

Extending the Energy Window – Moving away from LiNO₃ to Open Avenues for Ultra-high Energy Density Cells



James Robinson, Associate Professor
in Advanced Propulsion



Die Frühstückskarte...

- LiSTAR – The Lithium Sulfur Technology Accelerator
- Probing Trends in the Li-S Literature
- Emerging ‘Quasi-Solid-State’ Cell Performance to Move Toward Ultra High Energy Cells



LiSTAR 3 – The Problem Statement and Focus



There is a need to develop batteries which supersede the practical capabilities of Li-ion batteries to enable the electrification of applications including aerospace and heavier electric vehicles. While there are several realistic candidates the Li-S chemistry combines relative technical maturity with a practical limit that places the technology in a unique position to facilitate commercialisation.

Multiple approaches for cells:



- **Energy density**



- **Lifetime**



- **Rate performance**

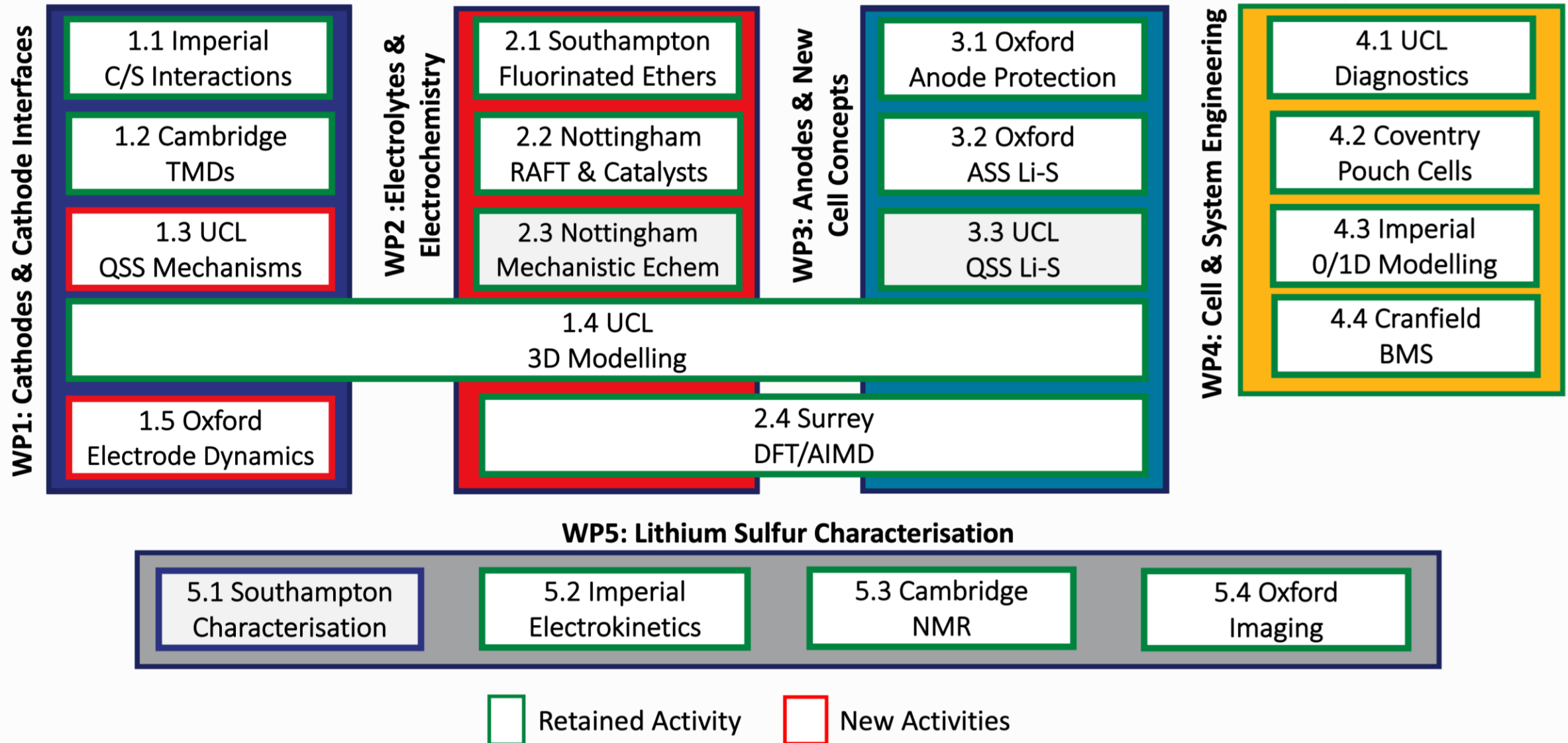
Project Aims

1. Improve routes to achieving ultra-high energy density with good lifetime
2. Remove LiNO_3 concerns
3. Ensure scalability & translatability considerations
4. Consolidate research & industrial activity in Li-S sector

LiSTAR 3 – Consortium Partners



LiSTAR 3a: Project Structure



Phase 3 Ambitions

-  Primary Targets
-  Secondary Targets
-  Potential Advantages

Faraday Institution Targets

KPI	Cost 	Energy Density 	Power Density 	Safety 	Lifetime 	Temperature 	Predictability 	Recyclability 
This Project								
Target Value (if defined)	TEA/LCA understood	Enabling >550-600 Wh kg⁻¹	Discharge: 2C capable, 4C pulse	No or not relevant volumes of LiNO₃	Enabling 500 Cycles as default	-20 – 60 °C	Demonstrate BMS vs Drive Cycle, Mission Profile	Designed for recyclability & linked to TEA

Additional Internal Project Targets

KPI	Capacity (mg cm ⁻²)	Sulfur Utilisation (%)	E/S Ratio (μL mg ⁻¹ s)	Technological Relevance of Demonstrators
Target Value	4-8	>75	<3	20 x 2 Ah Pouch Cell Tested vs Drive Cycles & Mission Profiles

Notes:

- Internal project targets are for conventional Li-S chemistry
- QSS & SS cells have wider routes to achieving aims which are modelled as required

The Project's Evolution

LiSTAR Phase 1

- Identify and develop promising research areas
- Explore high risk, high reward areas
- Build UK focussed Li-S research consortium
- Develop scientific and technical understanding of limiting factors which inhibit commercialisation
- Identify early applications of interest and engage partners in discussions

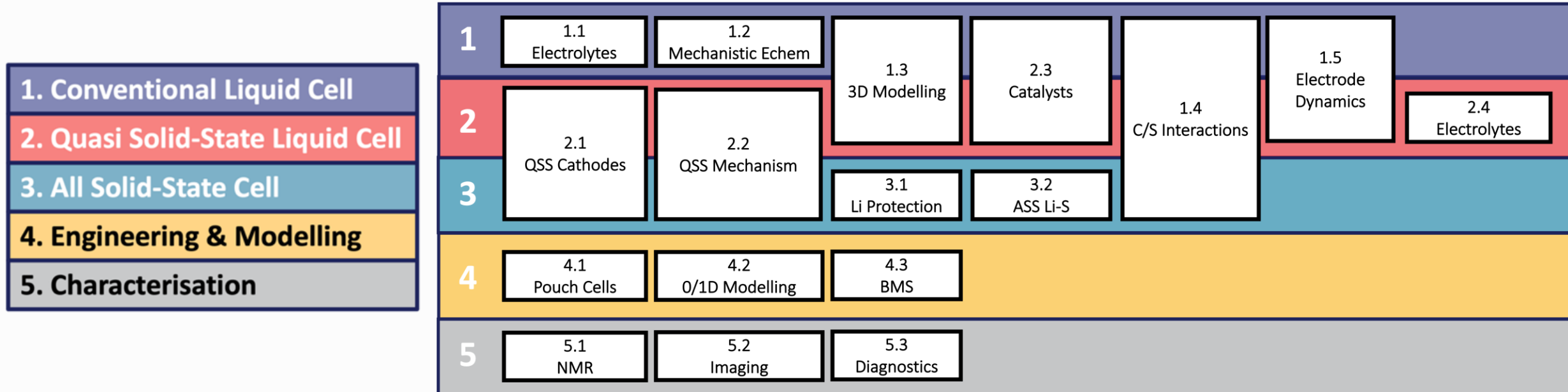
LiSTAR Phase 2

- Develop and optimise existing research areas to maximise commercialisation opportunities
- Investigate underserved research areas which may inhibit broader adoption
- Remove remaining barriers to commercial viability
- Cement and expand UK research efforts in Li-S technology
- Demonstrate developments in consolidated MVP cells

From 2025 to 2028

- Split project to focus on dual stream approach:
 - Research**
Lower TRL and research focus retained in LiSTAR
 - Commercialisation**
Higher TRL moved out of project
- Consider 'beyond early adoption' research inc. rate performance & recyclability
- Expand research focus in new cell concepts – QSS, SS

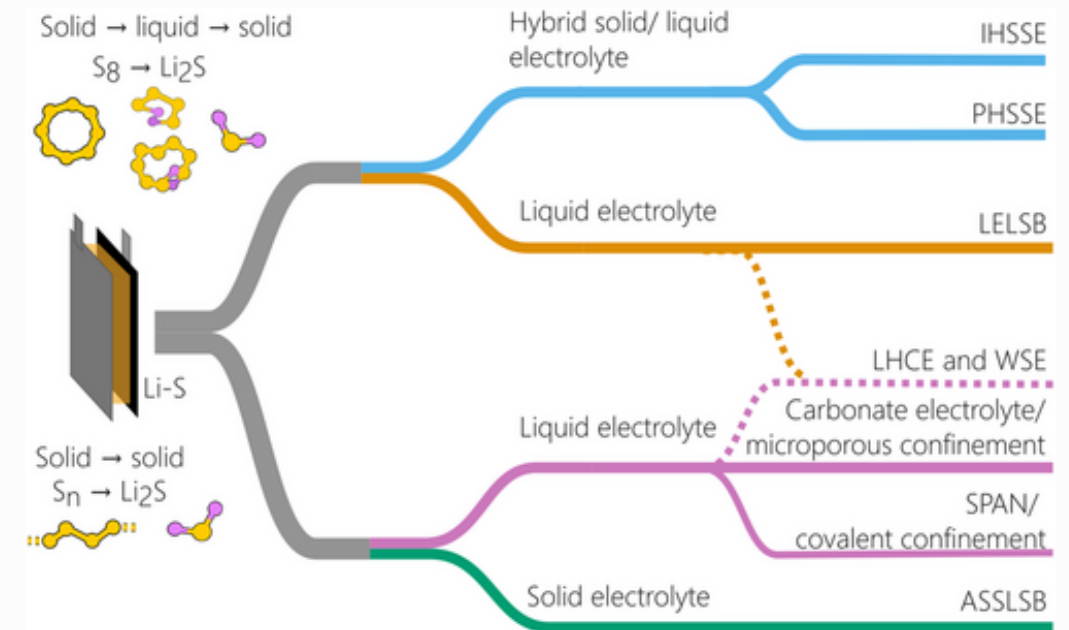
Evolving the Programme for 2026-2030



- Refocus programme toward specific cell formats, retaining underpinning characterisation and engineering activity
- Enable dynamic migration between cell formats as technology matures and opportunities are identified

An Increasing Separation in Li-S Technology

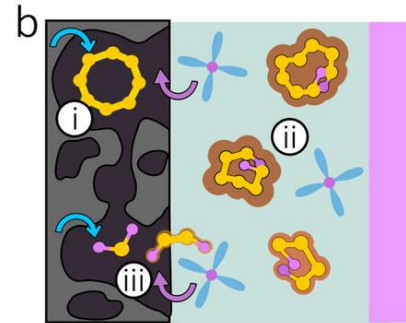
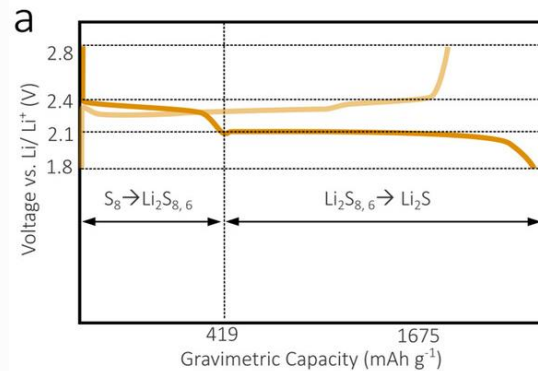
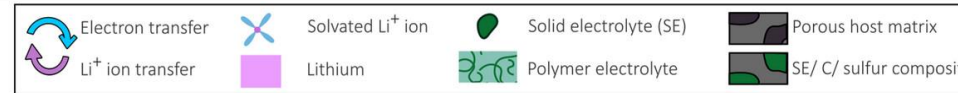
- Conventional cells still dominate the literature
- Emerging cell design focussed on:
 - Solid-state electrolytes (polymer/true solid-state)
 - Quasi-solid-state performance
- Conceptually attractive to:
 - Isolate electrodes
 - Maintain manufacturing similarity to state-of-the-art cells
 - Make cells cheaply
- Mechanistically this is challenging – liquids risk shuttle, solids/polymers move away from existing manufacturing routes
- Still using Li-metal!



