



9th Workshop “Lithium–Sulfur Batteries”

Challenges and Promises of Lithium Metal Anode in Practical Lithium–Sulfur Batteries

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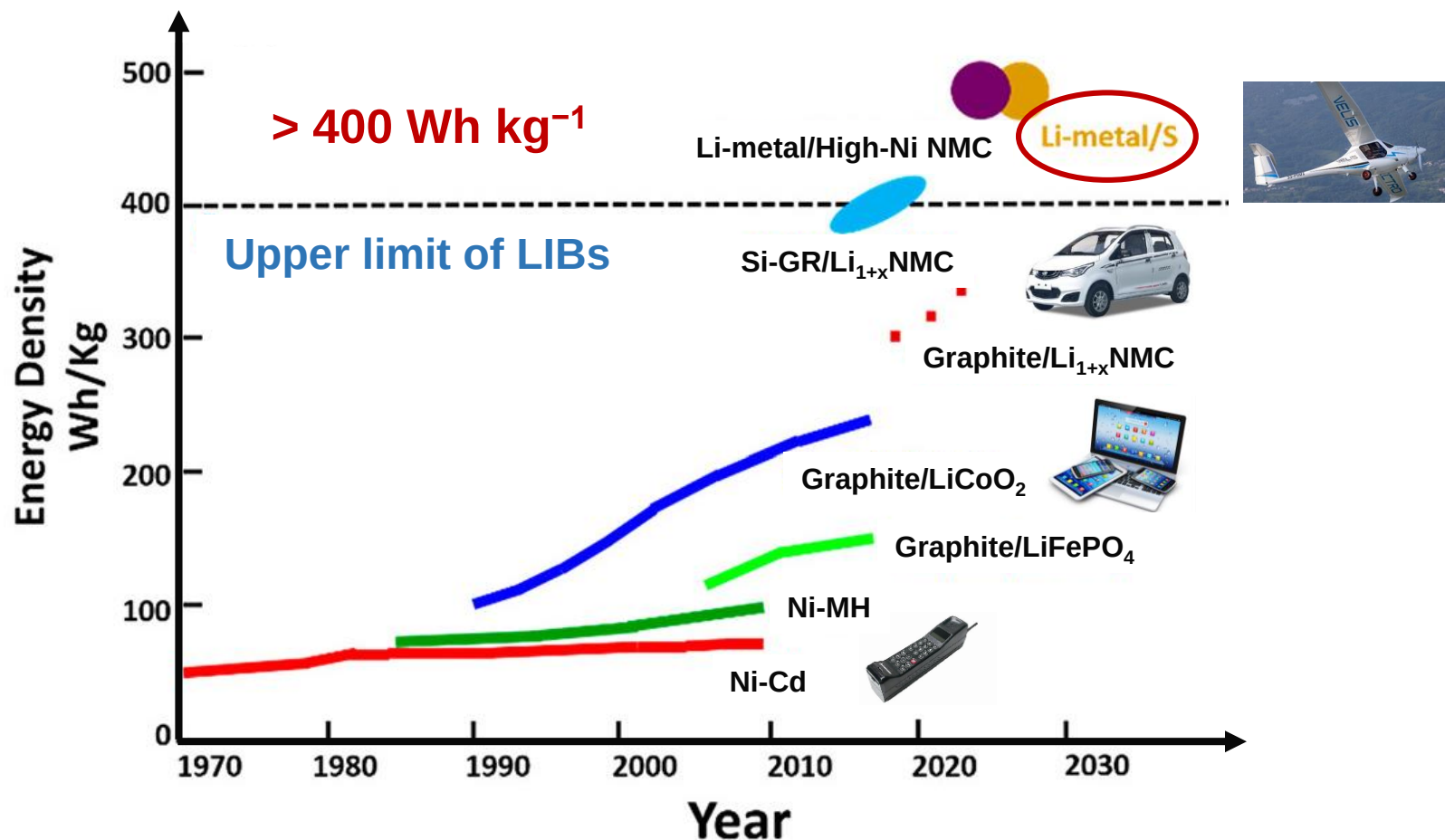


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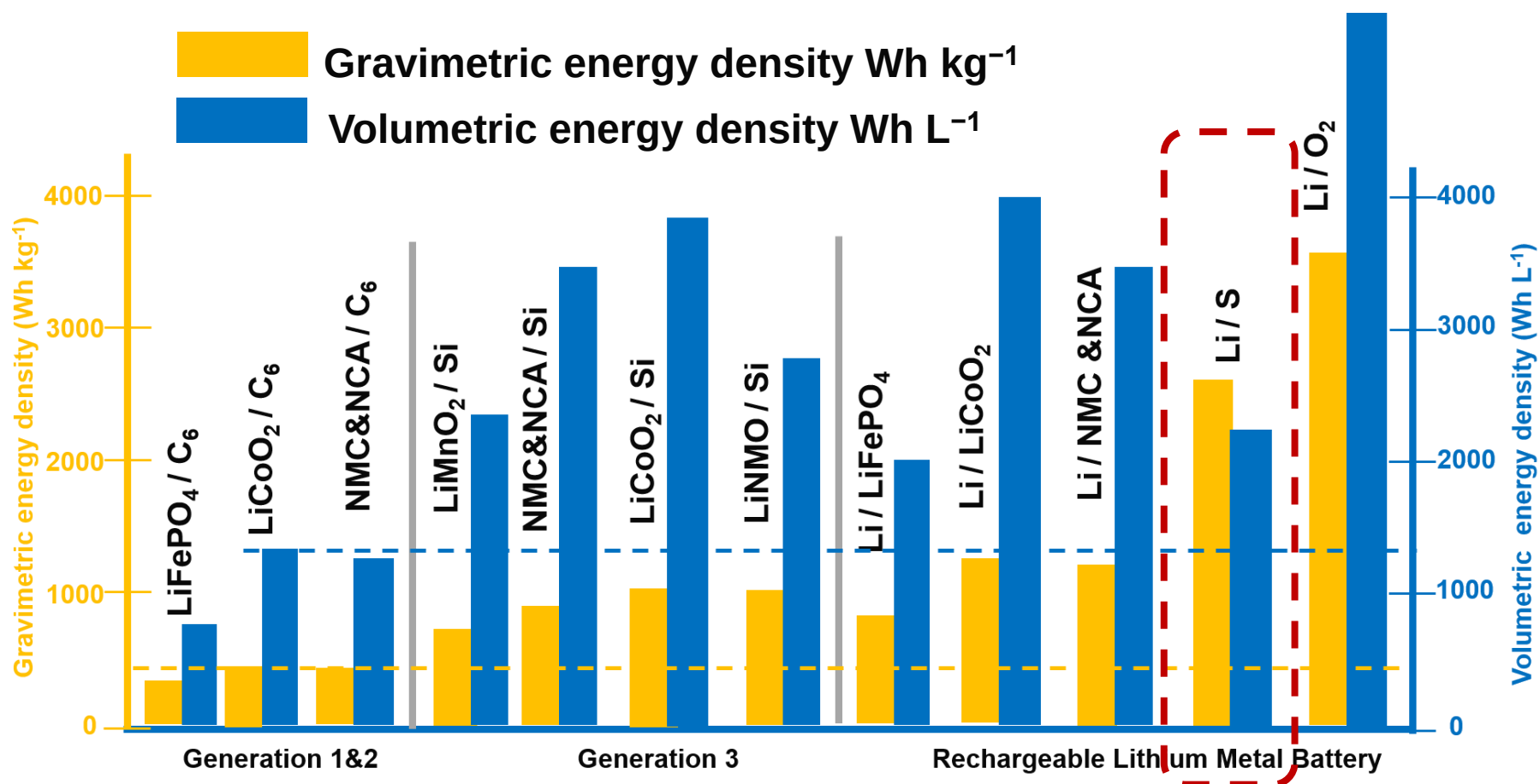
Batteries for sustainable energy

To break the energy density limit



Lithium–sulfur batteries

Lithium–sulfur batteries promise high energy density.



Lithium–sulfur batteries

Sulfur cathode



Atomic weight: 32.06 g mol^{-1}
Light yellow solid (2.07 g cm^{-3})
Non-toxic, “green” material
Abundant and cheap ($28 \$ \text{ ton}^{-1}$)
Theoretical capacity: 1672 mAh g^{-1}

Reaction path	
Anode	$\text{Li} \rightarrow \text{Li}^+$ solid – liquid
Cathode	$\text{S}_8 \rightarrow \text{S}_x^{2-} (x = 4-8) \rightarrow \text{Li}_2\text{S}$ solid – liquid – solid

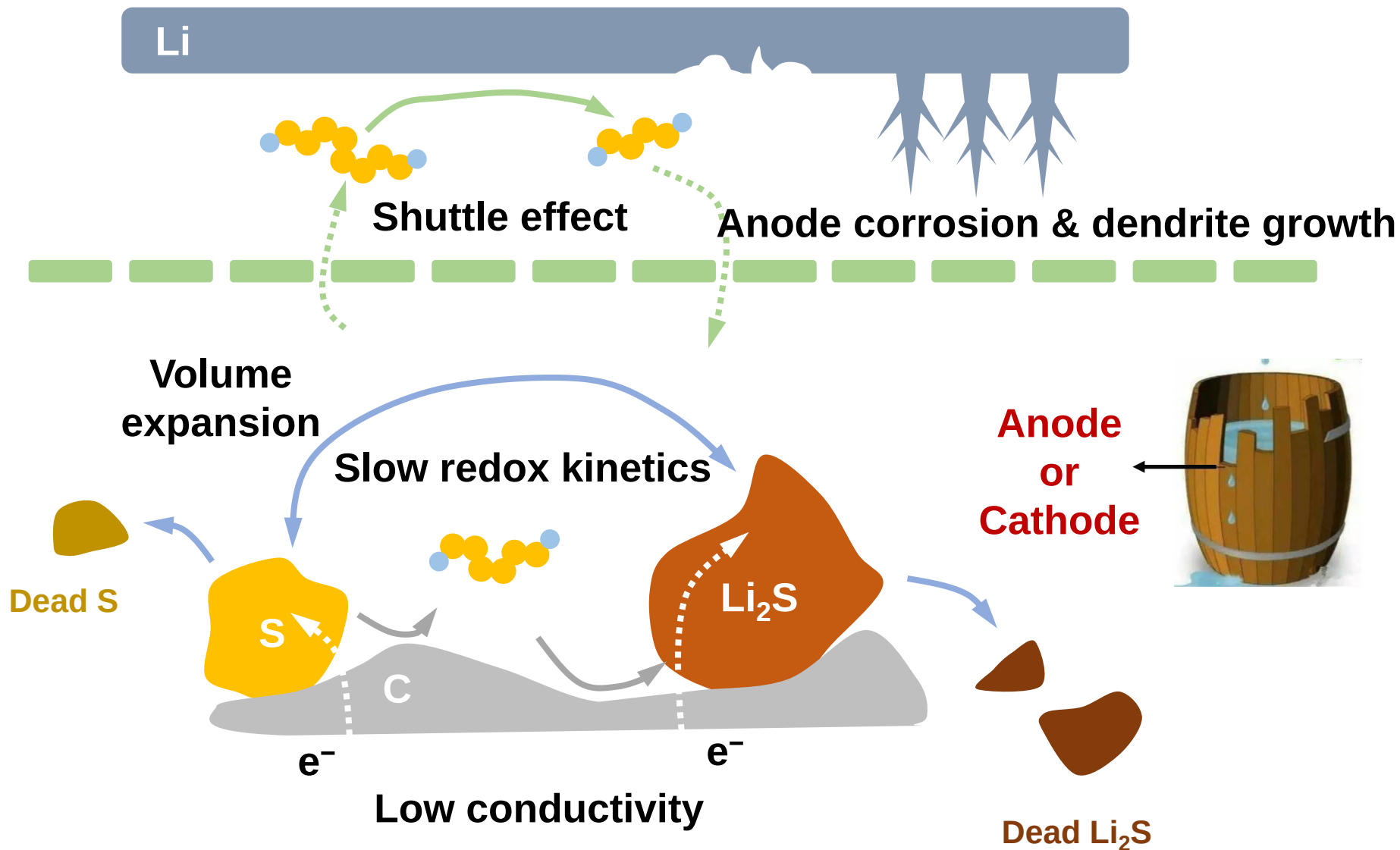
Lithium metal anode



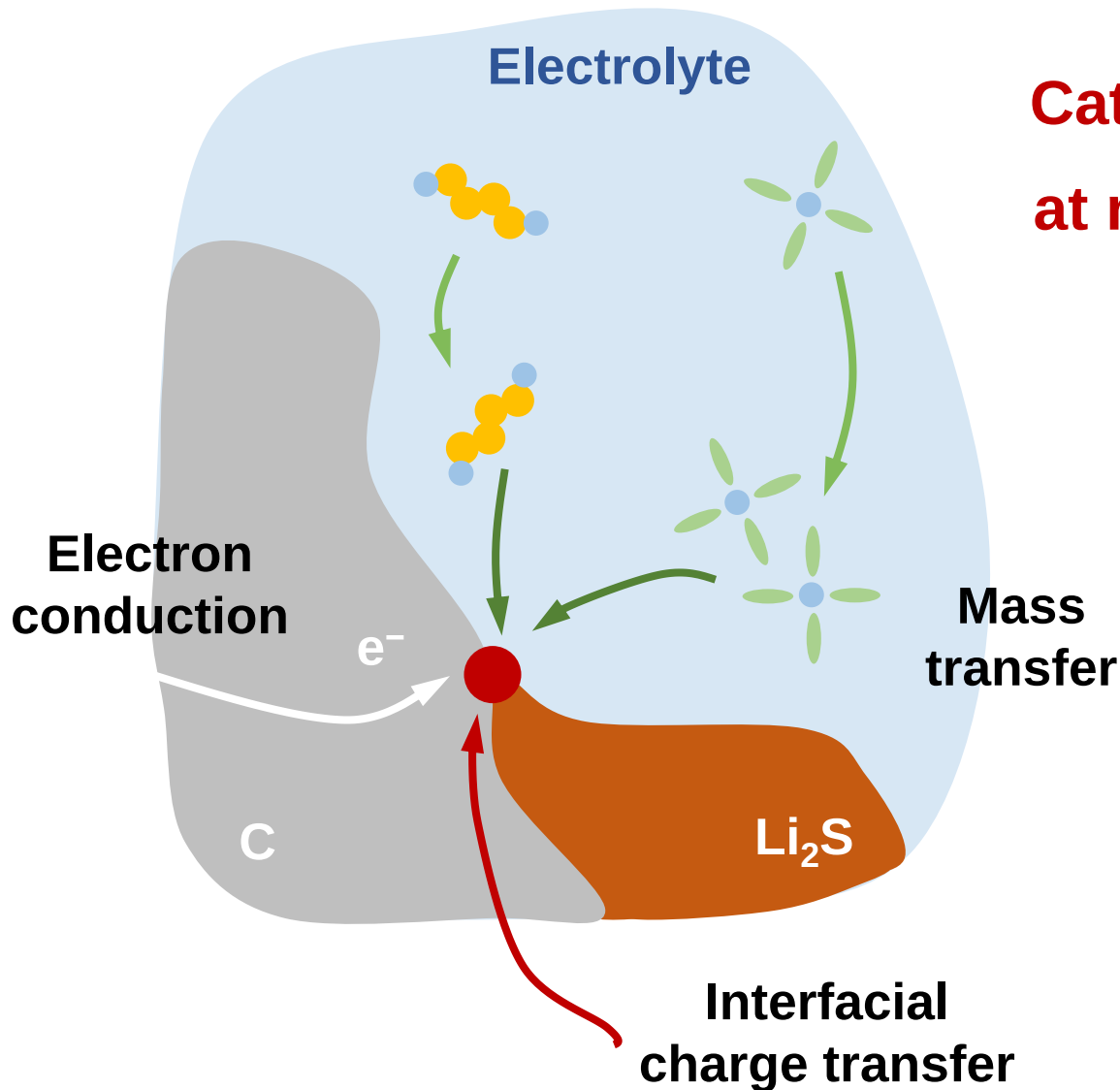
Atomic weight: 6.94 g mol^{-1}
Lightest alkali metal (0.54 g cm^{-3})
Silvery, metallic solid
Theoretical capacity: 3860 mAh g^{-1}
 $E = -3.04 \text{ vs. SHE}$

Energy density
 2600 Wh kg^{-1}

Lithium-sulfur batteries



Cathode kinetic regulation

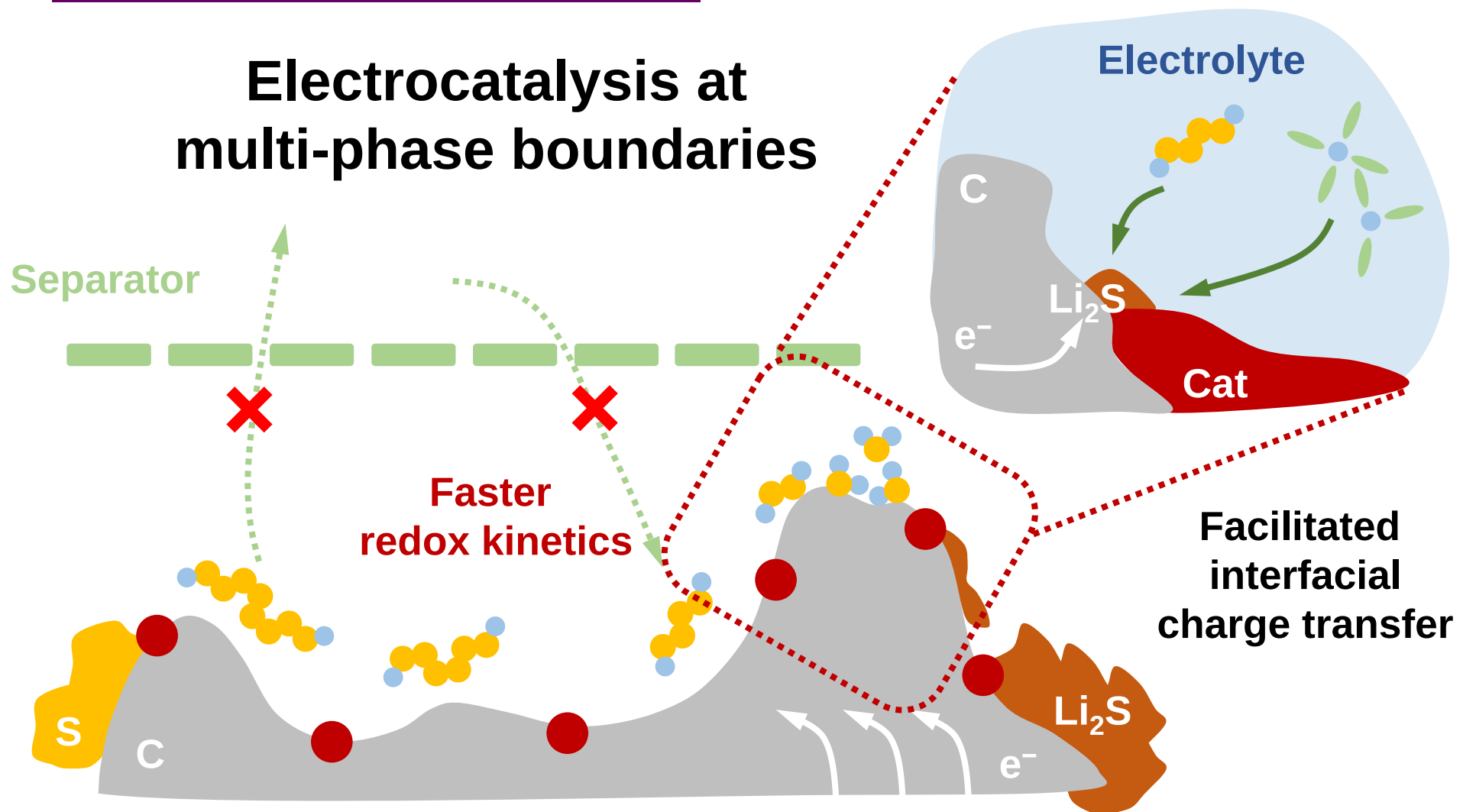


Cathode kinetic regulation at multi-phase boundaries

- High conductivity
- Fast mass transfer
- Reduced interfacial resistant
- Reduced activation energy
- Fast redox reactions
- High reversibility

