

Tom Boenke & Florian Schmidt, F. Hoffmann, S. Dörfler, T. Abendroth, B. Schumm, H. Althues

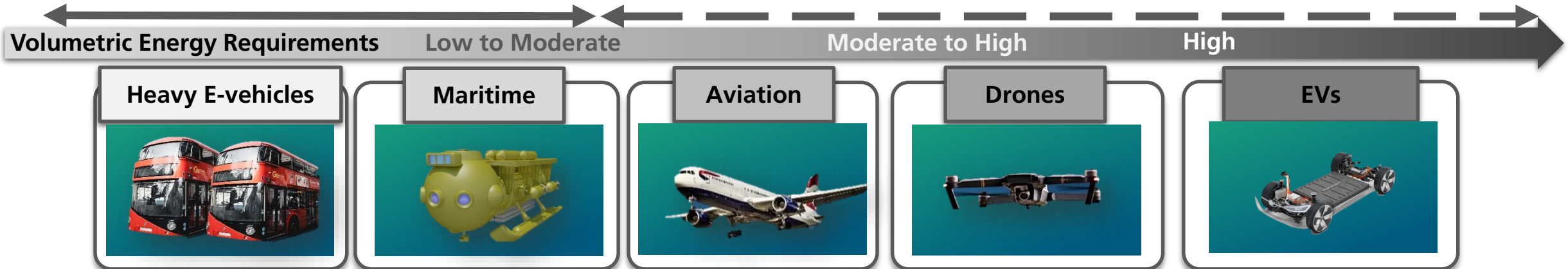
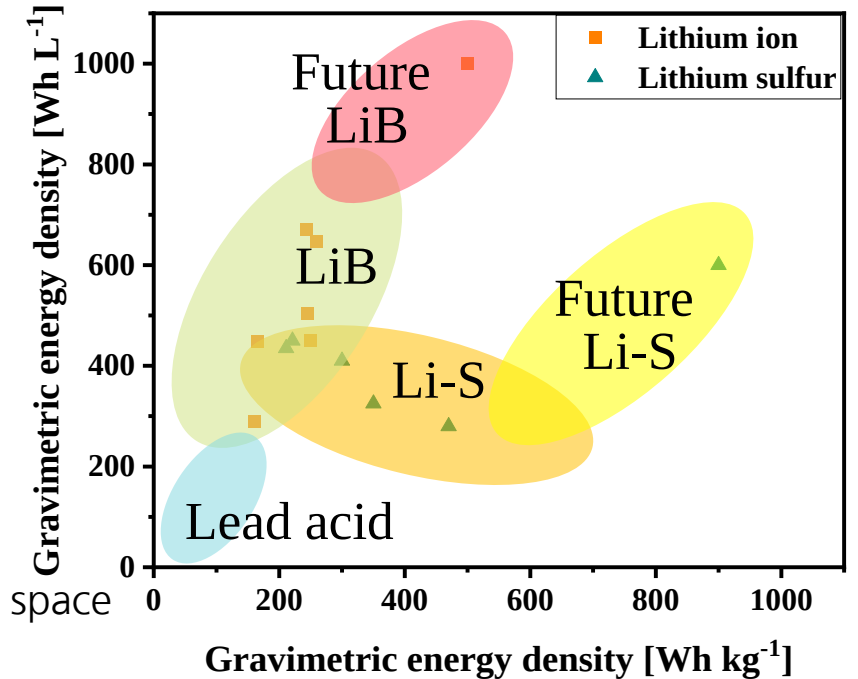
Impacts on the volumetric energy density of the Li-S batteries

Volumetric energy density

An overlooked key parameter

Lithium-Sulfur batteries

- Cost-efficient and abundant active material
- High Gravimetric** energy density
- Insufficient volumetric** energy density
- Volumetric energy density is a key parameter for applications with restricted space
 - Li-S: **Low density** of active material
 - Li-S: **High cathode porosity** & **low cathode density**



Solvent-free S/C cathode coating

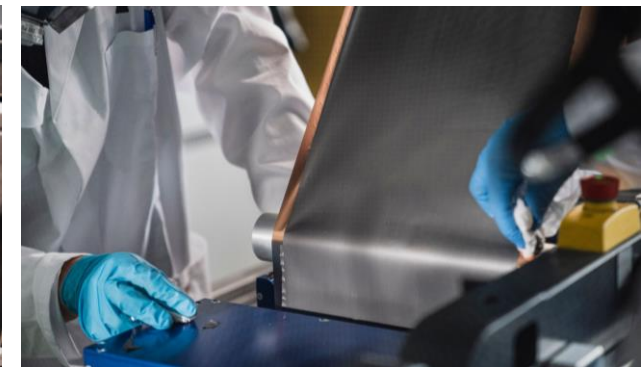
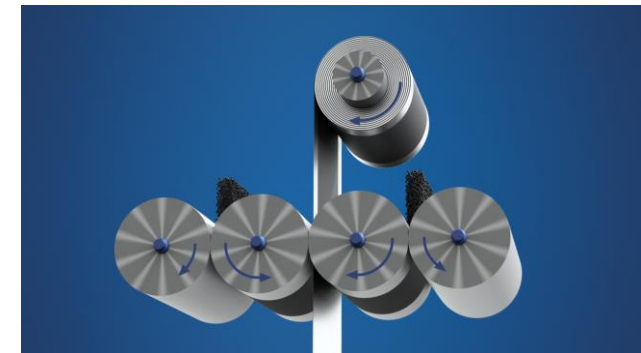
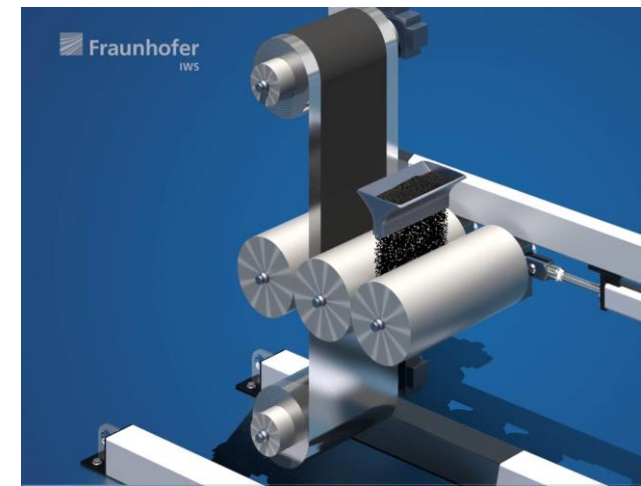
DRYtraec® process

Process advantages

- Green, **solvent-free** electrode coating
- **Low binder content** (3 wt-% and less)
- **No dryers** needed → reduced initial invest and footprint
- Cost-efficient / scalable production
- Wide variety of active materials

