

Identifying the fundamental causes limiting the performance of metal-sulfur batteries

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9th Workshop “Li-S batteries”
28-29 November 2022

Funding acknowledgements

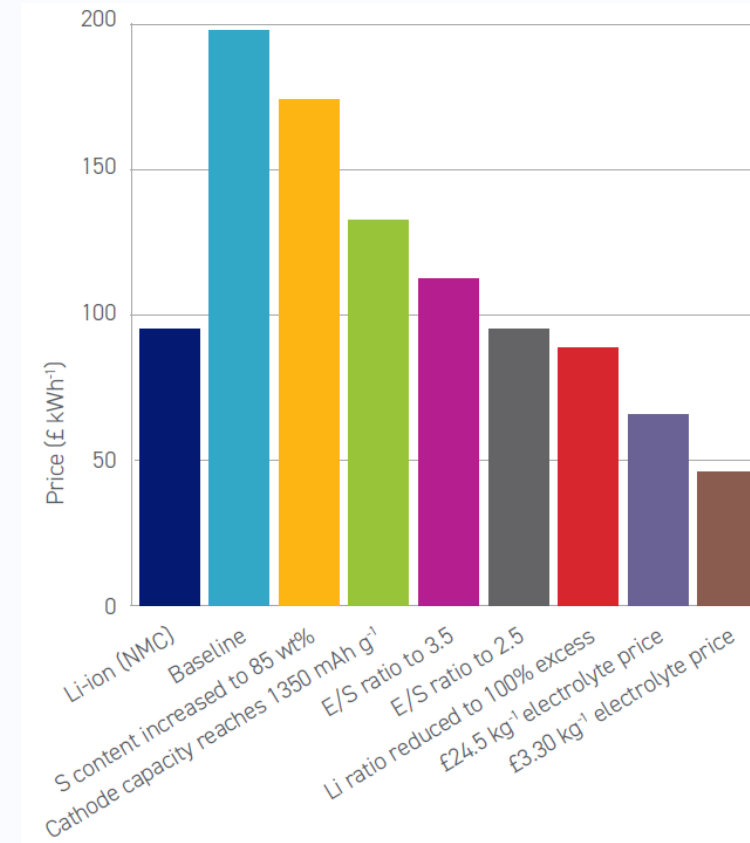
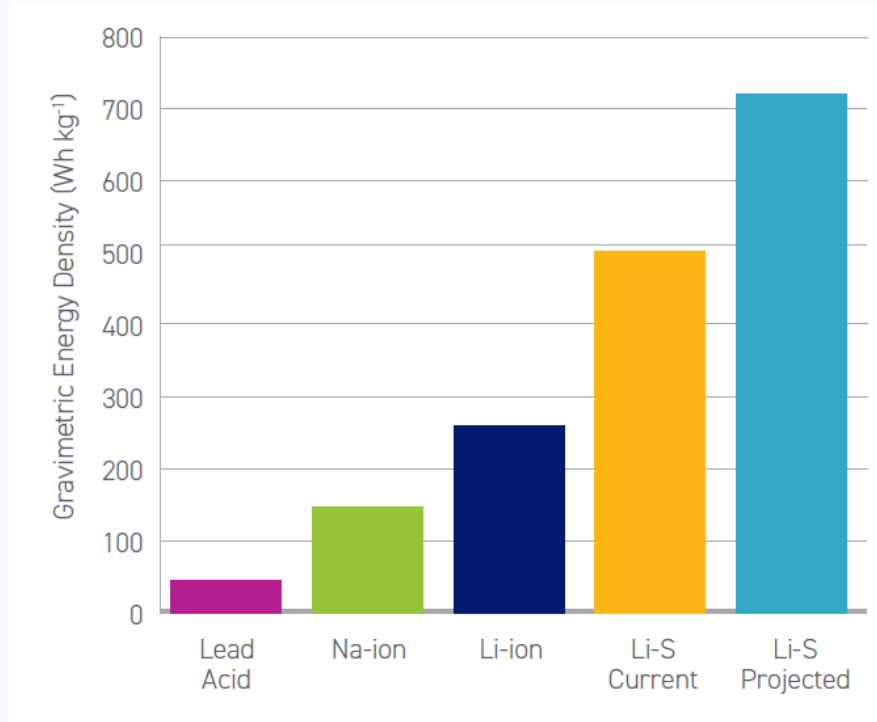
- Early-career fellowship by the EPSRC
- MESS project (Microgrid Energy Storage using Lithium-Sulfur Batteries), funded by Innovate UK and OXIS energy
- LiSTAR project (Lithium-Sulfur Technology AcceleratoR), funded by the Faraday Institution
- AMAPOLA project (A Marketable Polymer based Al-S battery) and SALBAGE (Sulfur-Aluminium Battery with Advanced Polymeric Gel Electrolytes) funded by the European Commission



Sulfur based battery chemistries

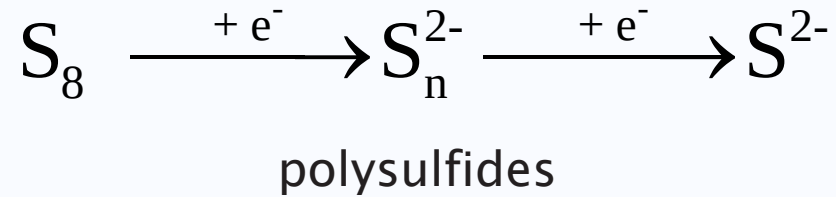
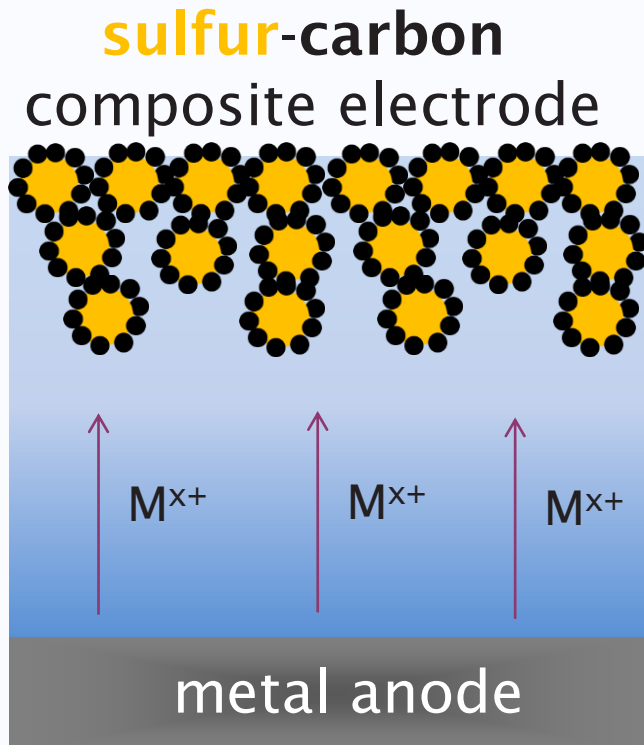


- ✓ High energy 😊
- ✓ Low projected cost 😊
- ✓ No scarce metals 😊



FARADAY INSIGHTS - ISSUE 8: JULY 2020
Lithium-sulfur batteries: lightweight technology for multiple sectors

Sulfur based battery chemistries

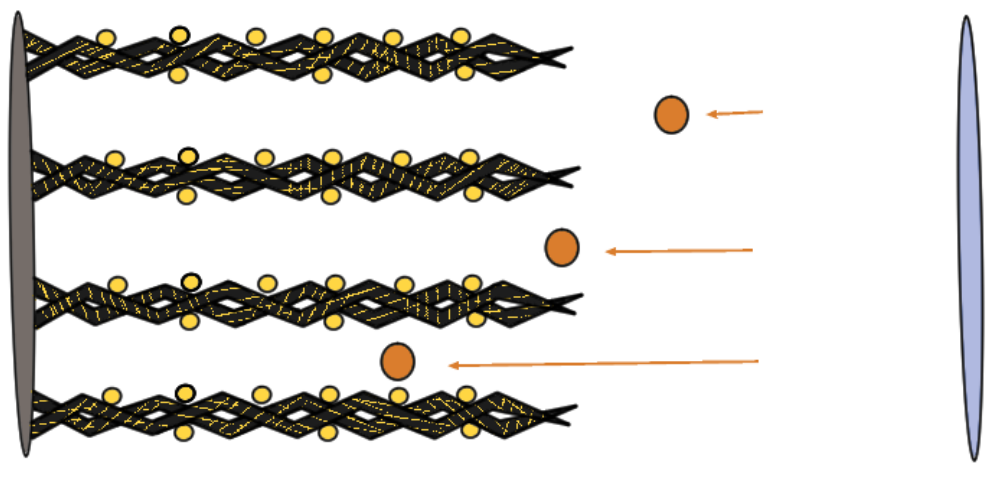


Discharge product: Li_2S , Na_2S , MgS , Al_2S_3 , etc.