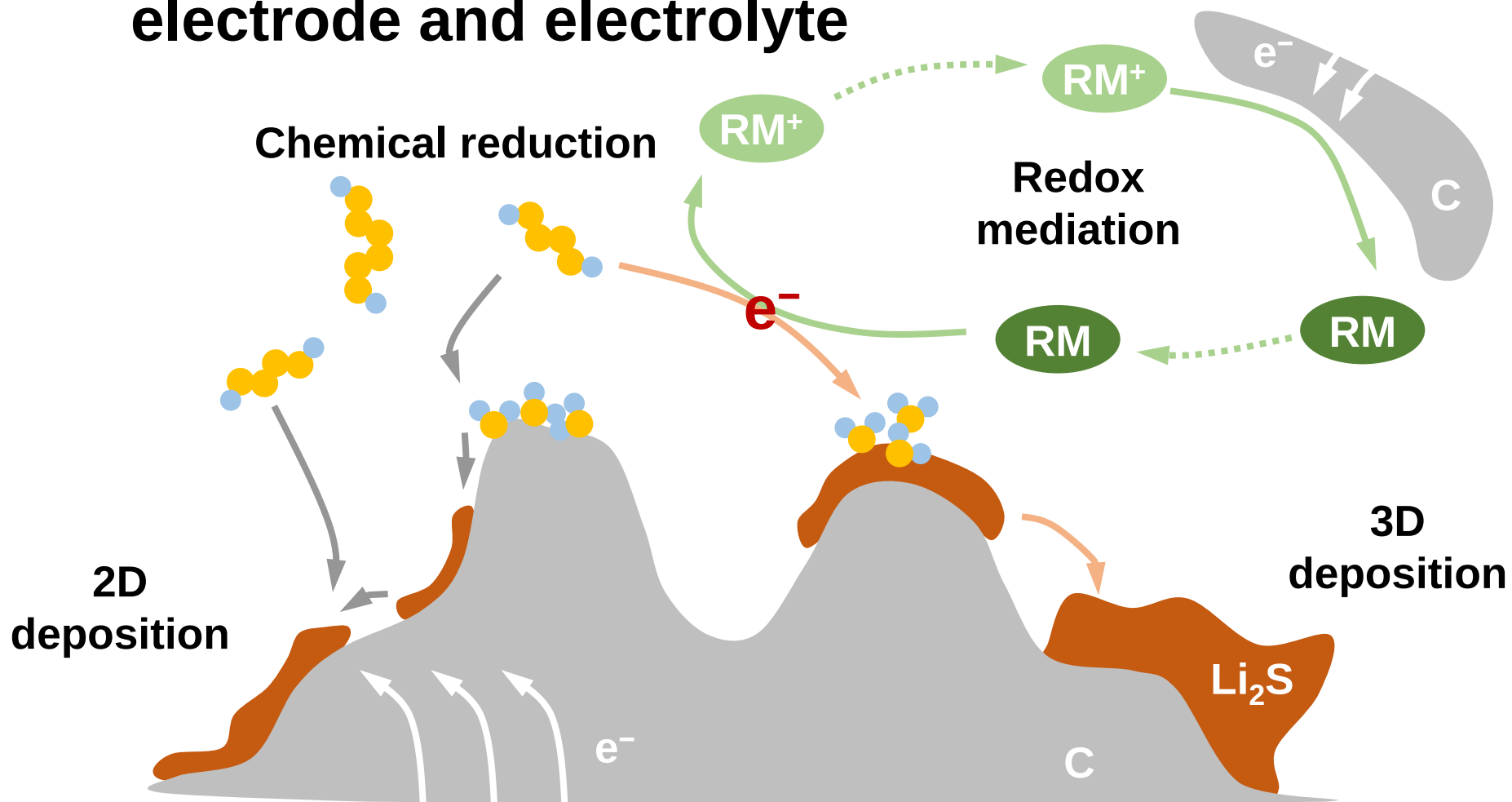
Cathode kinetic regulation

Electrocatalysis at multi-phase boundaries



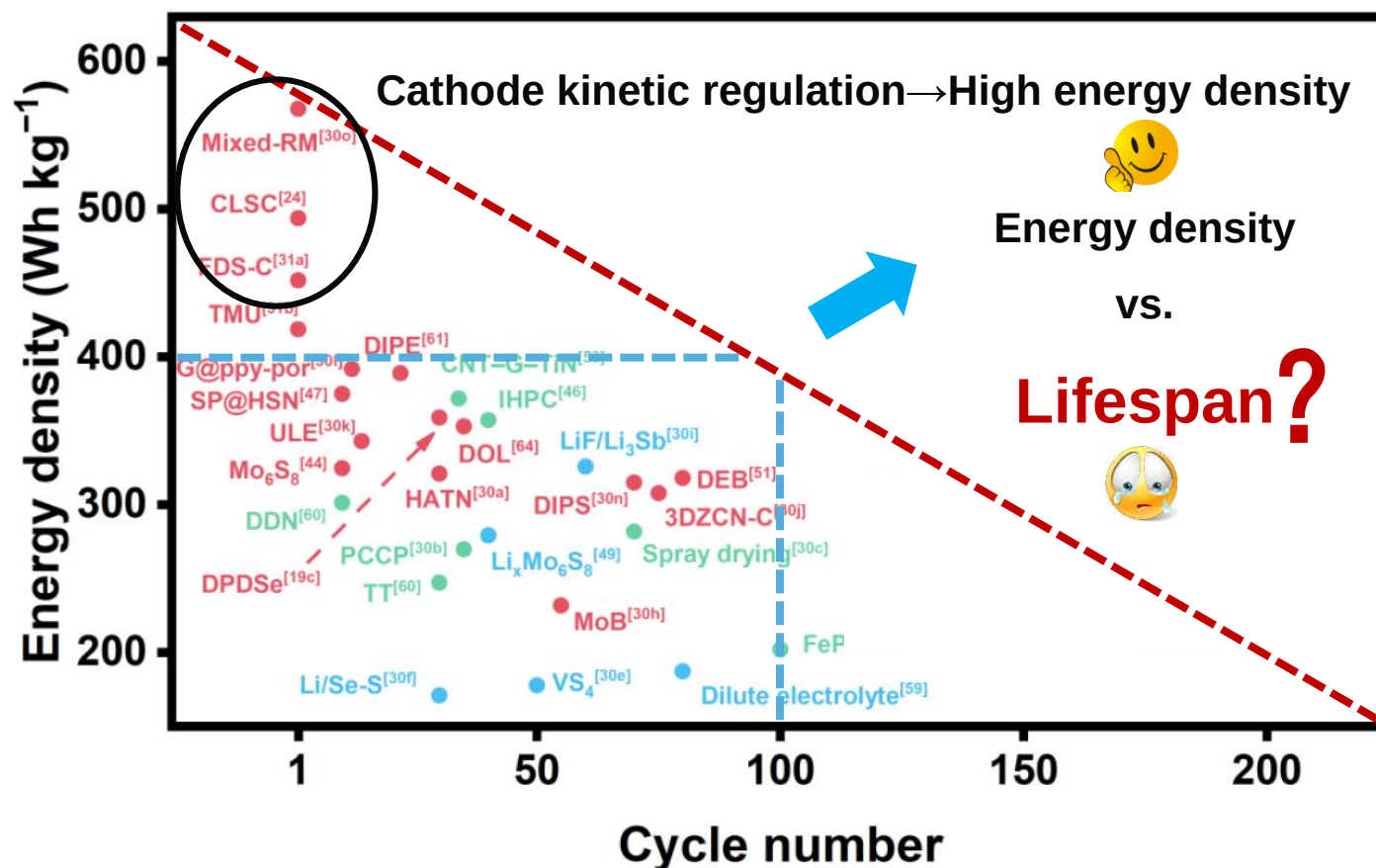
Cathode kinetic regulation

Redox mediation between electrode and electrolyte



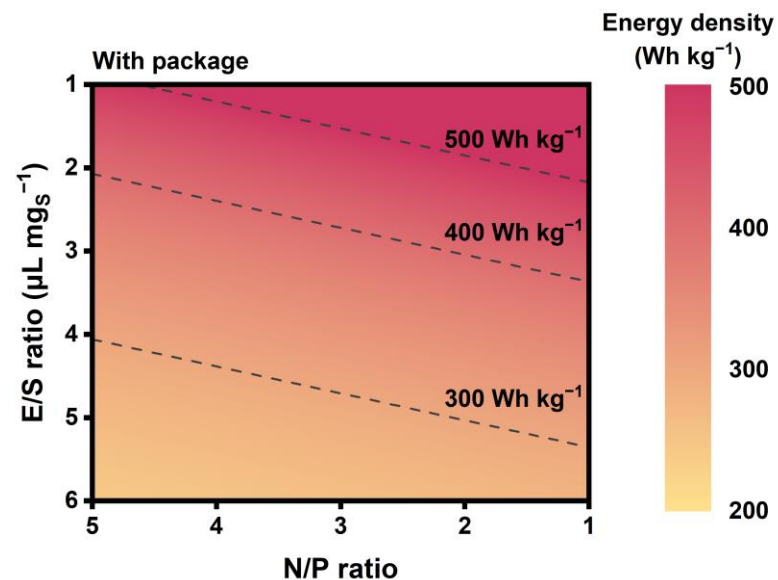
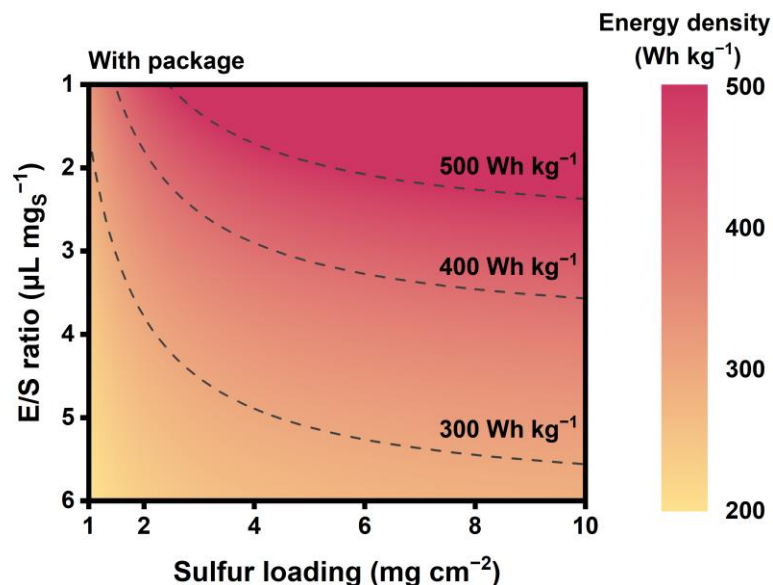
Challenges of practical high-energy-density batteries

Long lifespan is the prerequisite for practical Li-S batteries.



Challenges of practical high-energy-density batteries

Key parameters to design high-energy-density Li–S batteries



- High sulfur loading: $> 5 \text{ mg cm}^{-2}$
- Low E/S ratio: $< 3 \mu\text{L mg}_S^{-1}$
- Limited Li excess: N/P ratio < 2

Energy density: $> 400 \text{ Wh kg}^{-1}$

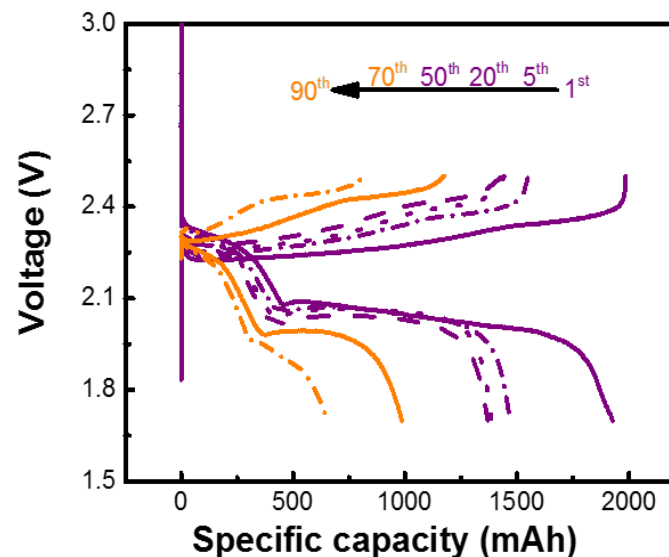
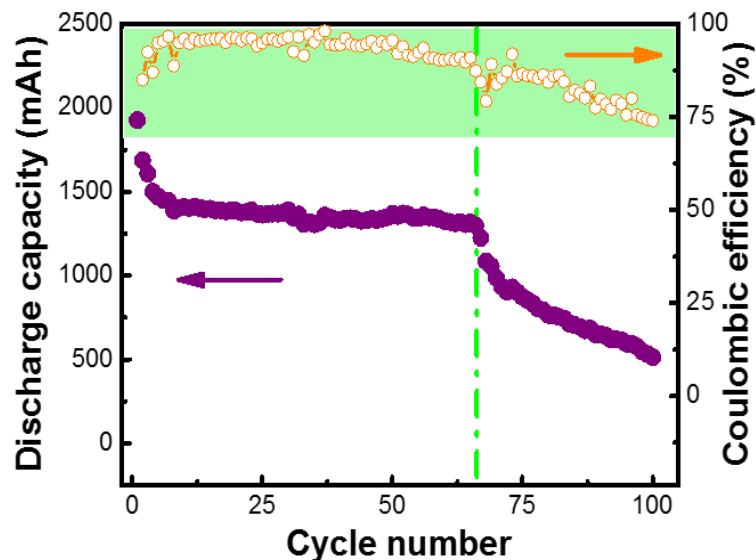
What is the failure mechanism?

Analysis on pouch cells is necessary.

Failure analysis of Li-S pouch cells

300 Wh kg⁻¹

Cycling performance of a 300 Wh kg⁻¹ Li-S pouch cell

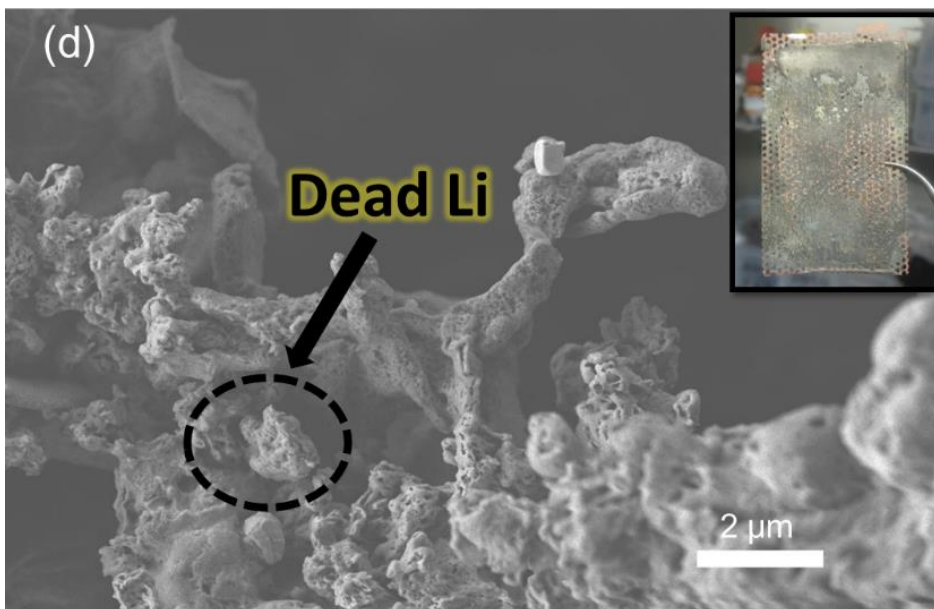
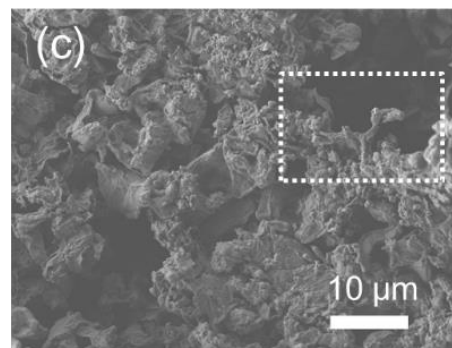
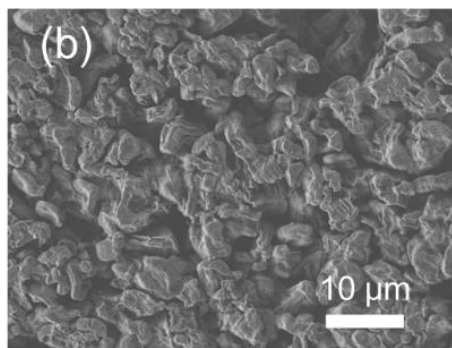
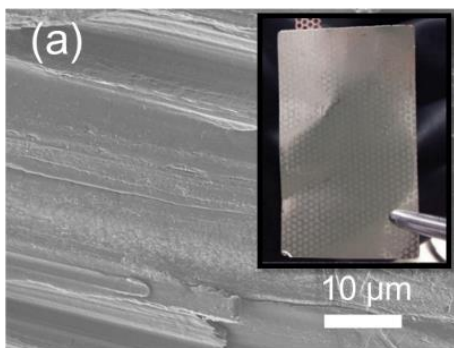


- Rapid capacity decay with reduced Coulombic efficiency
- Diminished second discharge plateau with growing polarization

Failure analysis of Li-S pouch cells

300 Wh kg⁻¹

Massive Li dendrite and dead Li are found on cycled anode.

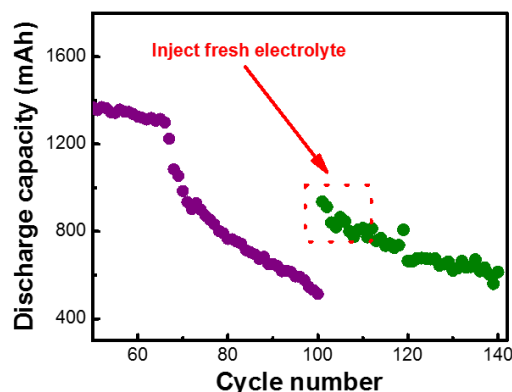


Failure analysis of Li-S pouch cells

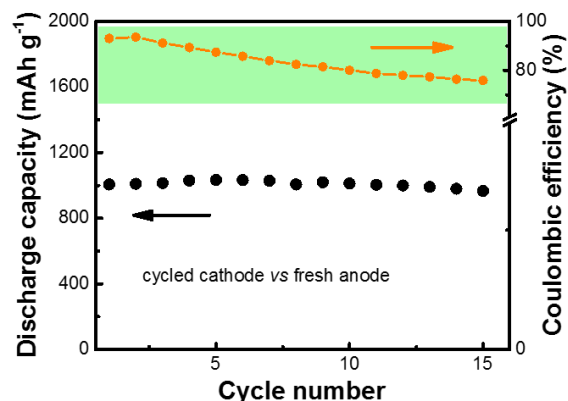
300 Wh kg⁻¹

The reaction between Li metal anode and electrolyte is the main reason for the failure of Li-S pouch cells.

