

Sulfurized Polyacrylonitrile (SPAN) Cathodes in Lithium-Sulfur Batteries: Investigating the Influence of Cathode Microstructure and Electrolyte System on Electrochemical Performance

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Motivation

Why Li-S batteries?

- High theoretical capacity of active materials
- Low cost and non-toxic raw materials
- High theoretical energy density: 2654 Wh kg⁻¹^[1]
practical energy density: >460 Wh kg⁻¹

Why Sulfurized Polyacrylonitrile (SPAN) as Cathode?

- Solid-solid conversion → prevents polysulfide dissolution and shuttling, improves performance
- High cycle life and thermal stability, excellent coulombic efficiency and reversibility

Employment of **Electrochemical Impedance Spectroscopy (EIS)** for identification, investigation and quantification of underlying mechanisms

Approach and methods

1. Cathode system

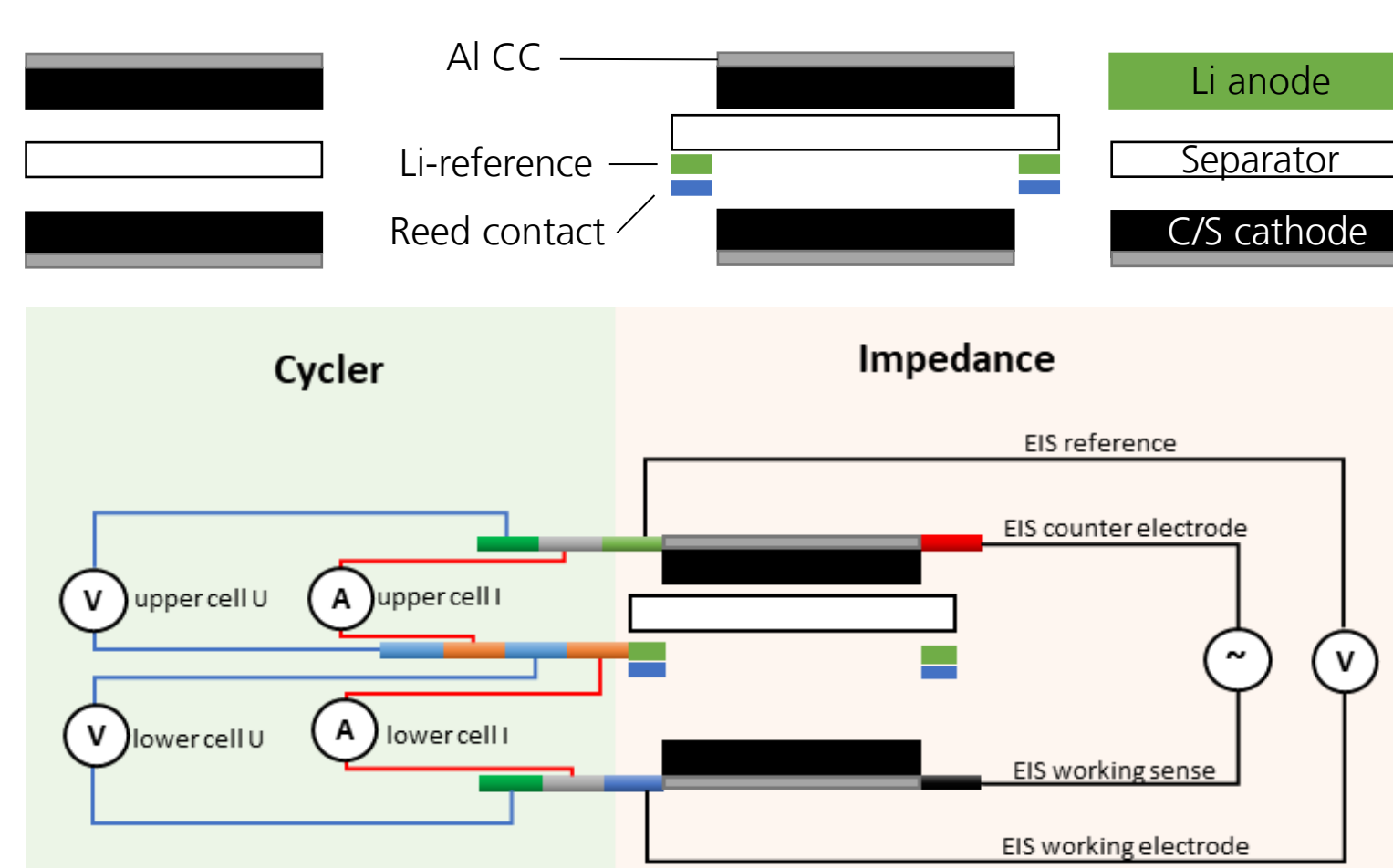
Sulfurized poly(acrylonitrile) SPAN compound (~38w%S) with 5% binder and 5% conductive agent