Sulfur-Carbon DRYtraec cathodes

- Use of elemental Sulfur as active material
- Industrially available carbons as host material
 - Ketjenblack EC600JD
 - Nanocyl CNT
- PTFE Binder
- Cathode composition: **S/C/MWCNT/PTFE: 60/30/7/3**



Increase of cathode density

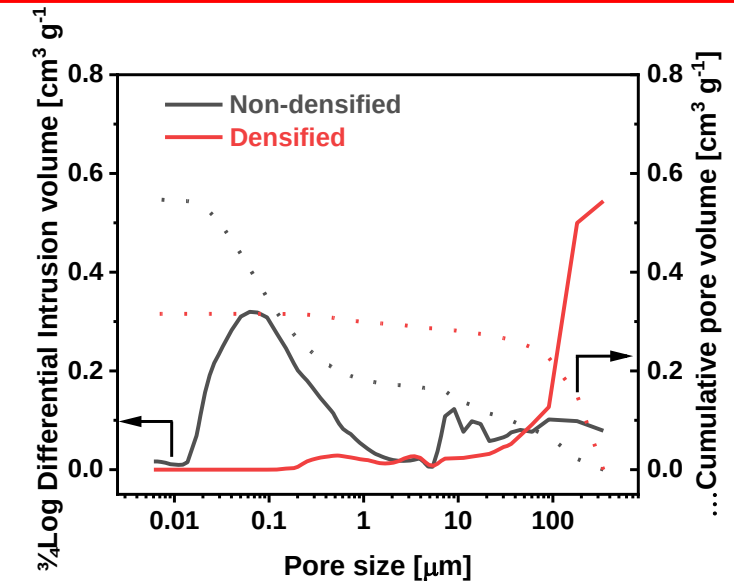
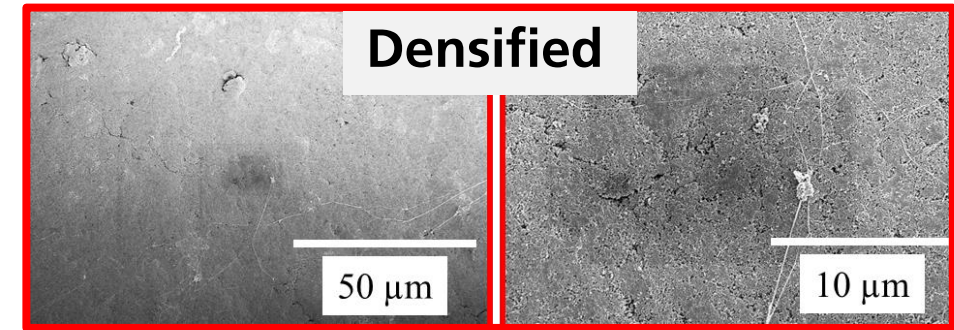
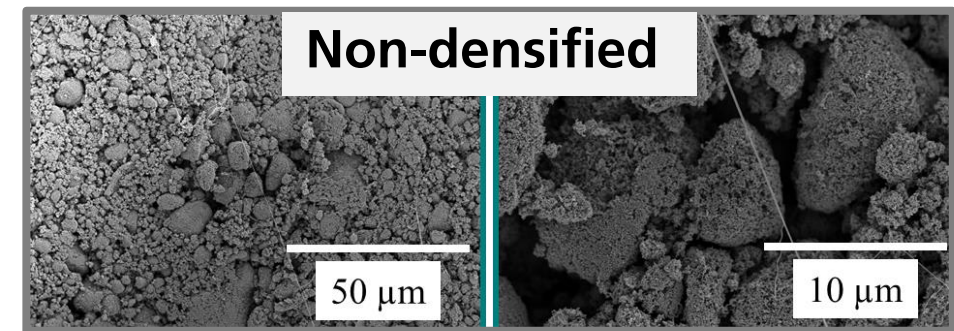
Calendaring and Porosity

Volumetric energy of Li-S limited by high cathode porosity

➤ Increase of cathode density by calendaring

- Increase of cathode density ($0.5 \rightarrow 1.0 \text{ g cm}^{-3}$)
- Decrease in Hg intrusion volume ($0.55 \rightarrow 0.31 \text{ cm}^3 \text{ g}^{-1}$)
- Reduction of pores below $10 \mu\text{m}$
- Contradicting impact of cathode density reported
- Evaluation in ether-based electrolytes

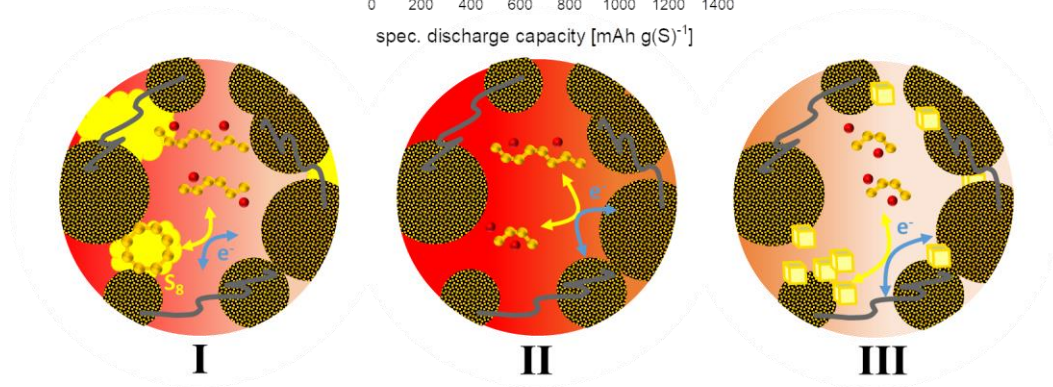
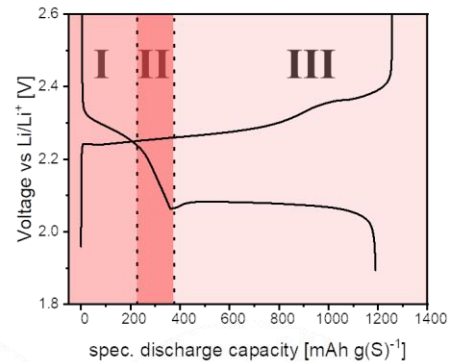
Cathode: 60 wt%(S); $2.8 \text{ mg(S) cm}^{-2}$