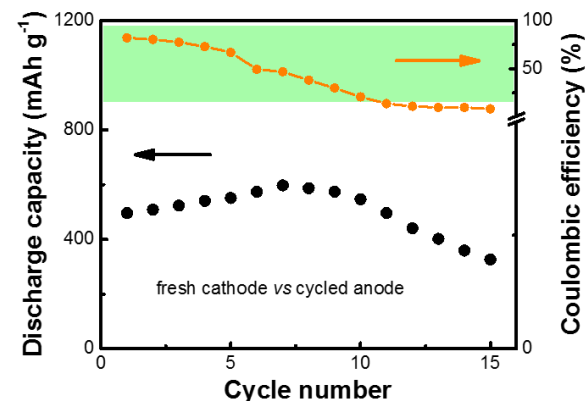
Depletion of electrolyte



No failure of cycled cathode



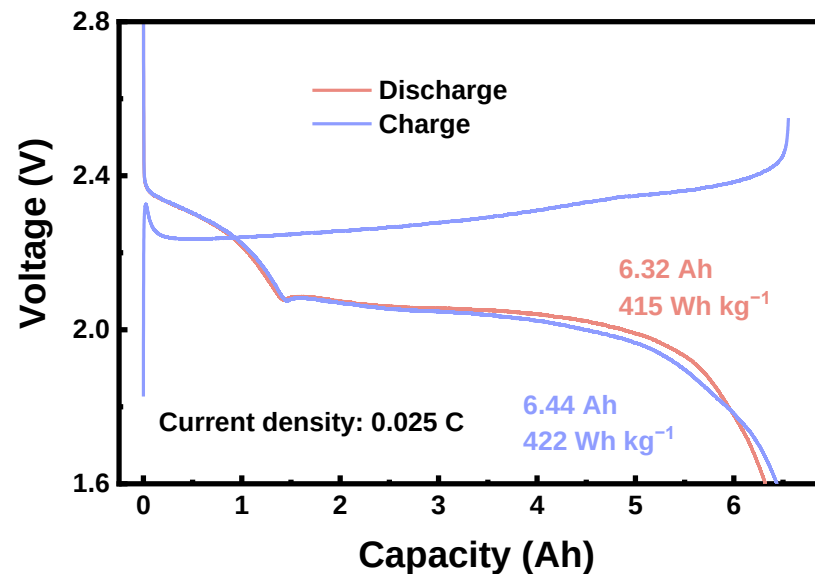
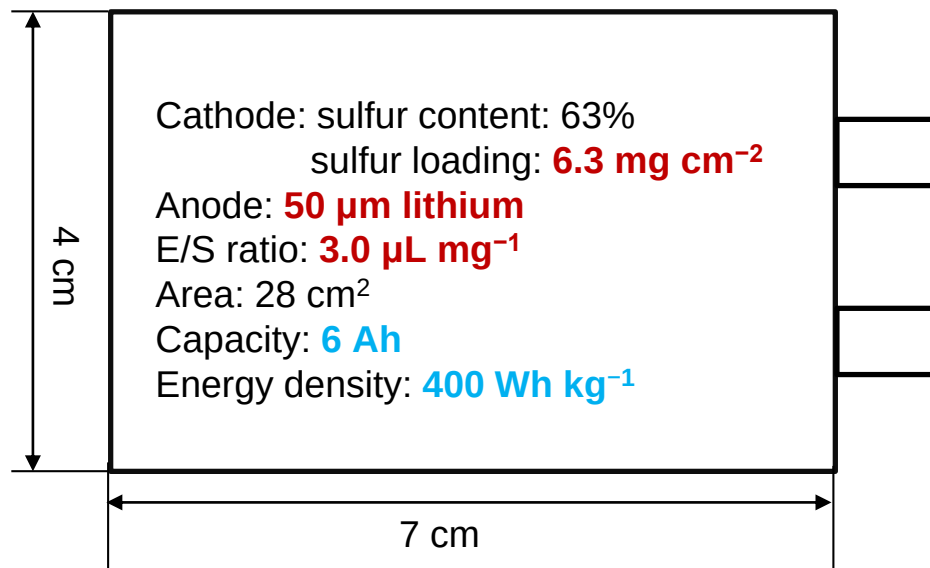
Failure of cycled anode



Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Constructing 400 Wh kg⁻¹ Li-S pouch cells under high sulfur loading, low E/S ratio, and ultrathin Li anode

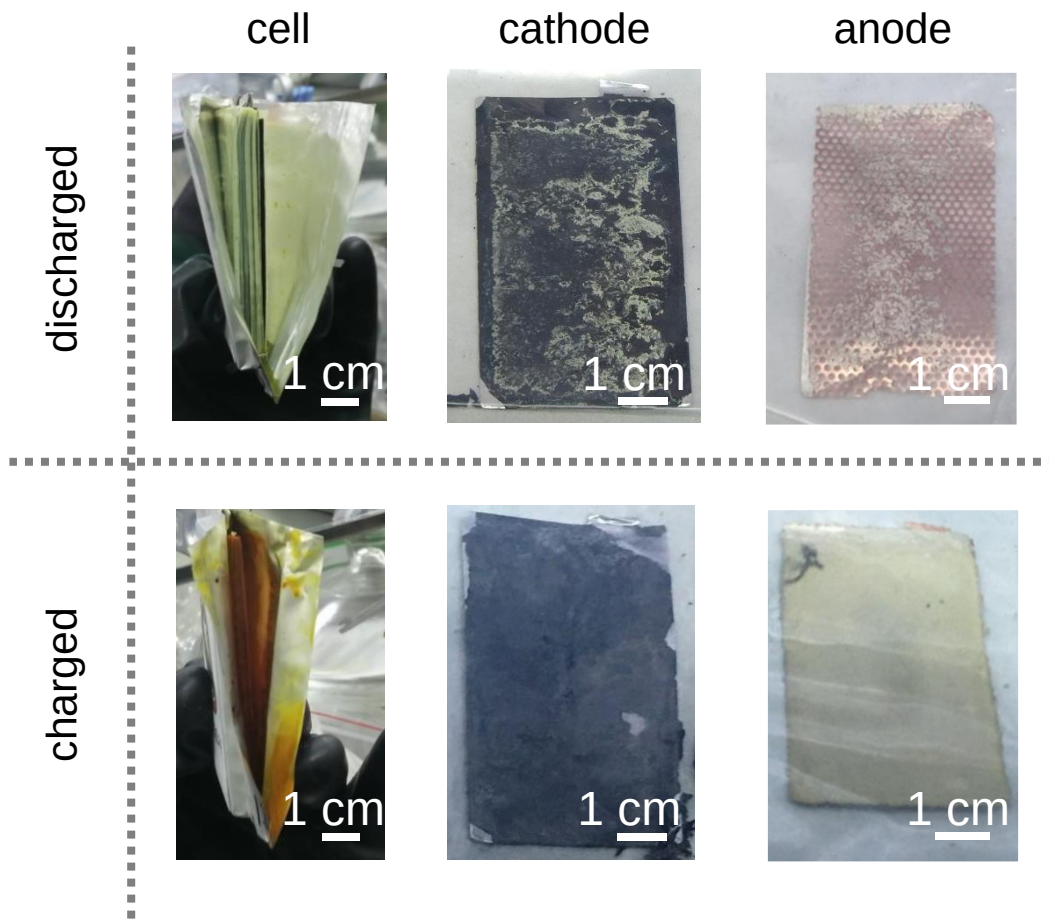


- Actual capacity: 6.44 Ah
- Actual energy density: 422 Wh kg⁻¹

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Morphology evaluation of electrodes after the 1st cycle



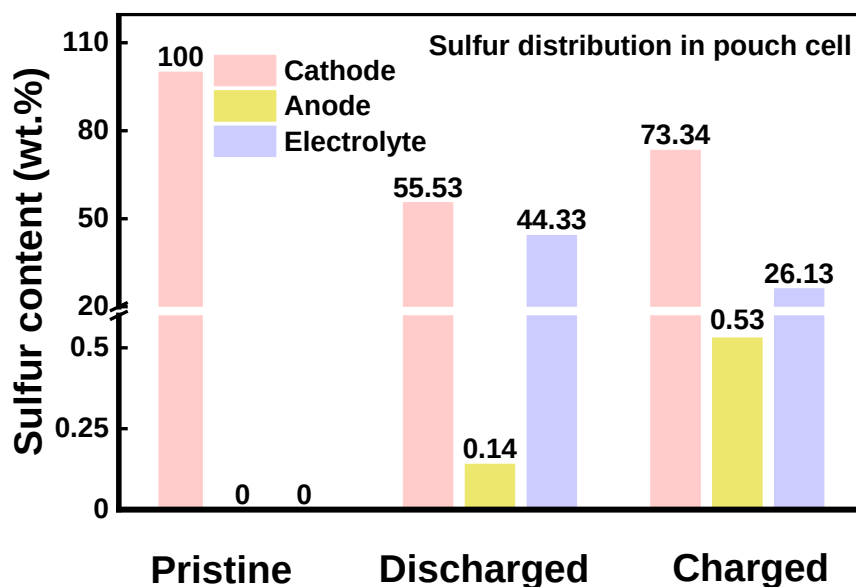
- Limited electrolyte after only 1 cycle
- Barely no left Li metal after 1st discharge
- No obvious change on cathode

Failure analysis of Li-S pouch cells

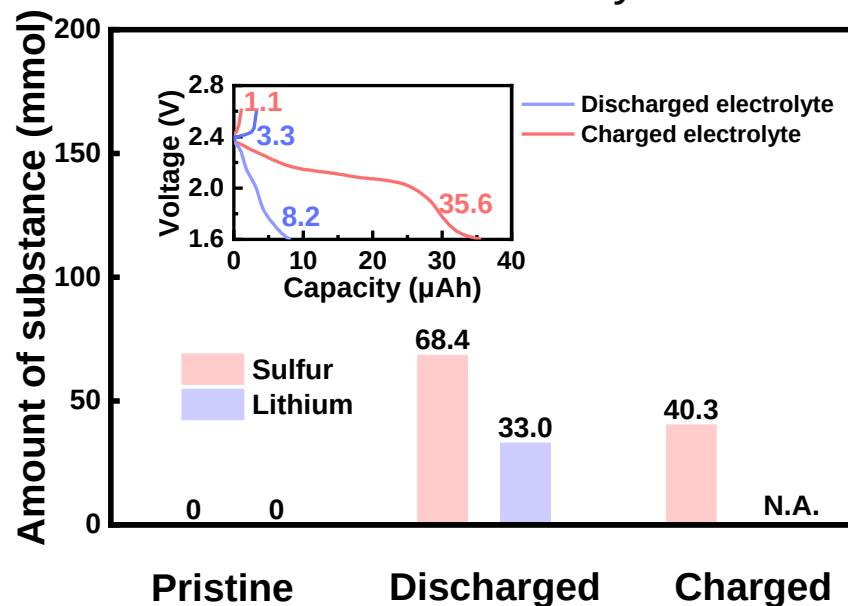
400 Wh kg⁻¹

Spatial and species analysis of sulfur

Spatial analysis



Sulfur in electrolyte

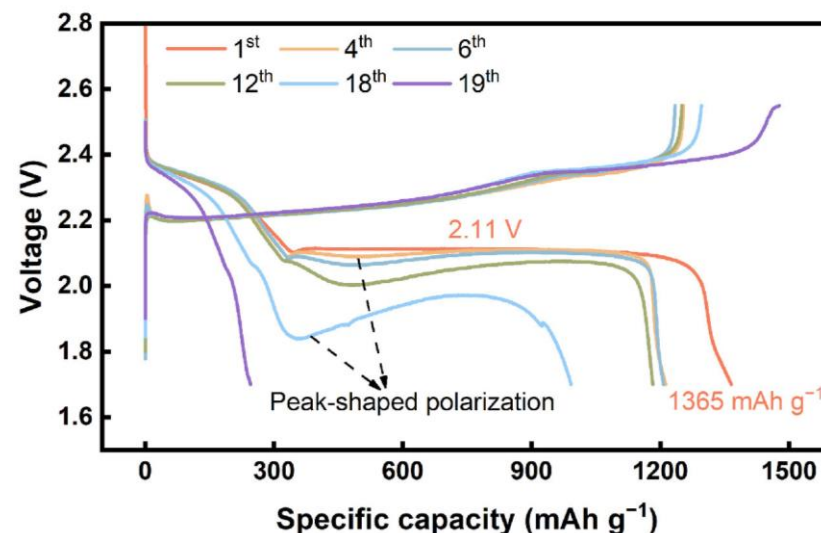
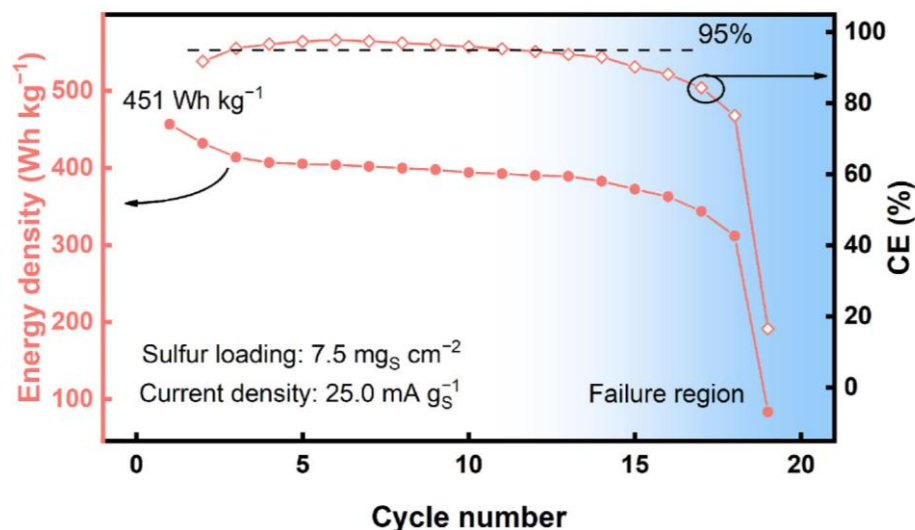


- Sulfur exists in cathode and electrolyte while limited amount on Li metal anode.
- Li₂S₄ and Li₂S₈ dominant in discharged and charged electrolyte, respectively

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Cycling performance of a 400 Wh kg⁻¹ Li-S pouch cell

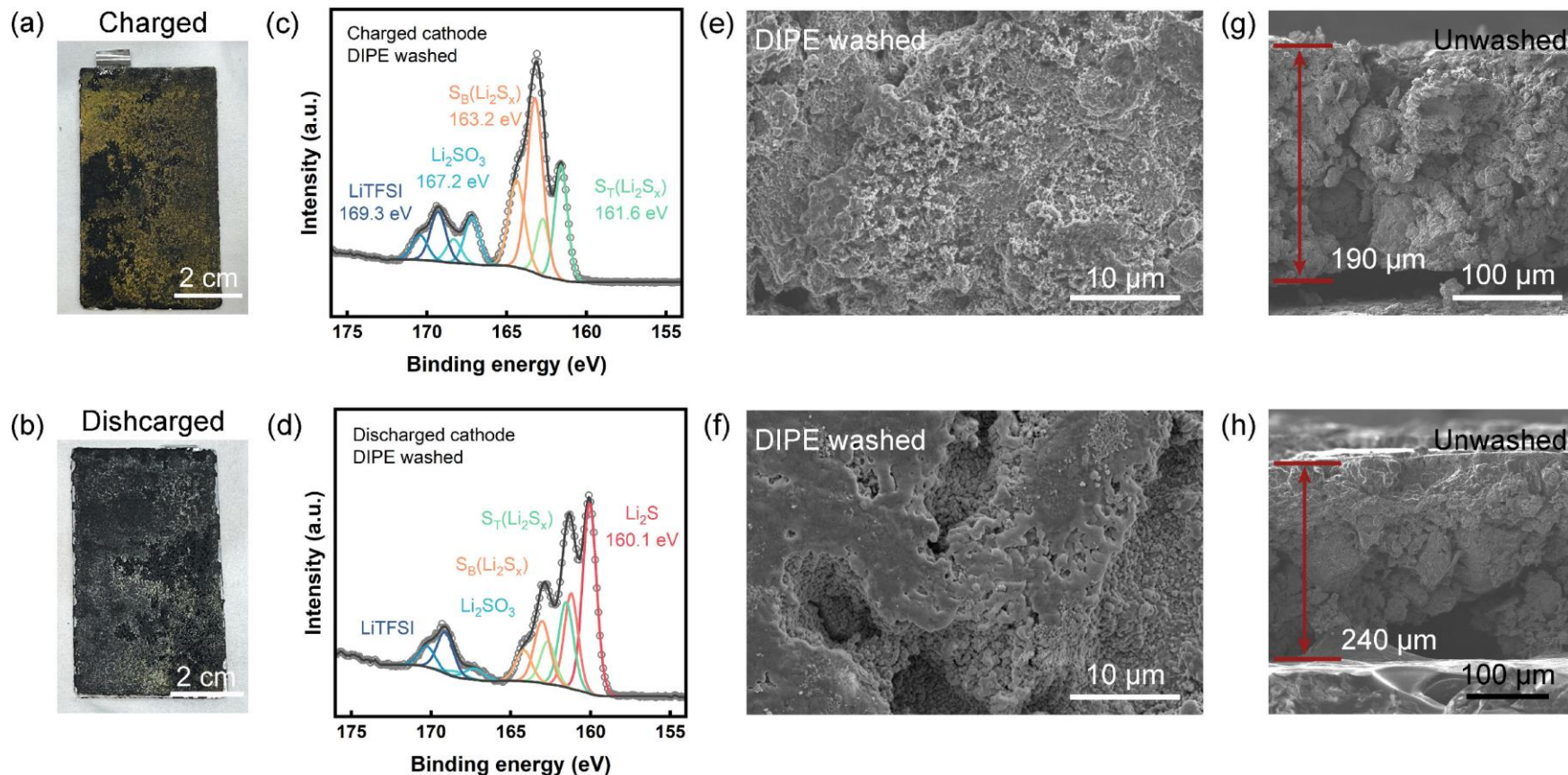


- Rapid capacity decay with reduced Coulombic efficiency
- Increased peak-shaped polarization at the second discharge plateau

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Analysis of cathodes after battery failure

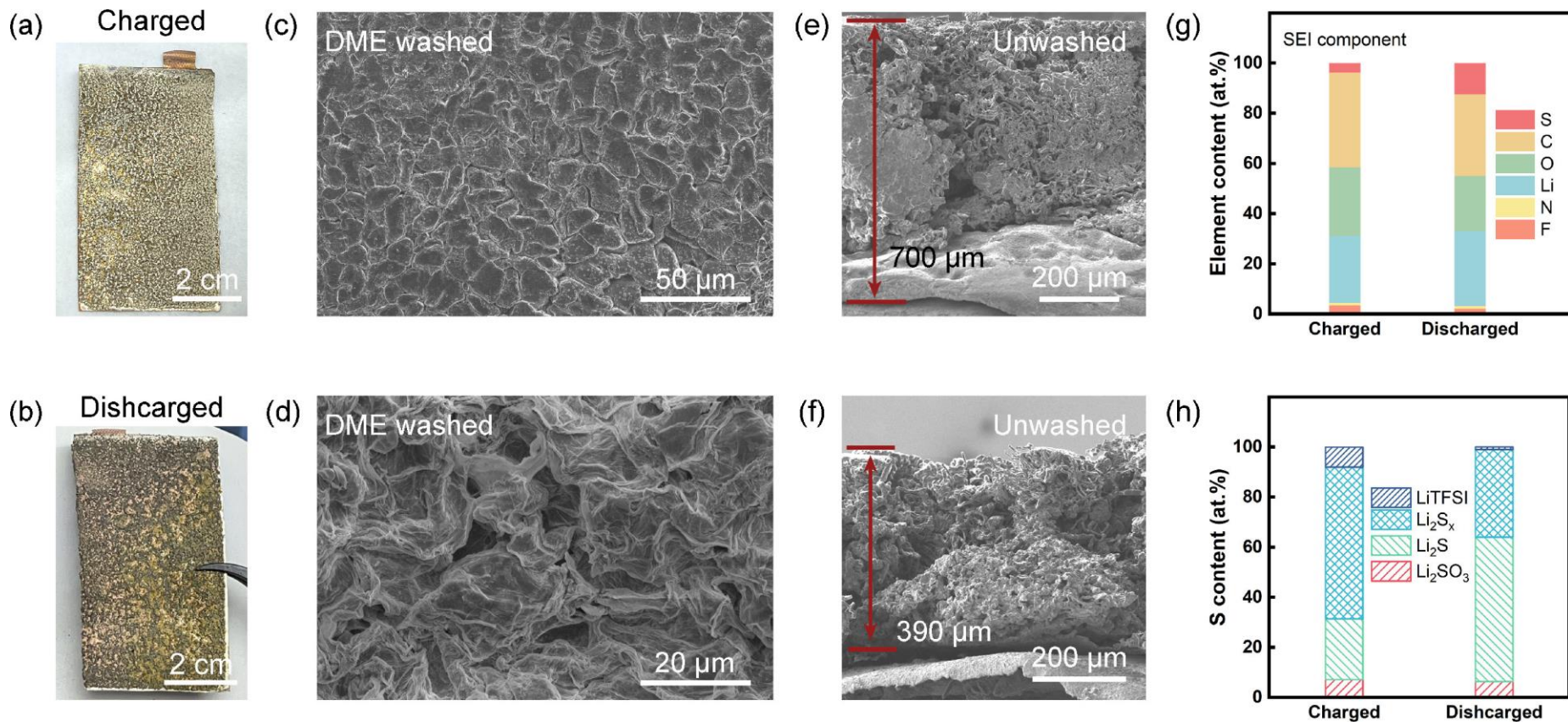


- Conductive surface and cathode structure are well-maintained.