An Increasing Separation in Li-S Technology

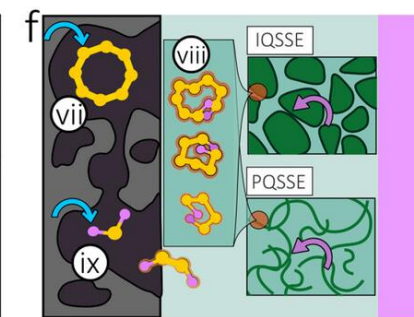
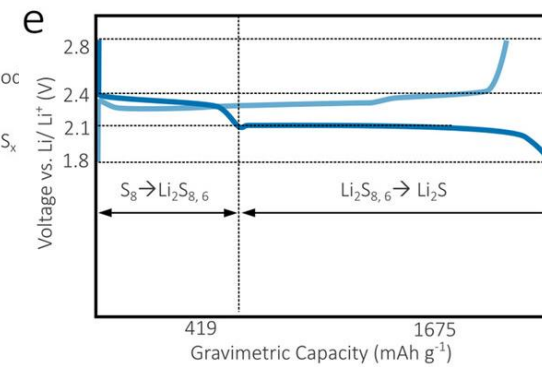


Four cell types, four different mechanisms



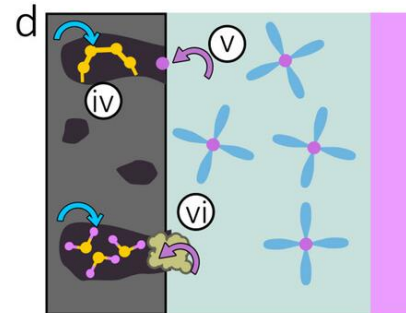
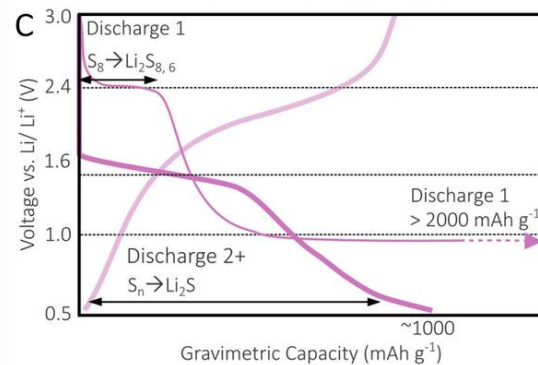
LELSB

- (i) Solid S_8 in porous cathode host matrix
- (ii) Diffusion of soluble Li_2S_x ($2 \leq x \leq 8$)
- (iii) Solid Li_2S



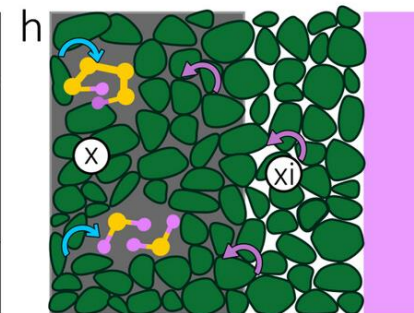
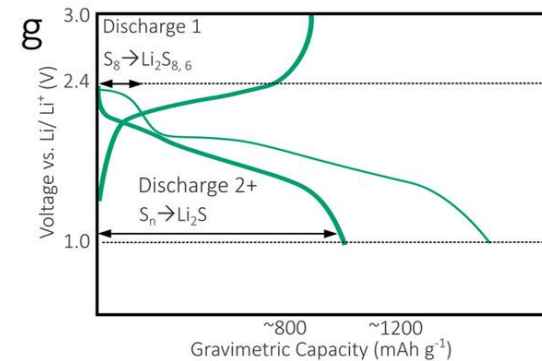
QSSS

- (vii) Solid S_8 in porous cathodic host matrix
- (viii) Soluble Li_2S_x ($2 \leq x \leq 8$) diffusion impeded by hybrid electrolyte
- (ix) Solid Li_2S



LEQSSM

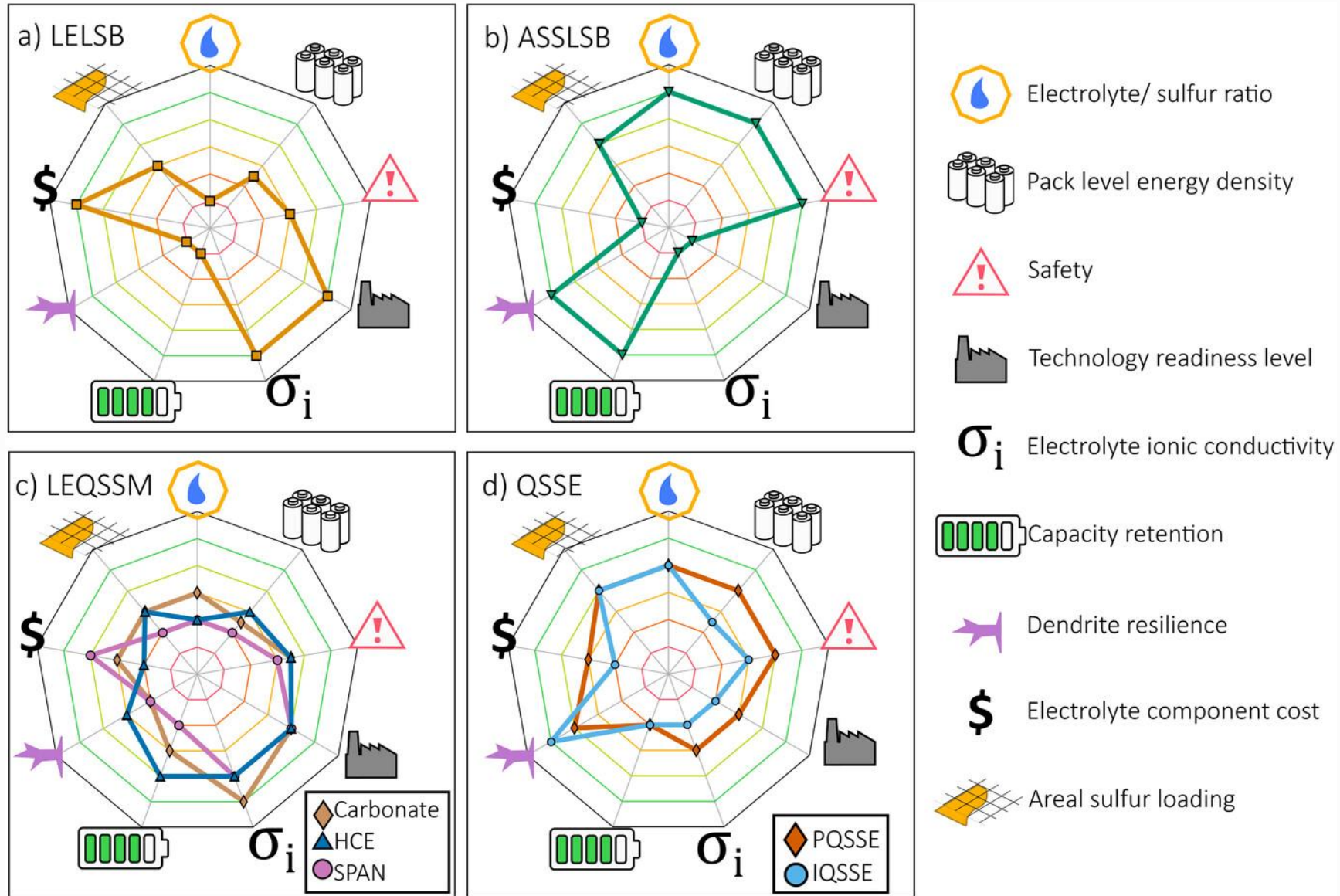
- (iv) S_n ($n \leq 5$) confined or covalently bonded to cathodic host matrix
- (v) Li^+ ion desolvates at micropore aperture
- (vi) Li^+ ion conductivity through CEI beyond charge 1



ASSLSB

- (x) Cathodic composite of sulfur, carbon, and solid electrolyte
- (xi) Ionically conducting solid electrolyte

Four Cell Types, Four Cell Profiles



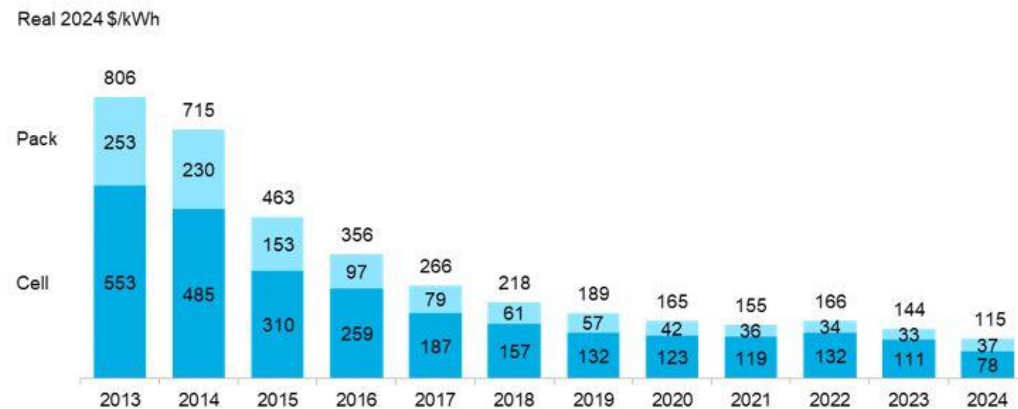
Assertion - A Problem [That We (I) Are (AM) Guilty Of]...



*'Li-S batteries (LiSBs) are among the most commercially mature of the 'beyond Li-ion' batteries, offering the prospect of cells that supersede **the intrinsic limits of Li-ion technology** along with the **potential for substantially reduced costs and improved safety.**' – Robinson et al., 2021*

Cost

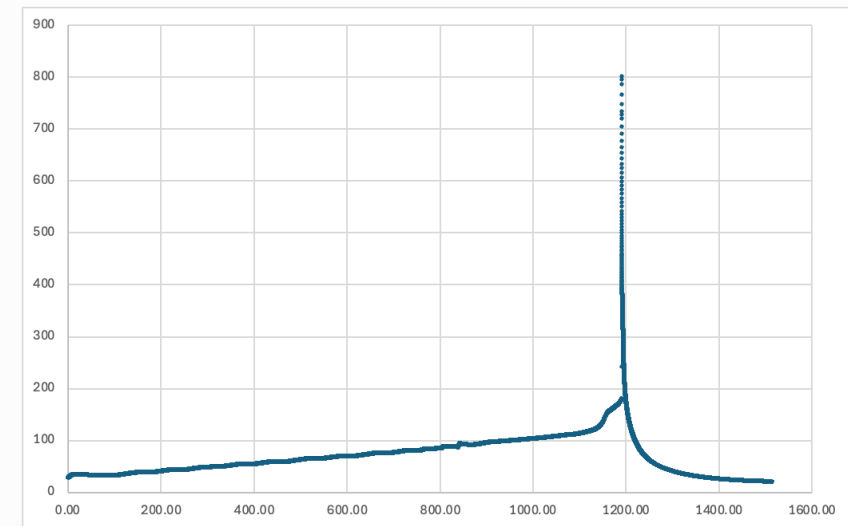
Figure 1: Volume-weighted average lithium-ion battery pack and cell price split, 2013-2024



Source: BloombergNEF. Note: Historical prices have been updated to reflect real 2024 dollars. Weighted average survey value includes 343 data points from passenger cars, buses, commercial vehicles and stationary storage.