Calendering to various compression grades (1x):

Compaction in gap [%]	Nominal calender gap [μm]	Compaction after calendering [%]	Density [g/cm ³]	Porosity [%]
Pristine	-	-	0.71	59.22
17	100	6	0.79	58.37
44	55	12	0.87	51.87
62	10	17	0.95	48.62

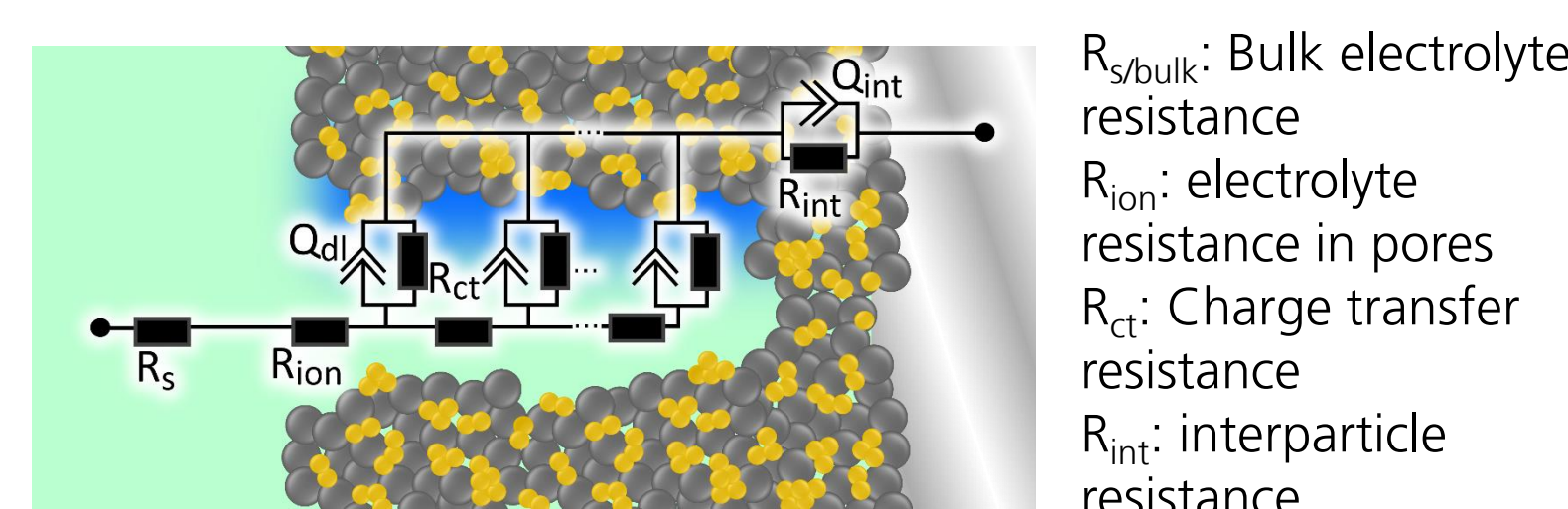
2. Cell configuration and Setup

Symmetrical 2E/3E or full cell in lab cell (EL-Cell)



