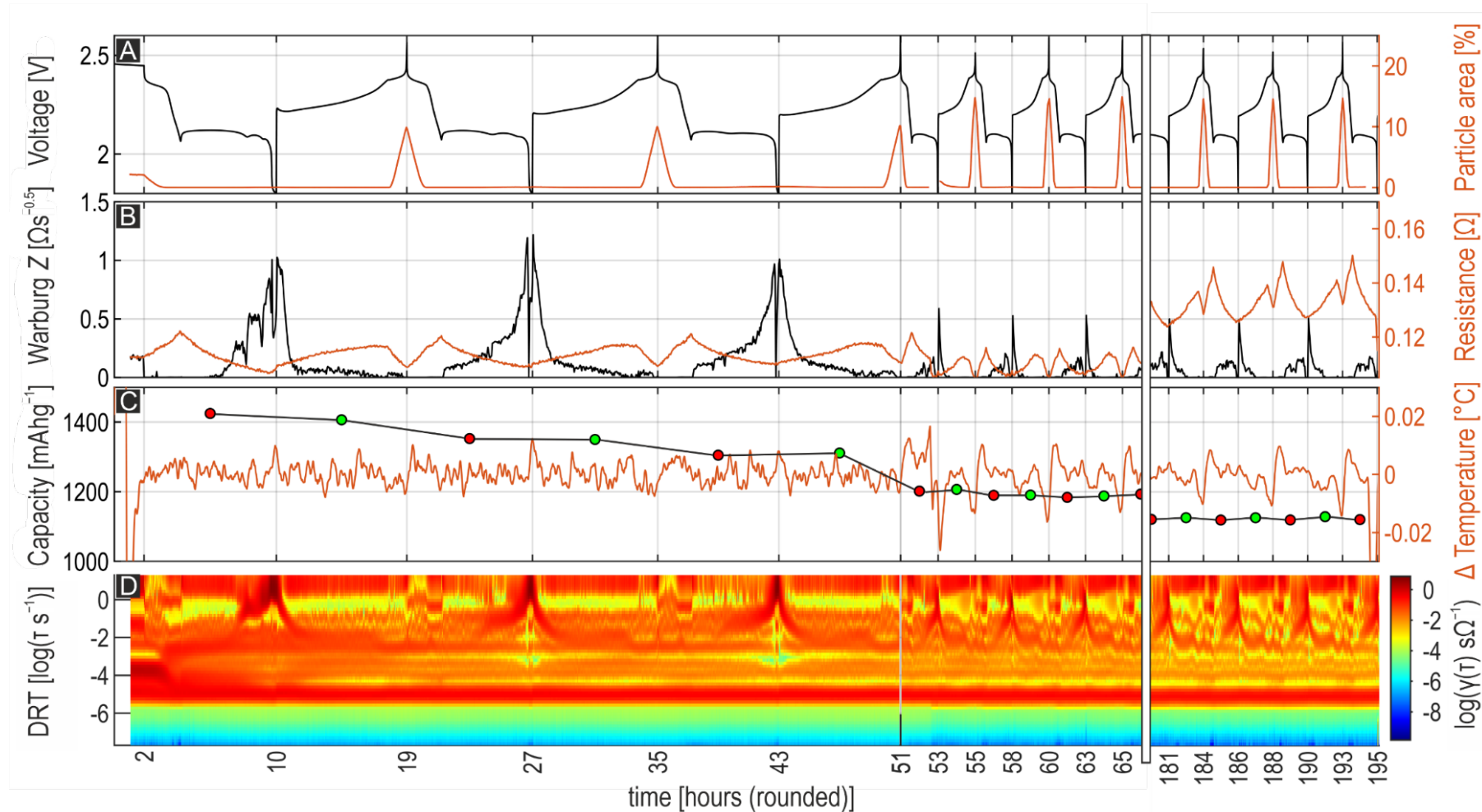
Rafael Müller

CORRELATION OF ELECTROCHEMICAL CURVES IN A LI/S POUCH CELL

Multimodal operando analysis