BloombergNEF, Dec 2024

Safety

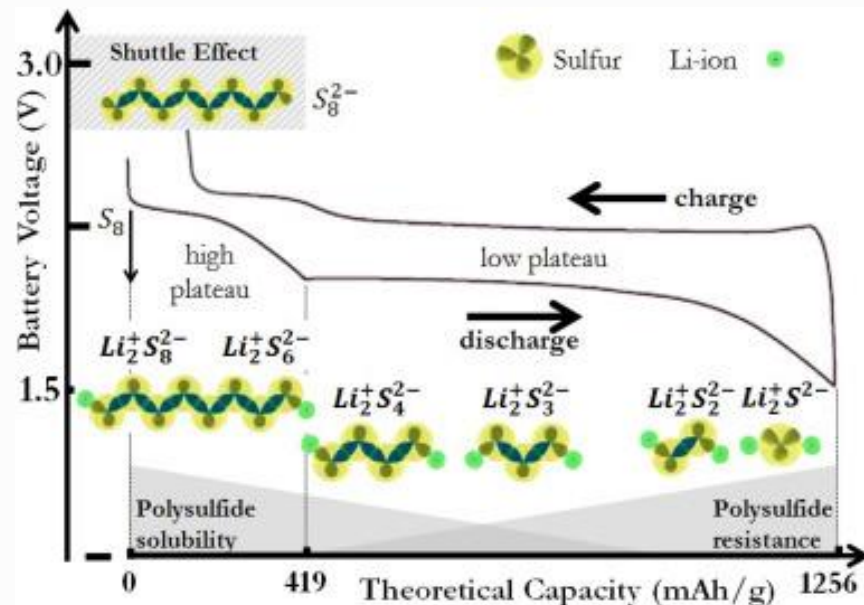
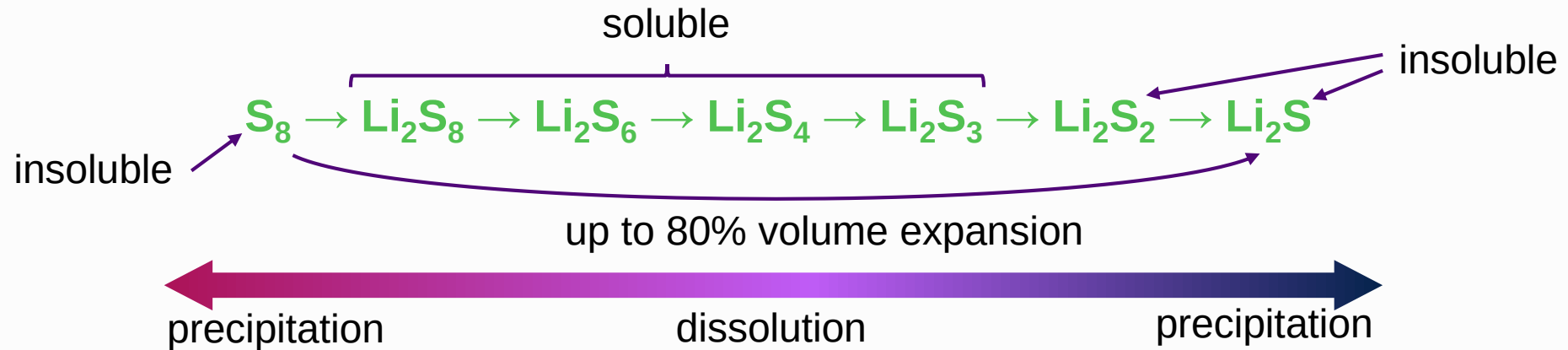


Li-S Pouch Cell with 0.25 M LiNO_3 ,
Kibler et al., In Submission

In isolation perhaps, but in a whole cell we need to think again...

Conventional Li-S...

S reduction takes place in multiple steps through several soluble intermediates to form Li_2S :

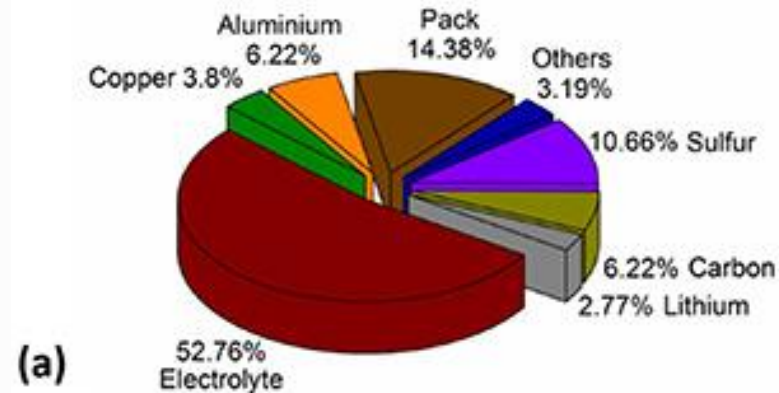


Challenges:

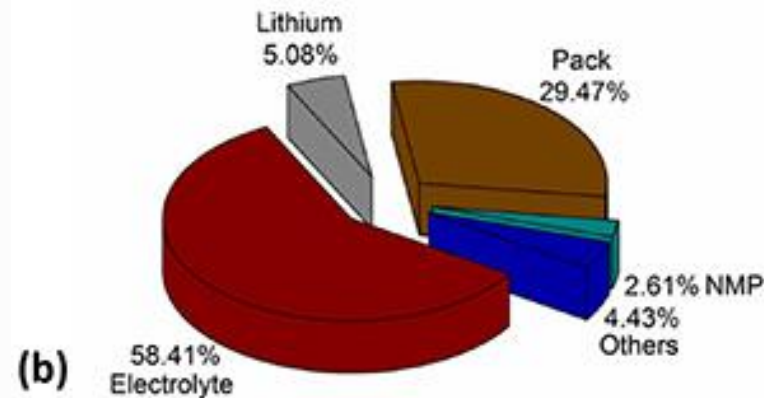
- Extremely low electrical conductivity of sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C),
- Polysulfide shuttle effect decreases capacity and rechargeability,
- Large volume expansion from S to Li_2S ,
- Large amount of electrolyte needed,
- Not compatible with conventional organic carbonate electrolytes,
- Slow kinetics from Li_2S_2 to Li_2S .

What Does This Practically Mean?

- Dissolving sulfur means we're restricted in solvent 'design space'
- That choice must also be compatible/stable with Li
- We need to maintain reasonable viscosity in electrolyte...so we need a reasonable amount....
- Which dominates the mass and cost of cells
- It also means we need relatively high sulfur loadings
- And relatively good utilisation
- And ways to inhibit shuttle/loss



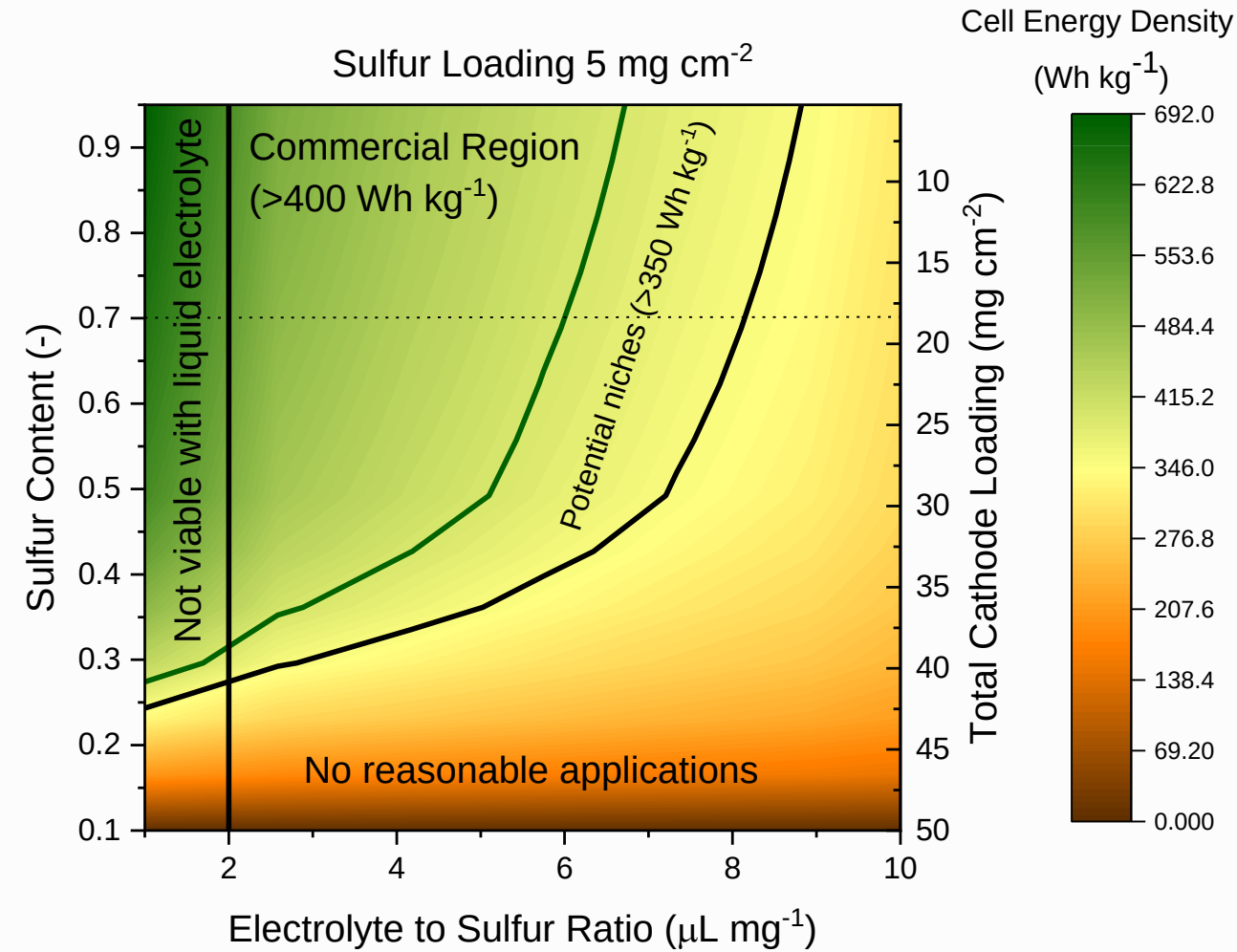
Others	
Material	Ratio (%)
Separator	1.87
Binder	0.89
Tab	0.42



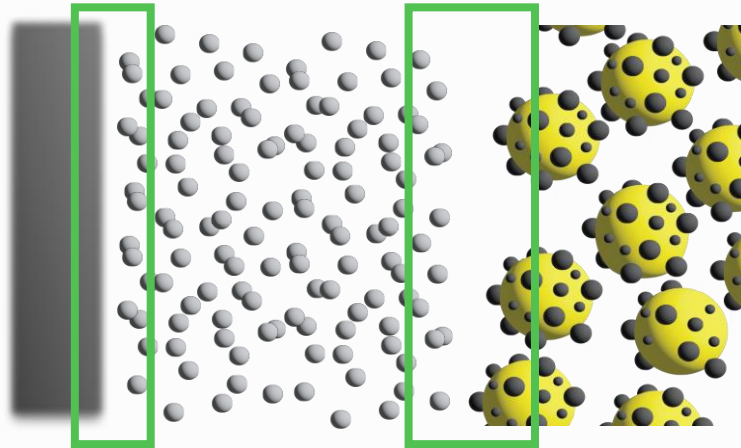
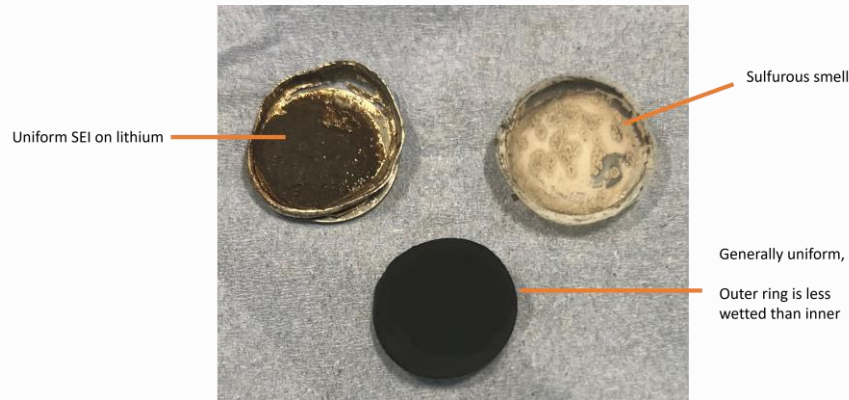
Others	
Material	Ratio (%)
Separator	1.47
Tab	1.16
Copper	0.91
Aluminium	0.41
Carbon	0.34
Binder	0.11
Sulfur	0.03

So, What About A Different Approach?