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Analysis of anodes after battery failure

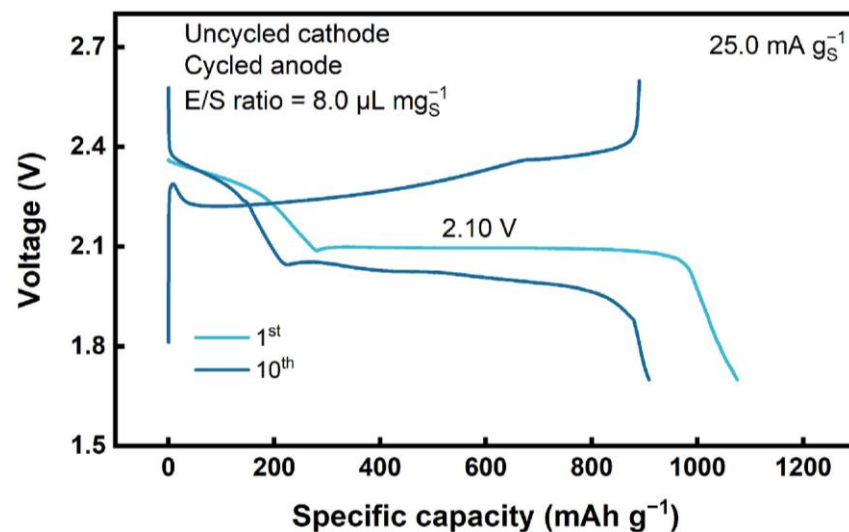
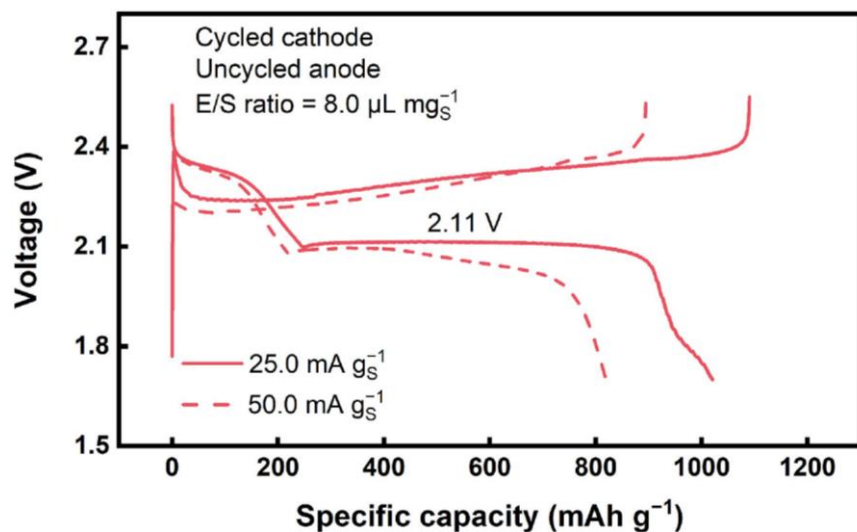


- Cycled anodes suffer huge volume variation.
- SEI is mainly composed of organic species with high C and O contents.

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Capacity analysis of electrodes after battery failure

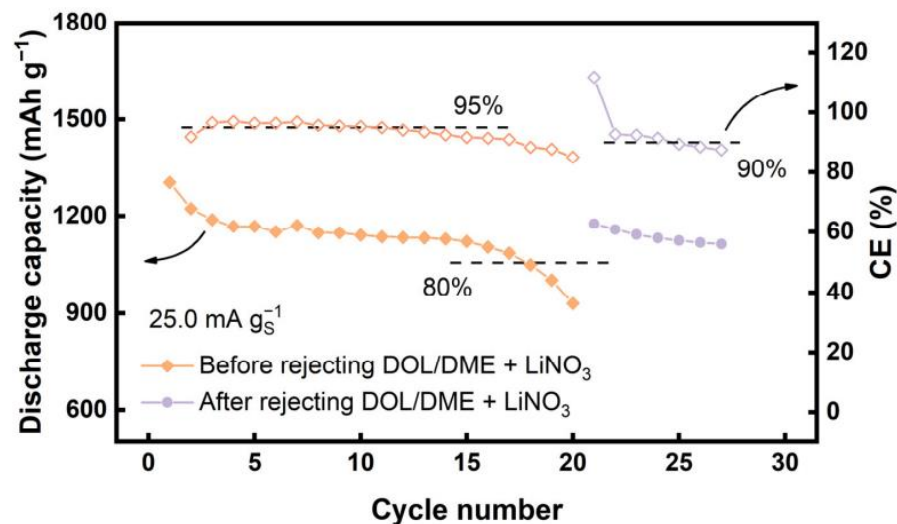
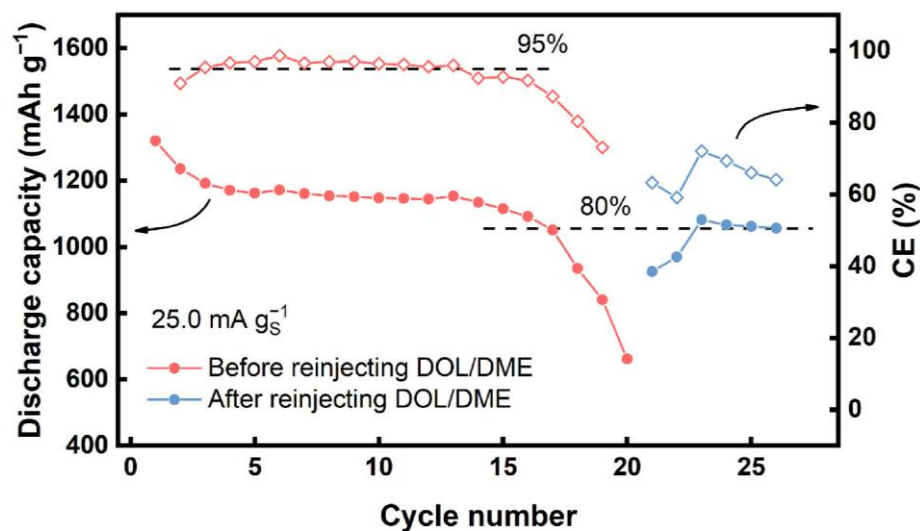


- Capacity of cycled cathodes and anodes is well-maintained.
- What is the failure reason?

Failure analysis of Li-S pouch cells

400 Wh kg⁻¹

Reinjecting electrolyte to recover the cycling of pouch cell

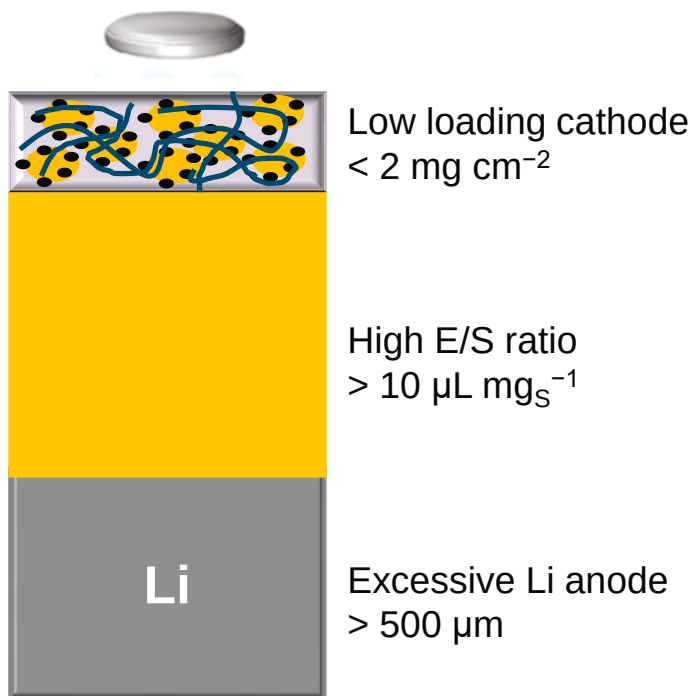


- Discharge capacity recovers after injecting solvent.
- Discharge capacity & CE recover after injecting solvent + LiNO₃.
- Electrolyte exhaustion is identified as the main failure reason.

Challenges of practical high-energy-density batteries

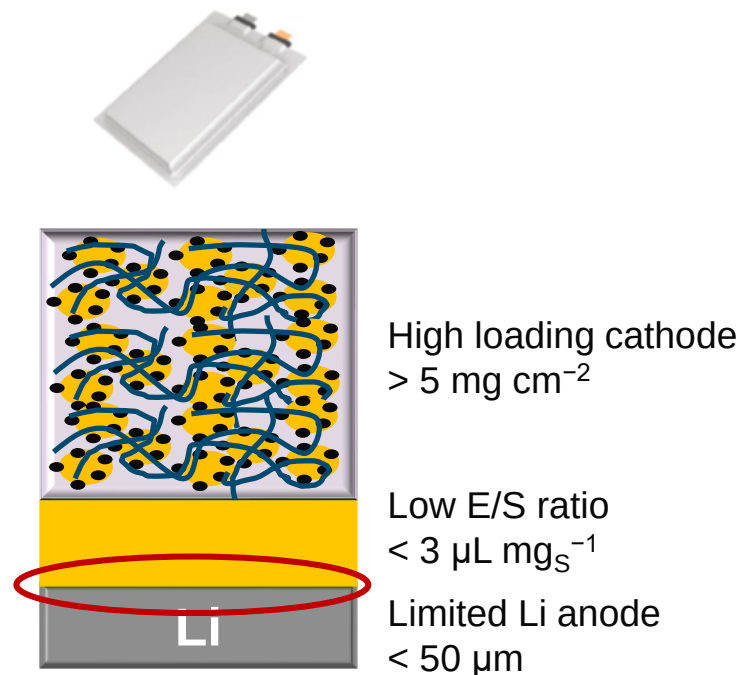
The reaction between Li metal anode and electrolyte hinders the long cycling of practical Li-S batteries.

Coin cell



Utilization ratio of Li $\sim 2\%$

Pouch cell



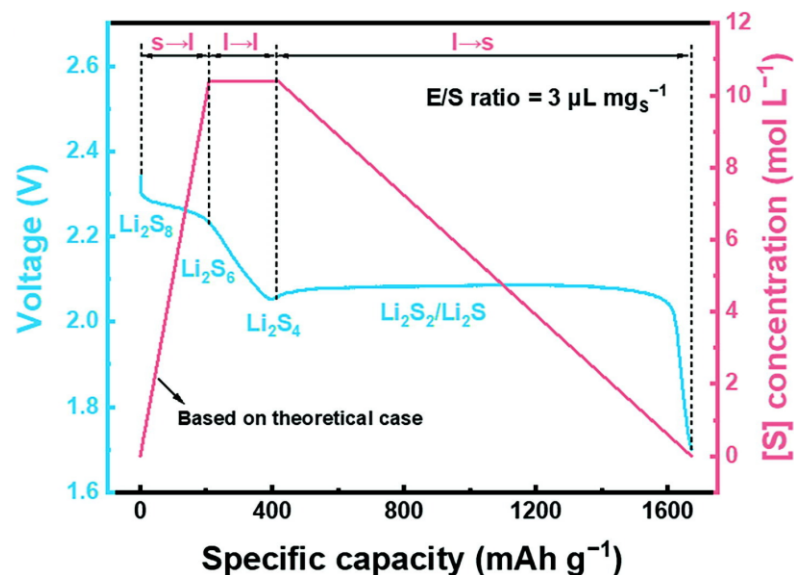
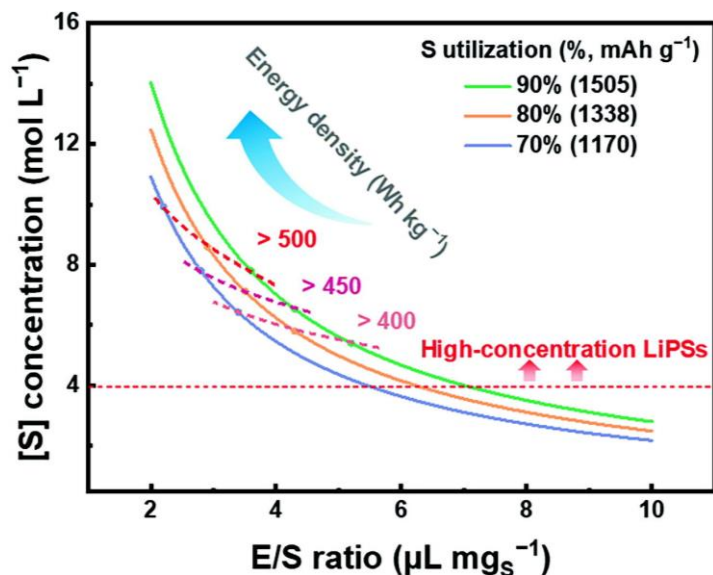
Utilization ratio of Li $\sim 50\%$

Challenges of practical high-energy-density batteries

Lithium polysulfide



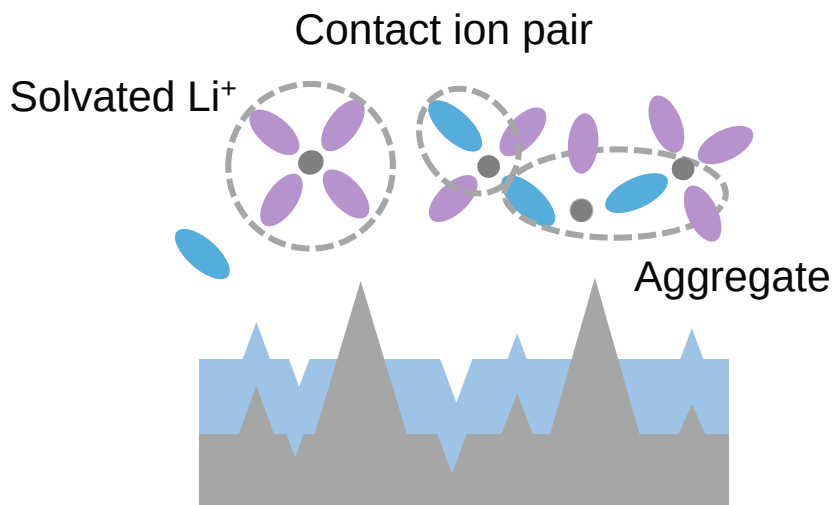
- High concentration ($> 6 \text{ M [S]}$)
- Multiple species ($\text{Li}_2\text{S}_{4-8}$)
- Dynamic change (0–10 M)



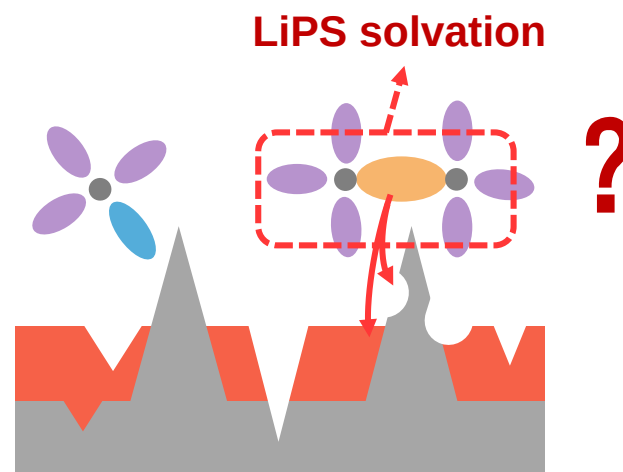
Polysulfide chemistry: Solvation structure of polysulfide

The solvation structure of LiPS is the key for electrolyte engineering and SEI regulation.

Other Li metal batteries



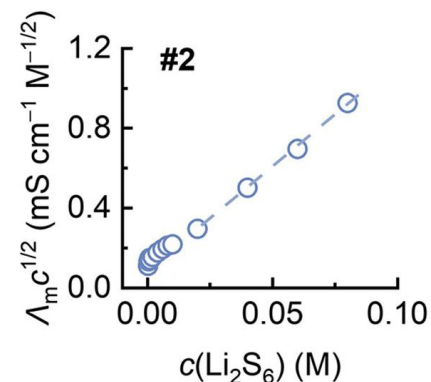
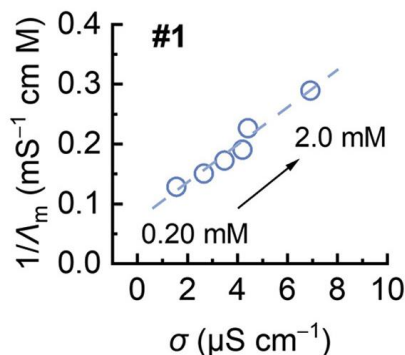
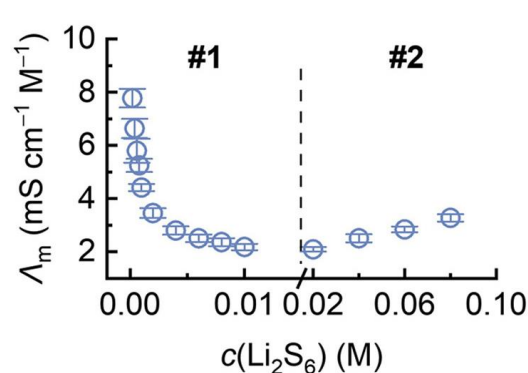
Li-S batteries



● Li⁺ ● Anion ● Solvent ● PS ■ SEI ■ Li metal anode

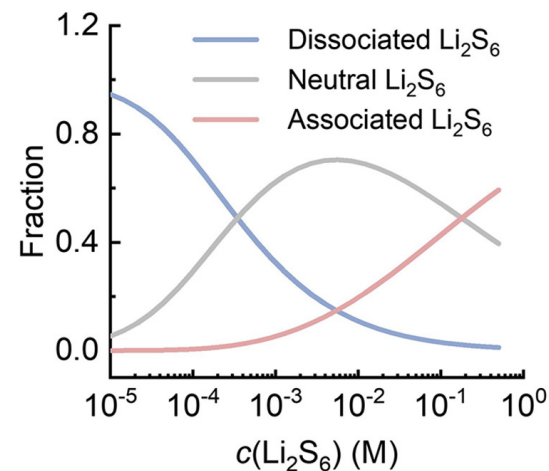
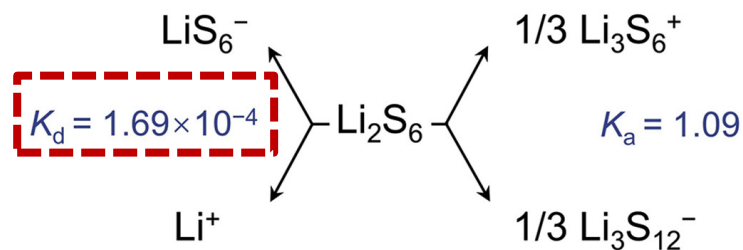
Polysulfide chemistry: Solvation structure of polysulfide

