Challenges and Solutions for Lithium-Sulfur Batteries

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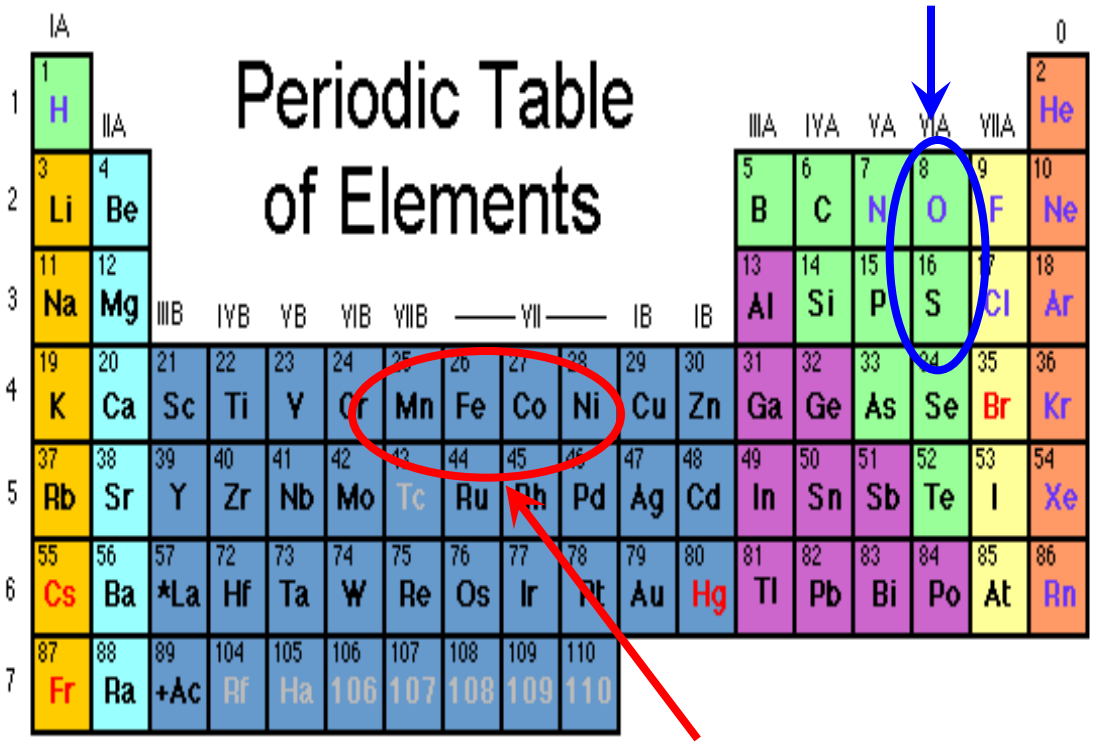
Battery Chemistry: Essential for Innovative Breakthrough for Li-Batteries

Ideal battery system: pure elements with every atom contributing to charge transfer and energy exchange. Li-S/ Li-O will be the systems of choice!

light elements



heavy compounds with O, P

Intercalation *vs* Conversion

Cathode material	Theoretical capacity [mAh/g]	Relative price
$LiCoO_2$	275	1
$LiNiO_2$	274	0.86
$LiMn_2O_4$	148	0.17
$LiFePO_4$	170	0.15
S_8	1675	0.017
O_2	1675 or 3350	free

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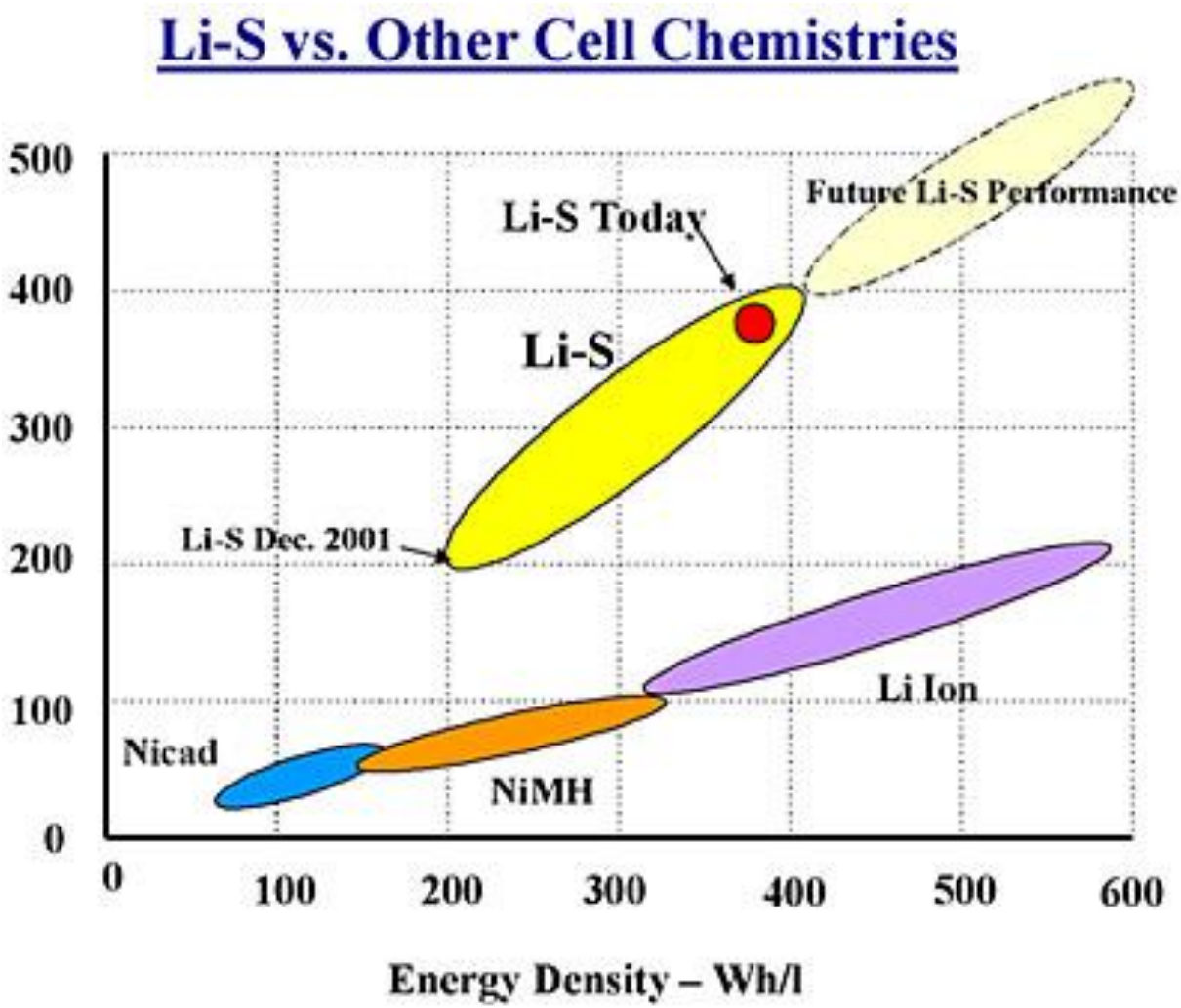
Li-S Batteries Hold the Promise for Next Generation of Battery Technology.