- If we can keep the sulfur in the cathode we can:
 - Decouple the electrodes
 - Explore more electrolytes
 - **Remove LiNO_3**
 - Ignore shuttle
 - Reduce the volume of electrolyte
 - 'Cheat' on the electrode formulation
- Close to exponential increase in energy density by reducing E/S ratio within regime of interest
- Variations in utilisation and loading less significant
- SS has many benefits but 'plug-in' nature of LE is attractive



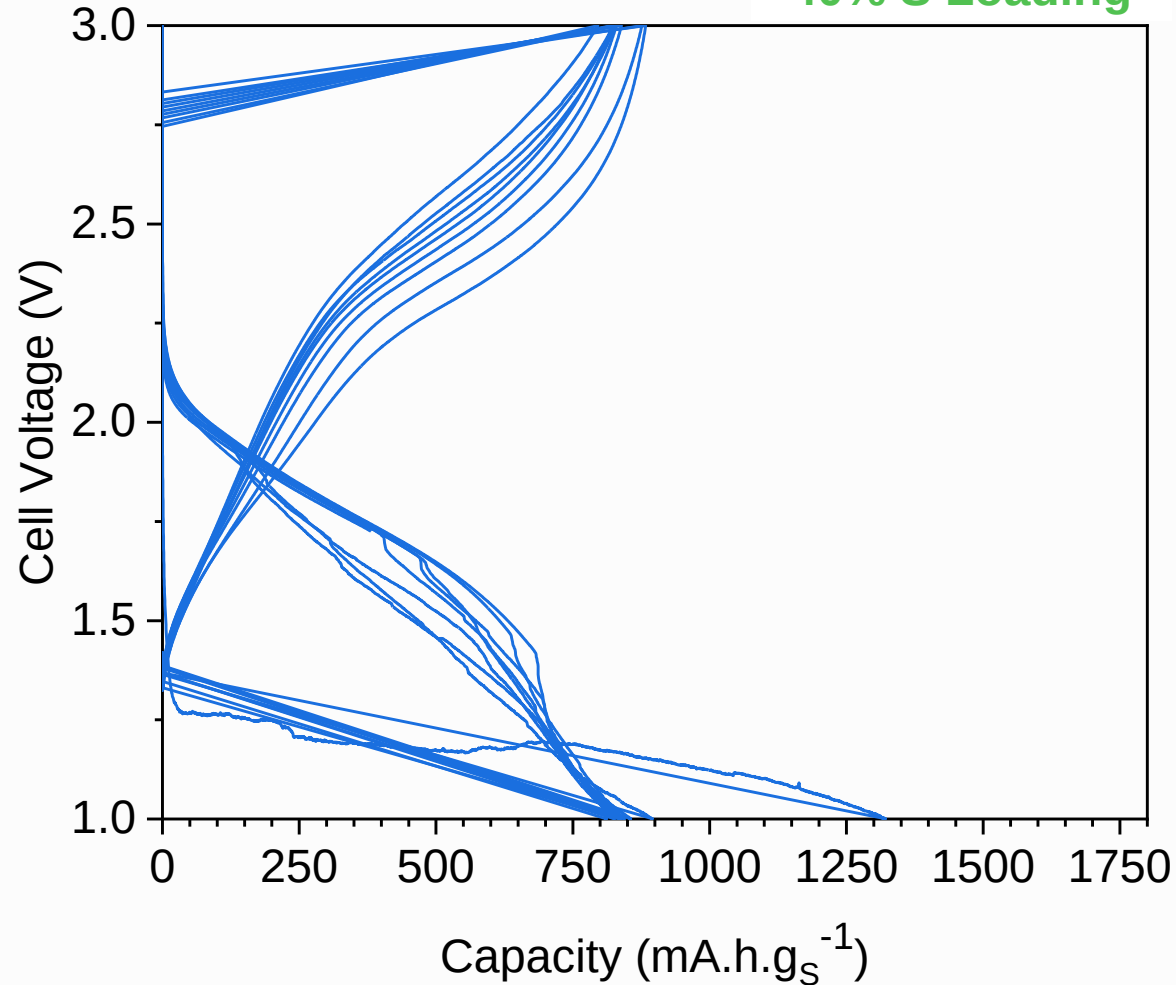
Some Considerations for this Approach



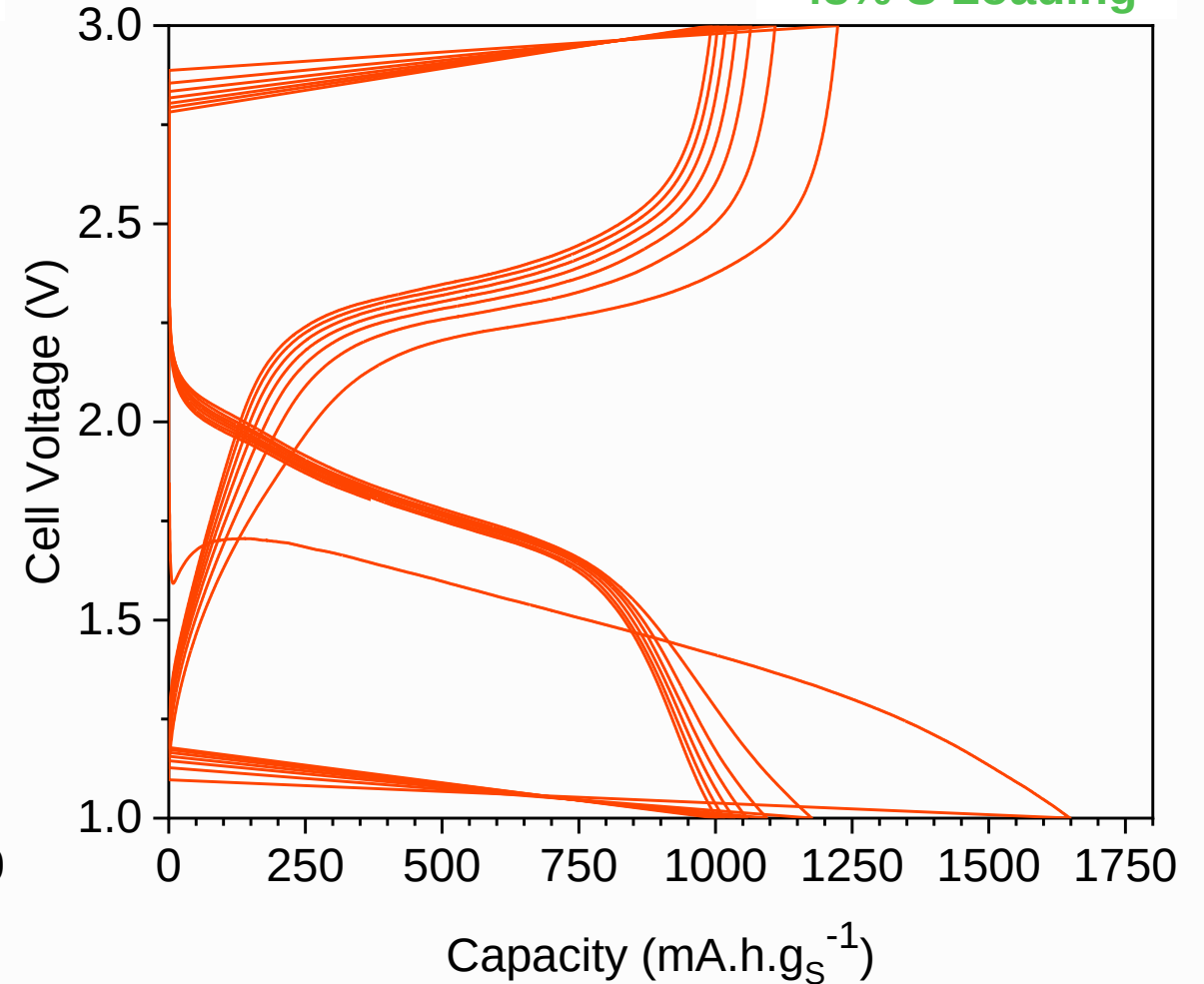
- ‘Solid state mechanism’ maintained in positive electrode
 - Expansion must be contained
 - Microstructure must be tailored to allow for three phases
 - Evidence of some polysulfide formation adjacent to positive electrode
- Electrolyte with sparing solubility but good viscosity, wetting, ionic conductivity etc.
- Cathode and anode ‘isolated’ from each other
- But individual interfaces become critical
 - Compatibility of electrolyte with anode and cathode crucial for performance & longevity
 - Wettability of electrolyte with cathode is important
 - Viscosity