Li-S Mechanism

Ether based electrolytes

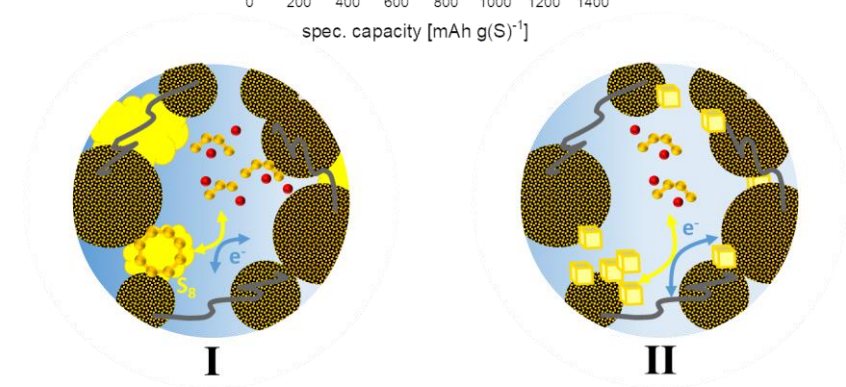
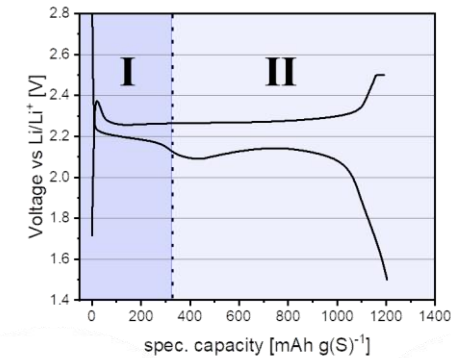
DME/DOL



Dissolution-precipitation mechanism

High PS solubility: $c_{\max} = 5.5 \text{ mol}_s \text{ L}^{-1}$

HME/DOL



Quasi-solid state conversion mechanism

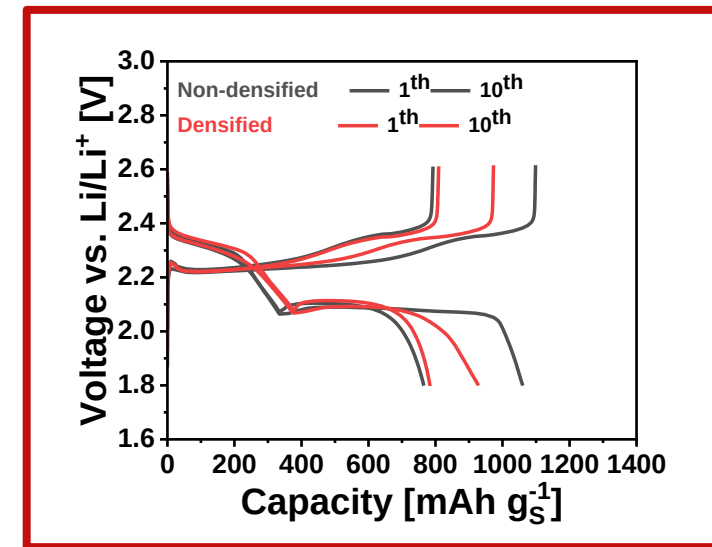
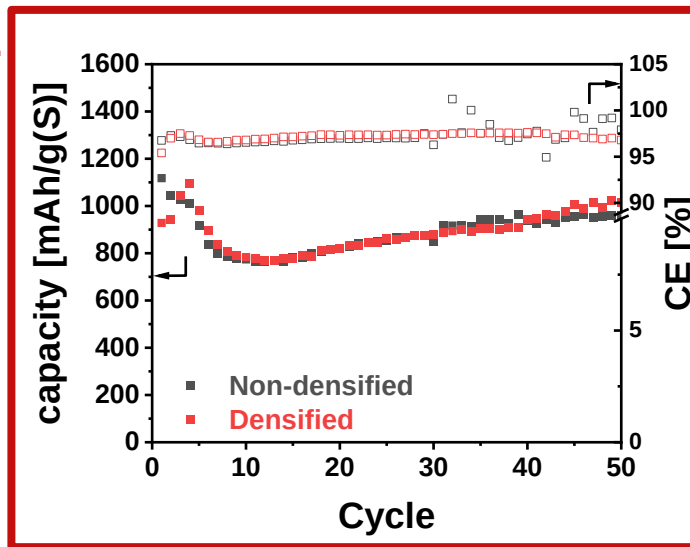
Low PS solubility: $c_{\max} = 0.36 \text{ mol}_s \text{ L}^{-1}$

Galvanostatic cycling

Coin cell testing

DME/DOL

- Initial capacity of compacted cathode lower
- 2nd plateau is reduced
- No discernible impact on later cycles



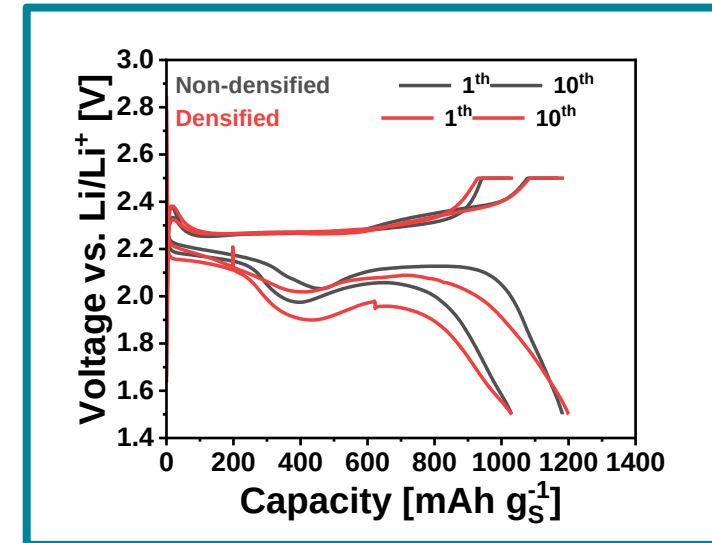
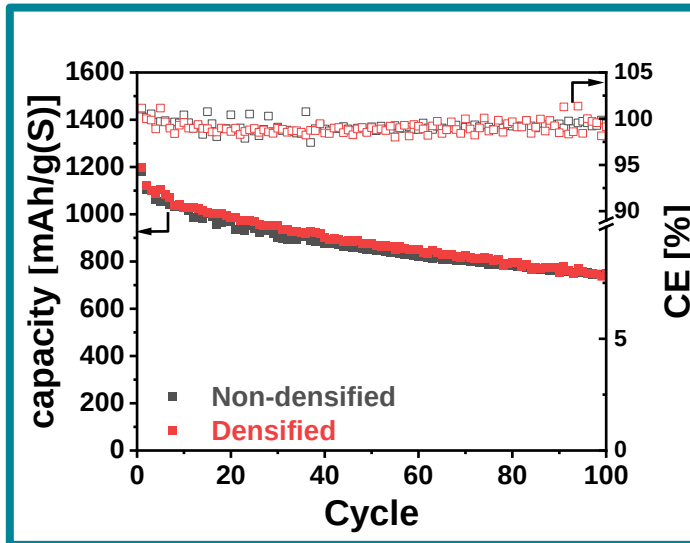
HME/DOL