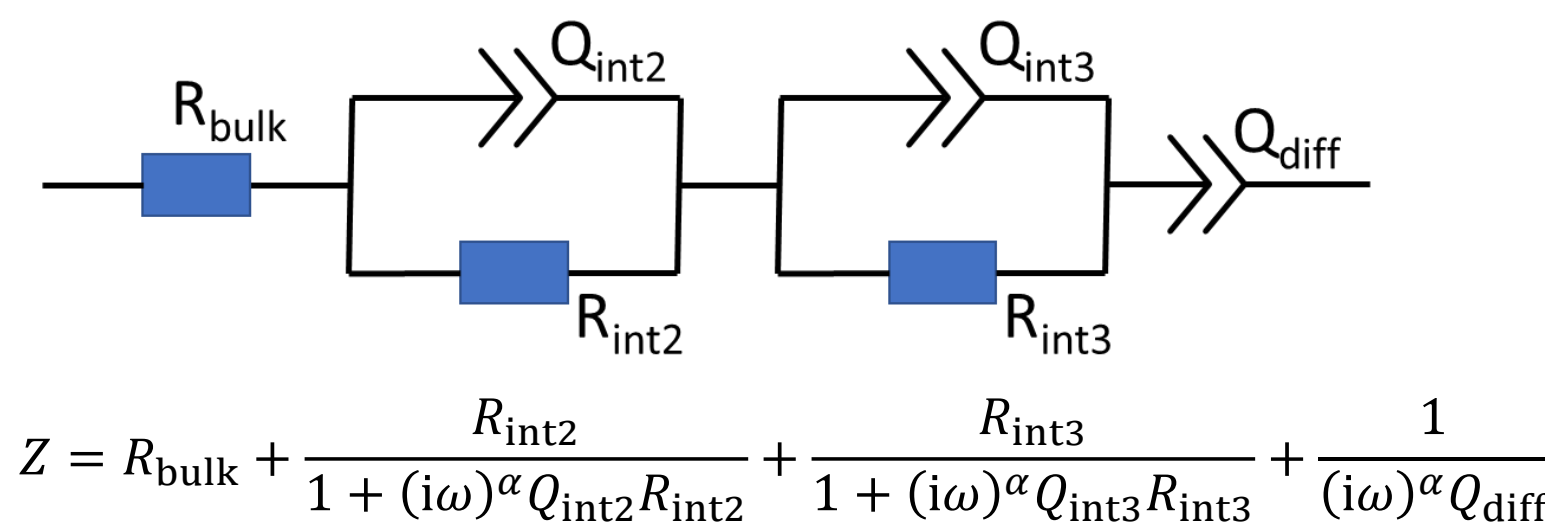
3. Fitting and Modelling

Transmission Line Model (TLM) for porous characteristics:



$$Z = R_s + [R_{ion} \cdot \zeta]^{1/2} \cdot \coth \left[L \left(\frac{R_{ion}}{\zeta} \right)^{1/2} \right]; \zeta = \left[\frac{1}{R_{ct}} + Q_{dl}(j\omega)^\alpha \right]^{-1}$$

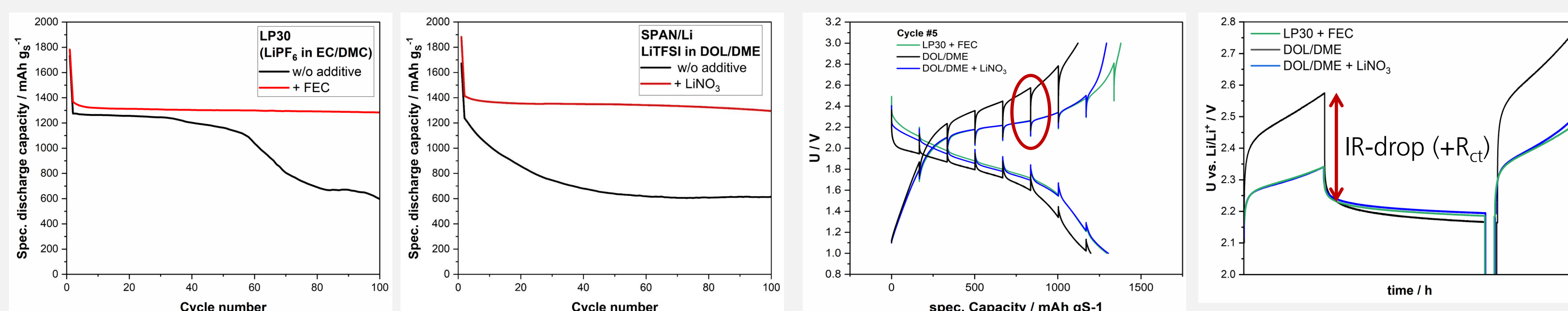
Simplified model for cathodes with inhomogeneous percolation network:



$$Z = R_{bulk} + \frac{R_{int2}}{1 + (j\omega)^\alpha Q_{int2} R_{int2}} + \frac{R_{int3}}{1 + (j\omega)^\alpha Q_{int3} R_{int3}} + \frac{1}{(j\omega)^\alpha Q_{diff}}$$