Transport of ions is essential!

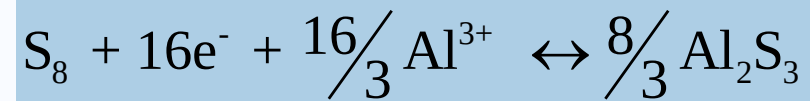
Ion transport limitations in Al-S cells

Sulfur-carbon composite

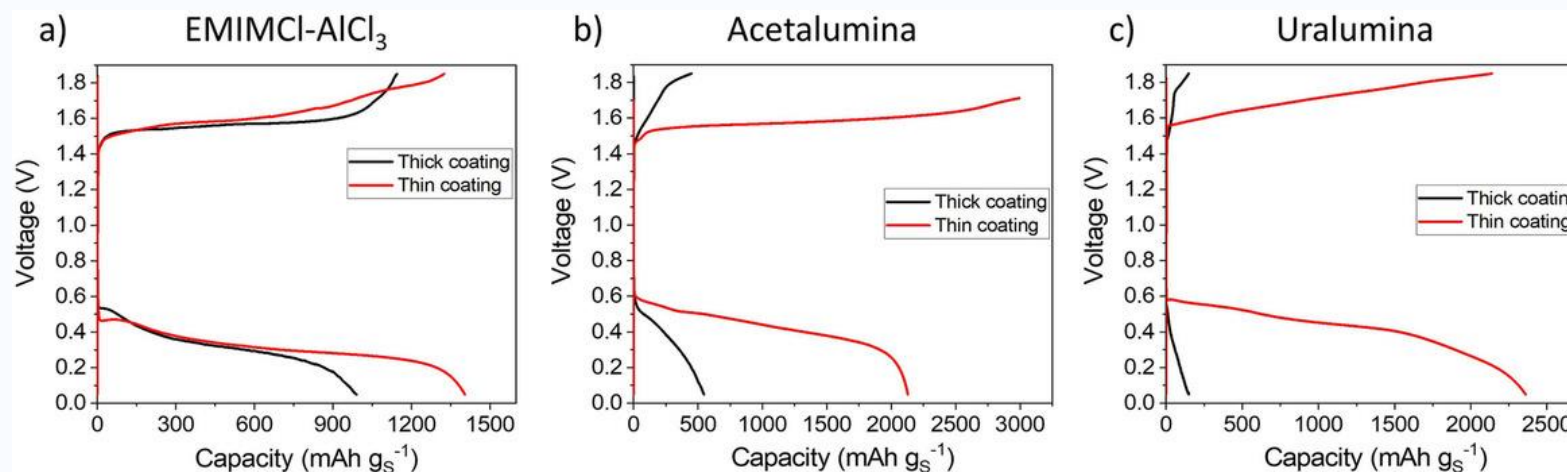


Separator

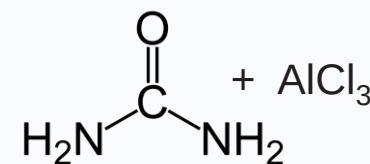
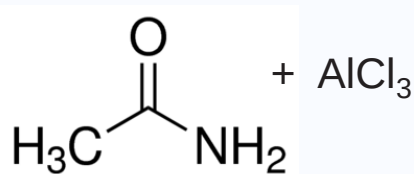
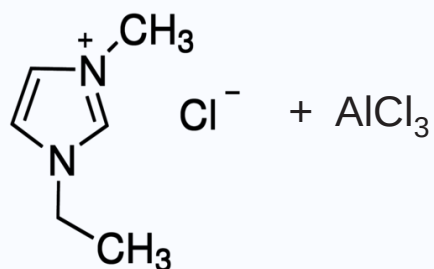
Transport of ions through the porous sulfur electrode limits the discharge of Al-S cells



Ion transport limitations in Al-S cells



50 mA/g_s
~C/33

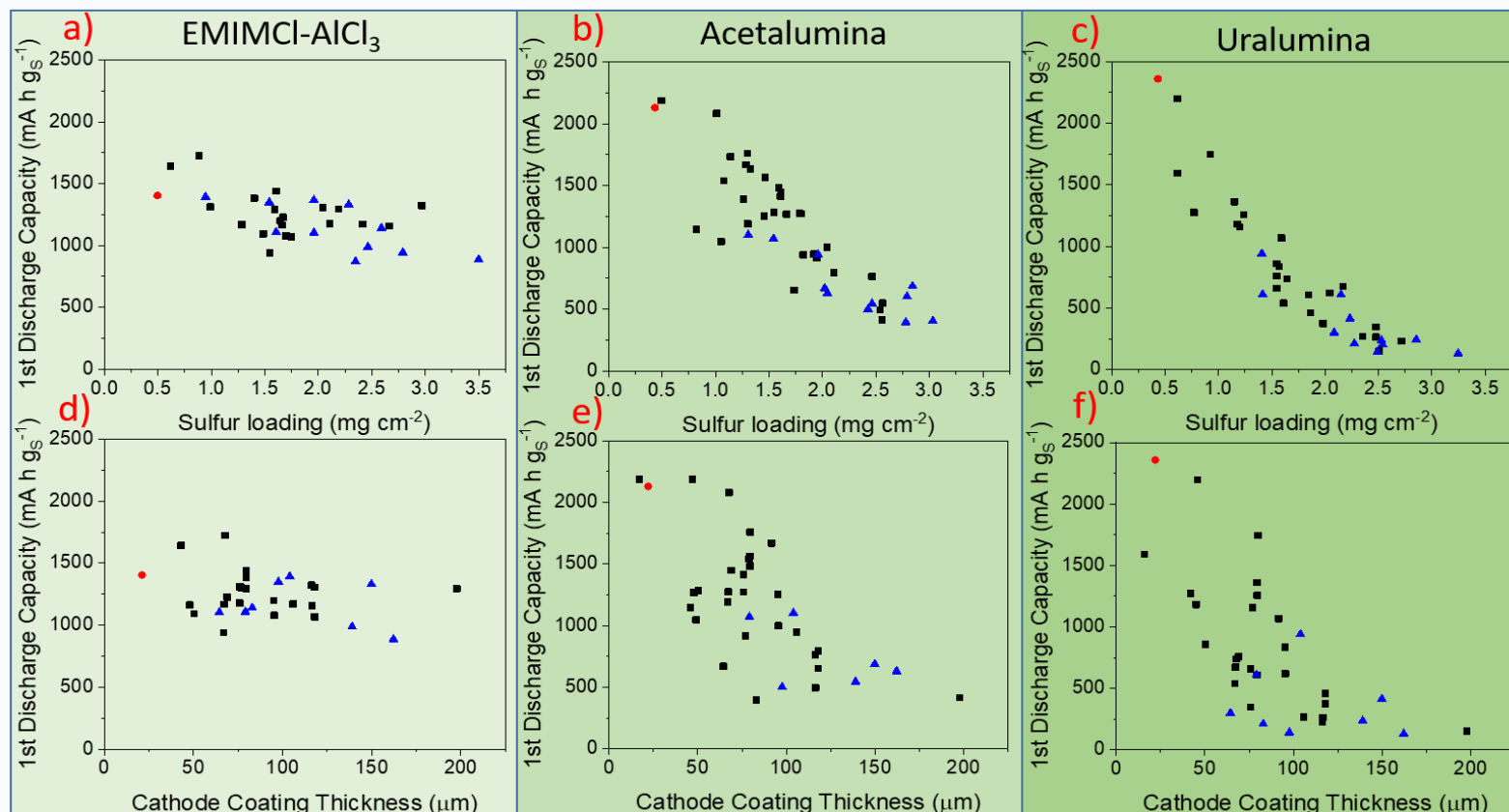


Viscosity



Lampkin, Li et al. *ChemSusChem* 2020, 13, 3514.