Early Work - SPAN

40% S Loading

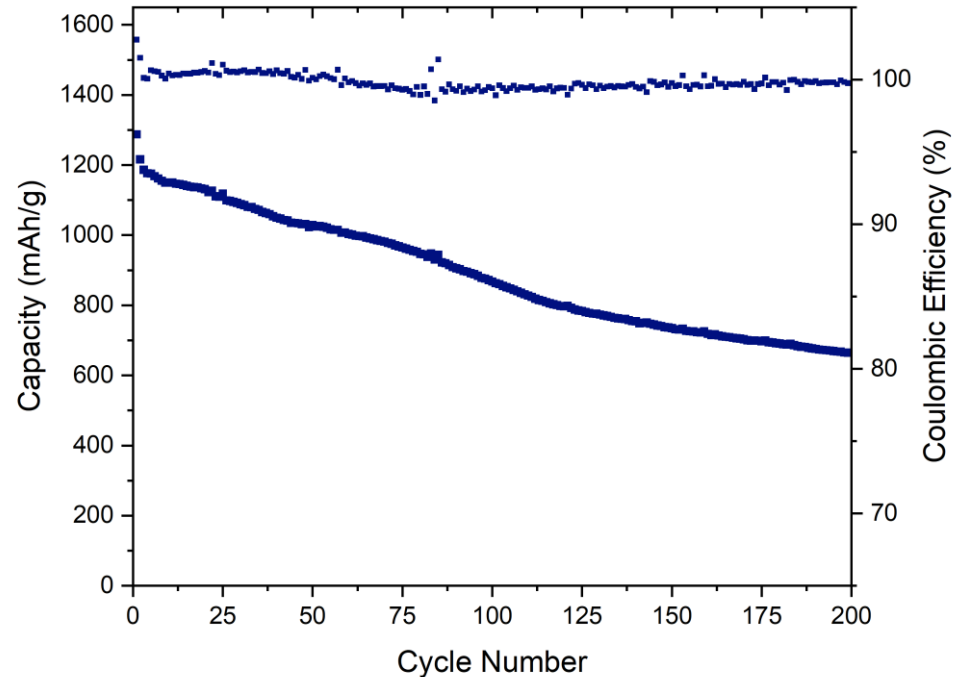
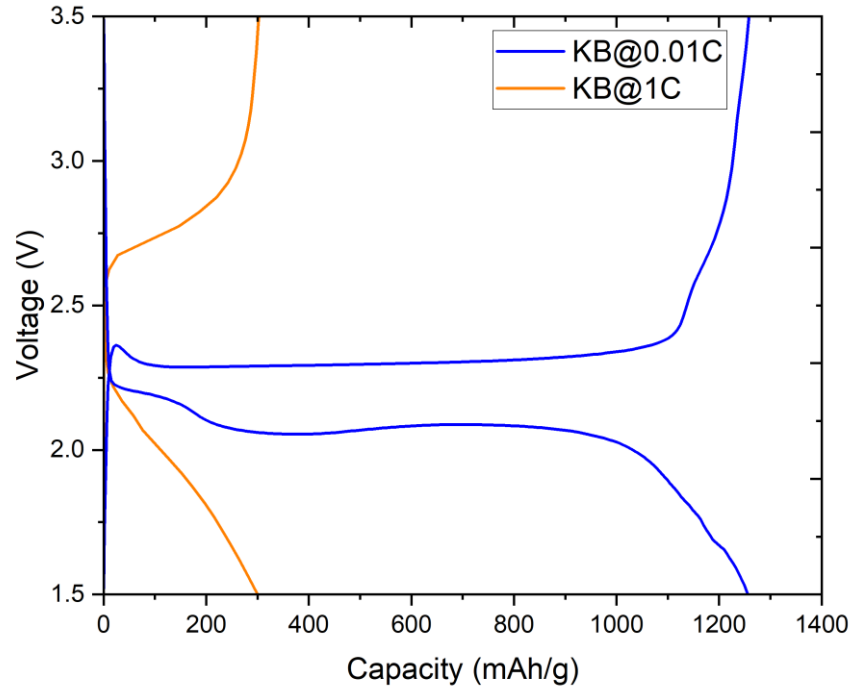


48% S Loading



Li-SPAN commonly discussed in the literature – accessible capacity but significant fade and limited scope for high energy density

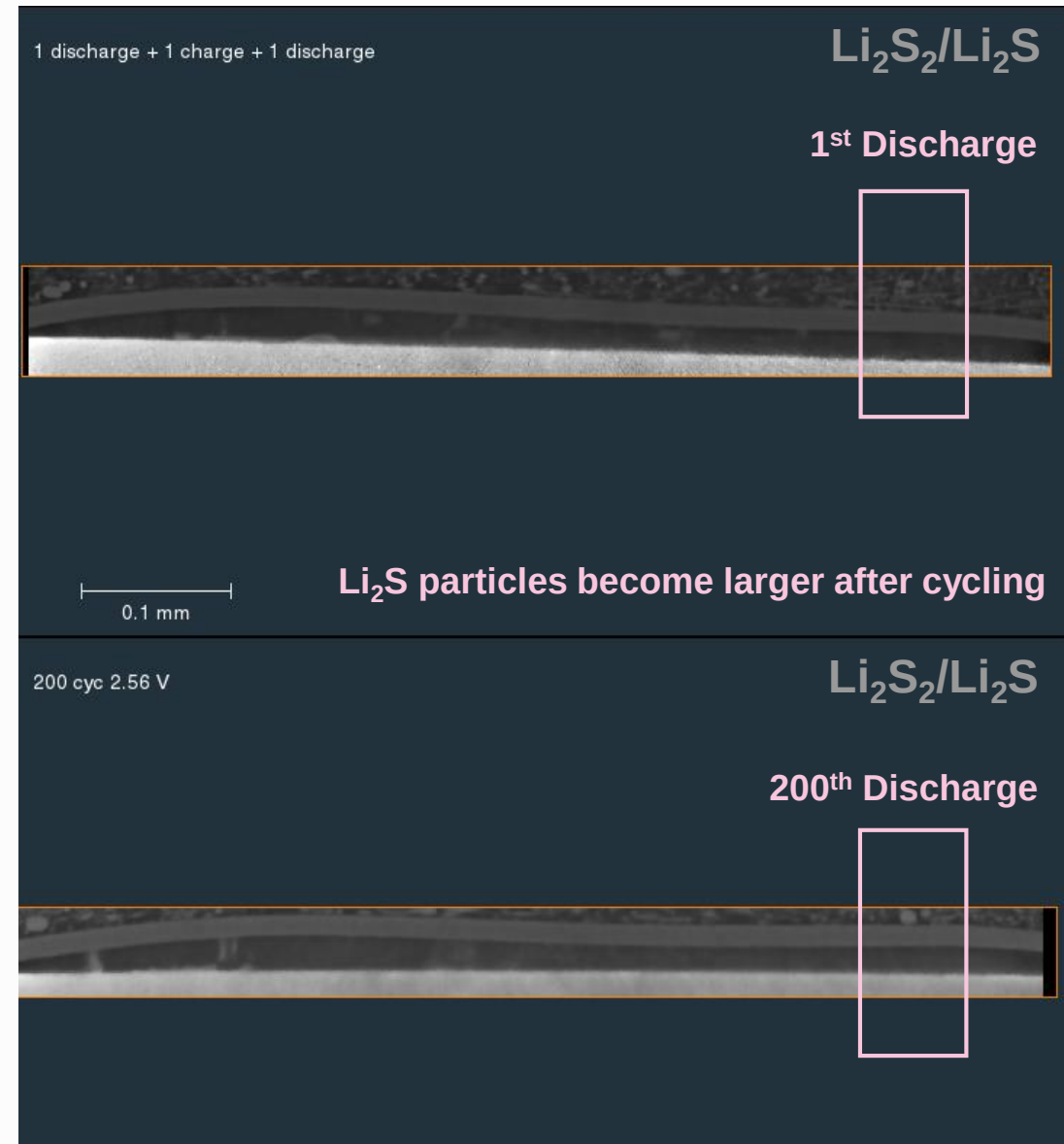
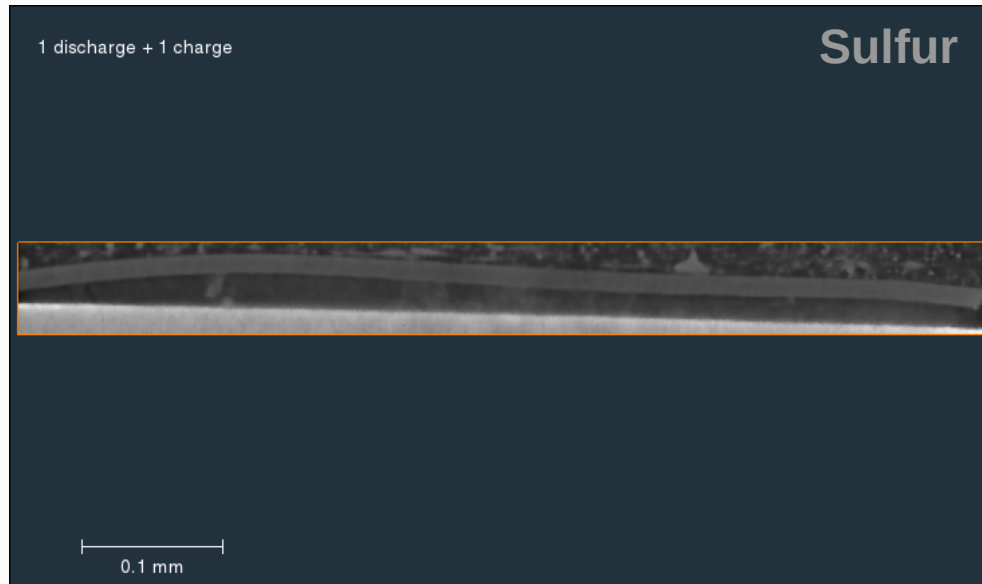
Sulfur/Ketjen Black Composite



- Cells manufactured with LiTFSI:G2:TTE (1.5:1:1 vol/vol) electrolyte
- Good capacity achieved though rate performance is relatively poor
- Degradation comparatively good for a Li-S cell though room for improvement
- What is the degradation mechanism?

CT Over 200 Cycles

- Using precommercial material testing pre and post cycling behaviour
- Evidence of material agglomeration, reduced sulfur utilisation over time
- Need to maintain ionic and electronic conductivity through the electrode for lifetime



Modifying the Electrode Architecture

Advantages:

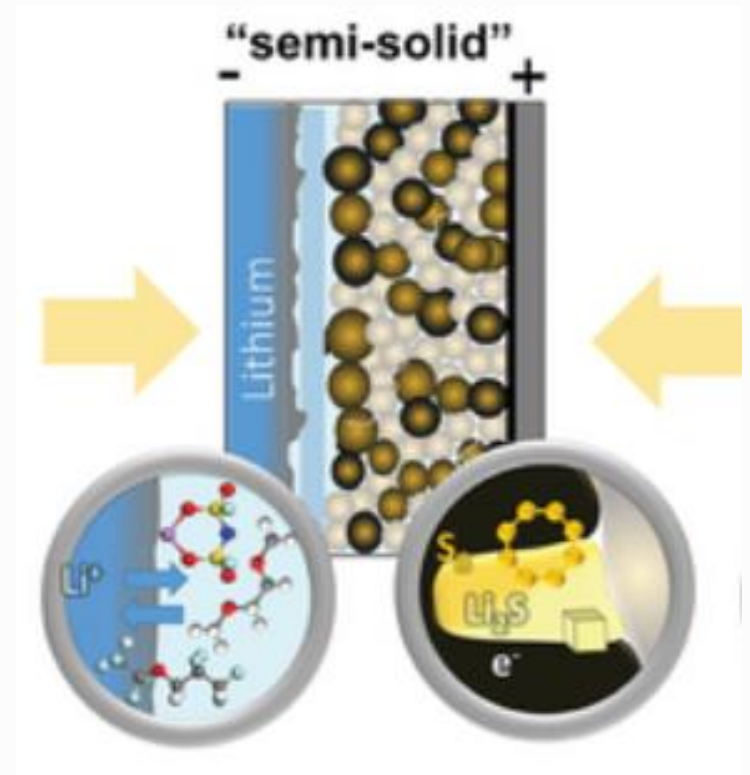
- The quasi-solid-state conversion of lithium polysulfides, results in better cycle stability compared to the conventional Li-S batteries.
- Higher energy density can be accessed

Issues:

- The overpotential of the QSS Li-S batteries is higher than the conventional Li-S batteries, due to the sluggish kinetics.
- Degradation appears to be multifaceted – with electrode pulverisation and incomplete sulfur conversion

Our Strategy:

Adding a solid-state electrolyte (e.g., LGPS) to the cathode to reducing the overpotential promote sulfur conversion



Advanced Energy Materials (2024): 2402204.

Developing a Feasible Manufacturing Route



LGPS in various solvents



Adding **ethyl acetate**

Adding various of solvents into LGPS in the glovebox. The NMP, cyrene, DMF, and DMSO are **Unstable**.

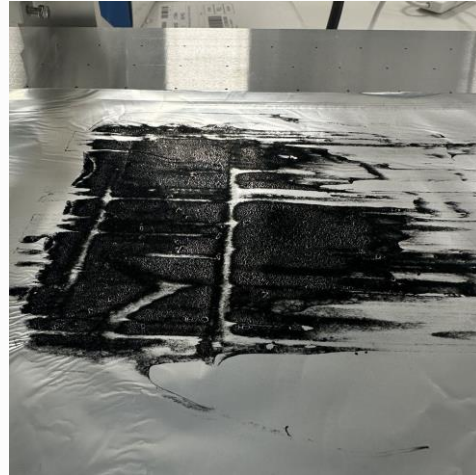
The **ethyl acetate** seems more Stable for both LGPS and LPSCl since no obvious colour change were observed.