Experimental Results

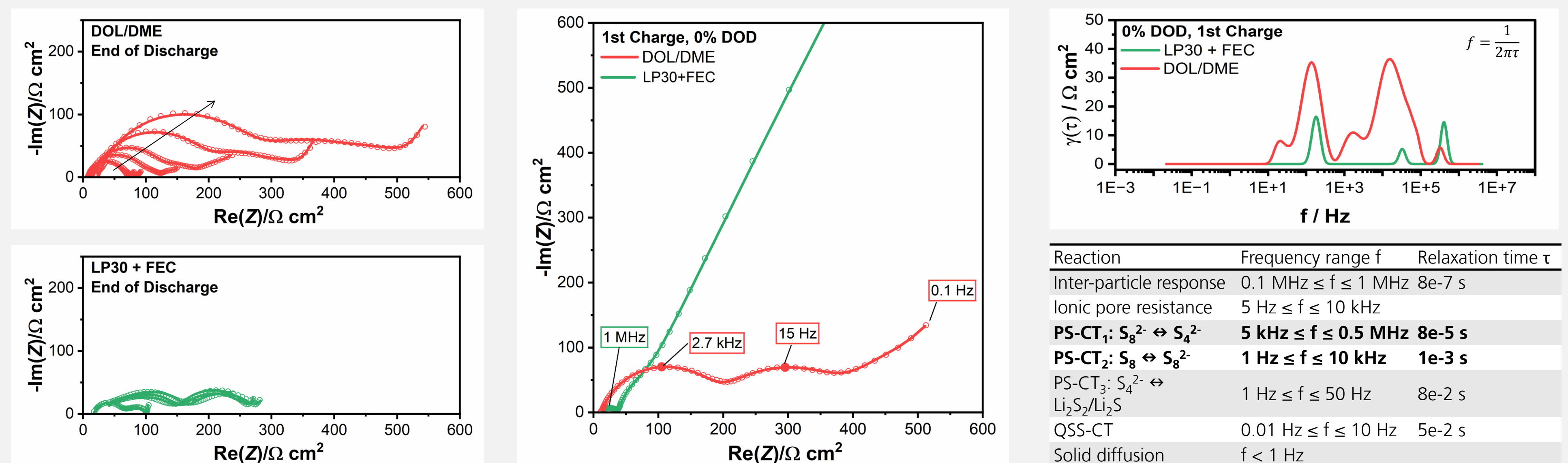
I. Effect of electrolyte and additive towards capacity, cycle stability and redox paths



- Carbonate electrolyte shows compatibility with SPAN electrode
- Pure 1M LiTFSi in DOL/DME (standard electrolyte for Li/S) shows rapid capacity degradation
- Significant improvements with additives in both systems
- High overpotentials for pure ether electrolyte, especially in charge
- Similar steady state potential for all systems
- Overpotential stemming mostly from initial IR-drop → lowered electrolyte conductivity due to polysulfides