- Higher overpot. of compacted cathode in the 1st cycle
- Only insignificant impact on later cycles

➤ **Pre-set cathode density has only a limited influence**

➤ **Only the 2nd plateau in the first cycles impacted**

HME/DOL



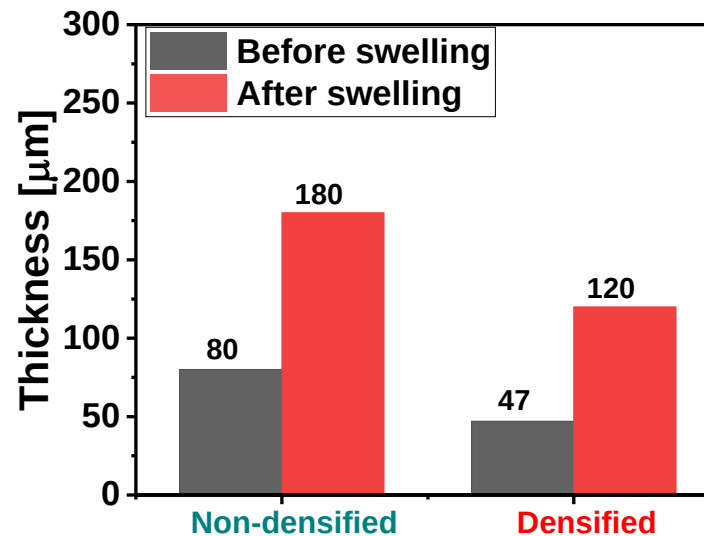
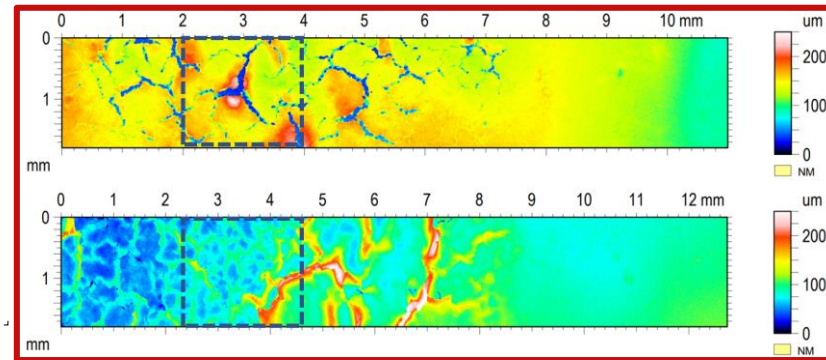
60 wt%(S); 2.8 mg(S) cm⁻²; E/S: 5 μ l mg(S)⁻¹

Cathode swelling

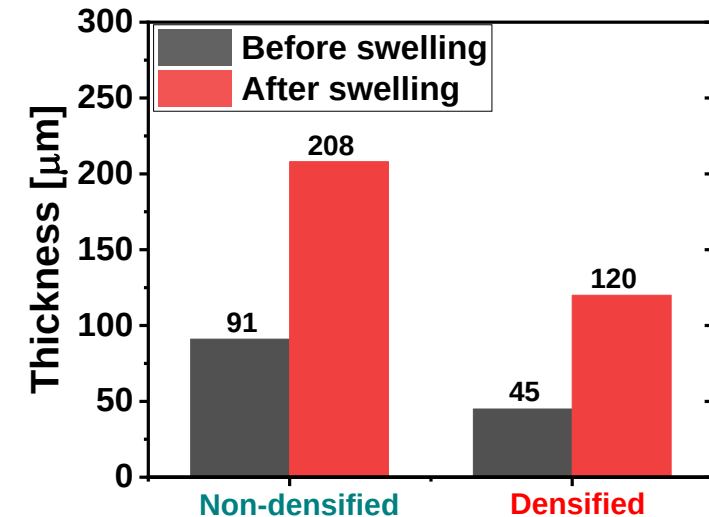
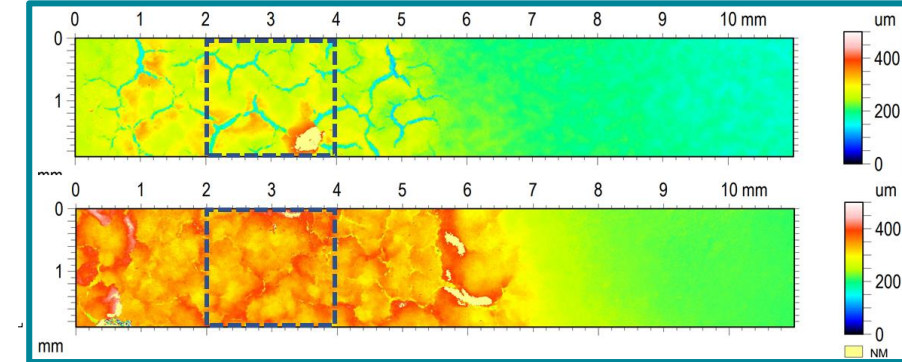
Dynamic swelling analysis

- Investigation of swelling via confocal microscopy
- Application of 10 μL electrolyte
 - Expansion and dry cracking observed
 - Swelling observed for both electrolytes
 - Density after swelling lower than initial