Developing a Feasible Manufacturing Route

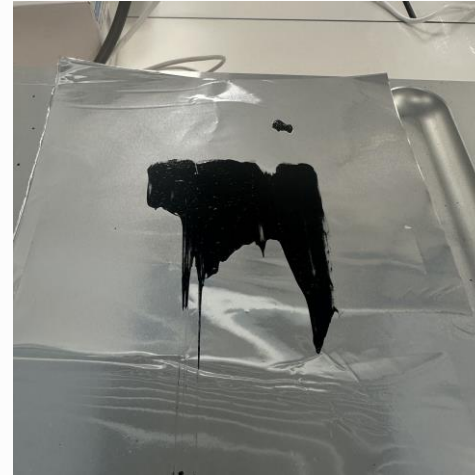
PVDF + ethyl acetate



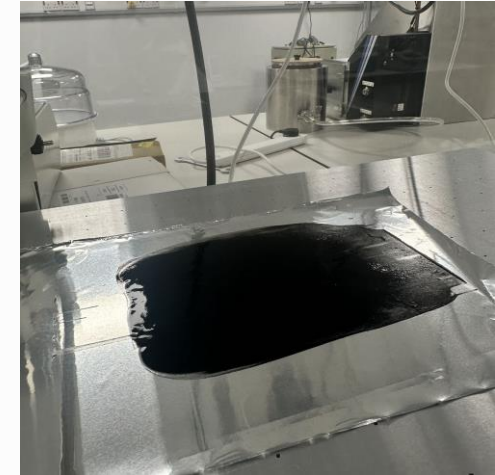
PVDF-HFP + ethyl acetate + HB (Hexyl butyrate)



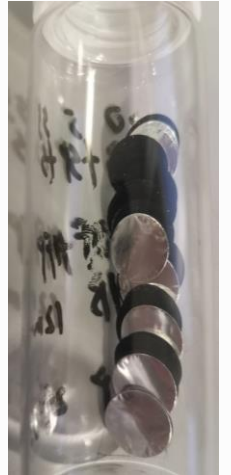
1st time



2nd time



Optimized coating

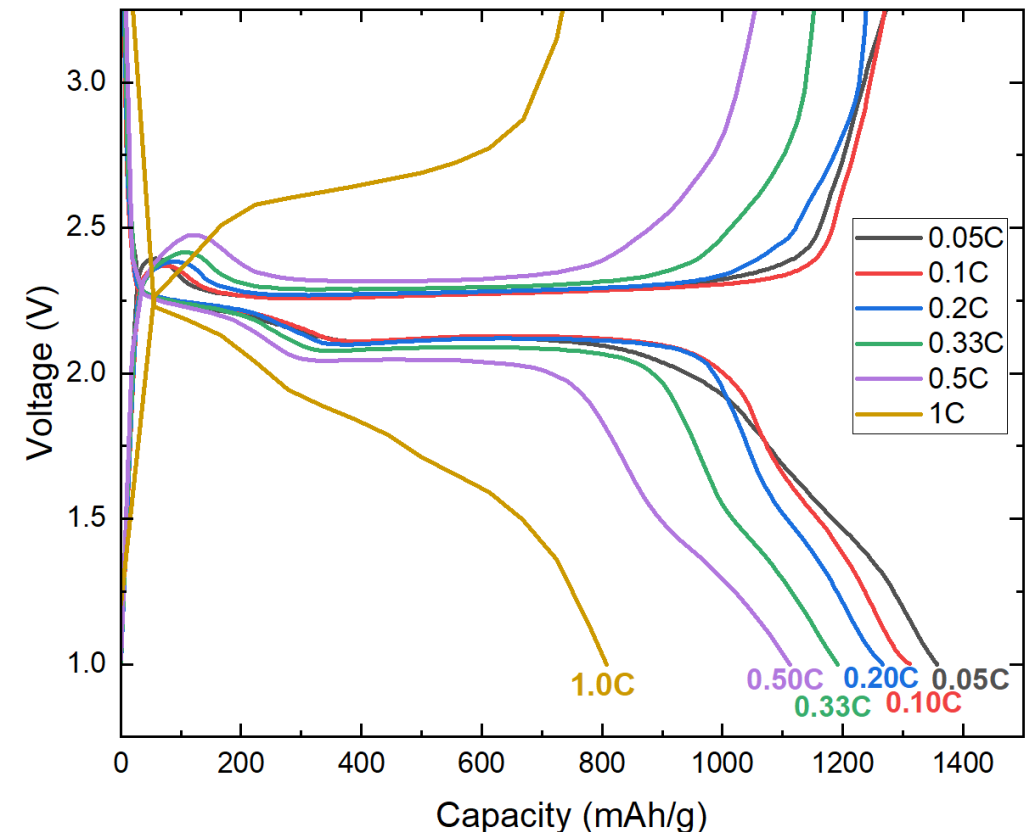


Electrodes

At the beginning, the powder always peeled off from the coated electrode after drying due to the incompatibility between the **PVDF** binder and the **ethyl acetate** solvent. After replacing the binder with **PVDF-HFP** and adding some **cosolvent HB**, coating is possible.

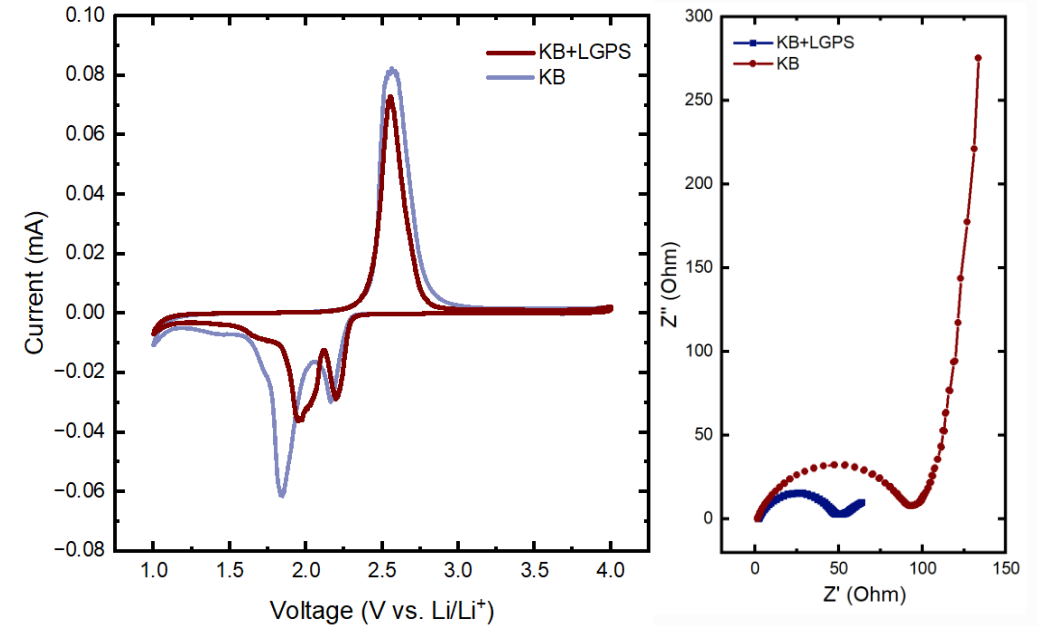
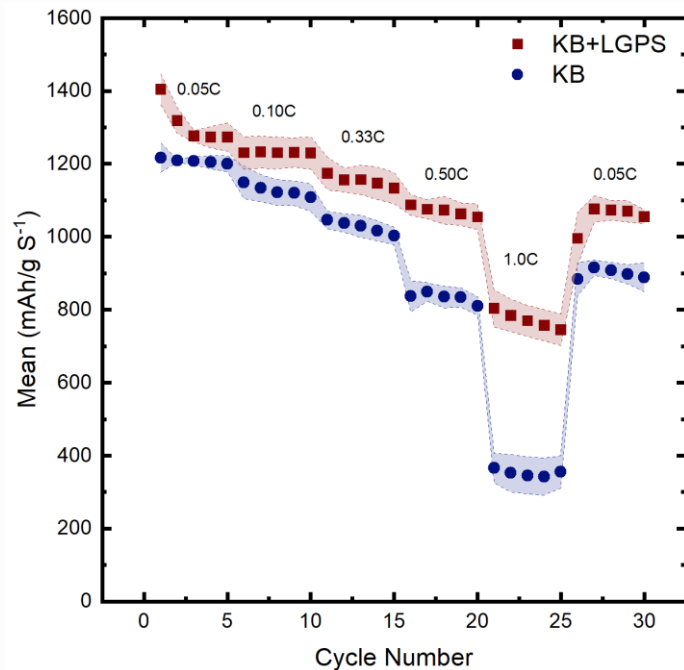
Electrode Performance

- Incorporation of LGPS into the electrode provides moderate enhancement of initial performance
- Significantly improved rate performance observed across the range tested
- Evidence of some polysulfide formation or dynamism in the resistance of the electrolyte occurring after ca. 400 mAh g⁻¹
- Open question regarding mechanism –
 - ‘Opening’ of the electrode to increase access to S?
 - Ion conducting pathways?
 - Improved triple phase boundary density?
- Observed from first cycle suggesting an active role in performance enhancement



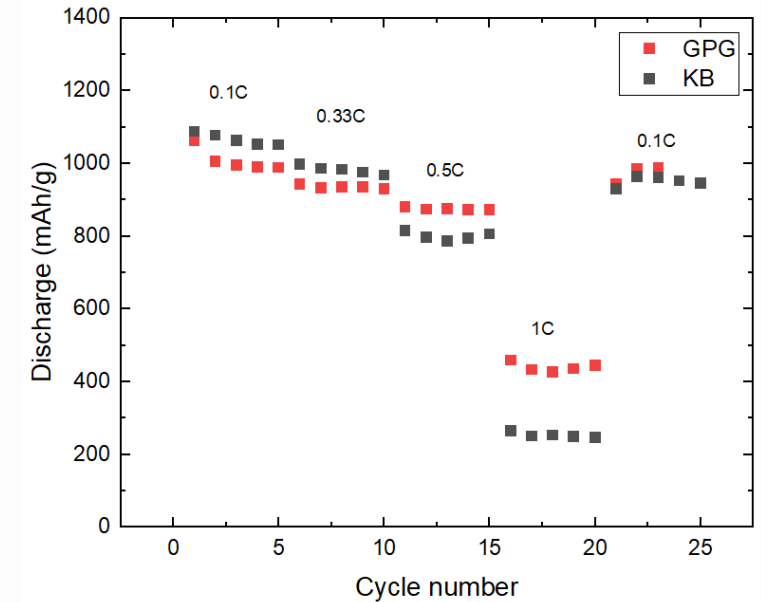
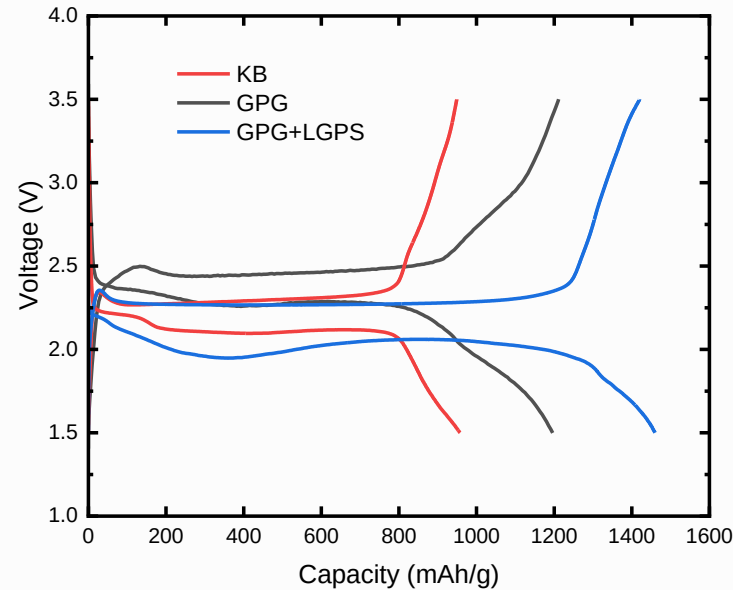
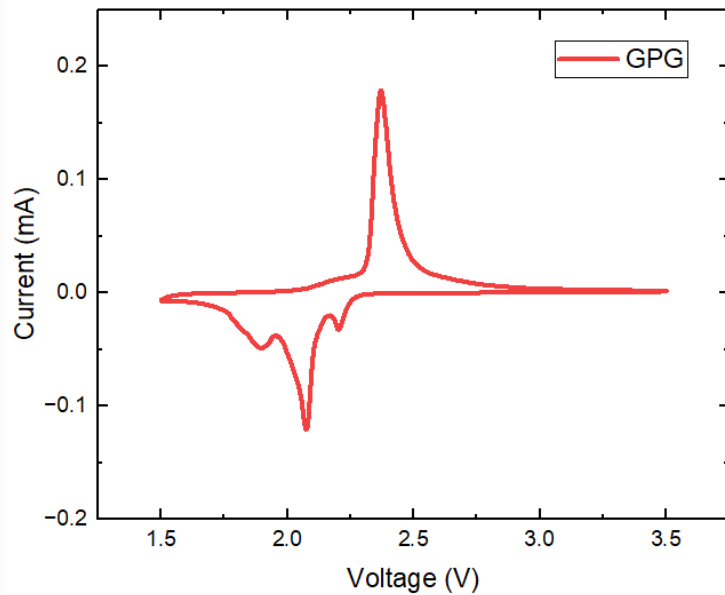
Comparative Performances