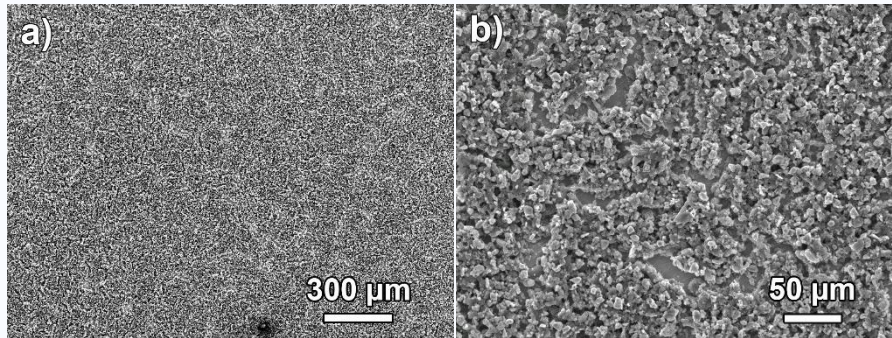
Ion transport limitations in Al-S cells



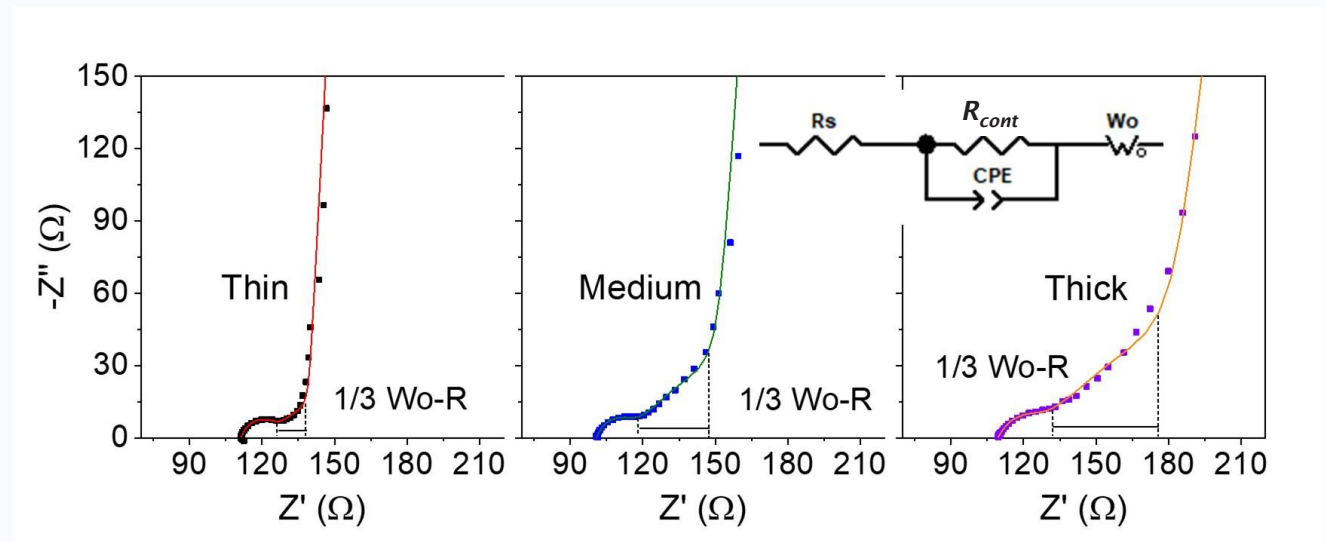
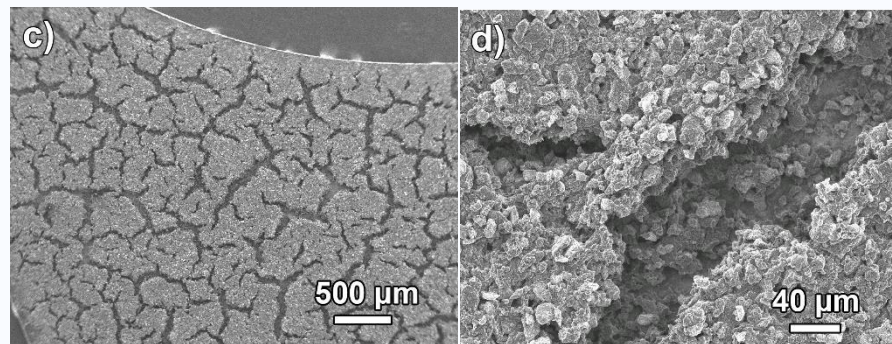
Thicker sulfur electrodes and more viscous electrolytes decrease the practical capacity