DME/DOL



HME/DOL

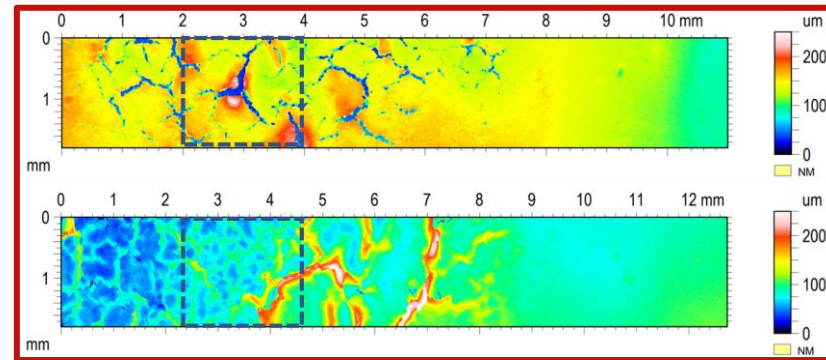


Cathode swelling

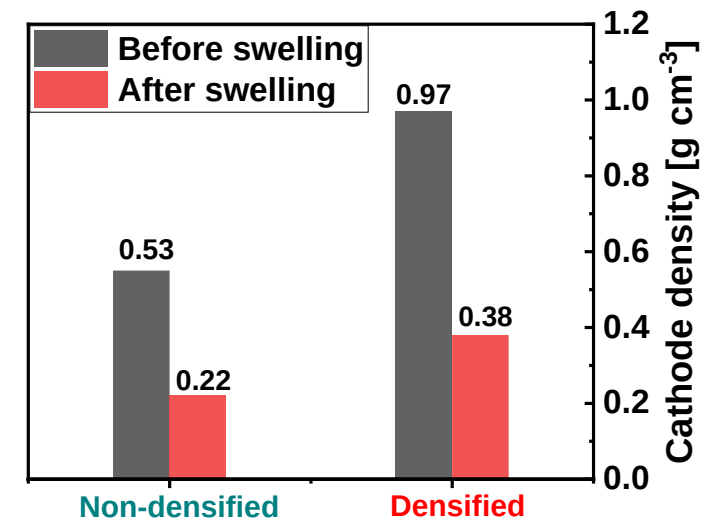
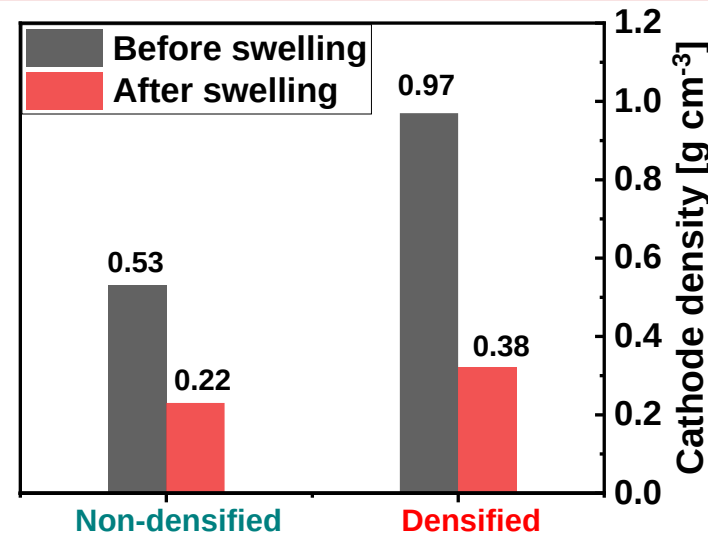
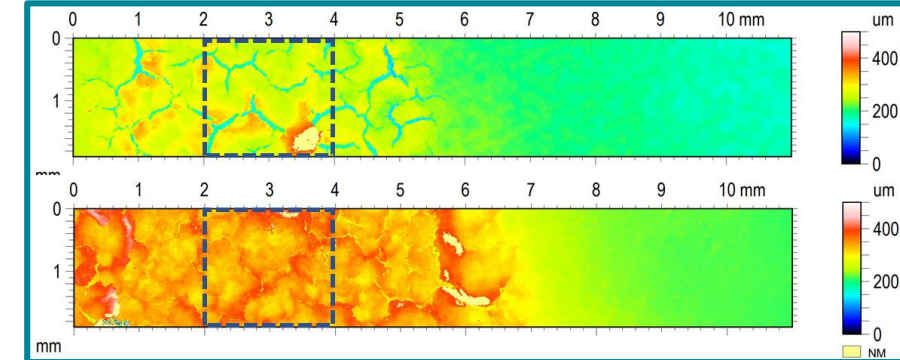
Dynamic swelling analysis

- Investigation of swelling via confocal microscopy
- Application of 10 μL electrolyte
 - Expansion and dry cracking observed
 - Swelling observed for both electrolytes
 - Density after swelling lower than initial

DME/DOL



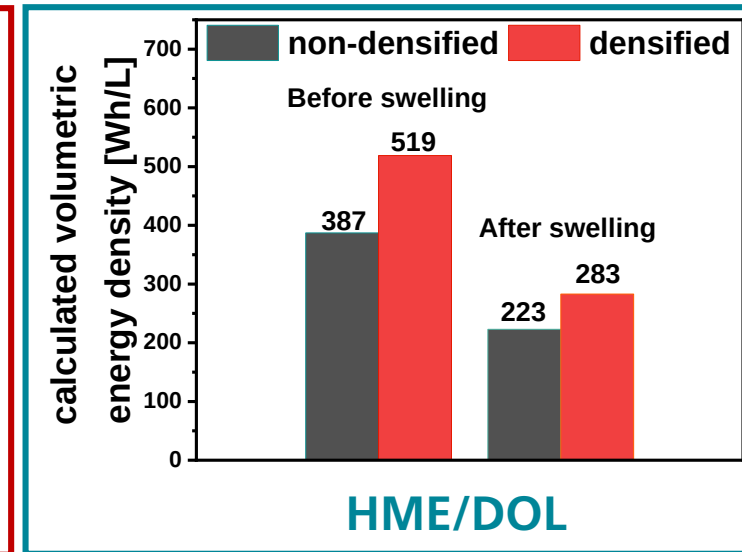
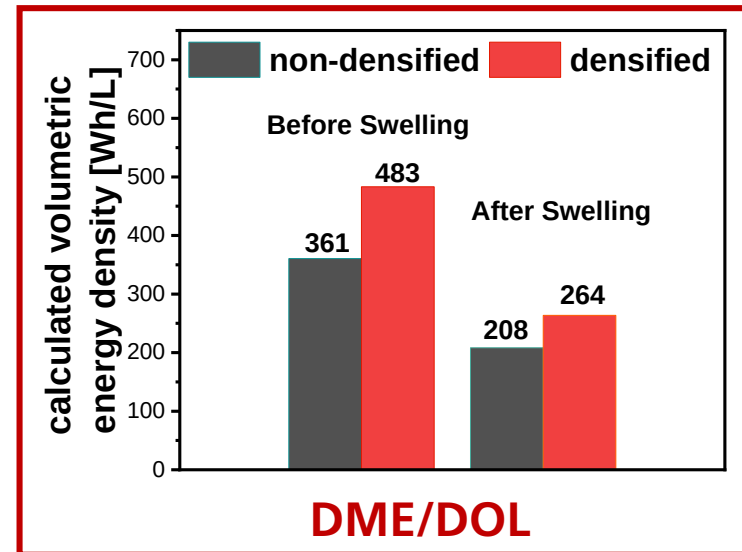
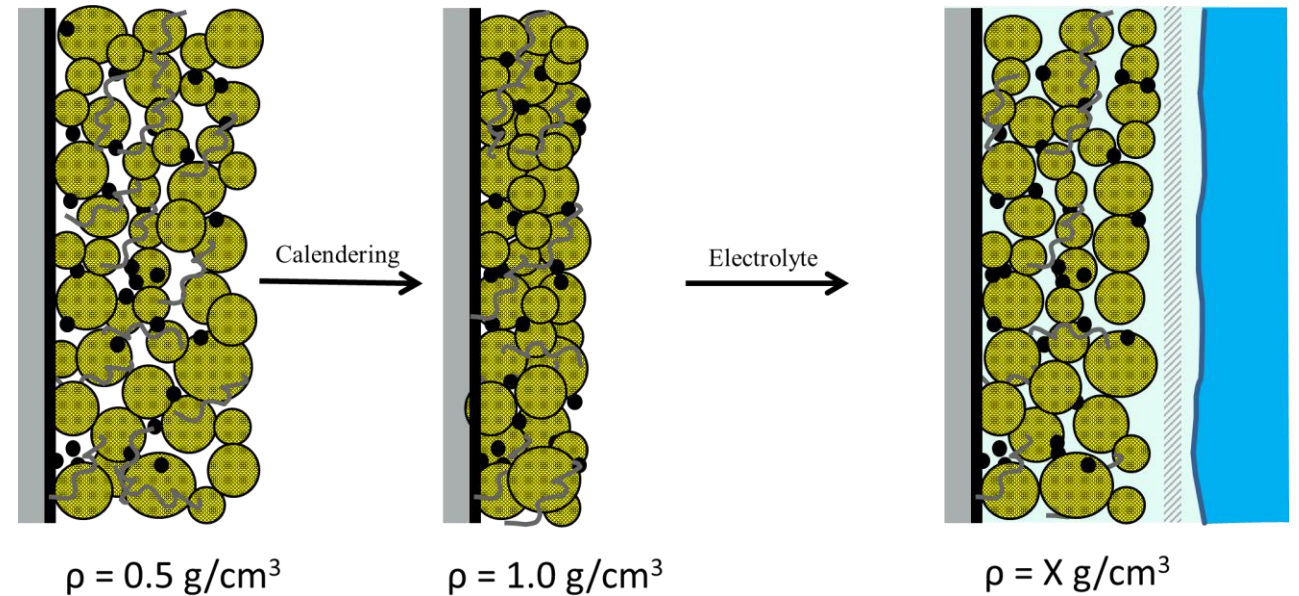
HME/DOL