Source: Sion Power

Theoretical Specific Energy

Li/S:
2600 Wh/kg

Features of Li-S

- High Capacity
  - High energy density
- Moderate Voltage
  - Safe
  - Compatibility
- Low Cost
  - High abundance

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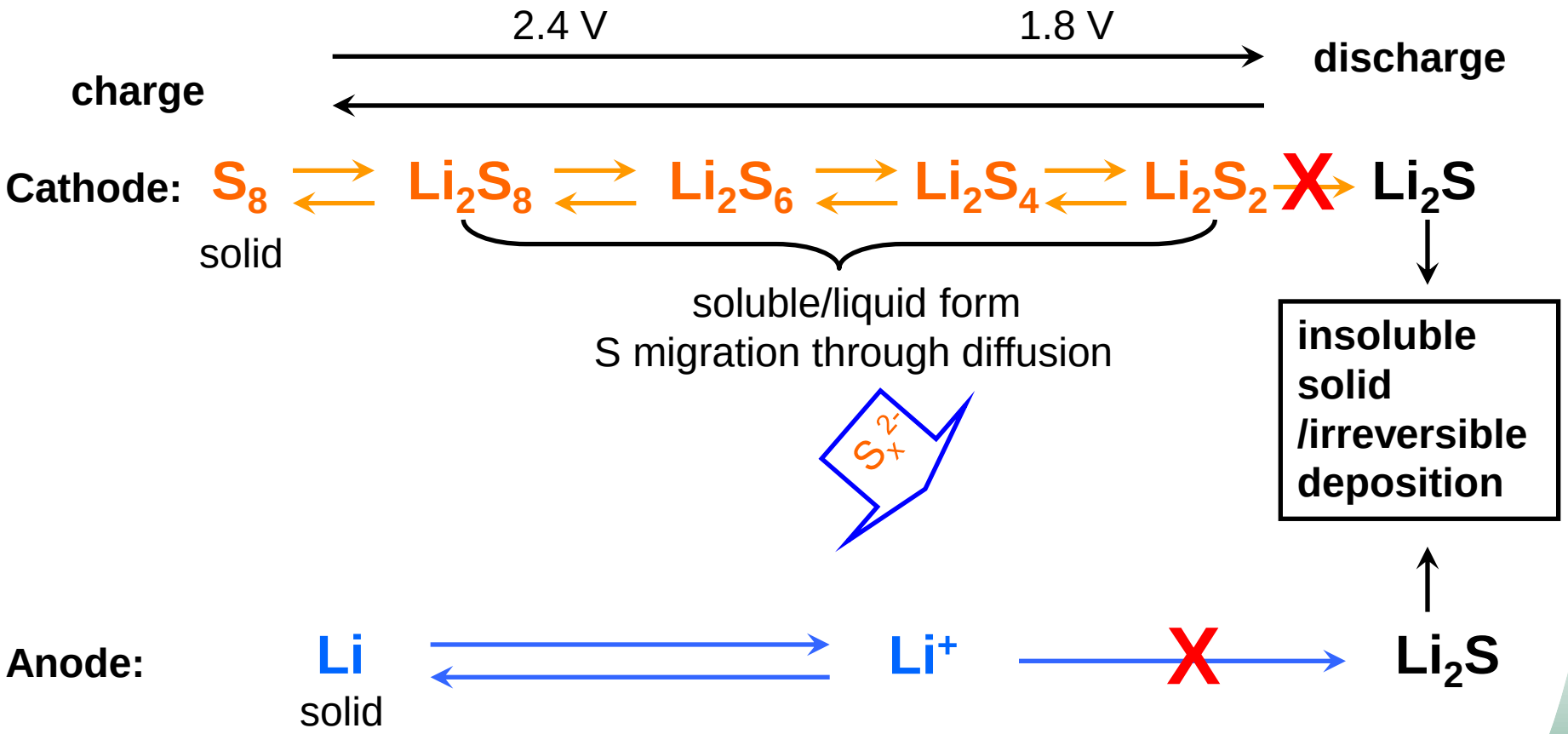
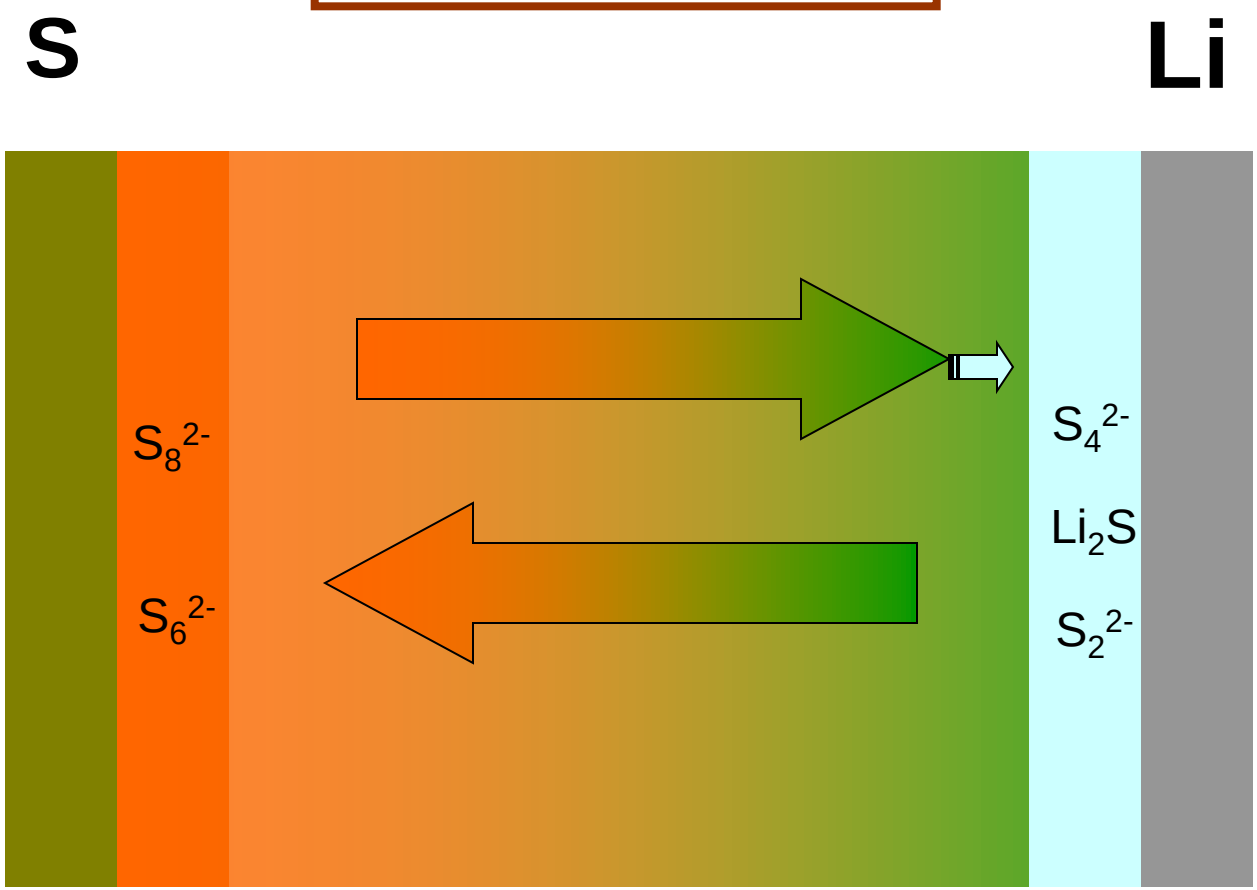
Migration of S Poses the Major Challenge for Li-S Batteries.