- CV shows shift in reduction peaks during cycling with reduced overpotential providing enhanced energy
- EIS shows reduced resistances associated with integration of LGPS



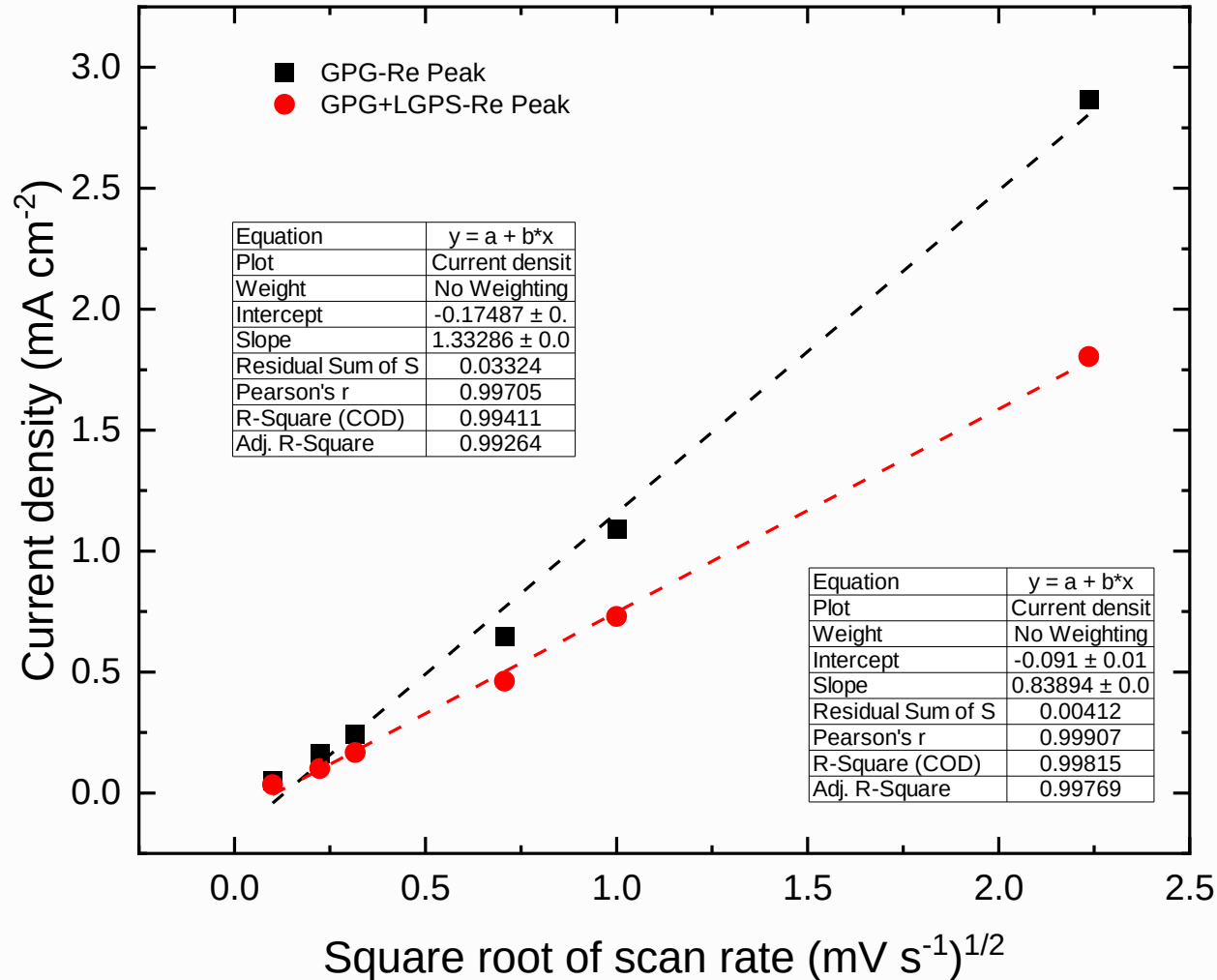
- Capacity enhancement sustained across all rates tested with difference becoming marked at elevated rates (0.5–1 C)
- Repeatability tested to ensure variation in sulfur loading etc is not factor

Alternative Carbons – Graphene-P-Phenyl-Graphene



- Performance retained with strong discharge capacity and reasonable rate performance
- Change in carbon results in emergence of third peak in CV
- Improved capacity, increased overpotential in GPG+LGPS
- Mechanism guided by composite and electrolyte – this is not a one shot solution!

Why The Difference – D_{Li} Calculations



Li⁺ ion diffusion coefficient

GPG: $D_{ox} (Li^+) = 3.73 \times 10^{-7} \text{ cm}^2/\text{s}$

GPG+LGPS: $D_{ox} (Li^+) = 2.35 \times 10^{-7} \text{ cm}^2/\text{s}$

LGPS:

$D (Li^+) \approx 1 \times 10^{-6} \text{ to } 1 \times 10^{-7} \text{ cm}^2/\text{s}$

$\sigma_e \approx 10^{-10} \text{ to } 10^{-8} \text{ S/cm}$

Kamaya, Noriaki, et al. "A lithium superionic conductor." *Nature Materials* 10.9 (2011): 682-686.

GPG:

$D_{ox} (Li^+) \approx 1 \times 10^{-6} \text{ to } 1 \times 10^{-7} \text{ cm}^2/\text{s}$

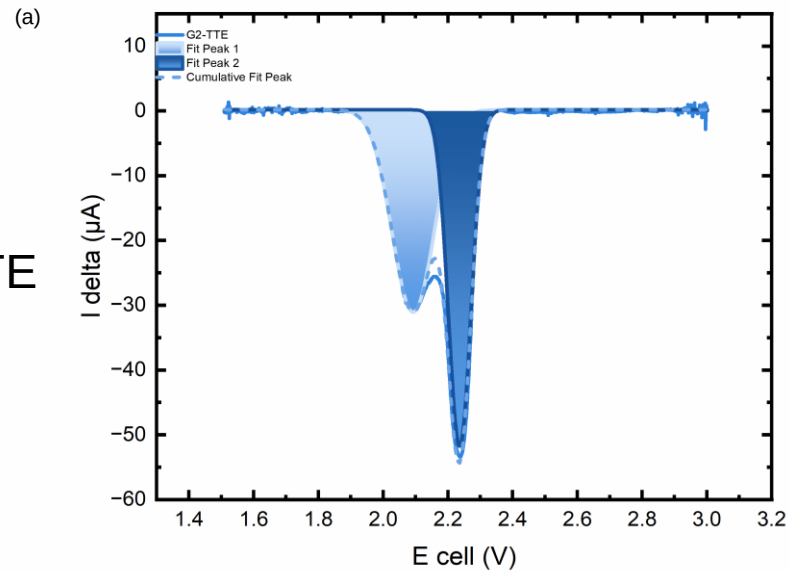
$\sigma_e \approx 31.55 \text{ S/cm}$

Li, H., et al. "Van-der-Waals-forces-modulated Graphene-P-phenyl-Graphene Carbon Allotropes." *Nature Communications* (2025). DOI: 10.1038/s41467-025-64971-1

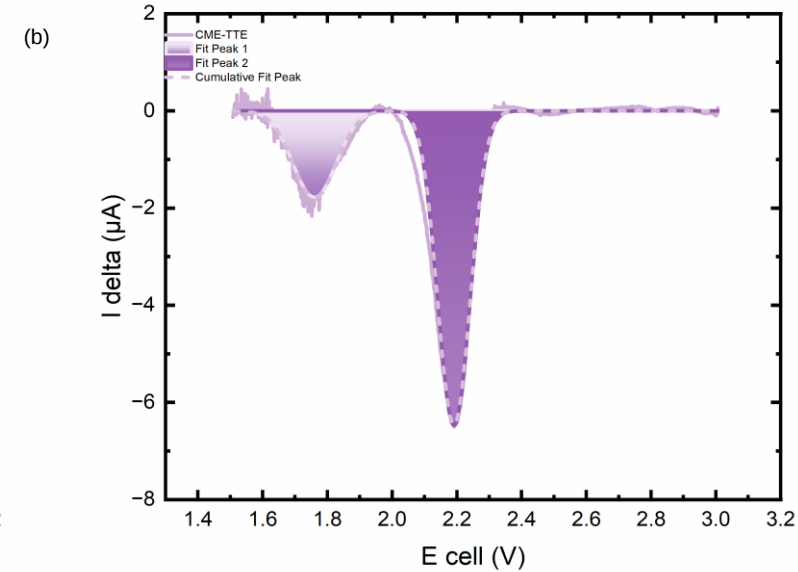
The Li⁺ diffusion coefficient (D_{Li}) in GPG is comparable to that of LGPS, whereas the electronic conductivity of GPG is over 10 orders of magnitude higher than that of LGPS.