Ion transport limitations in Al-S cells

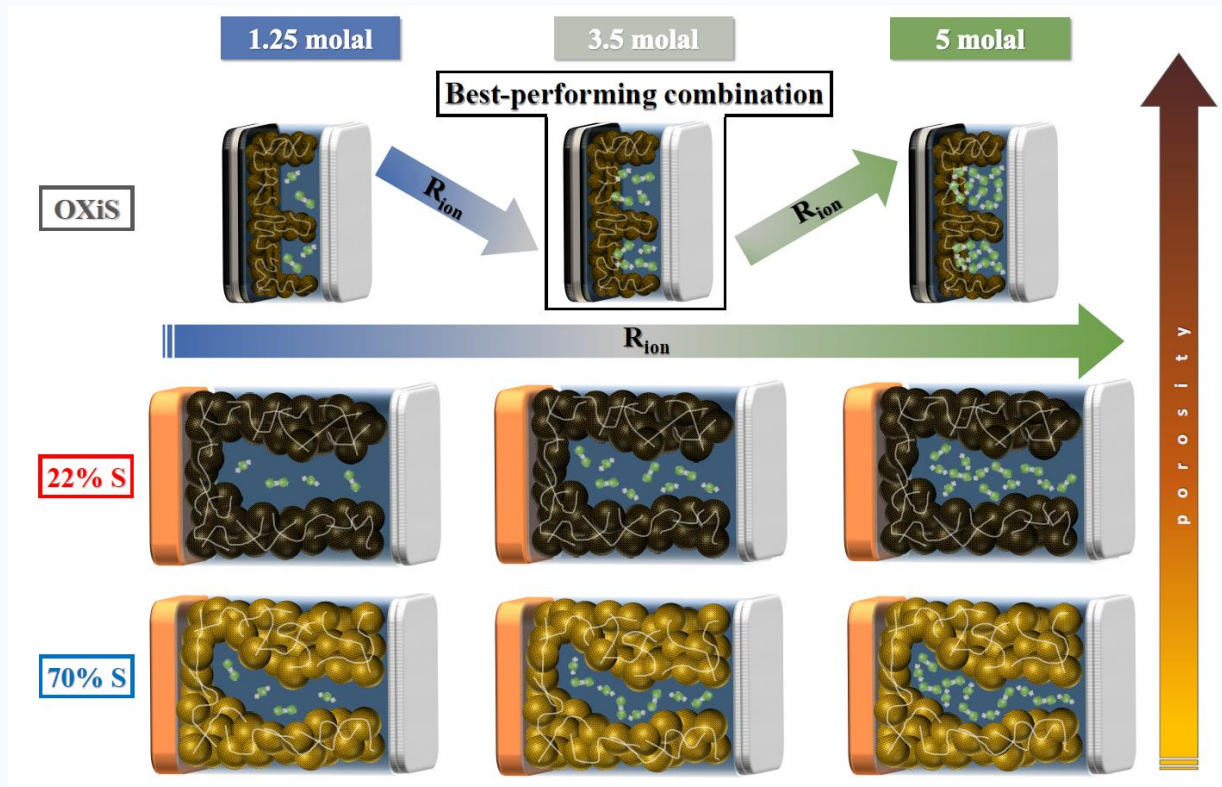
Thin electrode → ok



Thick electrode → cracks
→ slow ion transport



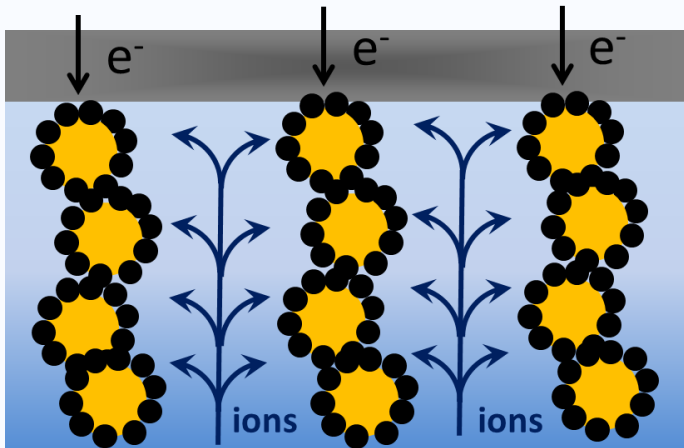
Ion transport limitations in Li-S cells



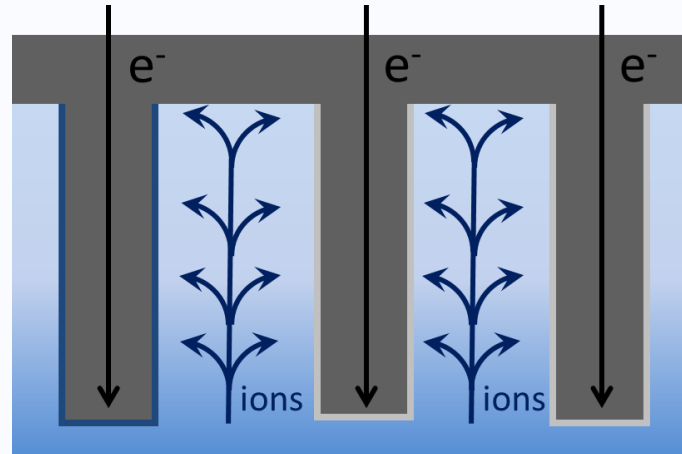
Electrode and electrolyte combinations with faster ion transport produce better Li-S battery performance

Ion transport limitations in Li-S cells

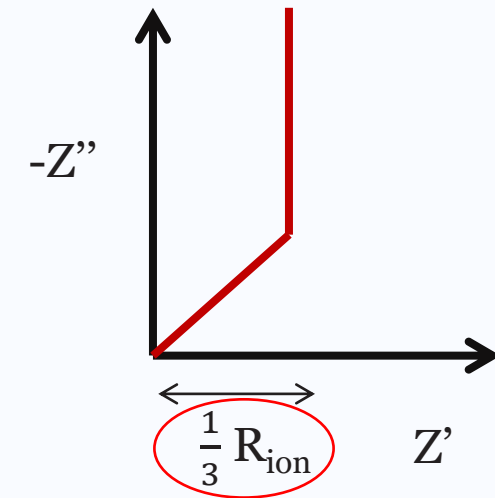
Sulfur-carbon composite electrode



Transmission line model
(de Levie)



Without charge-transfer reactions → porous supercapacitor:

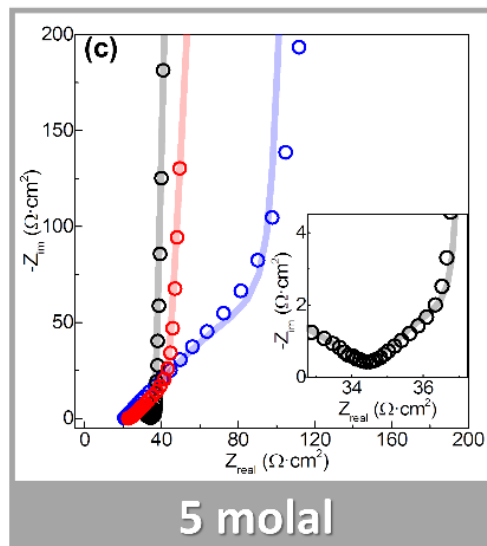
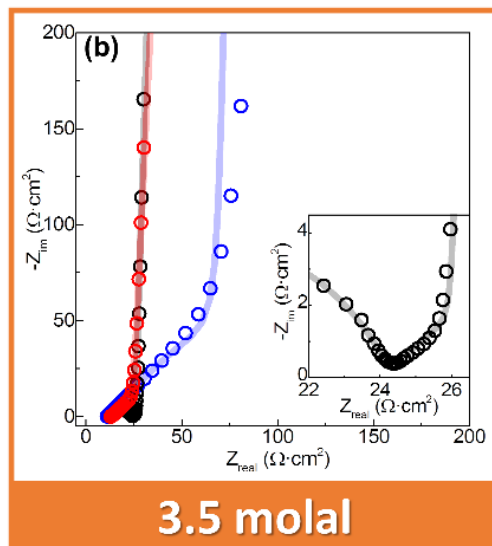
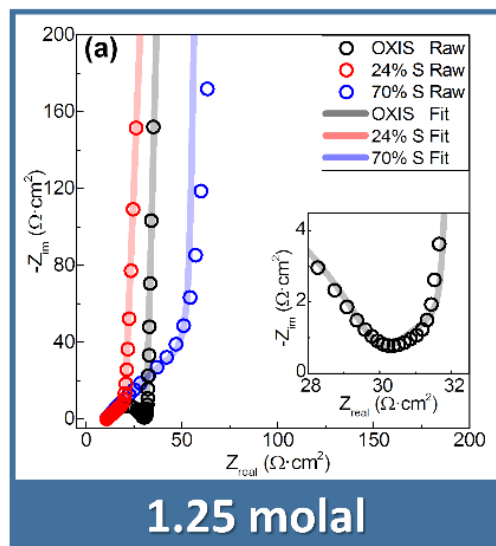


R_{ion} : resistance associated with ion transport within the pores of the porous electrode

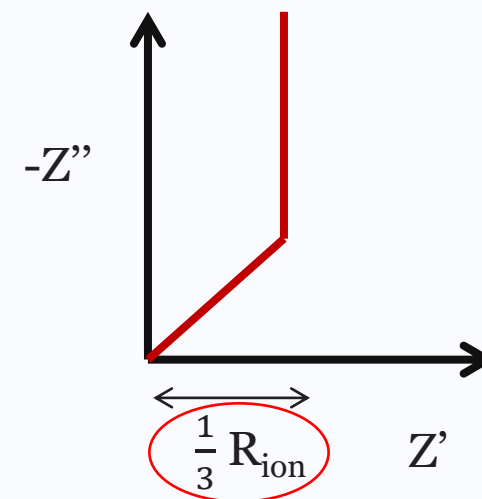
Ion transport limitations in Li-S cells

Symmetrical cell configuration

Electrolyte: x molal LiTFSI in 1,3-dioxolane

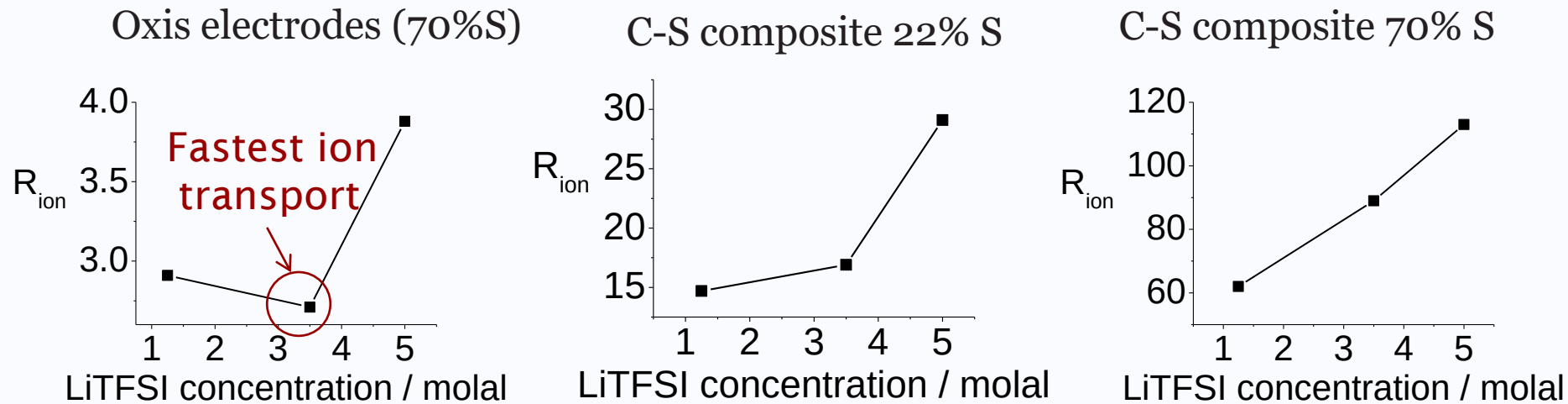


Without charge-transfer reactions → porous supercapacitor:



R_{ion} : resistance associated with ion transport within the pores of the porous electrode

Ion transport limitations in Li-S cells

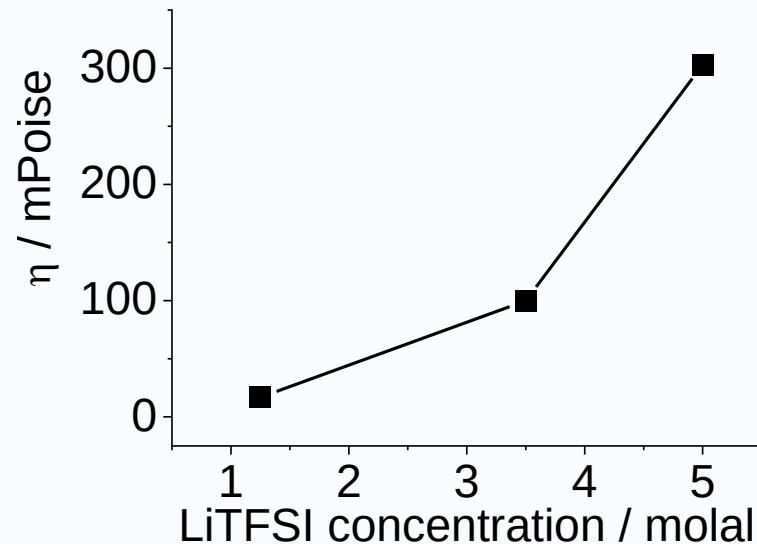


Faster ion transport → better Li-S battery performance

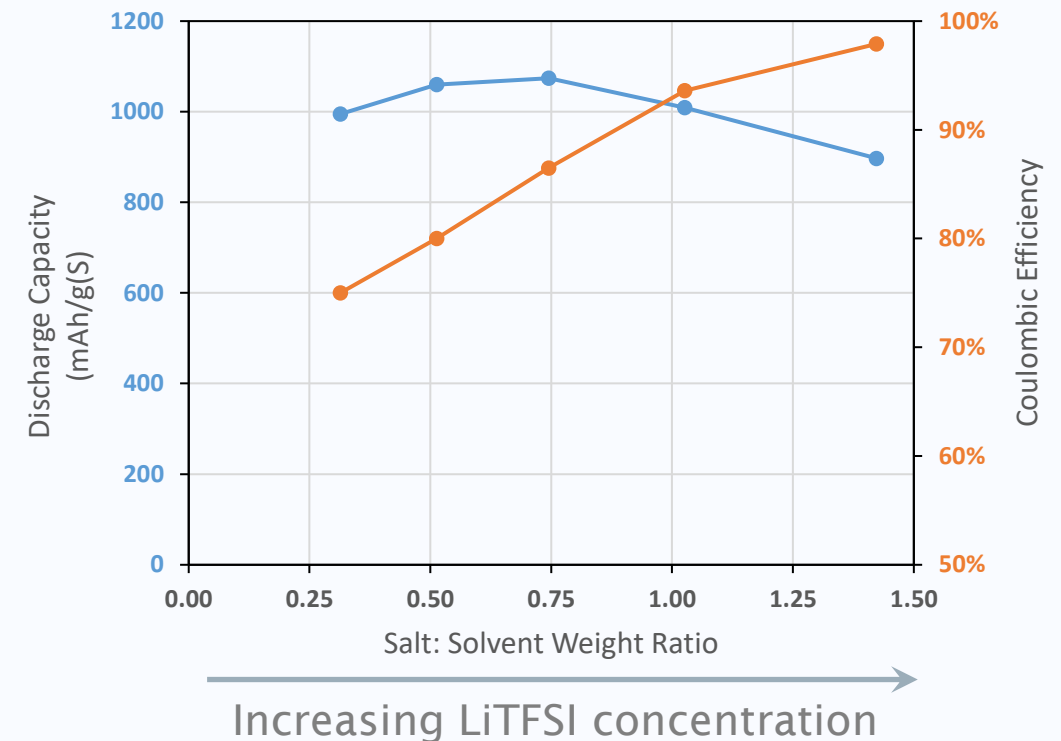
Ion transport limitations in Li-S cells



Bulk electrolyte **viscosity** of solutions of LiTFSI in 1,3-dioxolane



Li-S battery performance, OXIS pouch cells
OXIS electrodes with 70 wt.% sulfur

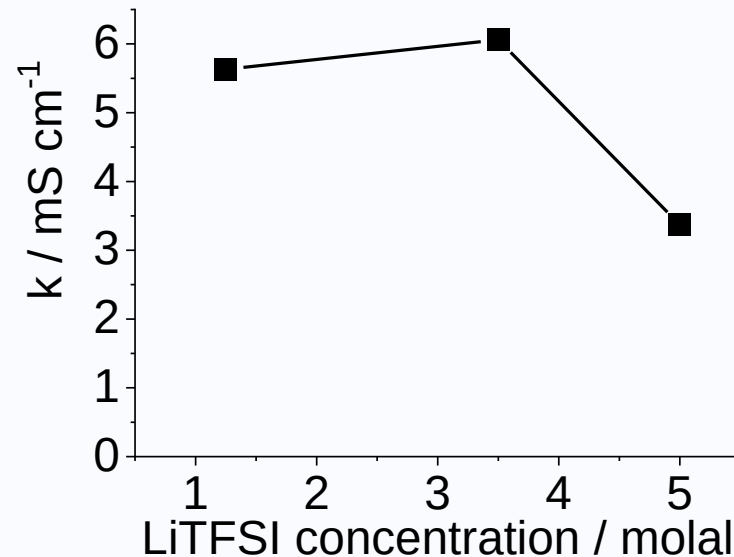


Raccichini et al. J. Phys. Chem. B 2018, 122, 267

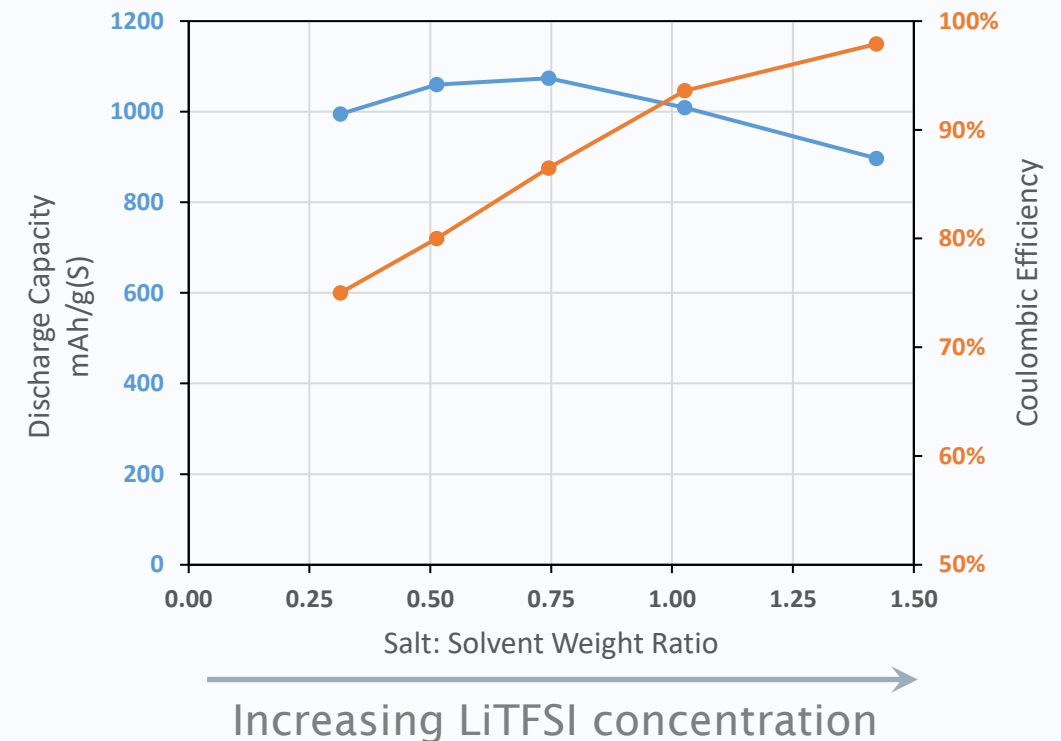
Ion transport limitations in Li-S cells



Bulk electrolyte **conductivity** of solutions of LiTFSI in 1,3-dioxolane



Li-S battery performance, **OXIS** pouch cells
OXIS electrodes with 70 wt.% sulfur