- **Intrinsic sulfur migration: liquid phase diffusion**
- **Irreversible Li_2S formation: both cathode and anode**
- **Poor Li anode cyclability: corrosion/ Li_2S deposition/ dendrites**

Why Li-S Cannot Cycle Long?

Polysulfide Shuttle



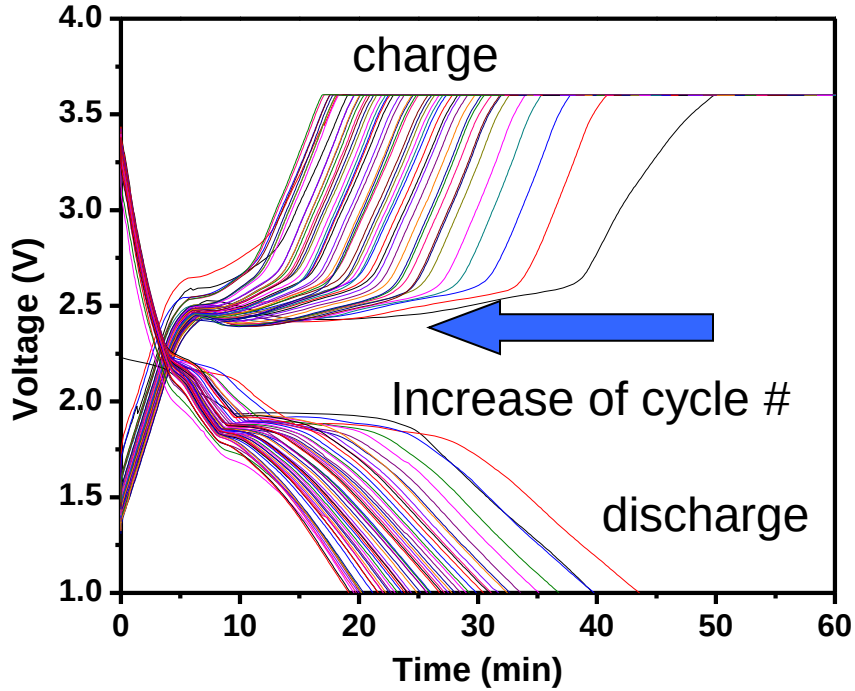
- Self-discharge
- Capacity fading
- Cell resistance increase
- Poor cyclability

- Passivate Li anode
- Decrease the diffusivity of ions
  - Gel electrolytes
  - Solid electrolytes
- Physically absorb S
  - High surface area carbons
  - Conducting polymers
- Chemically immobilize S
  - S-polymers
  - S-salts