LiPS: Weakly dissociated & Cationic



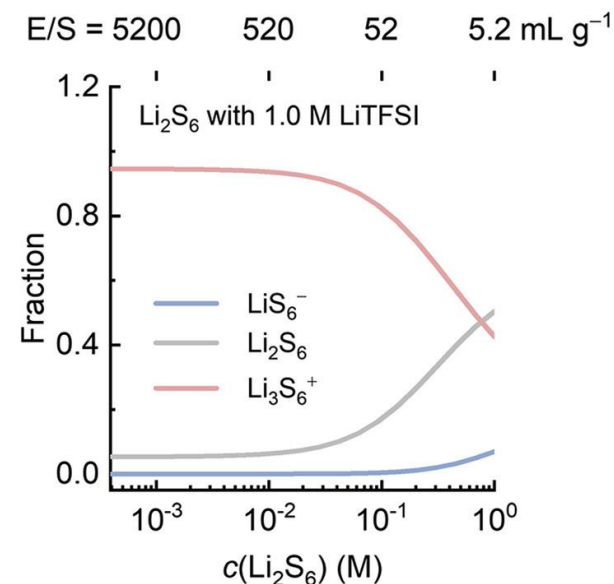
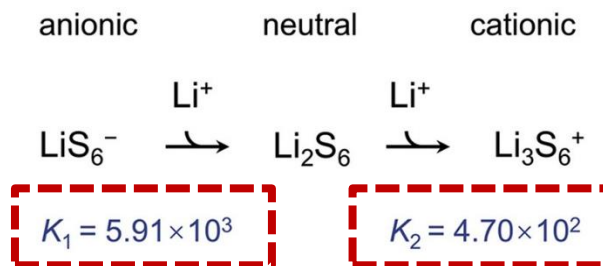
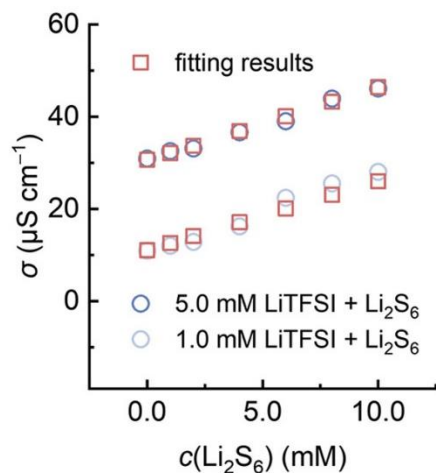
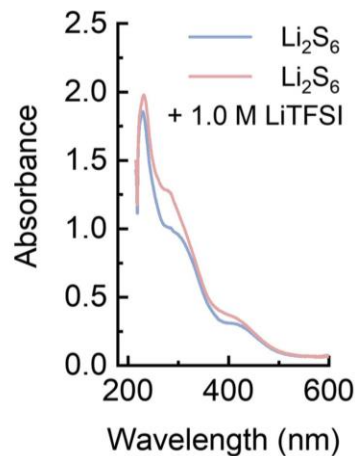
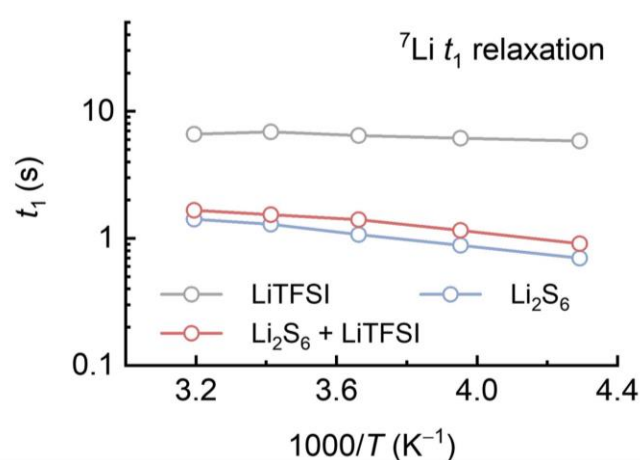
#1 Dissociation

#2 Triple ion association



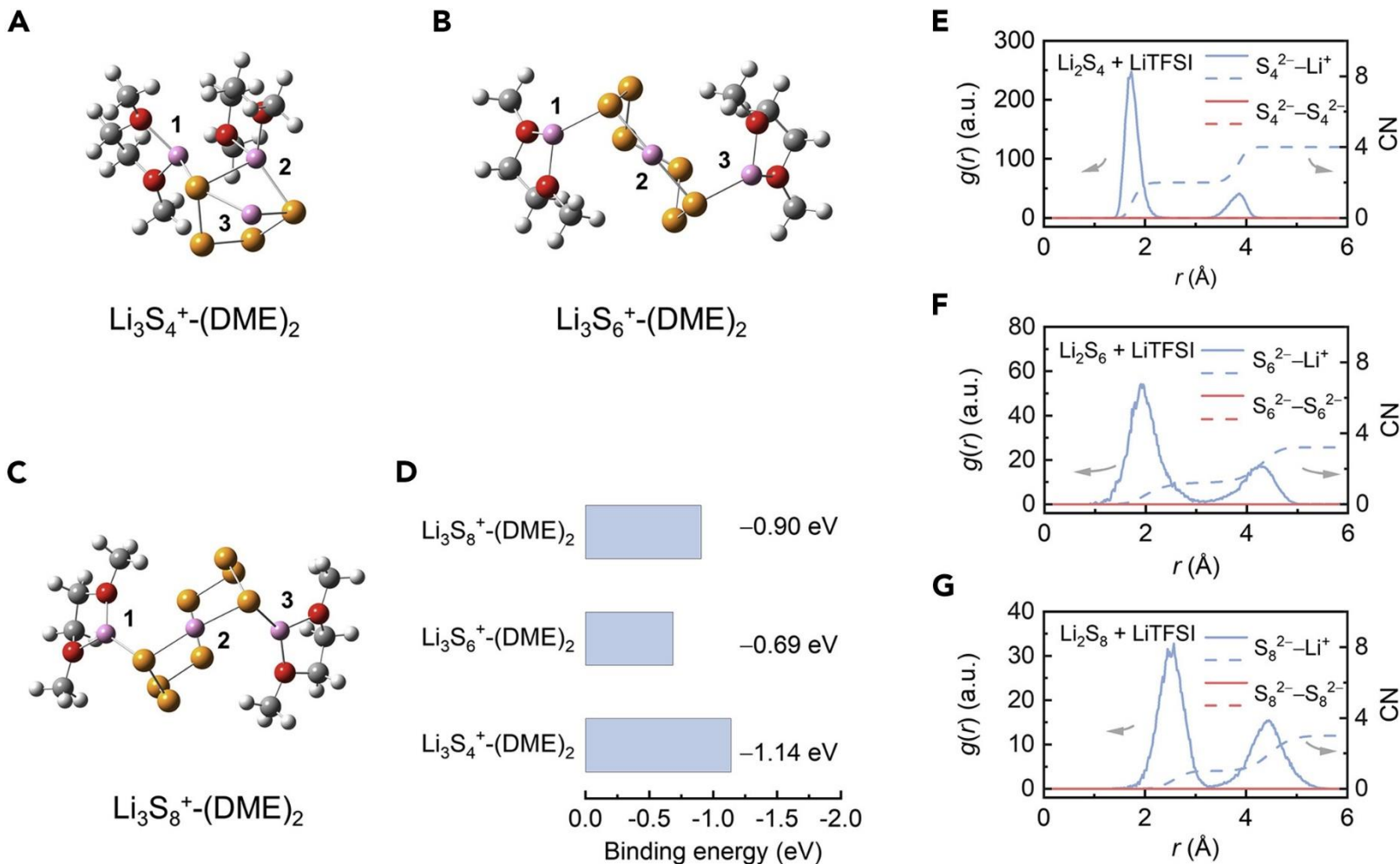
Polysulfide chemistry: Solvation structure of polysulfide

LiPS + Li salt: Neutral $\uparrow$ & Cationic $\uparrow$



Polysulfide chemistry: Solvation structure of polysulfide

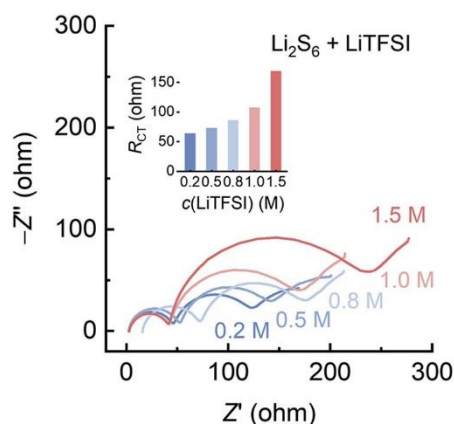
Cationic Li_3S_x^+ is thermodynamically favorable.



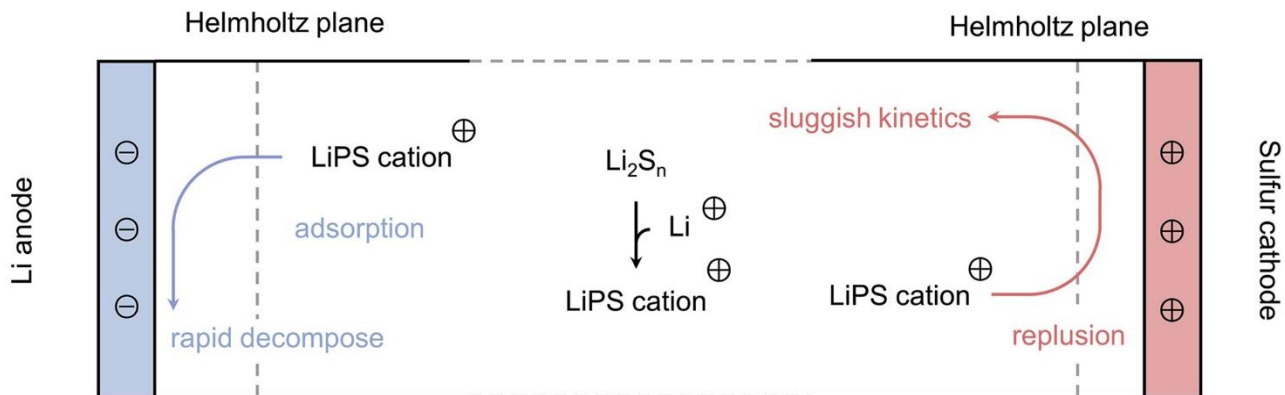
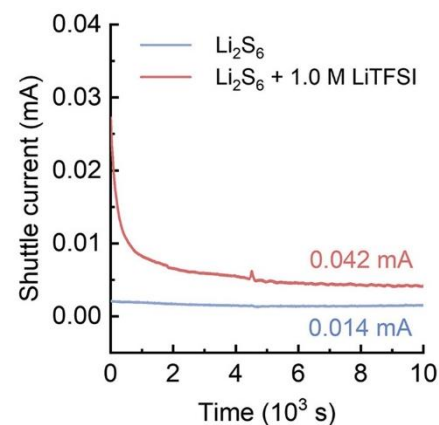
Polysulfide chemistry: Solvation structure of polysulfide

Cationic Li_3S_x^+ intensifies Li anode corrosion.

Decreased cathode kinetics



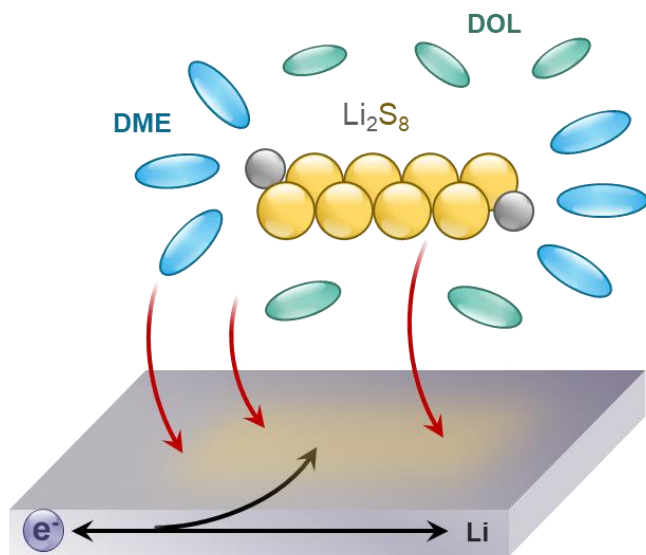
Enhanced Li corrosion



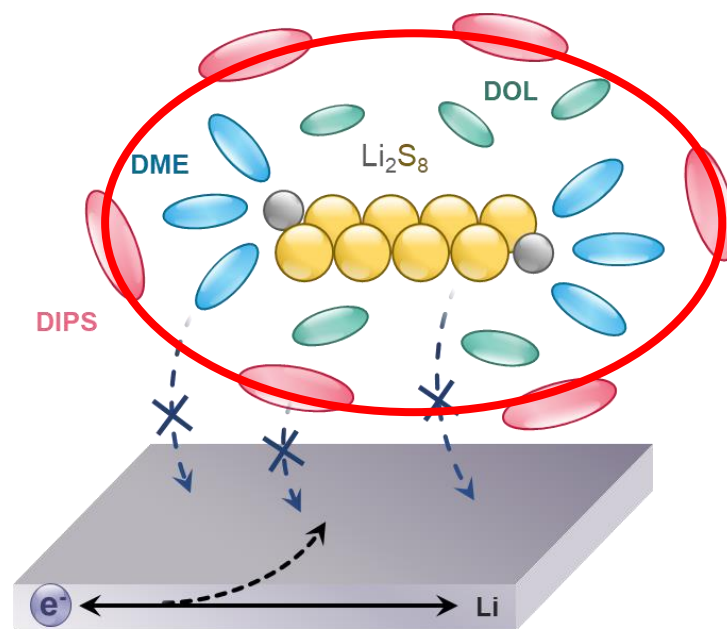
Anode protection: Encapsulating polysulfide electrolyte

Encapsulating polysulfide electrolyte (EPSE) to protect Li metal anode from LiPS corrosion

DOL/DME electrolyte



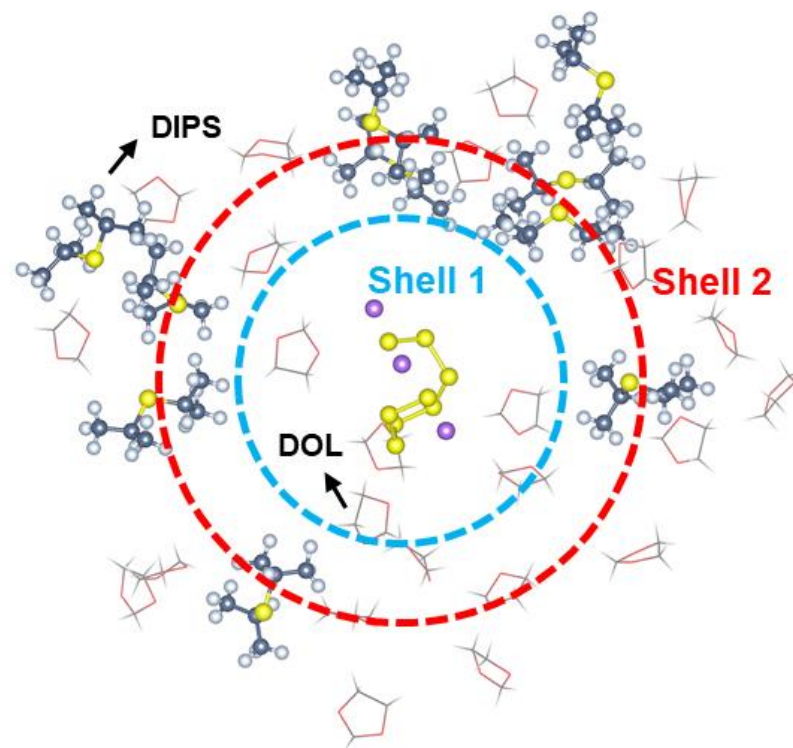
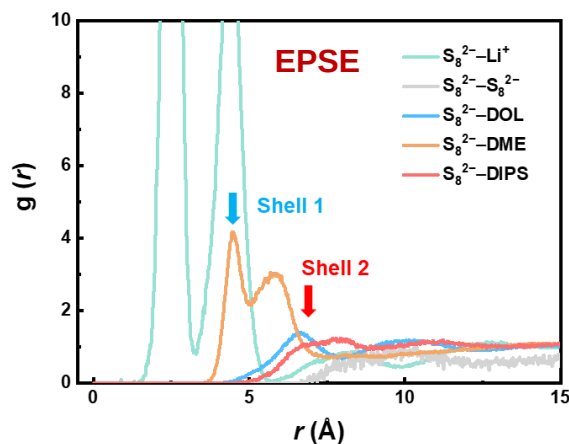
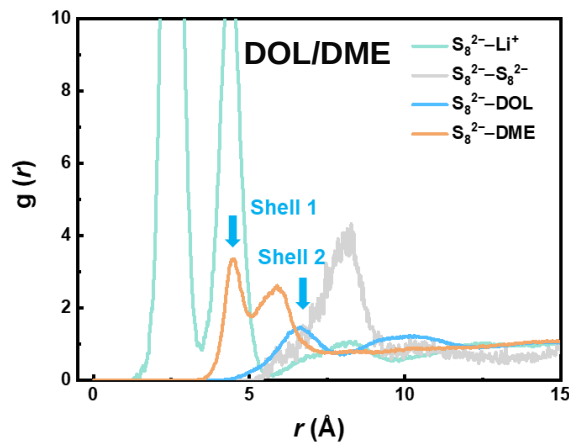
EPSE



- High reduction stability
- Weak solvation ability

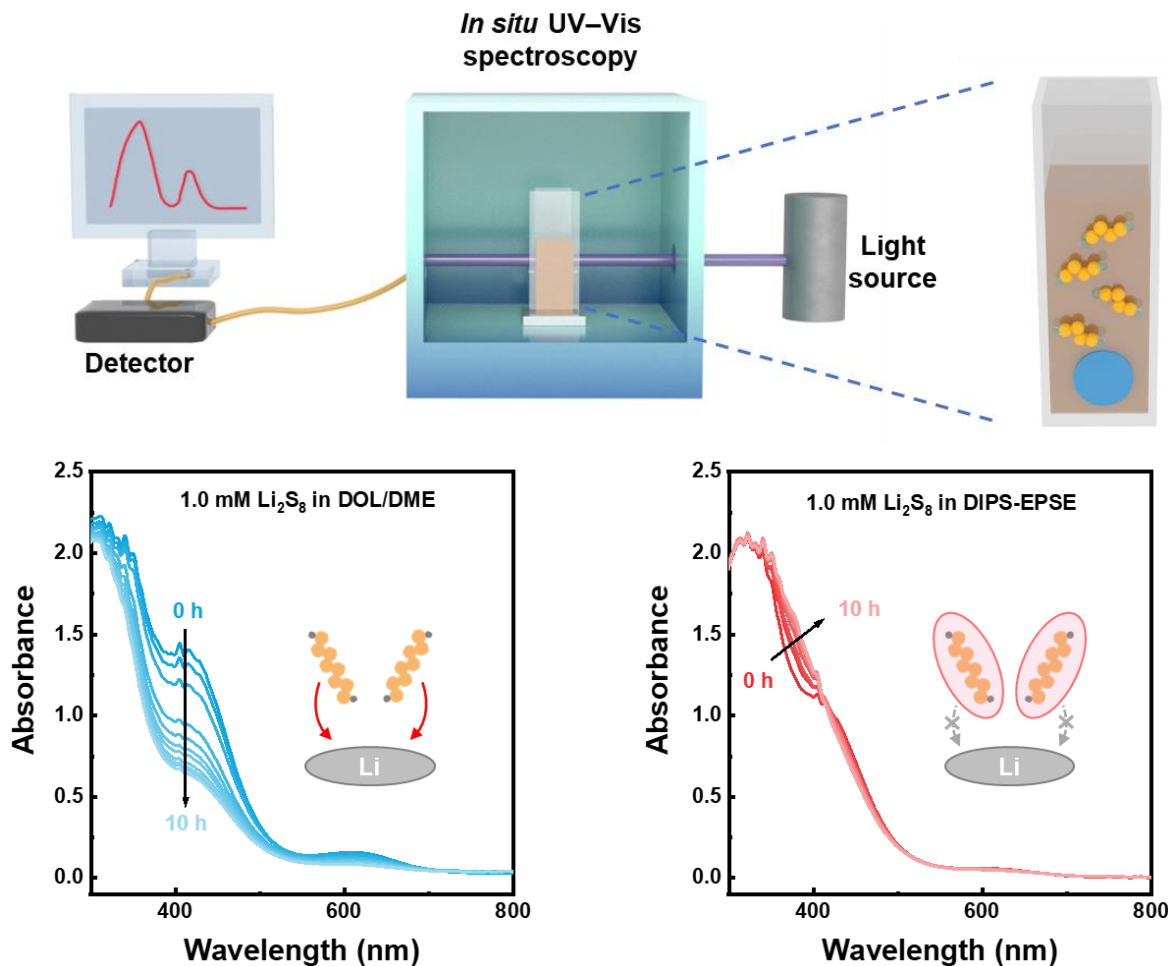
Anode protection: Encapsulating polysulfide electrolyte