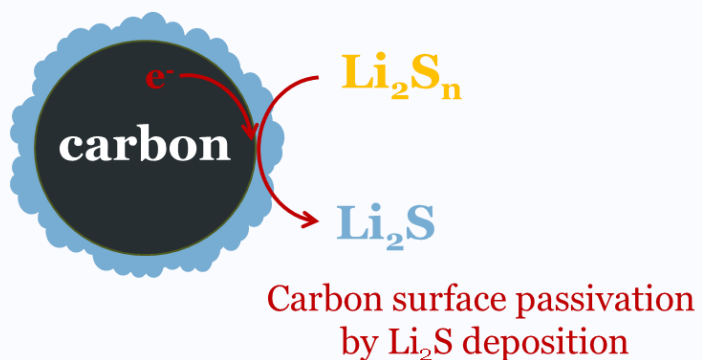
Raccichini et al. J. Phys. Chem. B 2018, 122, 267



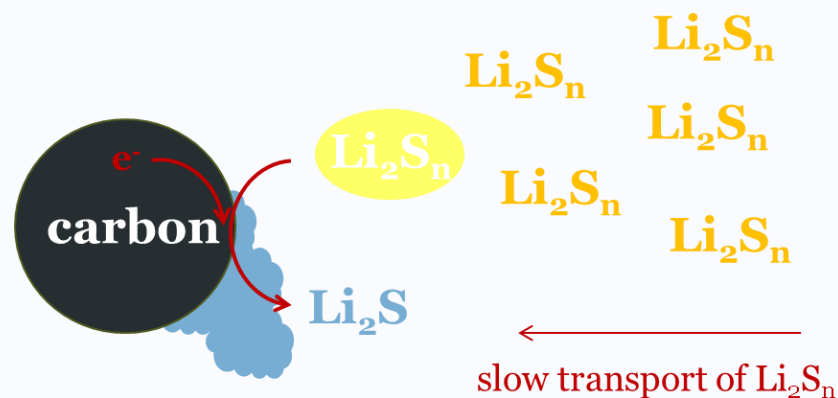
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Identifying the causes of Li-S cell death

Hypothesis #1:
passivation of the carbon
conductive additive



Hypothesis #2:
slow transport of electrolyte
species (e.g. polysulfides)

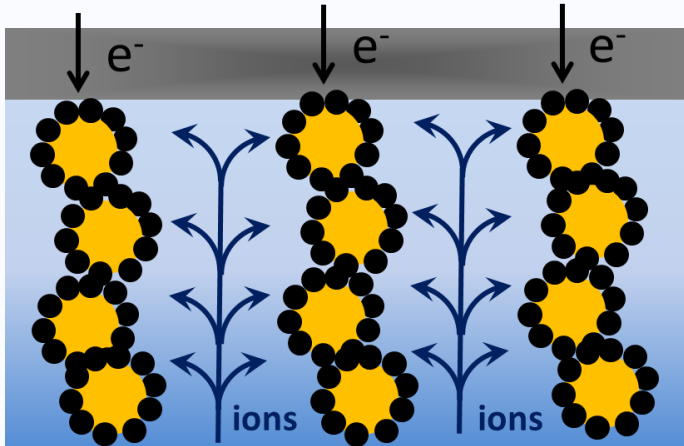


In collaboration
with Dr. Yu-Chuan
Chien, Prof. Daniel
Brandell, and Dr.
Matthew J. Lacey

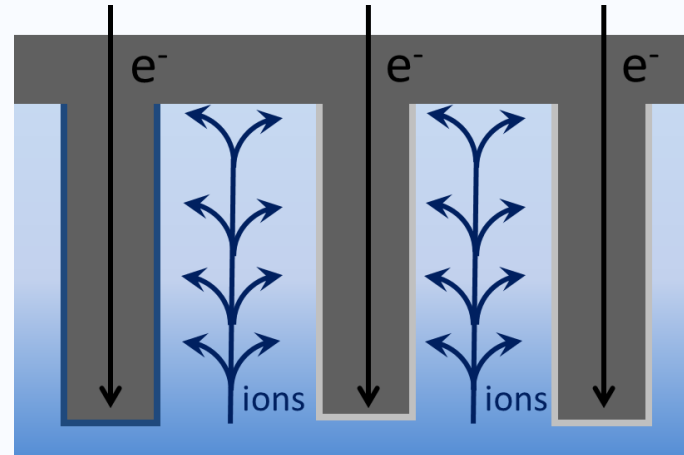
He, Lampkin, Chien et al. Electrochim. Acta 2022, 403, 139572.

Identifying the causes of Li-S cell death

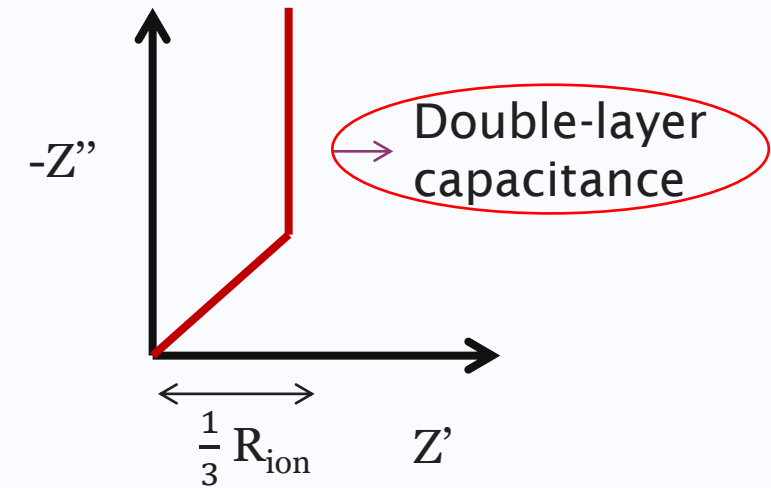
Sulfur-carbon composite electrode



Transmission line model
(de Levie)



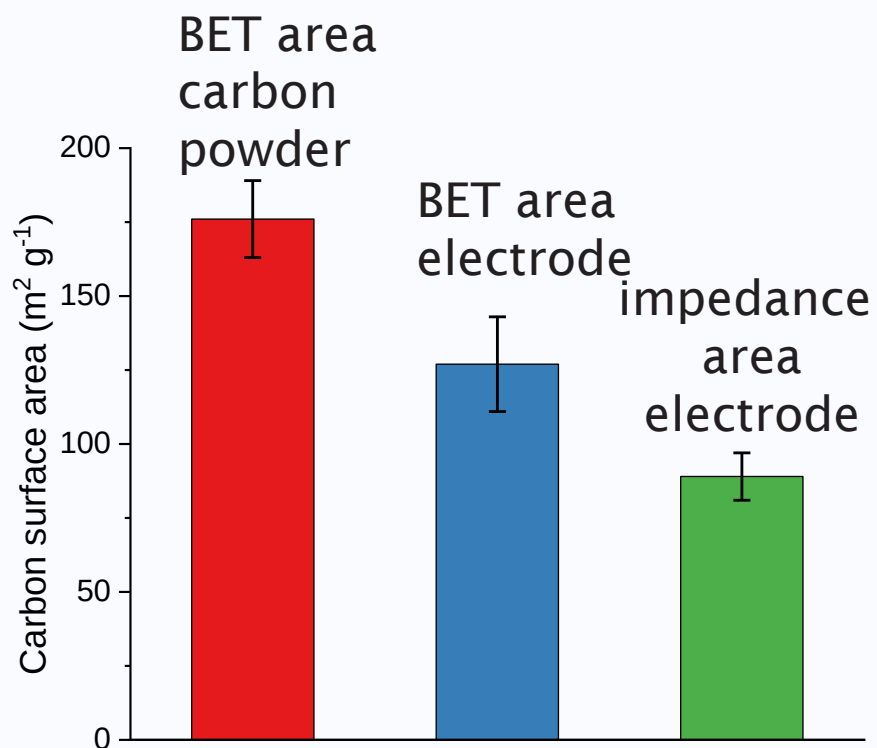
Without charge-transfer reactions → porous supercapacitor:



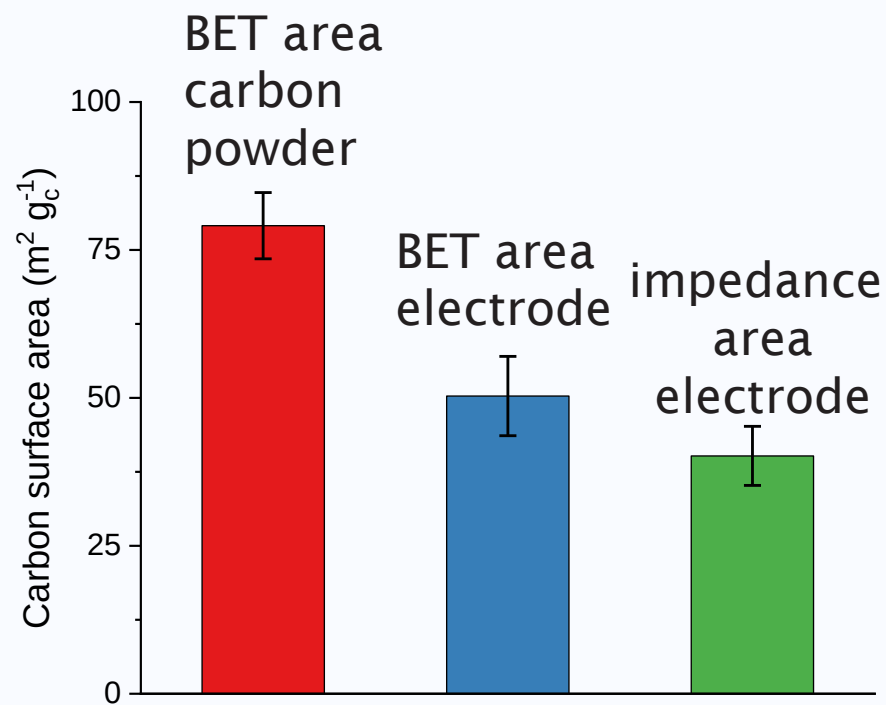
The double-layer capacitance is a measure of the electrochemically active area of carbon additive.

Validation of the determination of electrochemically active surface areas by impedance

Carbon nanotube electrodes



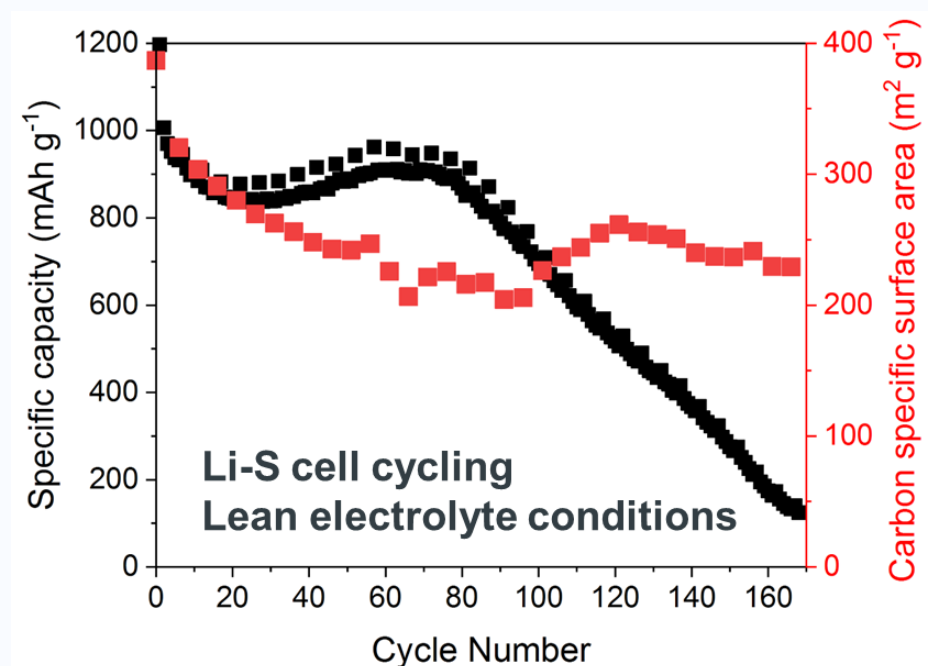
Acetylene black electrodes



Impedance → most **reliable** method to evaluate the electrode's real surface area in the electrochemical cell



Effect of passivation in Li-S batteries lifetime



- Rapid capacity decay because of stressed cycling conditions due to impedance measurements
- A cycle #160, the capacity has decreased by 90% whereas the electrochemically active carbon surface area remains high
- **Conclusion: carbon passivation is NOT the cause of capacity fade**



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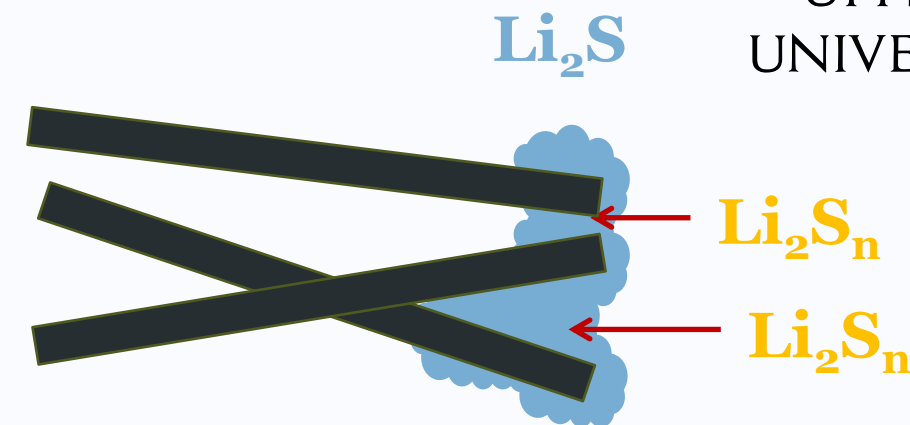
Effect of carbon network in Li-S batteries lifetime



Low electrode tortuosity

↓
Fast transport of electrolyte
species

↓
High amount of Li_2S
formation (high capacity)



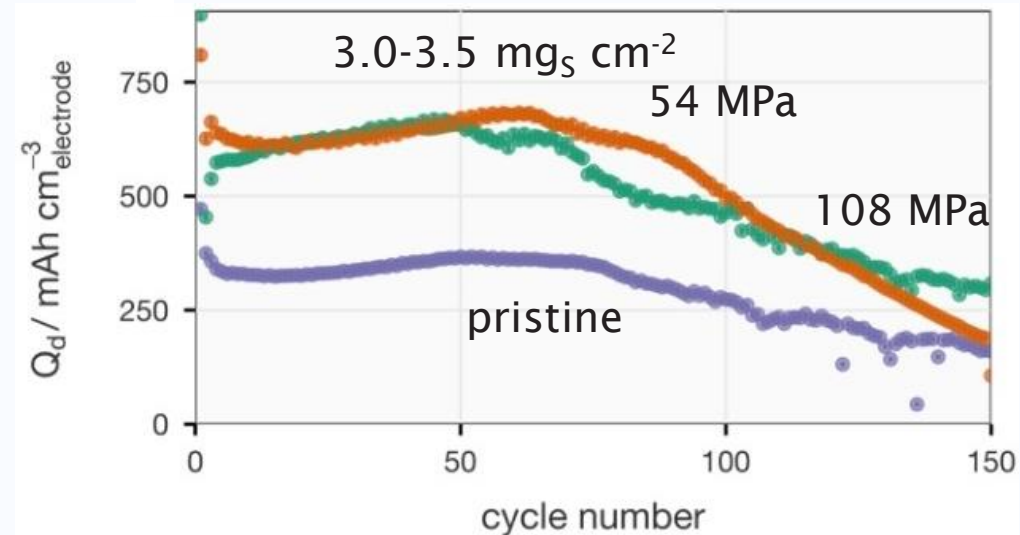
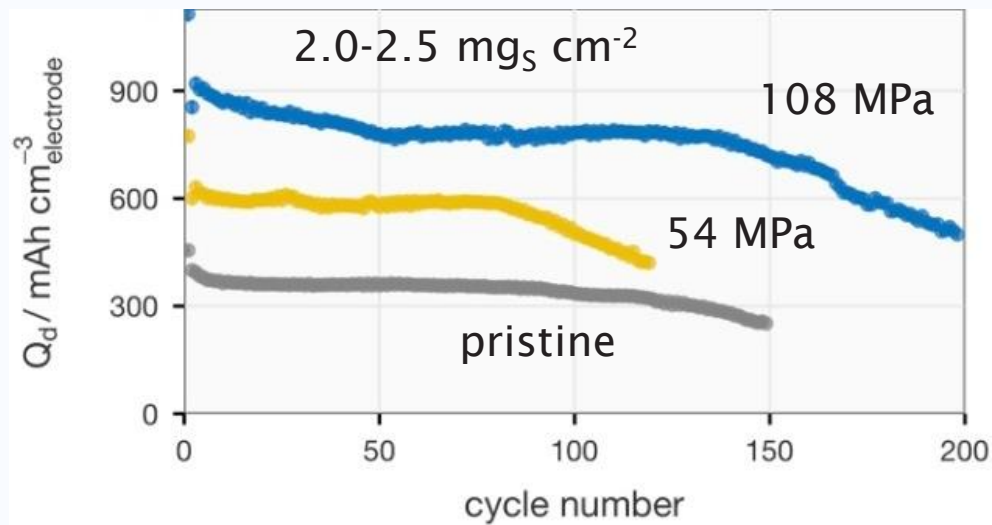
High electrode tortuosity