Cathode swelling

Impact of swelling on energy density

- Density is reduced via calendaring
- Increase in cathode thickness after electrolyte uptake
- Pre-set cathode density is altered by swelling
- Reduction of achieved energy density
- Density has no influence in swellable systems

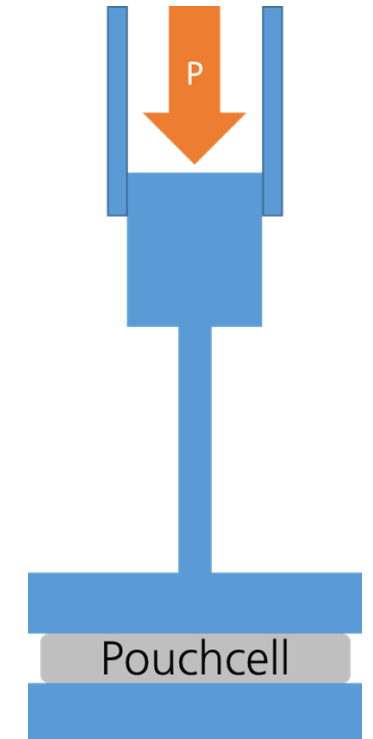
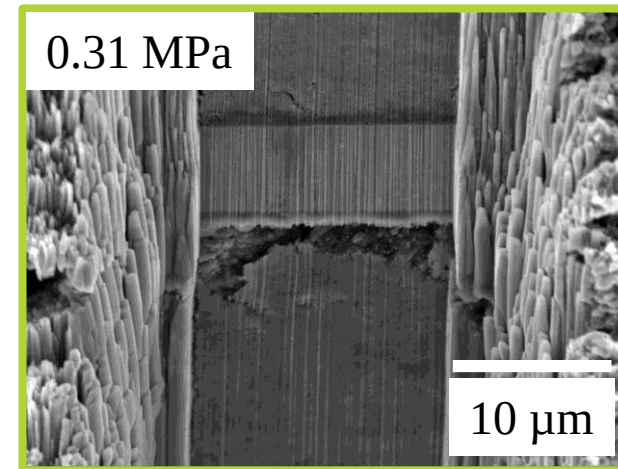
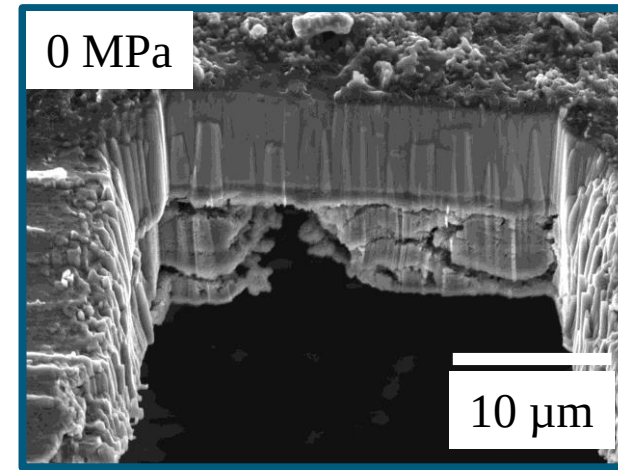


Effect on uniaxial external pressure

In-situ cathode compaction

➤ Prevention of swelling by external pressure

- Use of **non-densified cathodes**
 - Uniaxial pneumatic pressure
 - Pressure varied between 0 – 0.31 MPa
 - Post-mortem analysis after cycling
-
- **In-situ dry-film cathode compaction observed**



5 d-s cathodes, 60 wt%(S); $2.8 \text{ mg(S) cm}^{-2}$; E/S: $4.5 \text{ μl mg(S)}^{-1}$

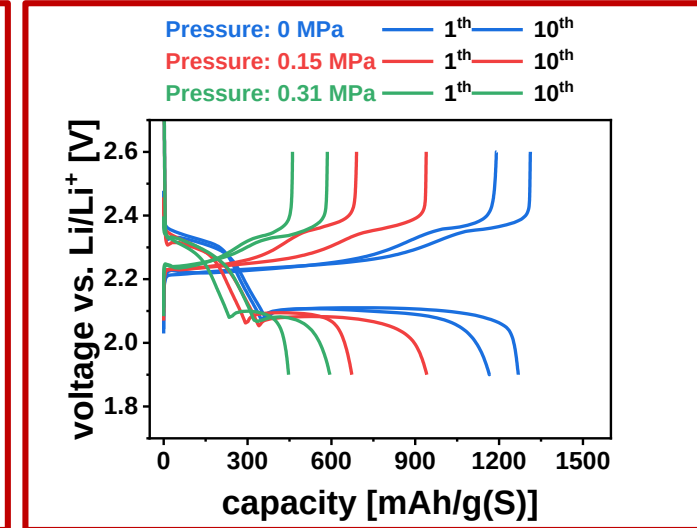
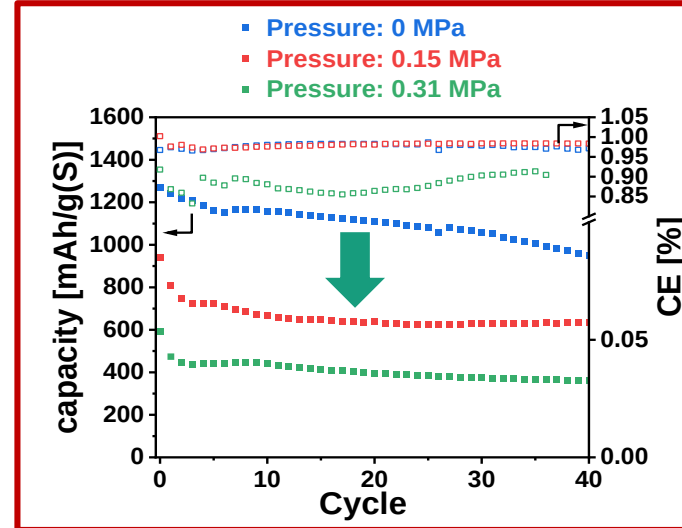
Effect on uniaxial external pressure