Rafael Müller



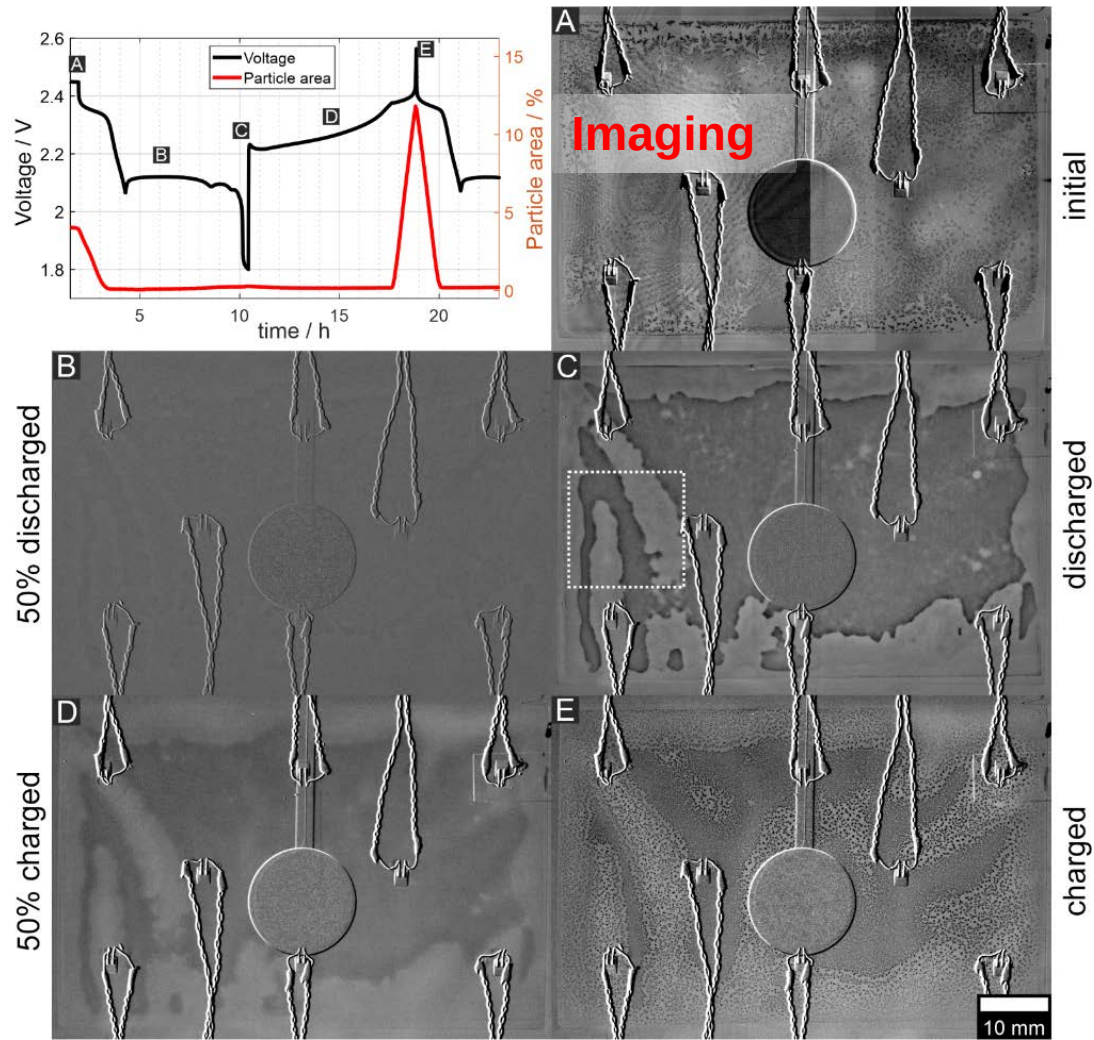
Dataset overview of a pouch cell with DOL/DME and 30% S loading.