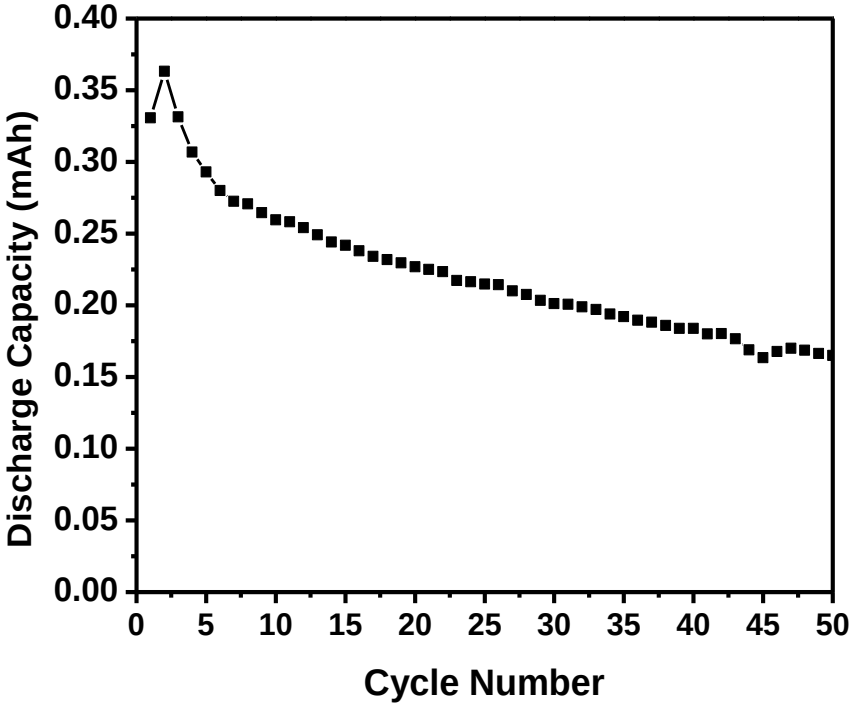
1) Cheon, S. E.; Choi, S. S.; Han, J. S.; Choi, Y. S.; Jung, B. H.; Lim, H. S. *Journal of the Electrochemical Society* 2004, *151*, A2067-A2073. 2)Mikhaylik, Y. V.; Akridge, J. R. *Journal of the Electrochemical Society* 2004, *151*, A1969-A1976.

Li-S Cell Has a Short Cycle-Life.

Charge/discharge curves



Cycle performance



Detrimental deposition of Li_2S :

- **Increase of cell resistance**
- **Decrease of cell capacity**

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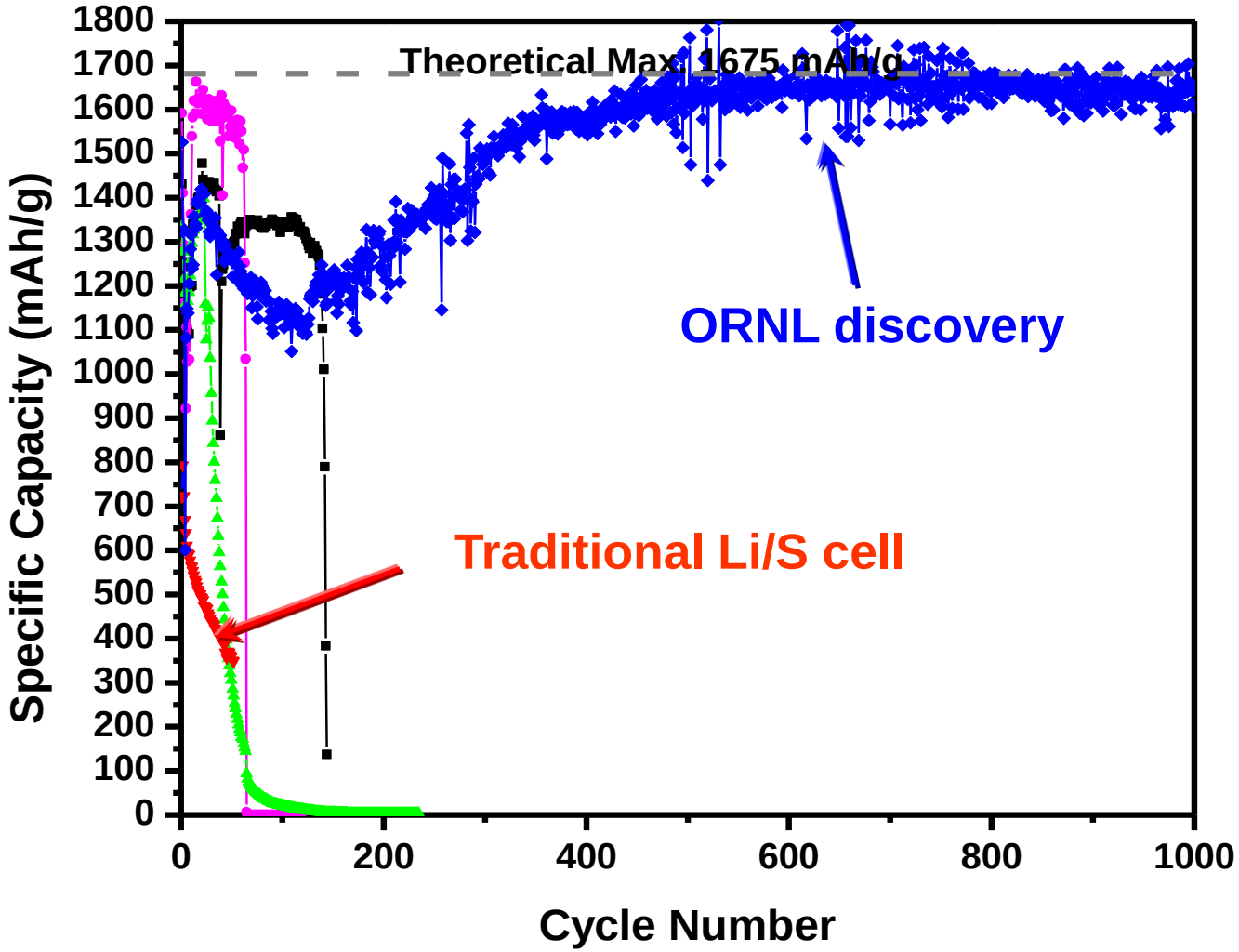
1000 Cycle-Life is Possible.