Double-shell solvation structure of LiPS: DIPS in the outer shell to reduce the reactivity of LiPS



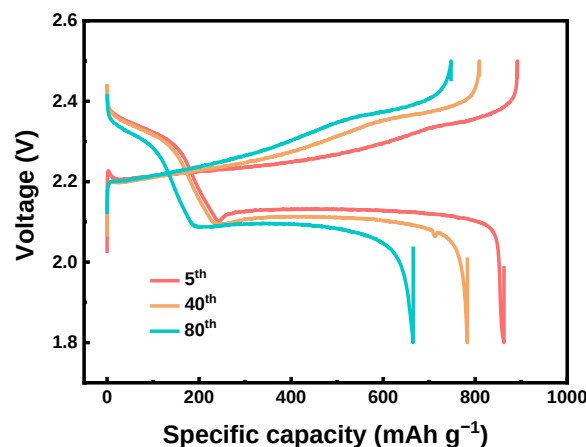
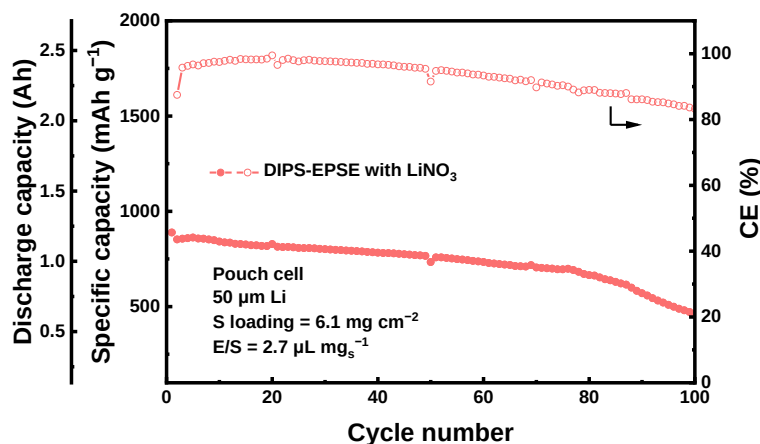
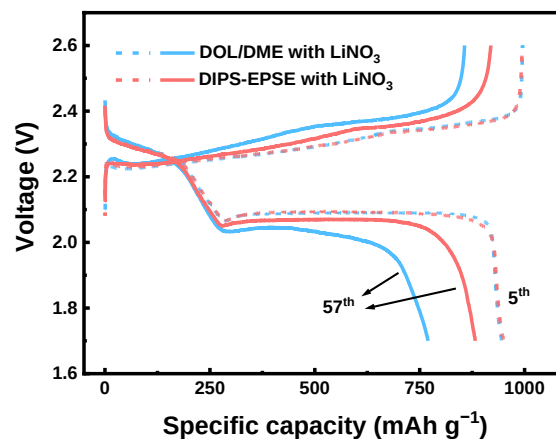
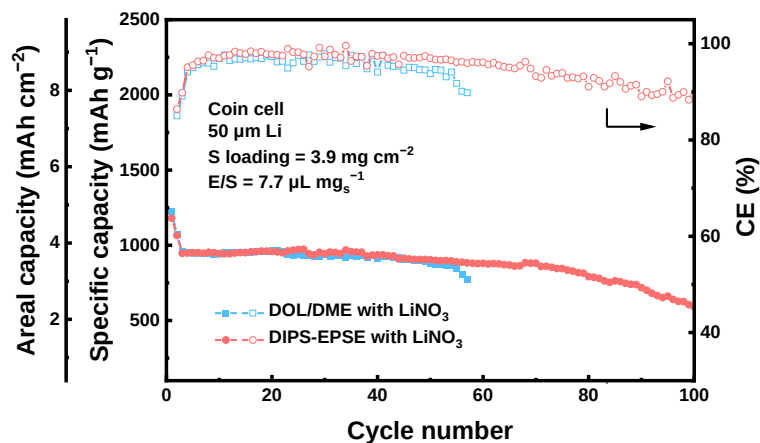
Anode protection: Encapsulating polysulfide electrolyte

EPSE relieves the corrosion of Li metal by LiPS.



Anode protection: Encapsulating polysulfide electrolyte

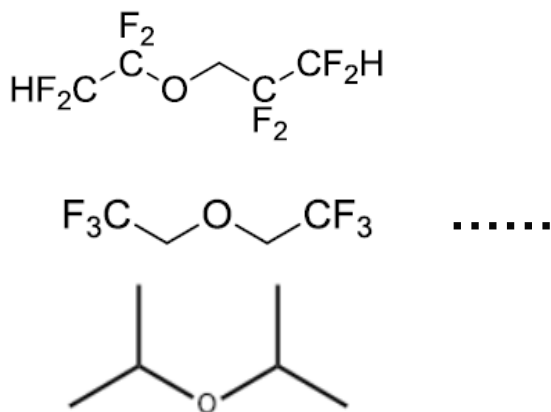
EPSE prolongs cycling stability in coin and pouch cells.



Anode protection: Encapsulating polysulfide electrolyte

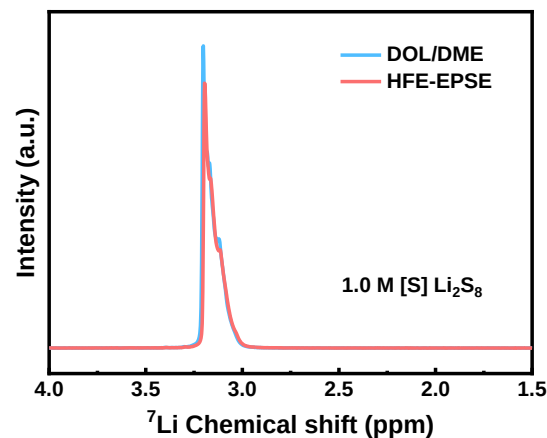
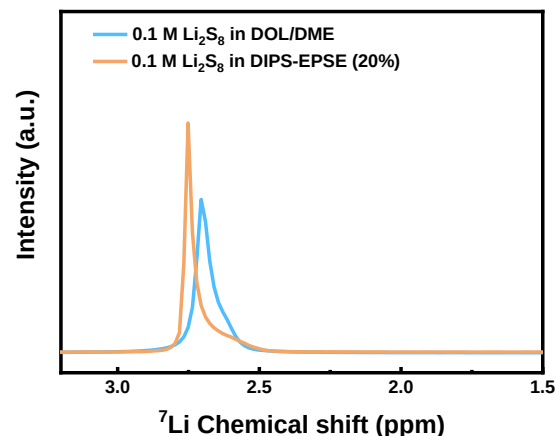
The general design of EPSE

Regulation of outer solvent shell



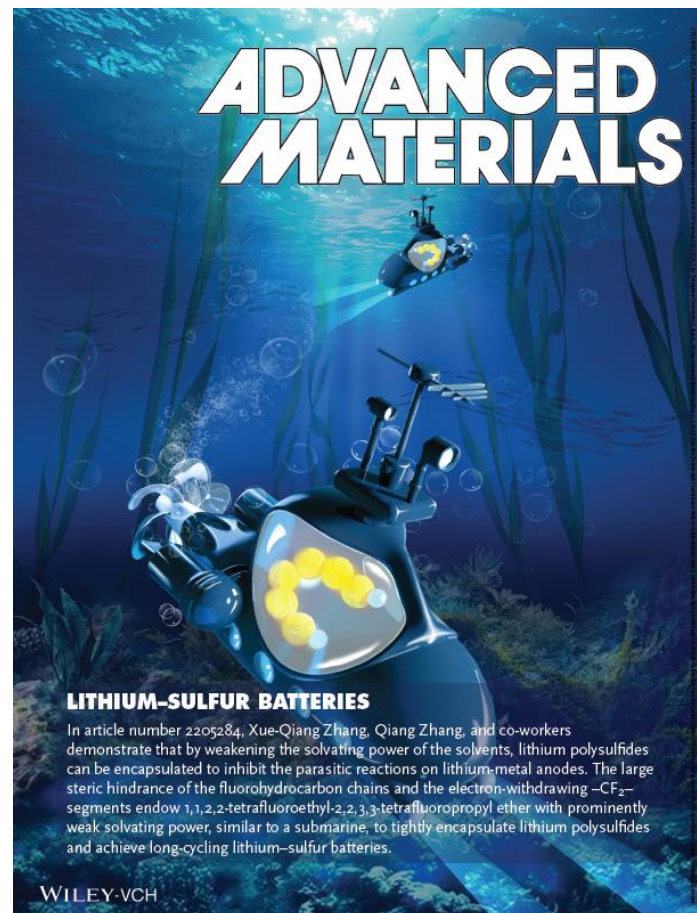
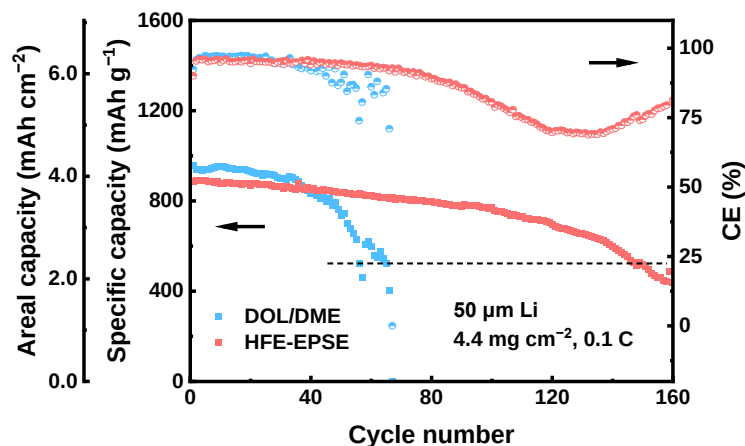
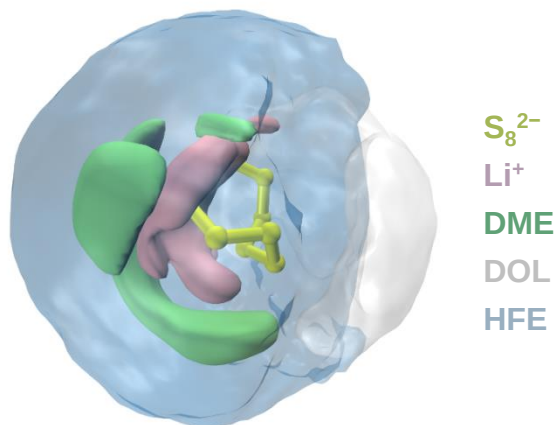
- High reduction stability
- Weak solvation ability HFE < DIPS

Weaking solvation ability



Anode protection: Encapsulating polysulfide electrolyte

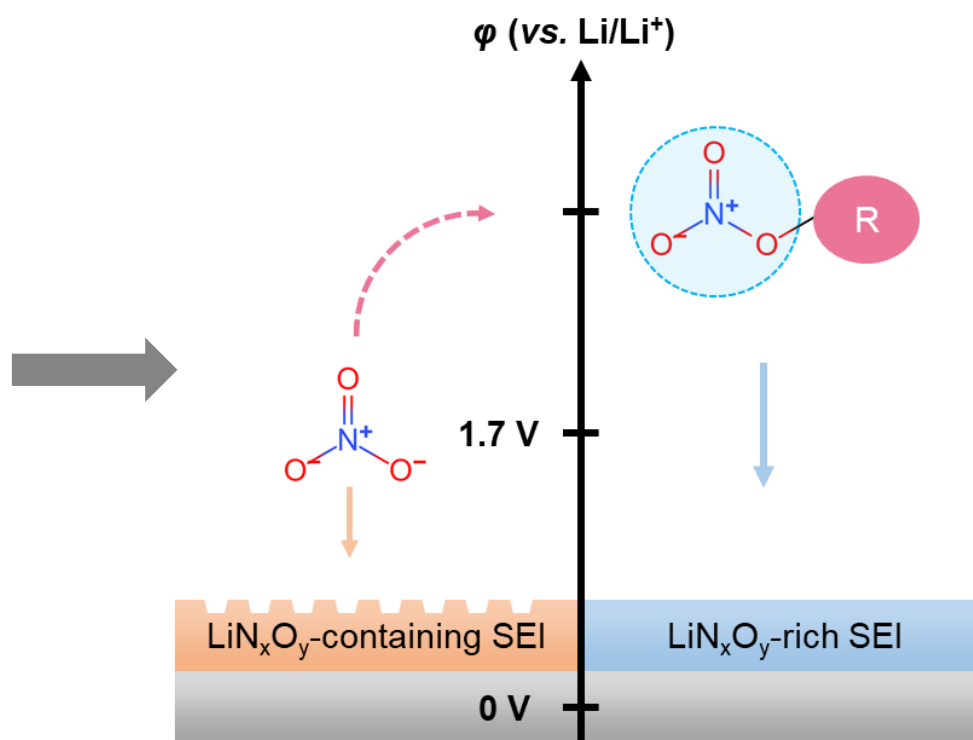
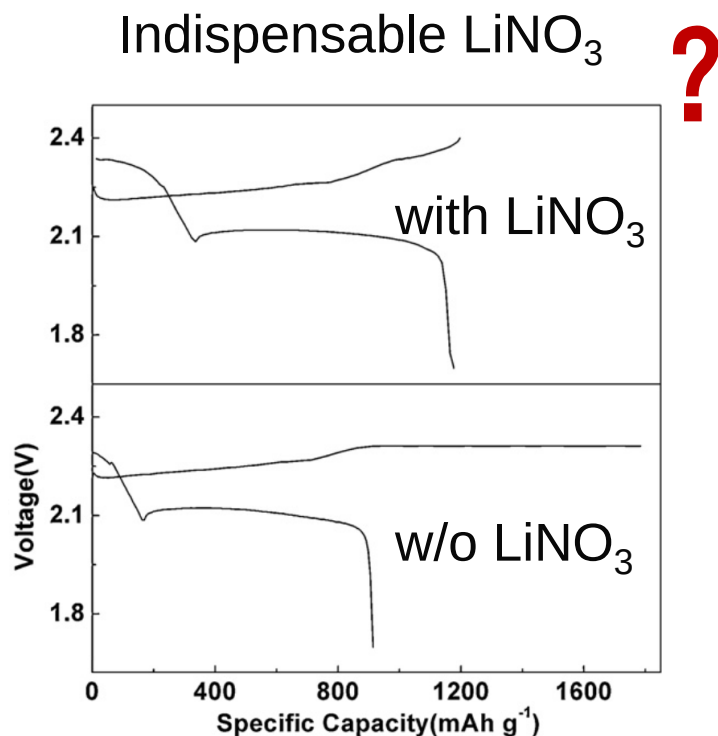
Weakening the solvating power of outer-shell solvents enables long-cycling Li–S batteries.



Anode protection: Regulation of SEI

LiN_xO_y in SEI

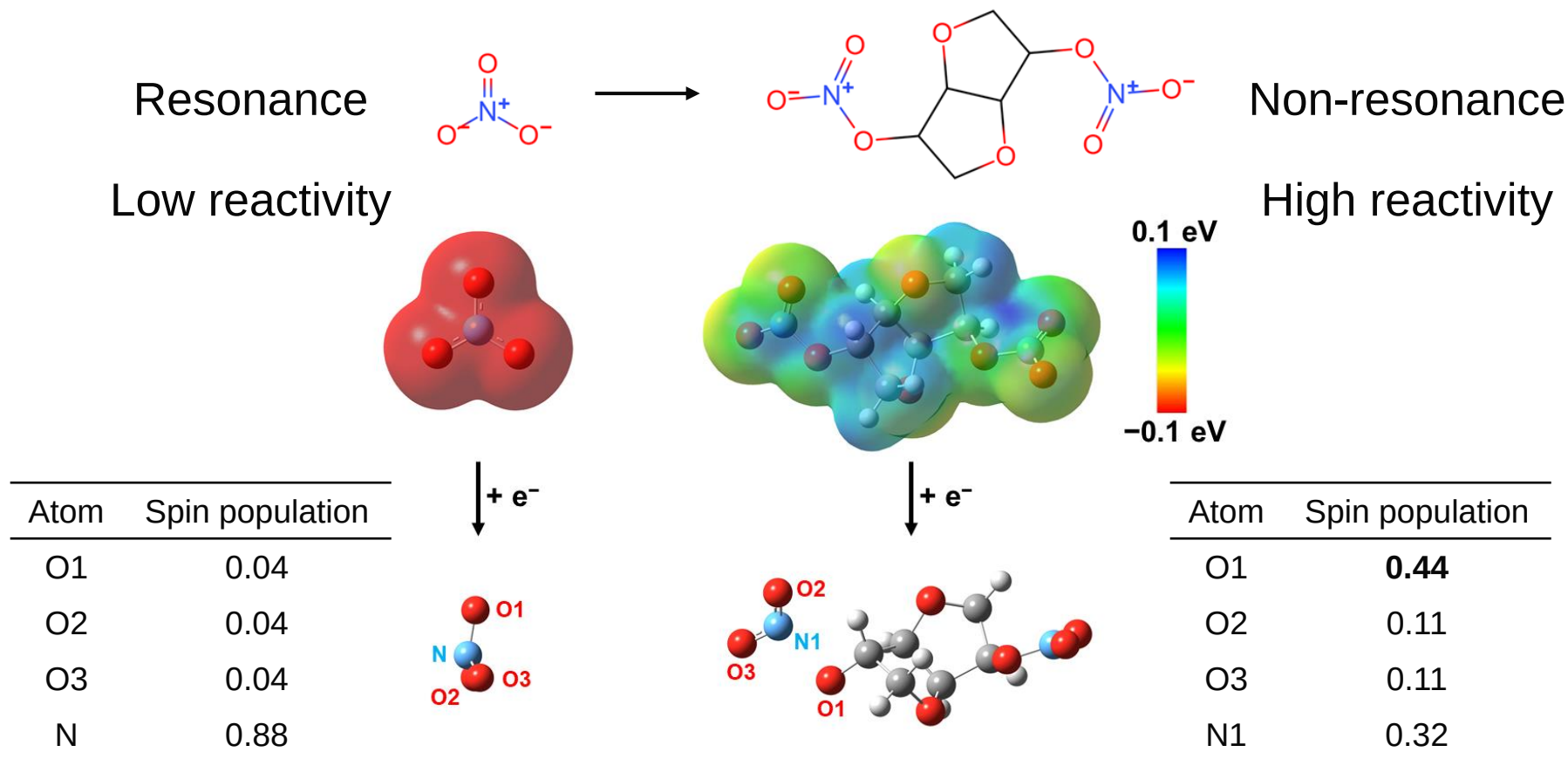
Modification of NO_3^- to form LiN_xO_y -rich SEI