Pouch cell cycling

DME/DOL

- Decrease of discharge capacity with rising pressure
- Slight reduction of sulphur utilization
- Hindered discharge reaction in the 2nd plateau
 - Slight overpotential in the 2nd plateau
 - Restriction of solid precipitation
 - Reaction terminated prematurely

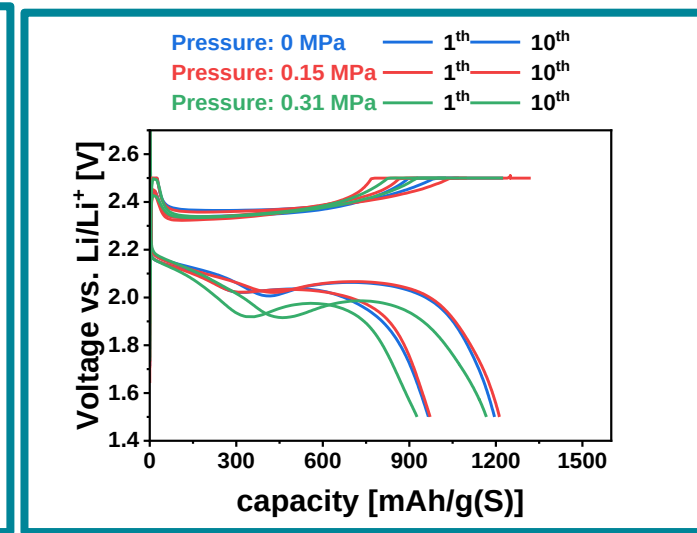
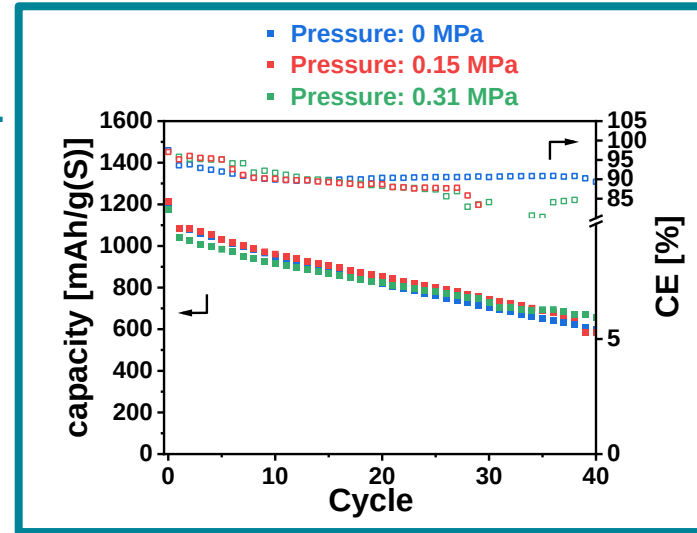
DME/DOL



HME/DOL

- No pronounced impact on performance

HME/DOL



➤ Why are the electrolytes affected differently

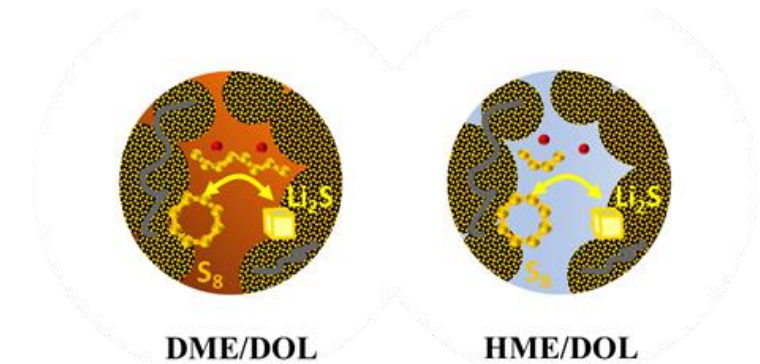
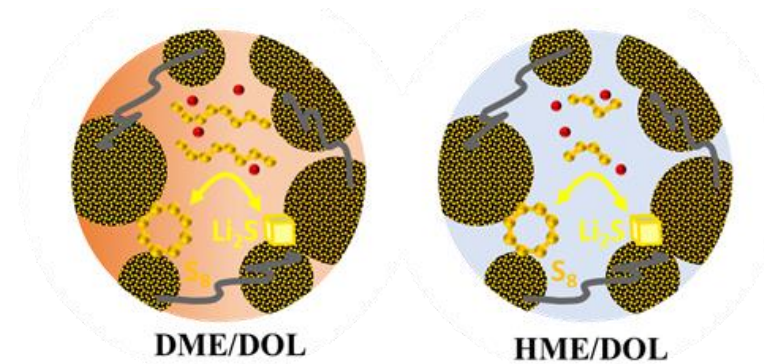
5 d-s cathodes, 60 wt%(S); 2.8 mg(S) cm⁻²; E/S: 4.5 μl mg(S)⁻¹