C-S composite along with an electrolyte additive can make a difference.

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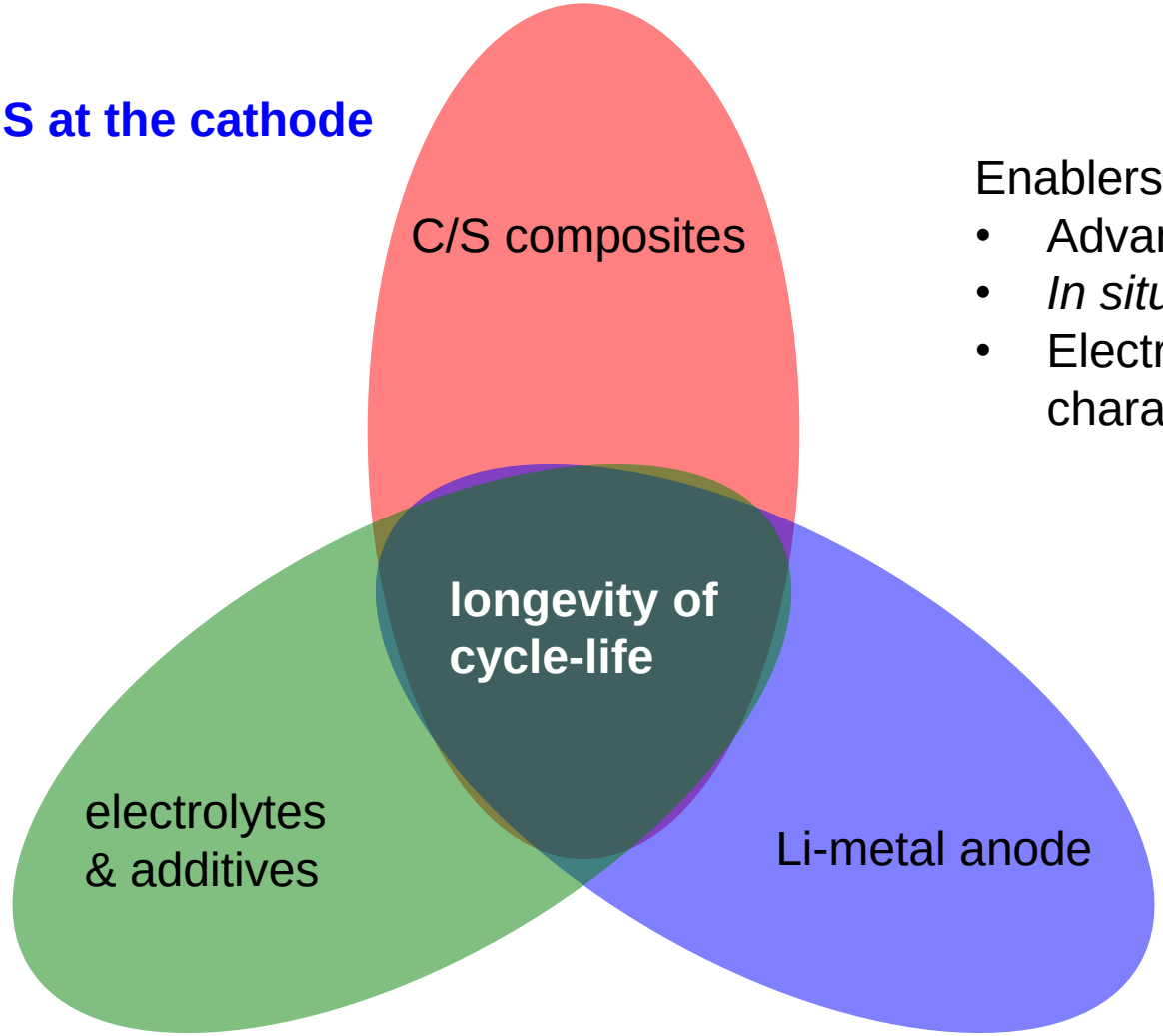
Approach to Improve Performance is Three-fold.

Goal: Understand and overcome the obstacles of cycling the Li-S battery

Retain S at the cathode



Enablers:

- Advanced synthesis
- *In situ* SEM
- Electrochemical characterization

Reverse Li_2S formation

Heal the damaged Li anode

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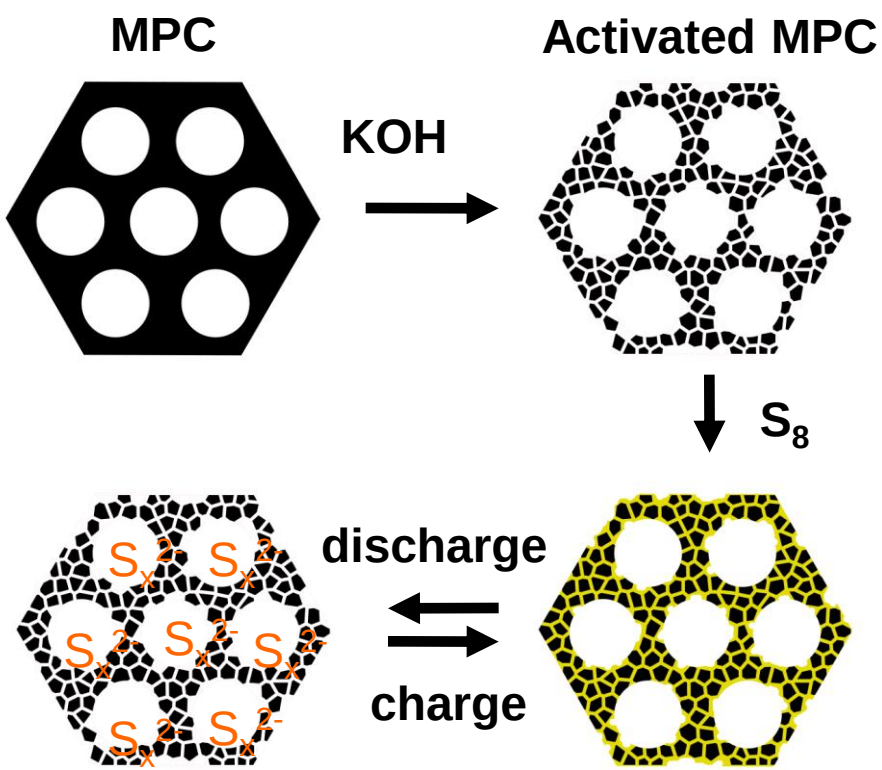
Activated Templated Carbon Gives Well Controlled Porosity for Sulfur Host.