SEI: Improved cycle life due to stabilization of Li anode

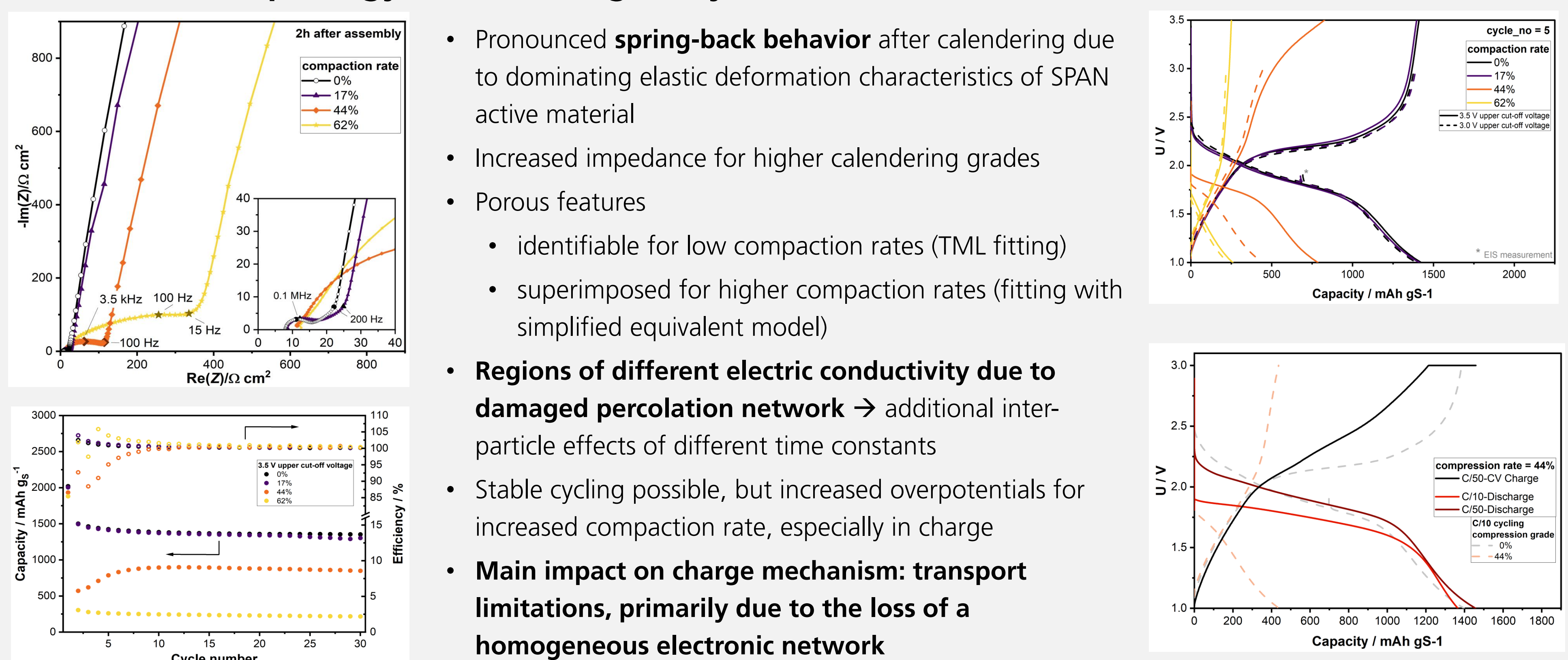
CEI: Improved capacity retention due to controlled polysulfide dissolution



- Continuously growing impedance response for pure ether electrolyte
- 1st end of charge impedance for pure ether electrolyte: High resistance and no blocking behavior
- DRT evaluation: Multiple contributions in high to mid frequency area
- Analogy to processes of mesoporous C/S composite cathodes with polysulfide-charge transfer reactions

→ Polysulfide generation in pure ether electrolyte

II. Effect of morphology – calendering study^[2]



- Pronounced **spring-back behavior** after calendering due to dominating elastic deformation characteristics of SPAN active material
- Increased impedance for higher calendering grades
- Porous features
 - identifiable for low compaction rates (TLM fitting)
 - superimposed for higher compaction rates (fitting with simplified equivalent model)
- **Regions of different electric conductivity due to damaged percolation network** → additional inter-particle effects of different time constants
- Stable cycling possible, but increased overpotentials for increased compaction rate, especially in charge
- **Main impact on charge mechanism: transport limitations, primarily due to the loss of a homogeneous electronic network**

Conclusion

- Importance of protective layer on both electrodes for capacity retention and cycle life: CEI and SEI
- Although the SPAN cathode is highly compatible with carbonate electrolytes regardless of additive presence, the high overpotentials and complex charge-transfer responses in ether electrolytes without additives suggest polysulfide formation despite the strong S–PAN covalent bonding.
- Highly elastic deformation behavior of SPAN active material and pronounced spring-back effect of cathode leads to destroyed percolative network and irreversible conductivity degradation.
- Inter-particle effects with larger time constants and higher resistance observed in the EIS of the calendered SPAN cathode corroborate the presence of an inhomogeneous electronic network and calendering-induced defects.
- Main impact and overpotential on charge mechanism: primarily due to the loss of a homogeneous electronic network rather than ionic conduction limitations

Acknowledgements

*This work is done in cooperation with the partners in the **SulForFlight** project.

This project has received funding from The Federal Ministry of Education and Research and Project Management Jülich under grant agreement No WABF03007422. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union nor the granting authority can be held responsible for them.

[1] Gerle, Nojabaei et al. J. Electrochem. Soc. 2022, 169 030505

[2] Gerle, Moschner et al. Adv. Sci 2025, 12, 2415436