Anode protection: Regulation of SEI

LiN_xO_y in SEI

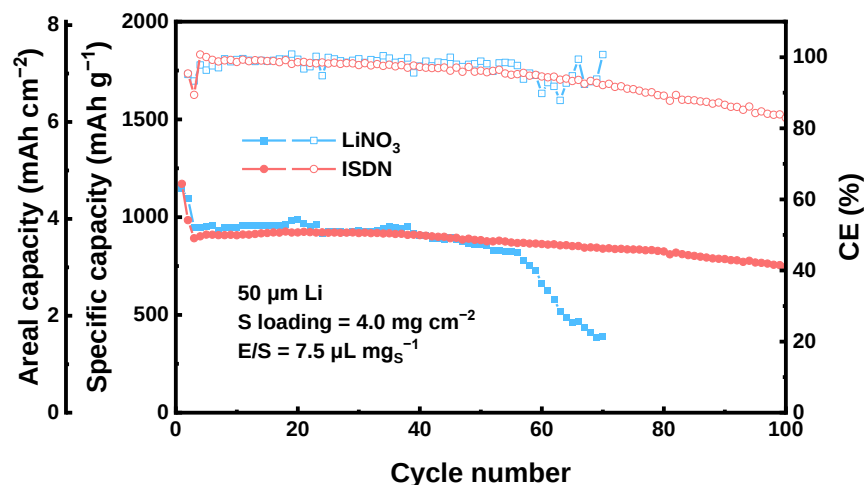
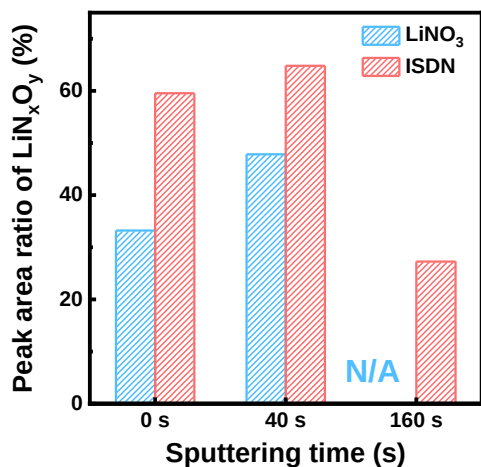
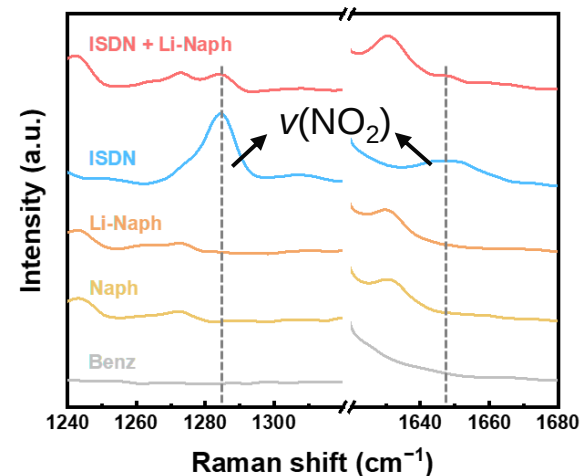
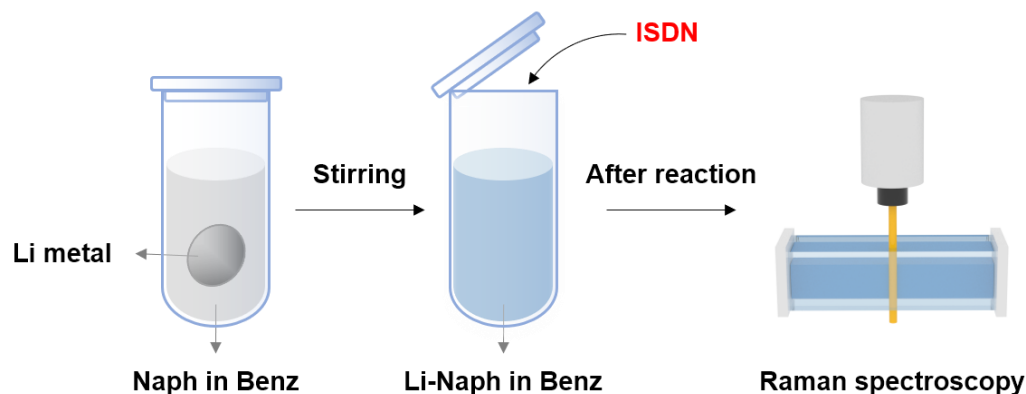
The preferential decomposition of ISDN vs. NO_3^-



Anode protection: Regulation of SEI

LiN_xO_y in SEI

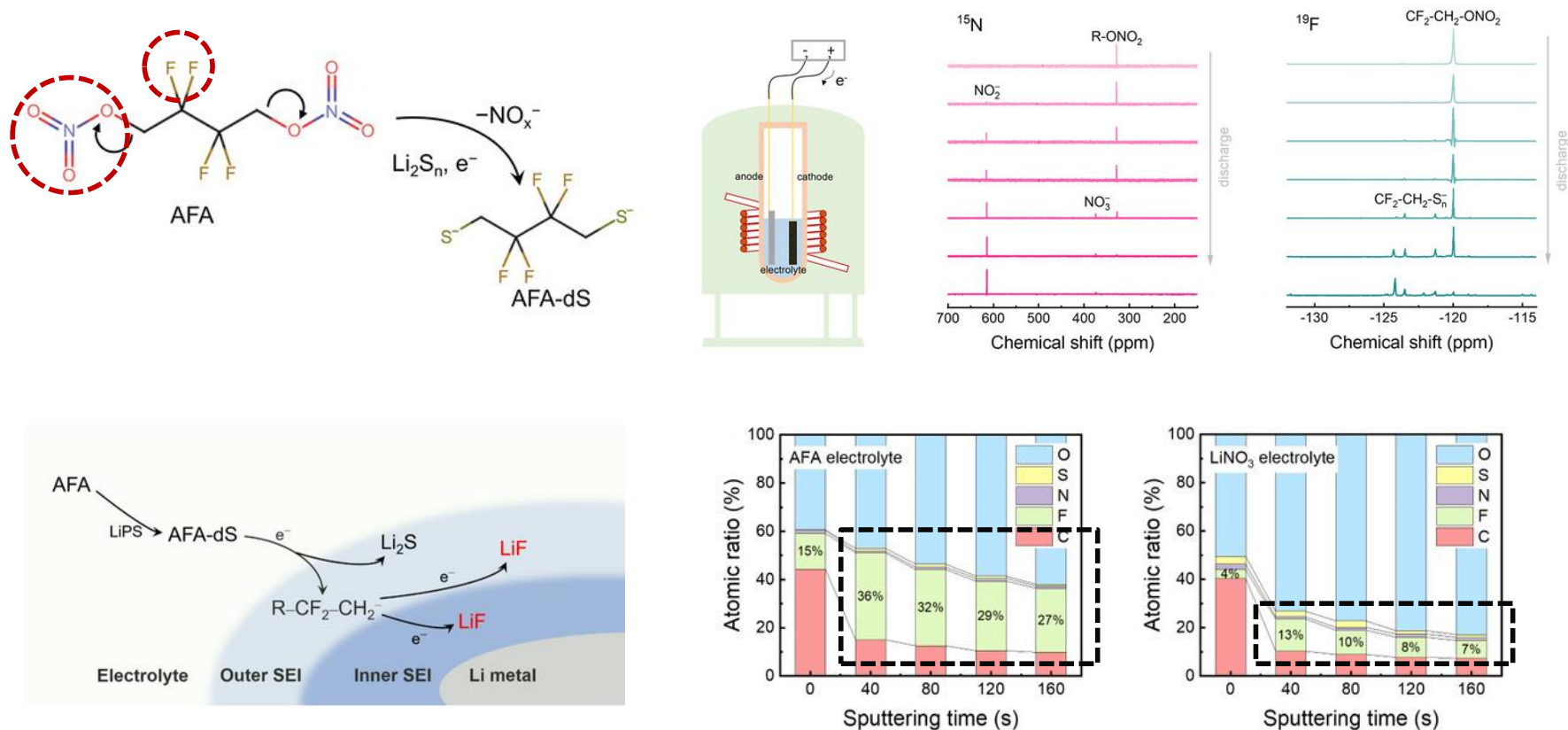
ISDN enables superior cycling stability than LiNO_3 .



Anode protection: Regulation of SEI

LiF in SEI

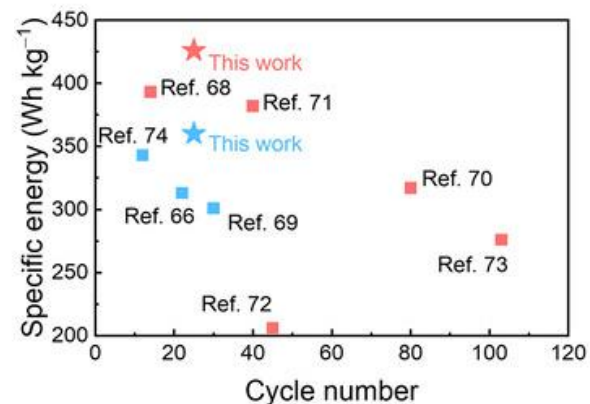
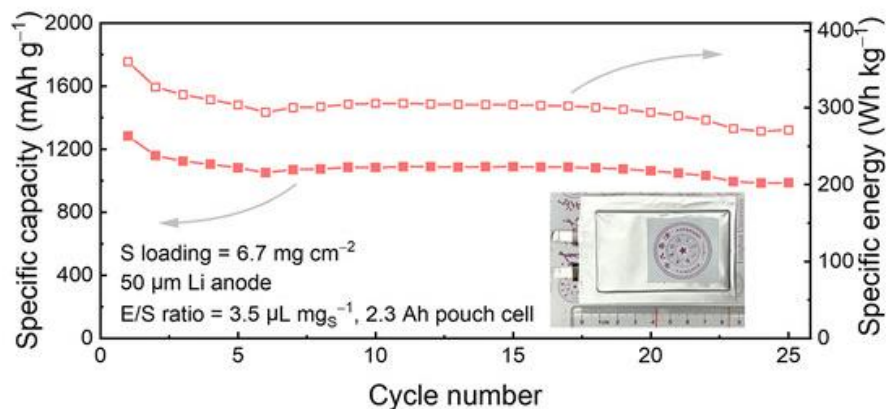
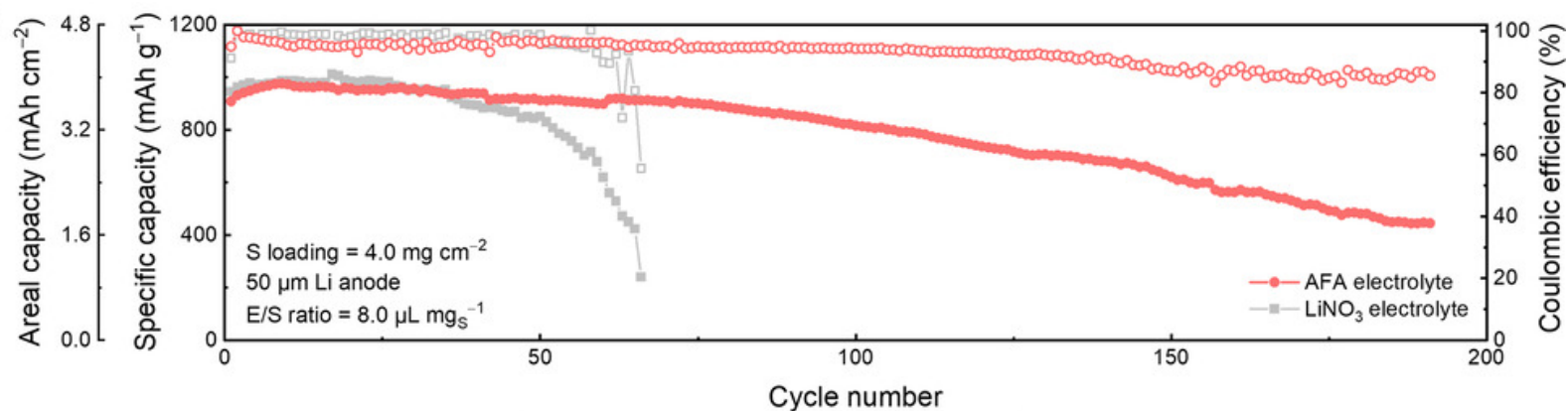
AFA renders fast and complete defluorination and generates uniform fluorinated SEI.



Anode protection: Regulation of SEI

LiF in SEI

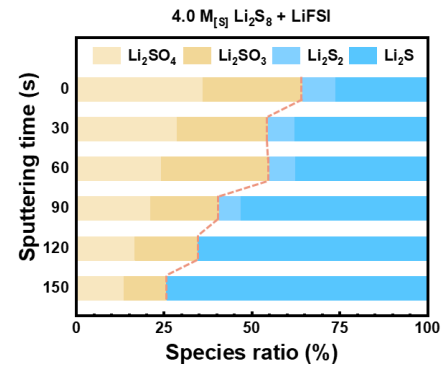
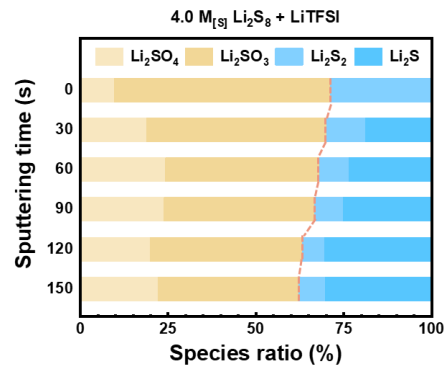
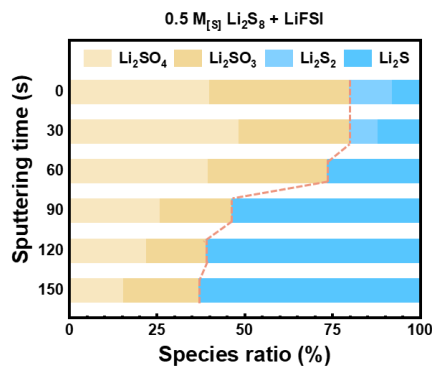
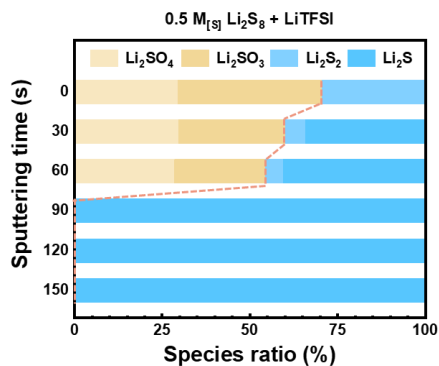
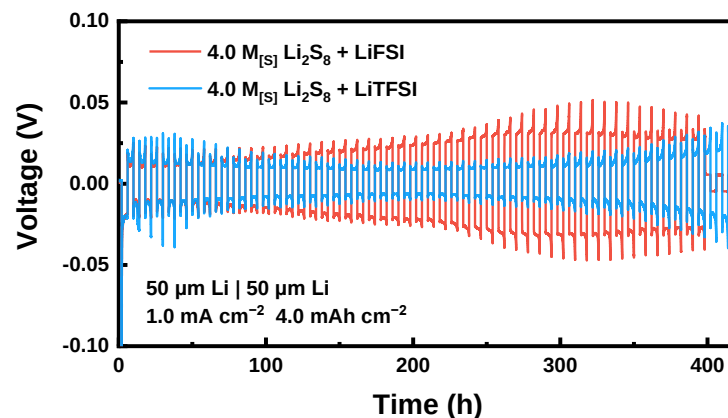
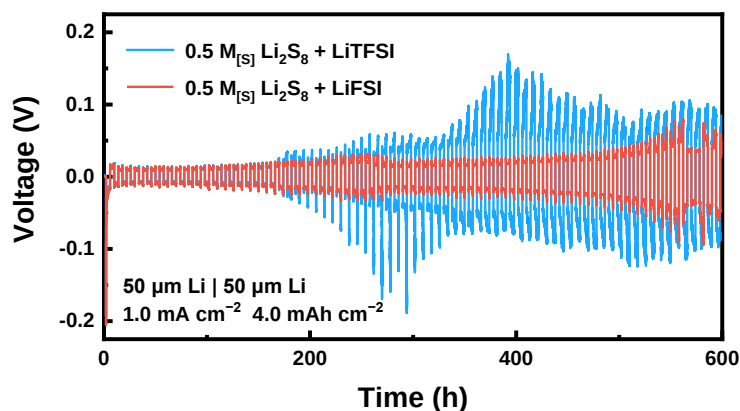
AFA enables superior cycling stability than LiNO_3 .



Anode protection: Regulation of SEI

$\text{Li}_2\text{S}_x\text{O}_y$ in SEI

S-containing species are indispensable in SEI. (LiPS & Li salt)

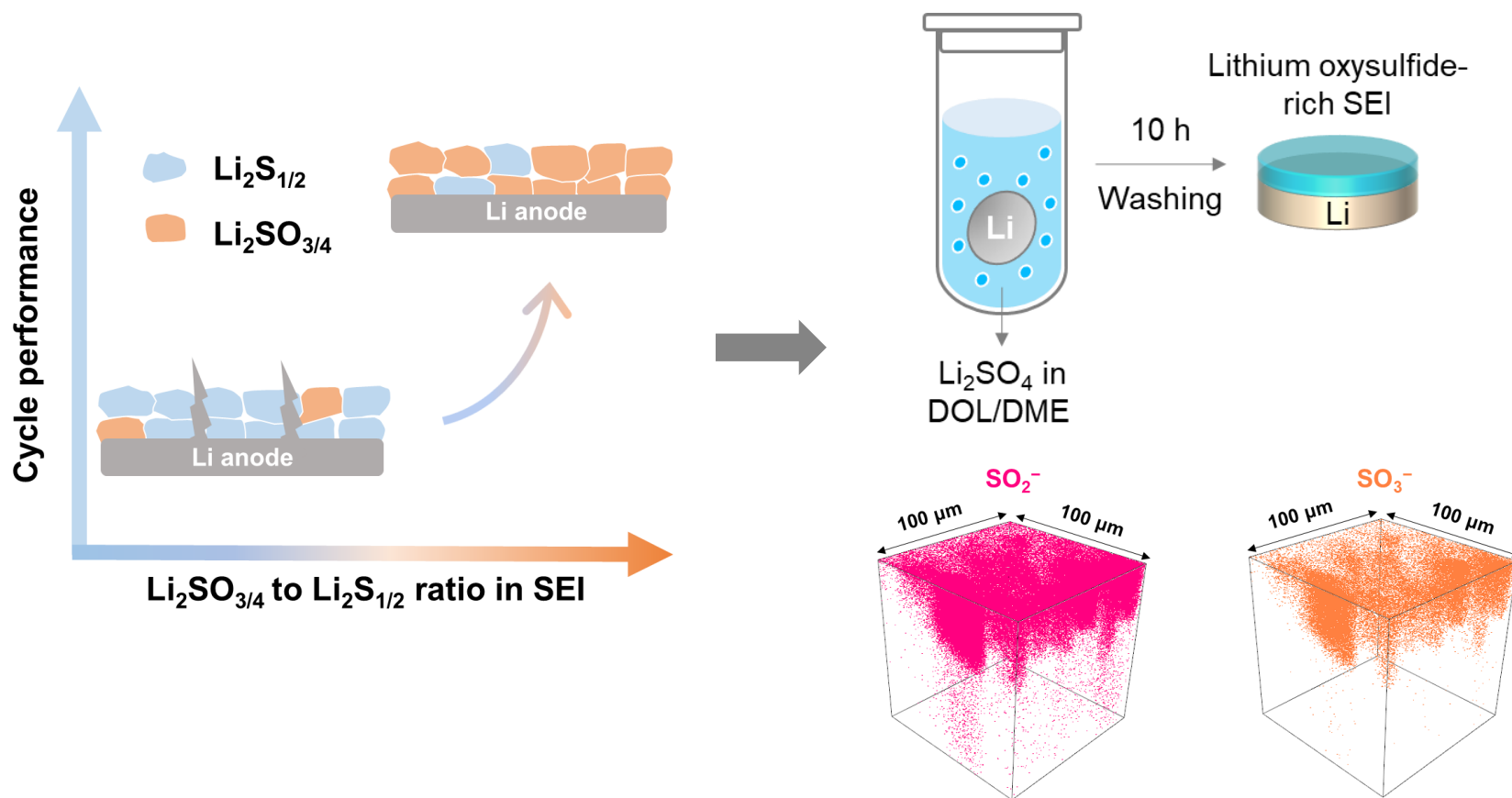


High content of $\text{Li}_2\text{S}_x\text{O}_y$ for superior cycling stability of Li metal anodes

Anode protection: Regulation of SEI

$\text{Li}_2\text{S}_x\text{O}_y$ in SEI

Li_2SO_4 is sustainably released to introduce abundant lithium oxysulfide components in SEI.