- **C/S composites by using bimodal porous carbon**
  - **Physical confinement of S in < 2nm pores**
  - **Electronic contact of S**
  - **Adsorption of polysulfides**
  - **Ionic path through mesoporous**

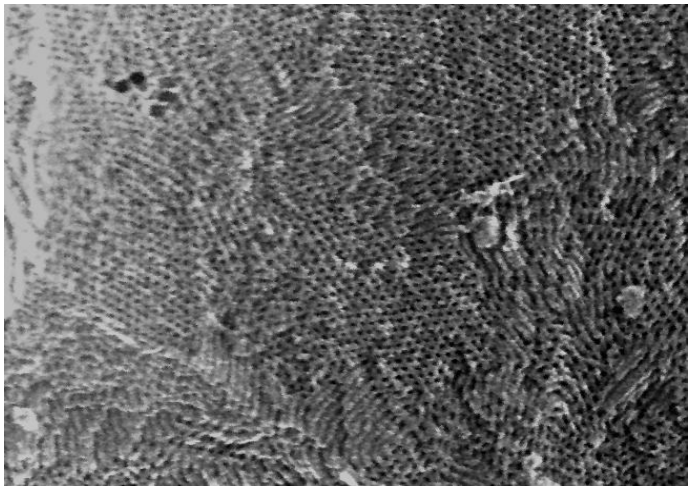


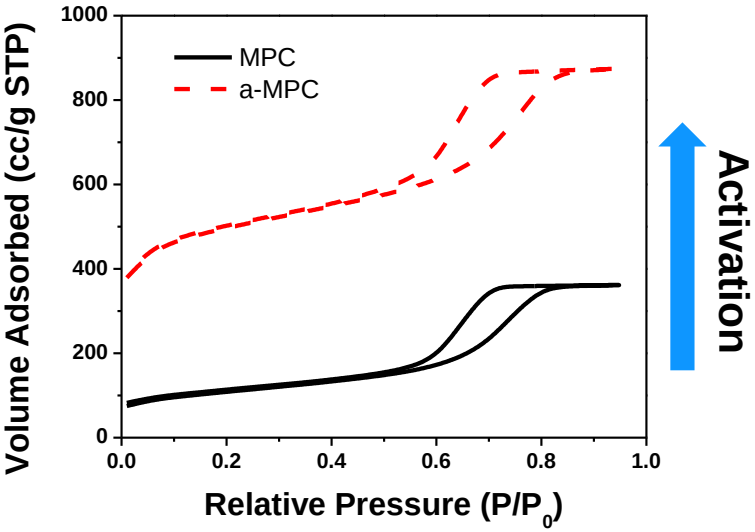
Micropores (<2nm): host sites for S
Mesopores (2-50 nm): path for Li^+ transport

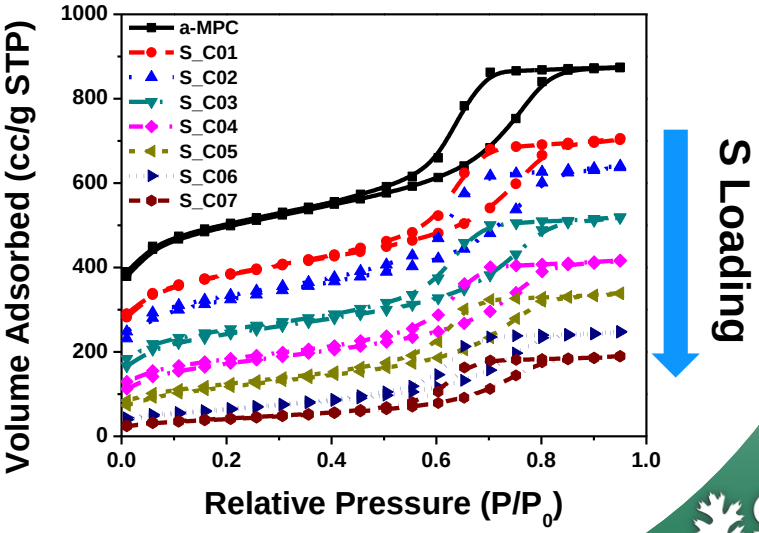
Simple Synthesis Procedure Eases the Preparation.