Early Mechanistic Studies – SWV

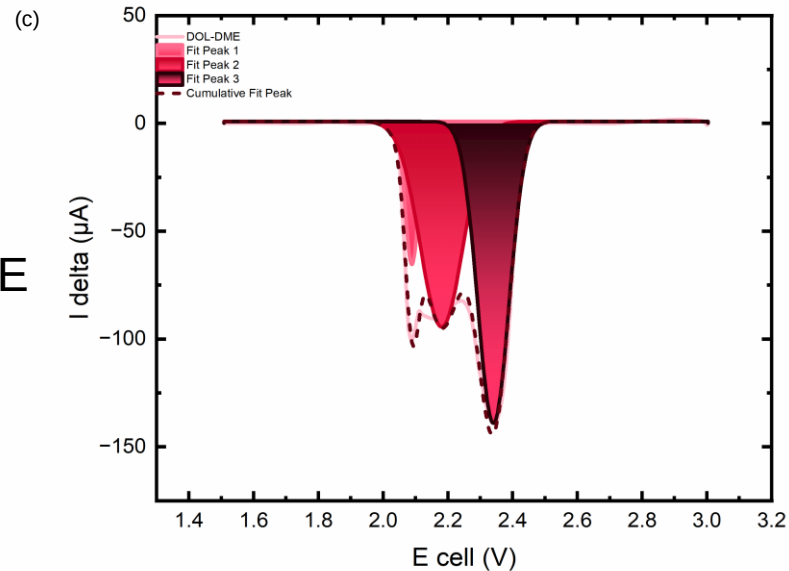
G2-TTE



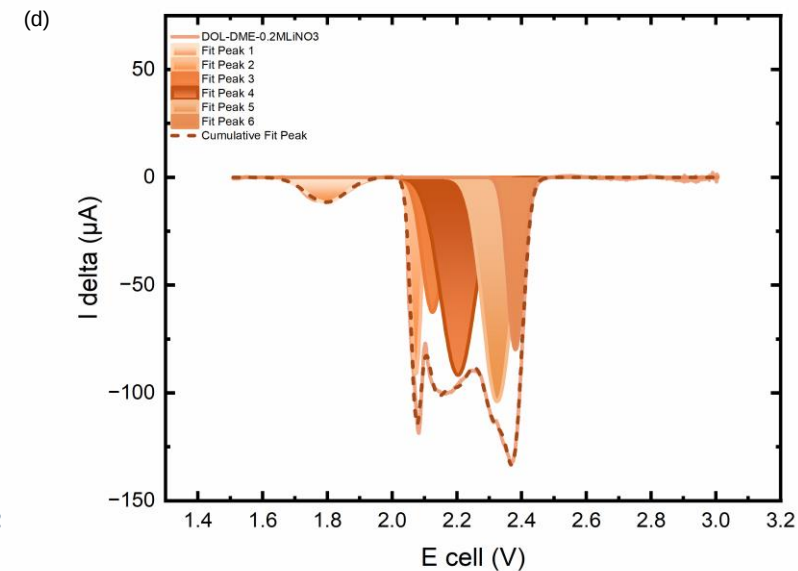
CME-TTE



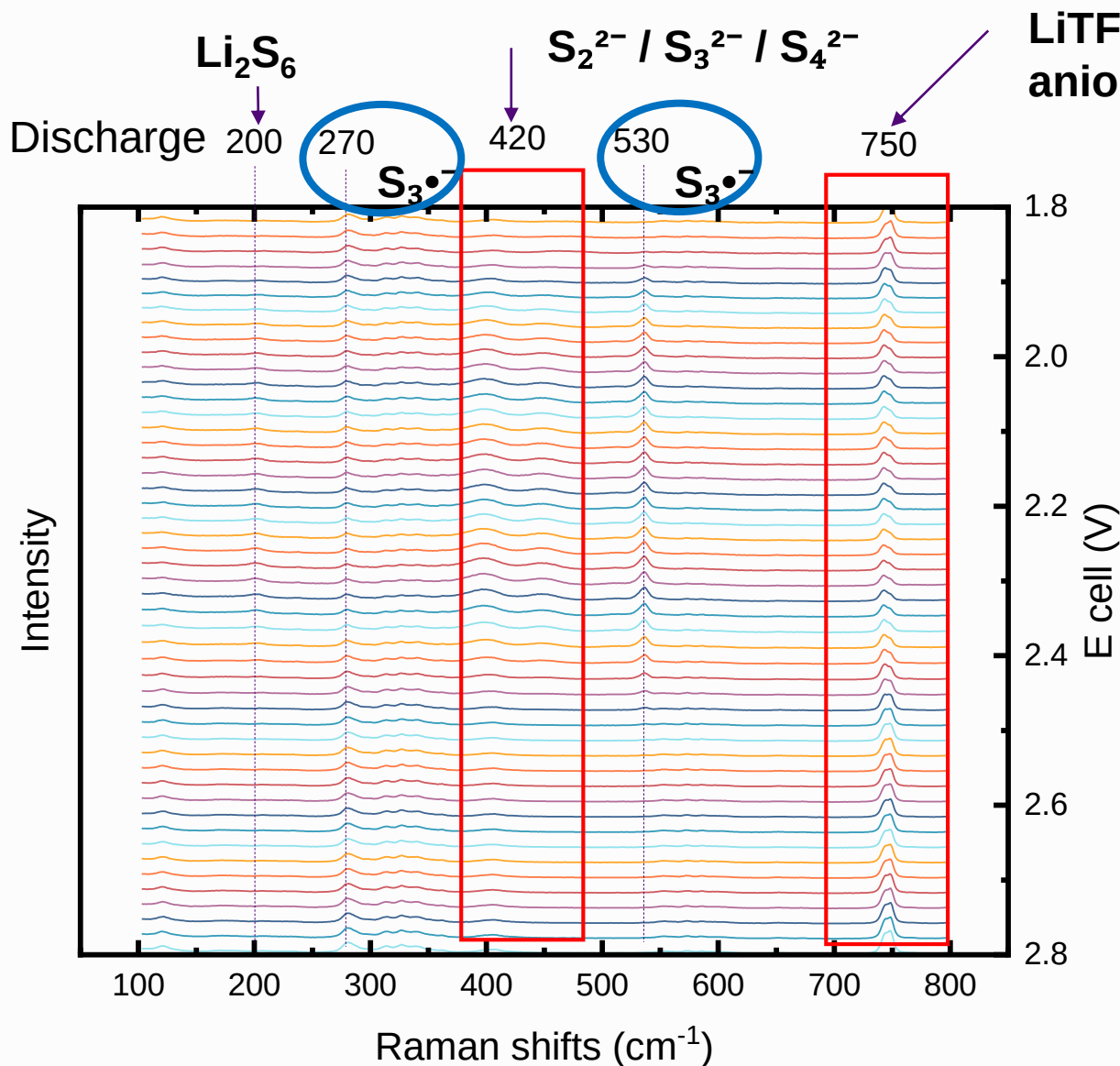
DOL:DME



DOL:DME
0.2M LiNO₃



Early Mechanistic Studies: Raman - Discharge



530/270: Tri-sulfur radical anion ($S_3^{\bullet-}$)

S_3 -type species (symmetric stretch)

420: Short chain sulfides

$S_2^{2-} / S_3^{2-} / S_4^{2-}$

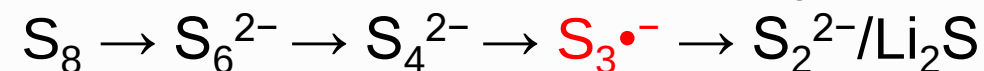
200: Short chain sulfides

Li_2S_6 dominated

750: Li solvated anion in electrolyte?

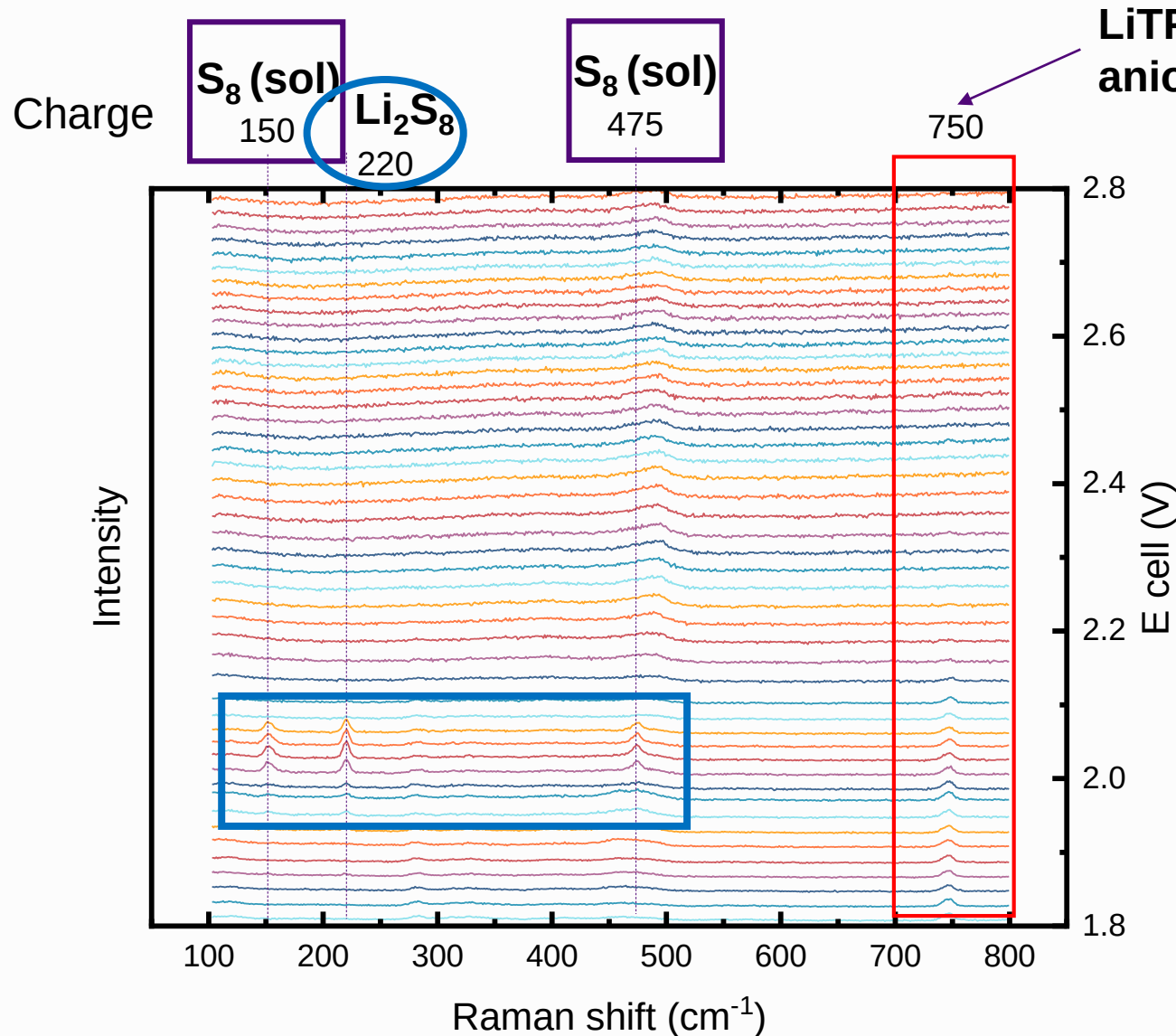
LiTFSI (highly possible)

Tentative Mechanistic Pathway:



The reproducible peaks observed at approximately 530 cm^{-1} are likely associated with the polysulfide of Tri-sulfur radical anion ($S_3^{\bullet-}$).

Early Mechanistic Studies: Raman - Charge



530/270: Tri-sulfur radical anion ($S_3^{\bullet-}$)

S_3 -type species (symmetric stretch)

420: Short chain sulfides

$S_2^{2-} / S_3^{2-} / S_4^{2-}$

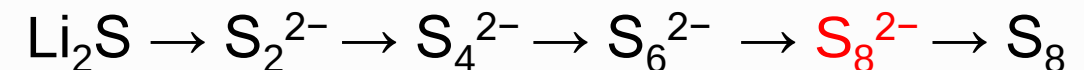
200: Short chain sulfides

Li_2S_6 dominated

750: Li solvated anion in electrolyte?

LiTFSI (highly possible)

Tentative Mechanistic Pathway:



The reproducible peaks observed at approximately 530 cm^{-1} are likely associated with polysulfides that have yet to be identified.

In Summary

- G2-TTE based electrolyte yields reasonable performances using S/C composite
- Addition of LGPS enables extension of cycle life and significant improvement in rate performance
- Though mechanism of degradation is uncertain
- Mechanistic shifts associated with electrolyte change explored using SWV
- Ultimately there is a need to move beyond LiNO₃ as an additive:
 - Use alternative solvents
 - Use alternative additives
- LiSTAR researching aspects of the whole cell – crucial to consider wider impact on cell performance when developing in isolation

A Word of Thanks



Boyi Pang, Huanxin Li, Huw Parks and all of the wider APL team based at UCL

(Please consider this an invite to visit!)



Paul Shearing (Oxford) ,Liam Bird (UCL/Oxford), Yiheng Shao (Oxford)



Sylwia Walus (Faraday Institution), Tony Burrell (NREL, Faraday Institution)

A Word of Thanks