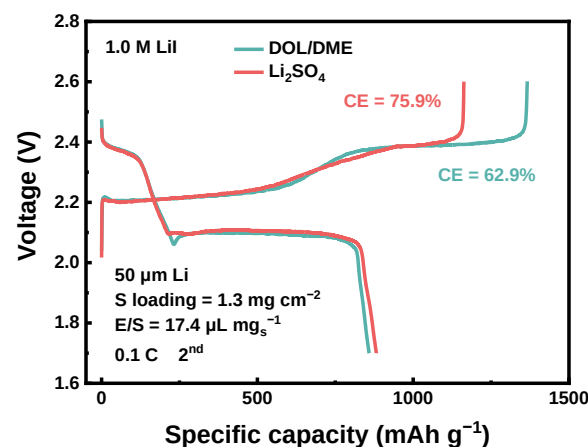
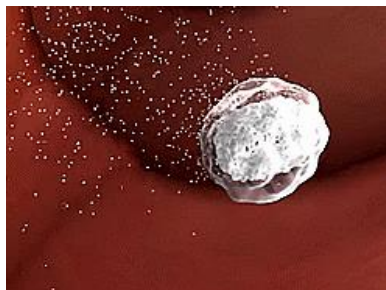
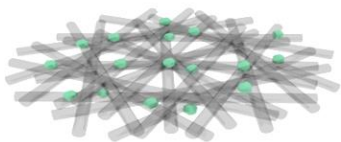


Anode protection: Regulation of SEI

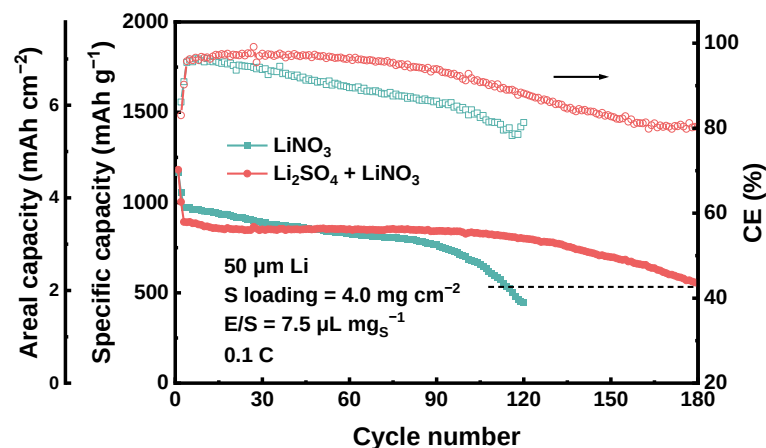
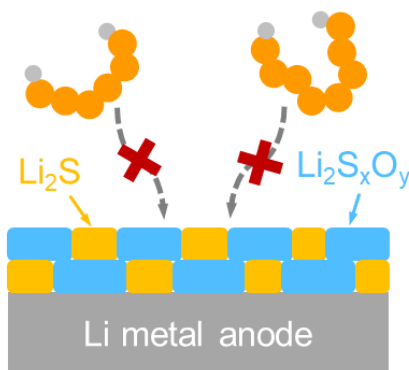
$\text{Li}_2\text{S}_x\text{O}_y$ in SEI

$\text{Li}_2\text{S}_x\text{O}_y$ -rich SEI achieves long cycling stability of Li-S batteries.

Li_2SO_4 in
non-woven fabrics

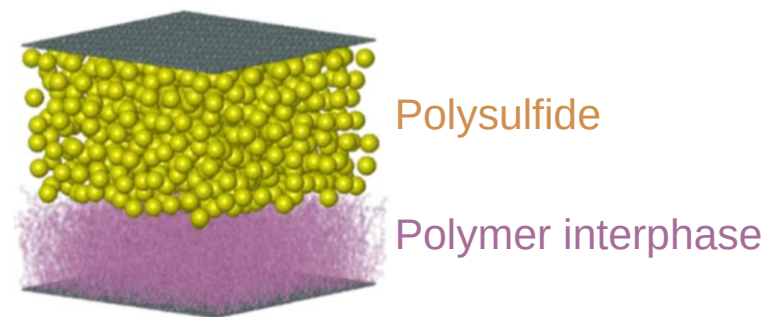
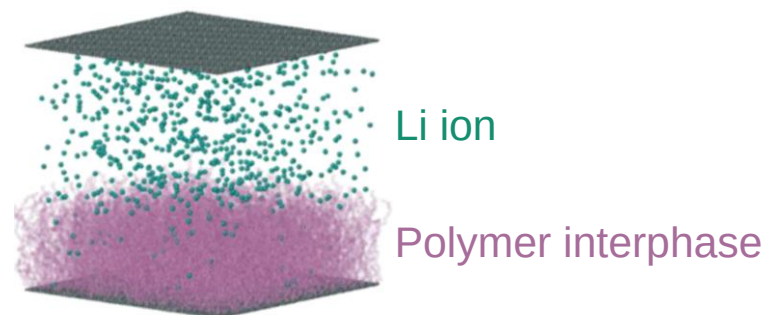
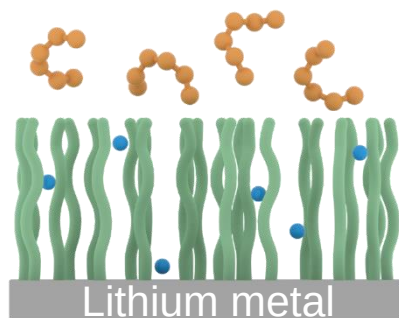
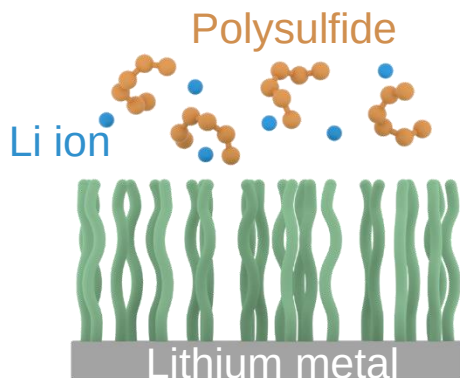


Lithium oxysulfide-rich SEI



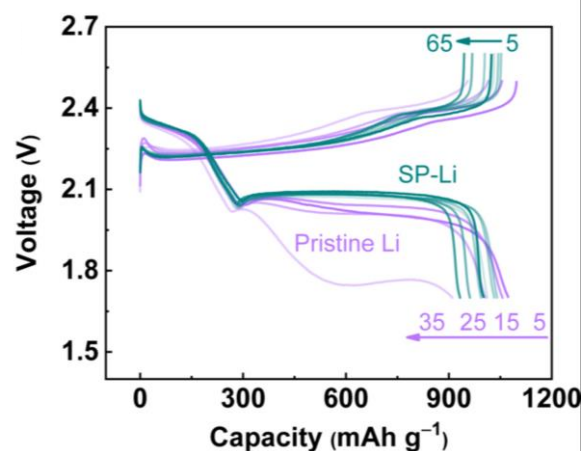
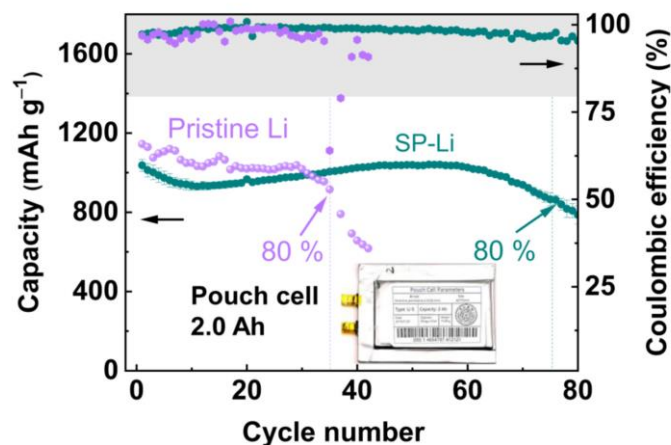
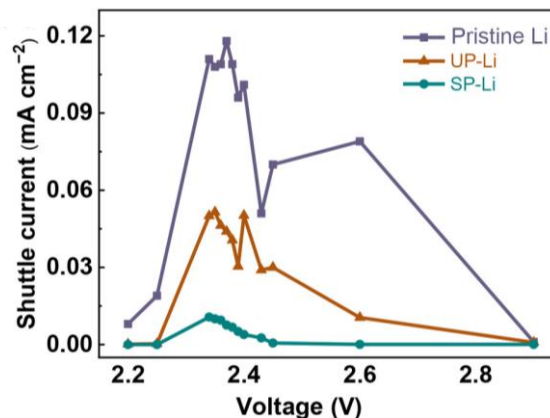
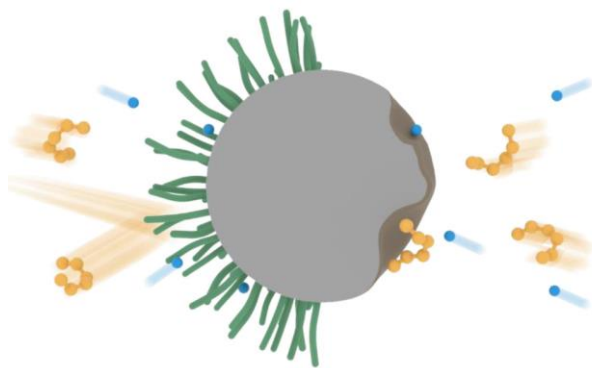
Anode protection: Artificial SEI

PDMS-based artificial SEI as protective layer to repulse LiPS and exclusively permit Li^+ transportation



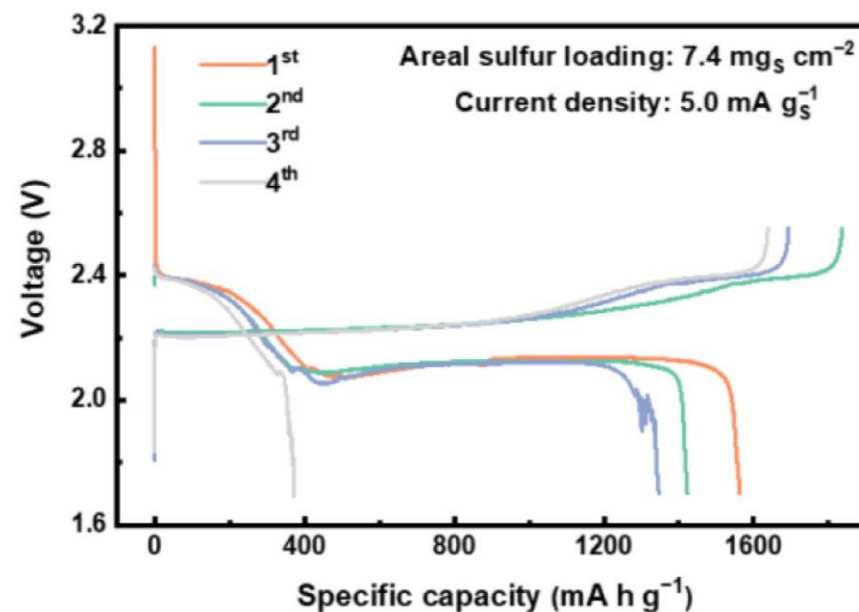
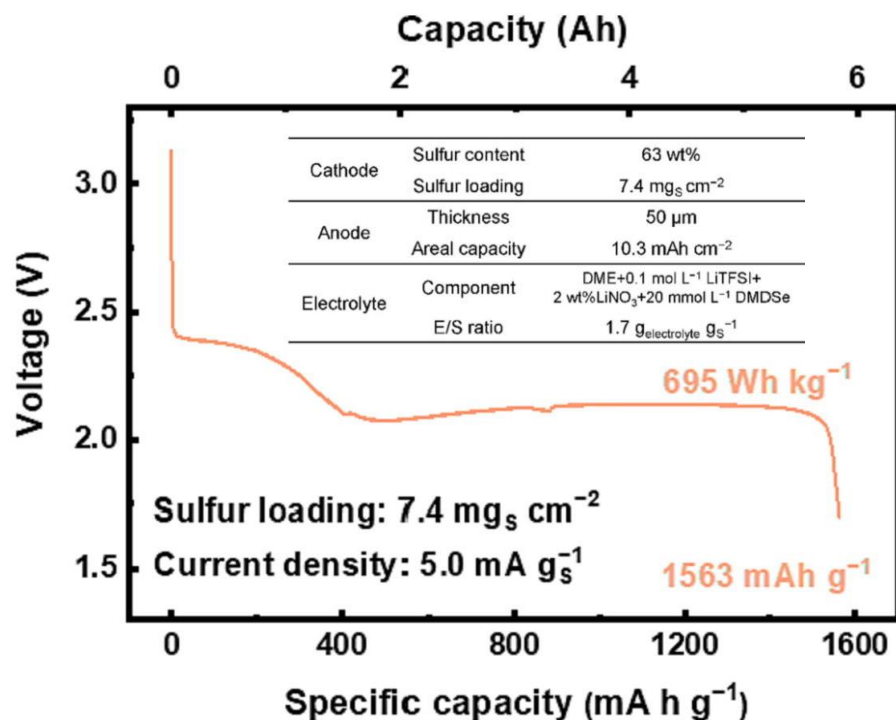
Anode protection: Artificial SEI

PDMS-based artificial SEI promotes the cycling stability of Li metal in pouch cells.



Pouch cell evaluation

Constructing recyclable 700 Wh kg^{-1} Li-S pouch cells

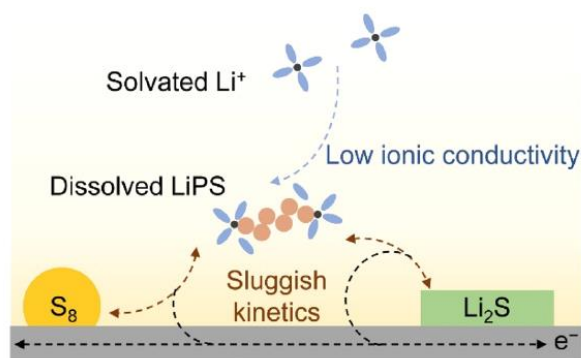


- Long lifespan is still a big challenge.

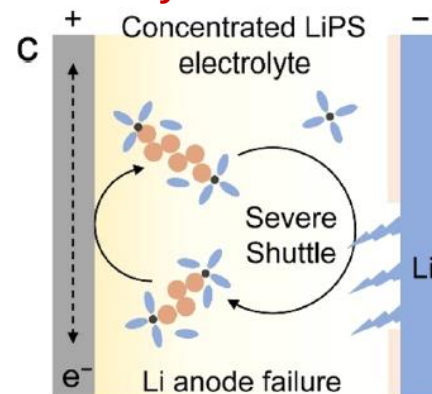
Perspective

Three emerging challenges under practical conditions

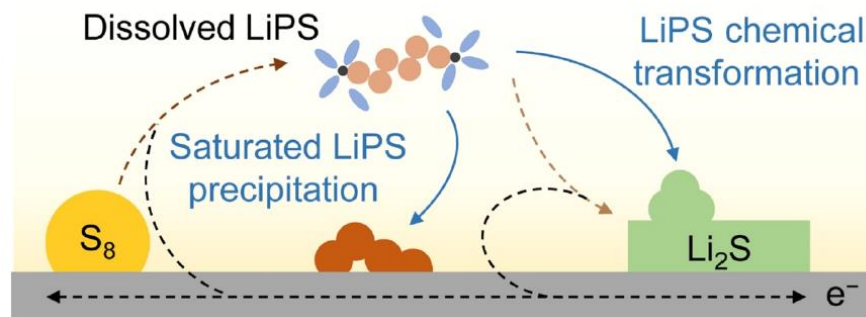
Abrupt change of electrolyte properties



Severe reaction of electrolyte and anode



Slow kinetics under lean-electrolyte conditions



Conclusion

1. Li–S batteries are promising high-energy-density energy storage systems.

The most promising system to achieve $> 400 \text{ Wh kg}^{-1}$

2. Li metal anode/electrolyte interphase is key for long cycling.

Sulfur insulation, volume expansion, and sluggish LiPS redox kinetics are being solved.

Rapid decay of anode interphase hinders long cycling of high-energy-density batteries.

3. Investigation at pouch cell level is necessary.

High sulfur loading, limited anode excess, and lean electrolyte are necessary.

Electrolyte and active Li exhaustion is the main failure reason for 300 Wh kg^{-1} pouch cell.

Electrolyte exhaustion is the main failure reason for $> 400 \text{ Wh kg}^{-1}$ pouch cell.

3. Polysulfide chemistry & Anode interphase regulation prolong lifespan.

Basic understanding of solvation structure of polysulfide (Neutral & Cationic)

Encapsulating polysulfide electrolyte (EPSE) to inhibit LiPS corrosion on Li anode

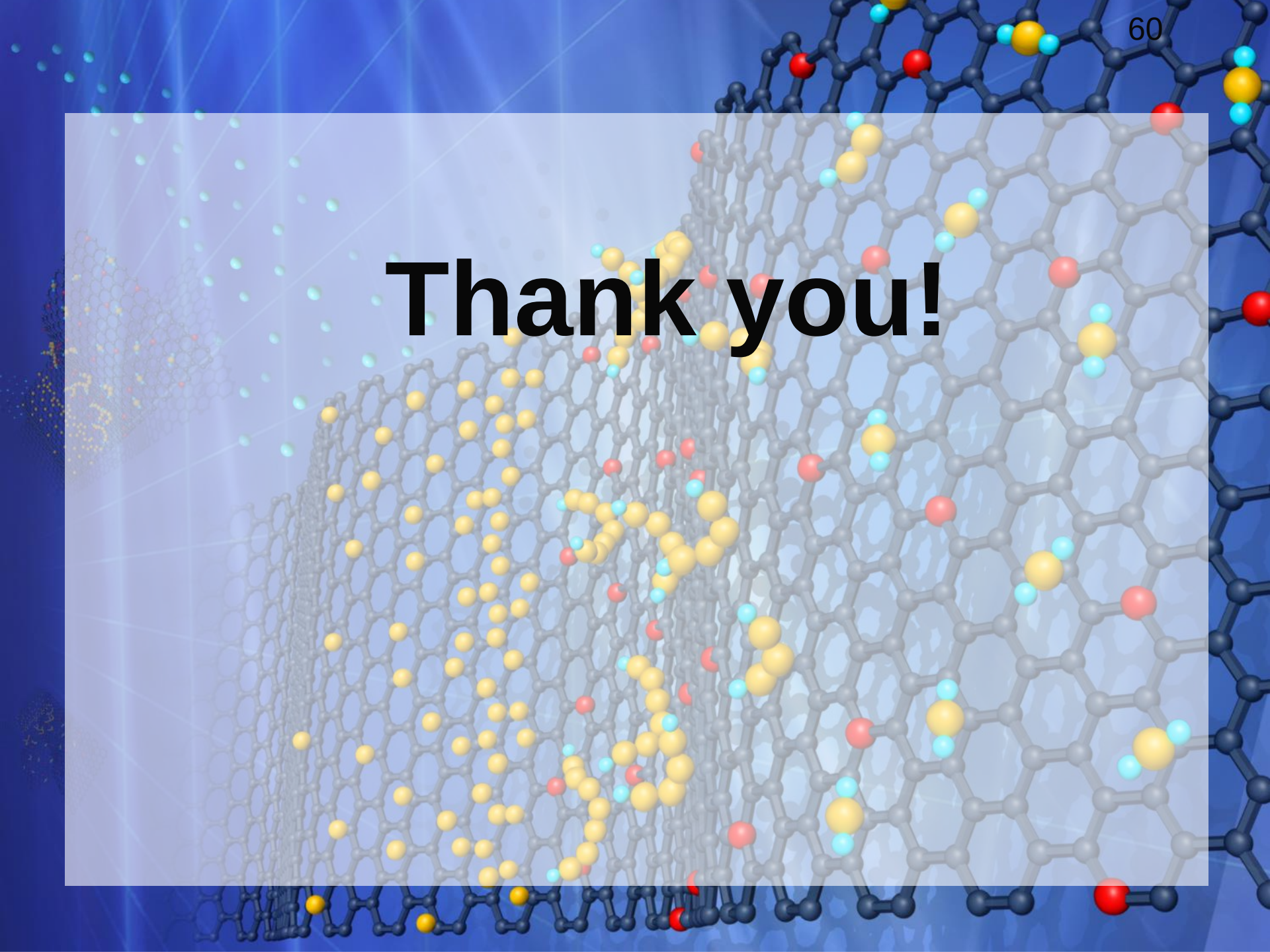
In situ SEI regulation (crucial components) & Artificial SEI to protect Li anode

4. Basic chemistry of Li–S system still needs to be explored.

Unique non-equilibrium system

Complex coupled process including mass transfer and electron conduction

Spatially uneven and irreversible pathway



Thank you!