Three-step Synthesis of Carbon/Sulfur Composite

1. **Soft-template synthesis of mesoporous carbon**
2. **KOH activation**
3. **Sulfur infiltration**

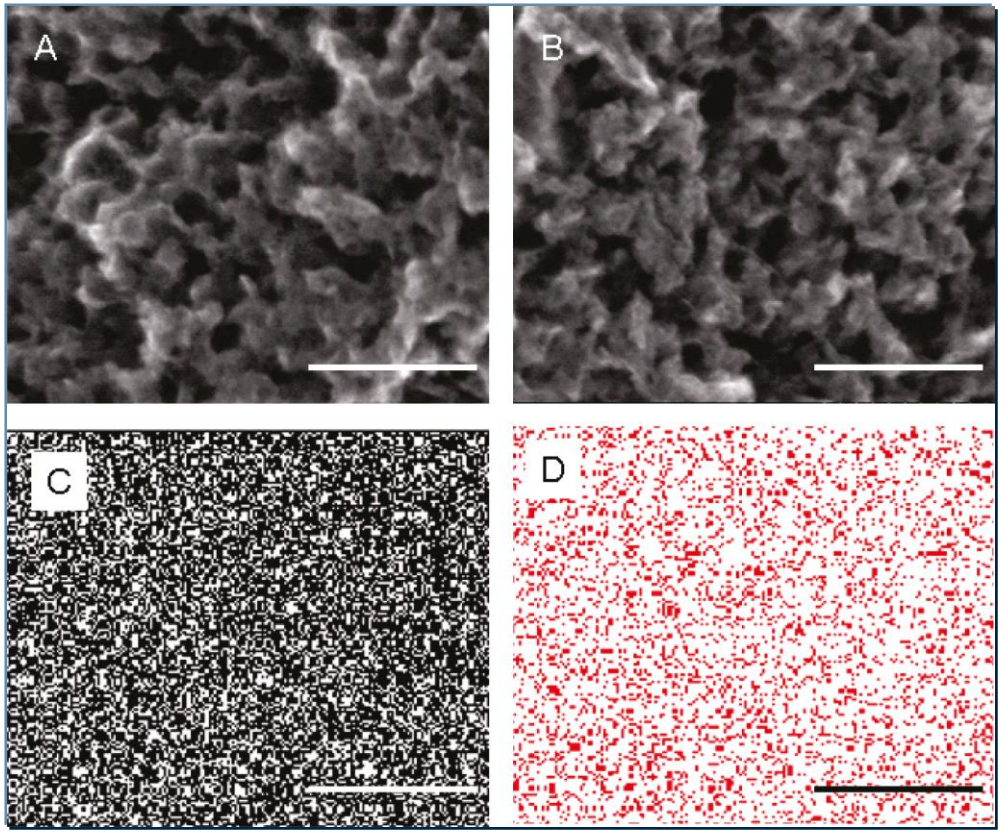




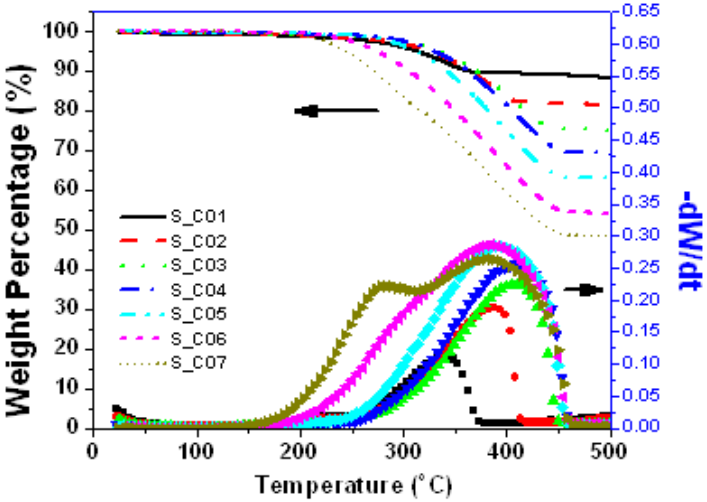


Sulfur Loading is Precisely Positioned.

SEM and Elemental Maps



TGA analysis of Sulfur Loading



Elemental S is precisely controlled within the micropores

Business Sensitive

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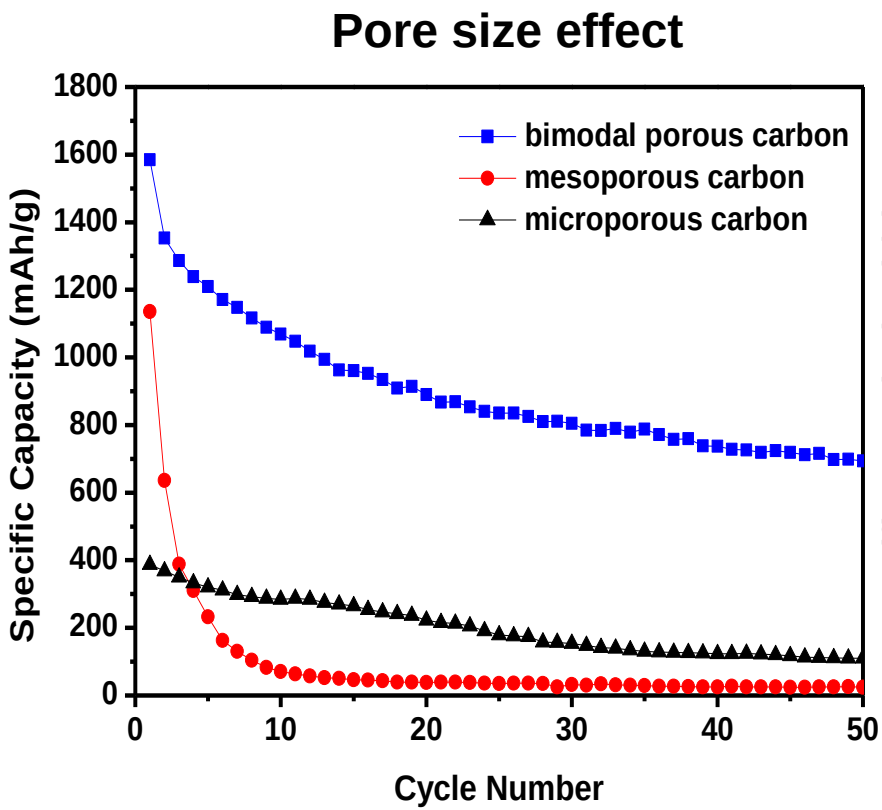
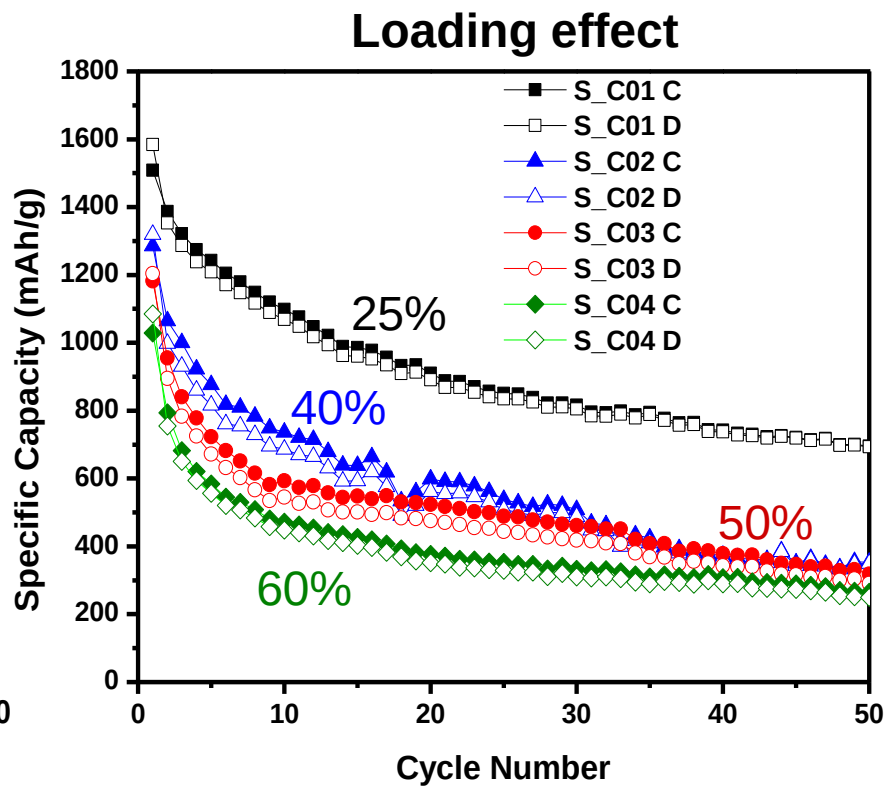
Cycling Performance (without Electrolytes Additives) is Greatly Improved by Nano-engineered Carbon Host which Retains Sulfur.