Correlation of independent information channels

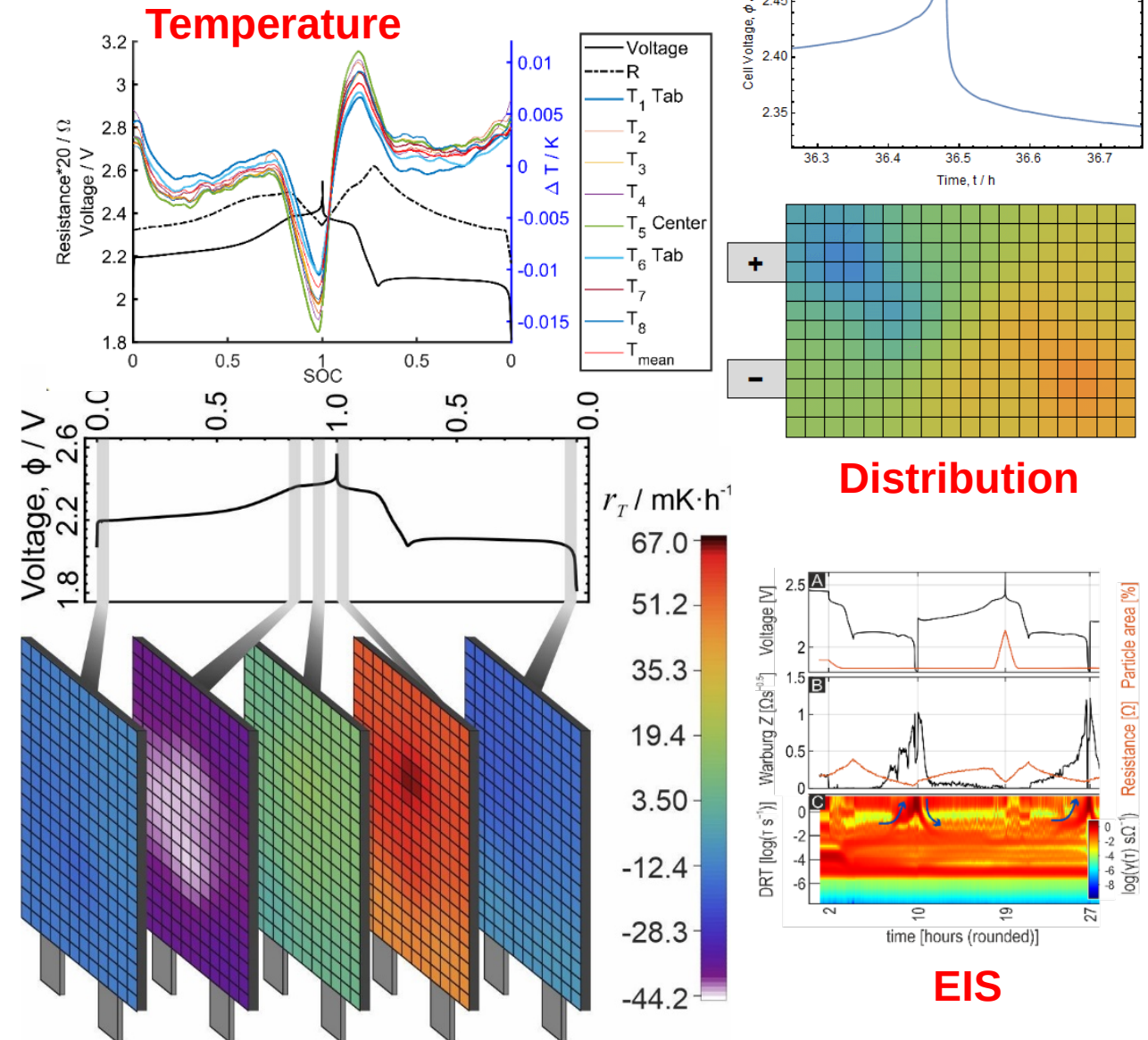
- Ideal for Li/S model validation
- Pressure sensor not sensitive enough for monolayer cell but first results for multilayer cells
- DRT from opEIS is a valuable extra information channel

SUMMARY - LI/S POUCH CELL

Time resolved dependences



Pouch cell DOL/DME and 30% S loading.



DISCUSSION & CONCLUSION

Lessons learned, Outlook, Cooperations ...

Contact: sebastian.risse@helmholtz-berlin.de

Lessons learned:

- Multimodal Operando analysis is a suitable tool for process understanding in Li/S batteries and
- We must mitigate parasitic reactions at the lithium metal anode
- We need sulfur electrode structures enabling fast transport of active species in tailored electrolytes
- Stronger cooperation between synthesis, operando analysis and simulation/modelling

Outlook:

- Experiments with multimodal operando setups and multilayer pouchcells (SkaLiS)
- Precise force/strain measurements for detection of phase precipitation
- Quantitative measurements for better simulation input (OpMetBat)
- Algorithms for high throughput data analysis (OpMetBat)

Cooperations:

- We are always looking for novel Li/S battery material concepts and exciting scientific questions!

Thank you for your kind attention!