Pouch cell compression

Effect of PS solubility

Reduction of pore volume

Reduction of electrolyte volume



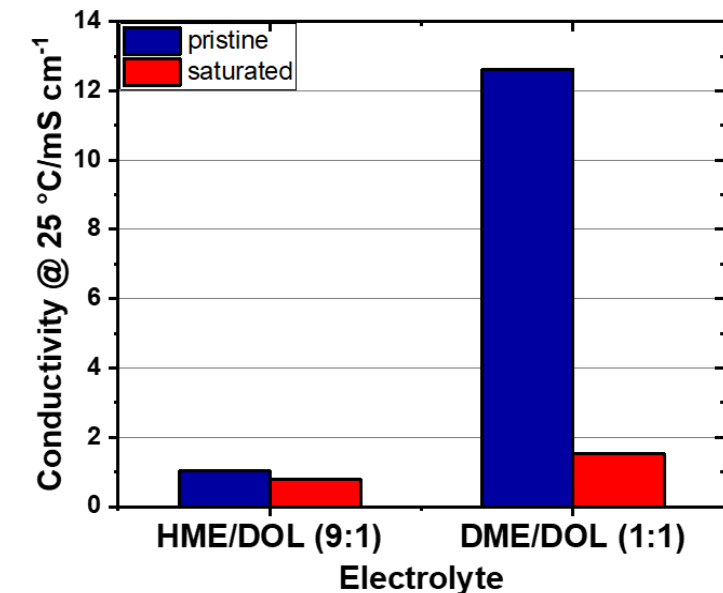
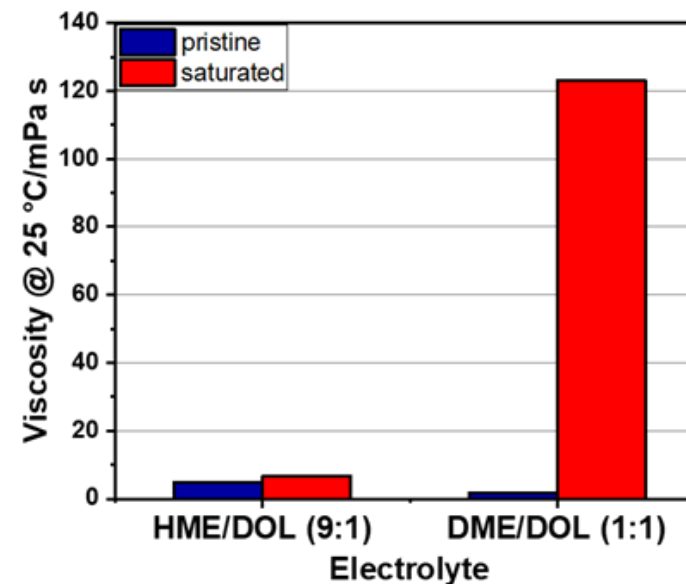
DME/DOL

- High PS solubility
- Decrease in conductivity and rise of viscosity
- Fast oversaturation, lower electrolyte volume
- Termination of reaction

HME/DOL

- Low PS solubility
- Slight effect on conductivity and viscosity
- Negligible impact on reaction

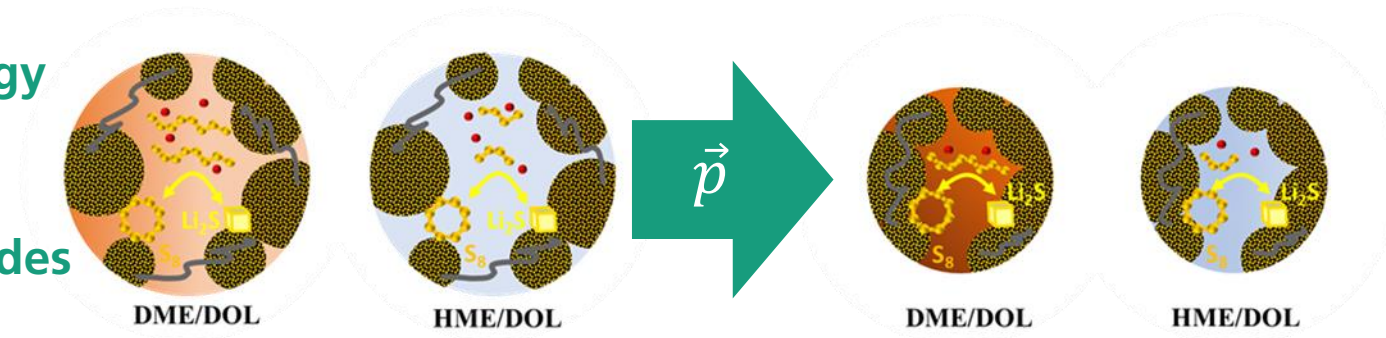
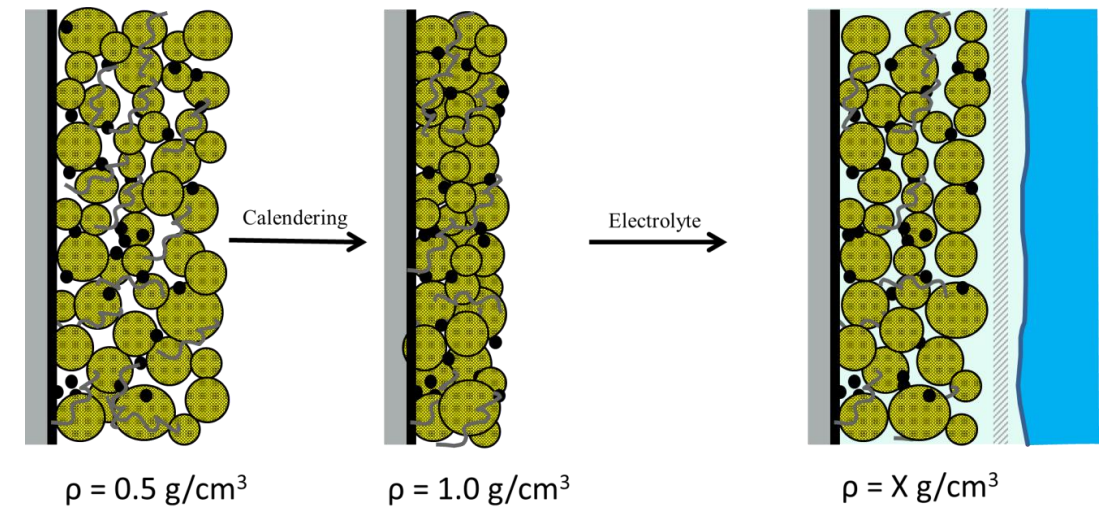
Impact of polysulfide-saturation in electrolytes



Volumetric energy density

Conclusion & Outlook

- Pre-set cathode density affected by swelling
- New method to observe interaction developed
- External pressure suppresses swelling
- Varying impact of external pressure on energy density
- HME/DOL enables use of high-density cathodes
- Development of new low density electrolytes



Advanced Battery Technology Center (ABTC)

Contact

M.Sc. Florian Schmidt
Telefon +49 351 83391 3530
florian.schmidt@iws.fraunhofer.de

Fraunhofer Institute for Material and Beam Technology IWS
Winterbergstraße 28
01277 Dresden
www.iws.fraunhofer.de



Fkz: 03XP0254A



GA No. 814471

#lightatwork

Follow us!

Fraunhofer-Institut für Werkstoff- und Strahltechnik IWS
Winterbergstraße 28
01277 Dresden



www.iws.fraunhofer.de