↓
Slow transport of electrolyte
species and pore clogging

↓
Low amount of Li_2S
formation (low capacity)

He, Lampkin, Chien et al. Electrochim. Acta 2022, 403, 139572.

Enhancing Li-S energy density via compression



- Smaller electrode volume
- Similar specific capacity
- **Higher volumetric capacity**



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Enhancing Li-S energy density via compression

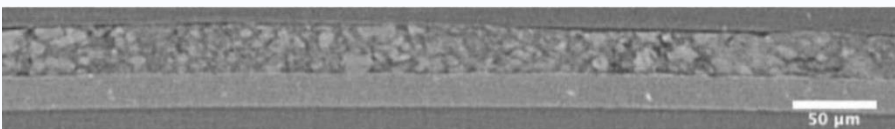
2.0-2.5 $\text{mg}_\text{S} \text{ cm}^{-2}$

Pristine



Tortuosity: 2.5

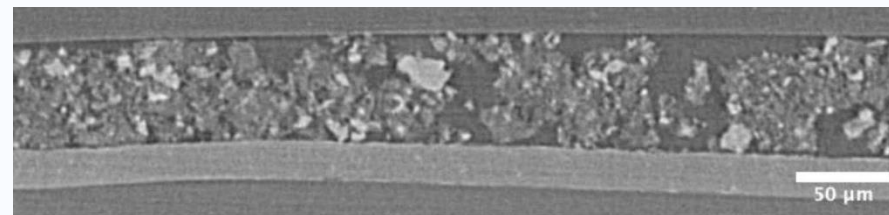
108 MPa compression



Tortuosity: 4.5

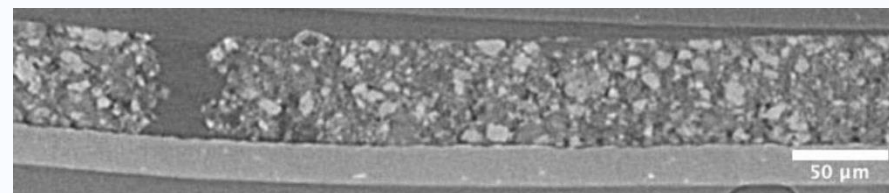
3.0-3.5 $\text{mg}_\text{S} \text{ cm}^{-2}$

Pristine



Tortuosity: 2.2

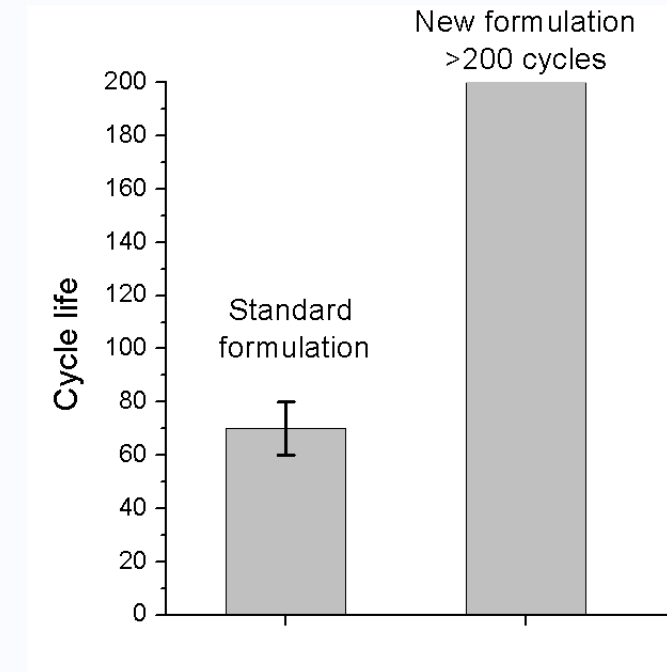
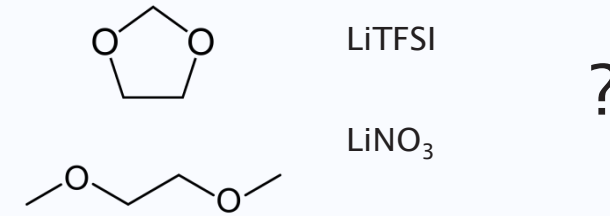
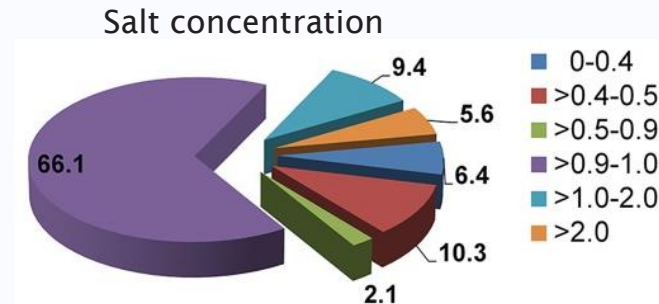
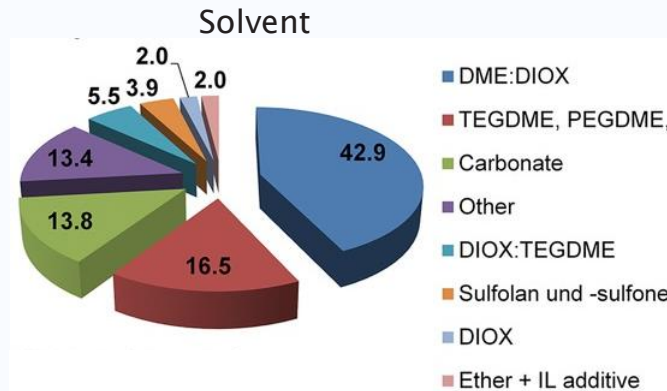
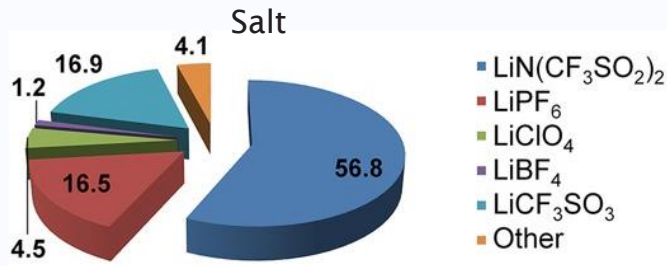
108 MPa compression



Tortuosity: 3.7

Large cracks → tortuosity underestimation

Improving Li-S batteries via electrolyte development



Adv. Energy Mater. 2015, 5, 1401986.

Conclusions

- High performance sulfur electrodes require fast transport of electrolyte species
 - Low tortuosity
 - Good interaction with the electrolyte (wettability)
- Passivation of the carbon is not a cause of cell death
 - Higher carbon surface area is NOT needed
- Sulfur electrode compression can enhance energy density and cell life
- New electrolytes can lead to improvements in cycle life

Thank you!