Note: specific capacity is per gram sulfur. Theoretical is 1675 mAh/g.

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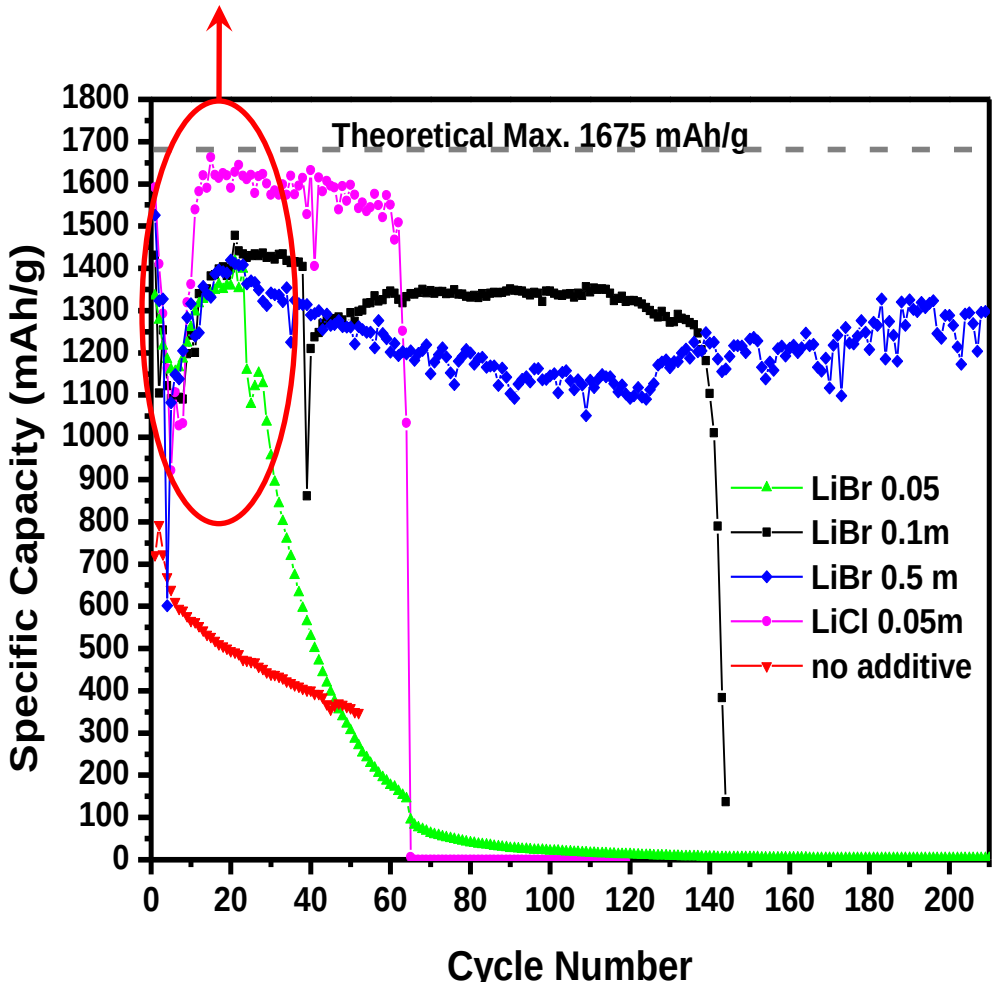
Electrolyte Additives Can Reverse Li_2S Formation, Improving Cycle Life of Li/S Half-cells.

Polymerization of electrolytes after 10 cycles



Traditional approach:
Avoid the formation of Li_2S

Our approach:
Allow the formation of Li_2S and make it reversible through a catalytic process

- Additives improve the reversibility of Li_2S formation
- The polymerization of the electrolytes plays an important role on the cyclability of Li-S cells

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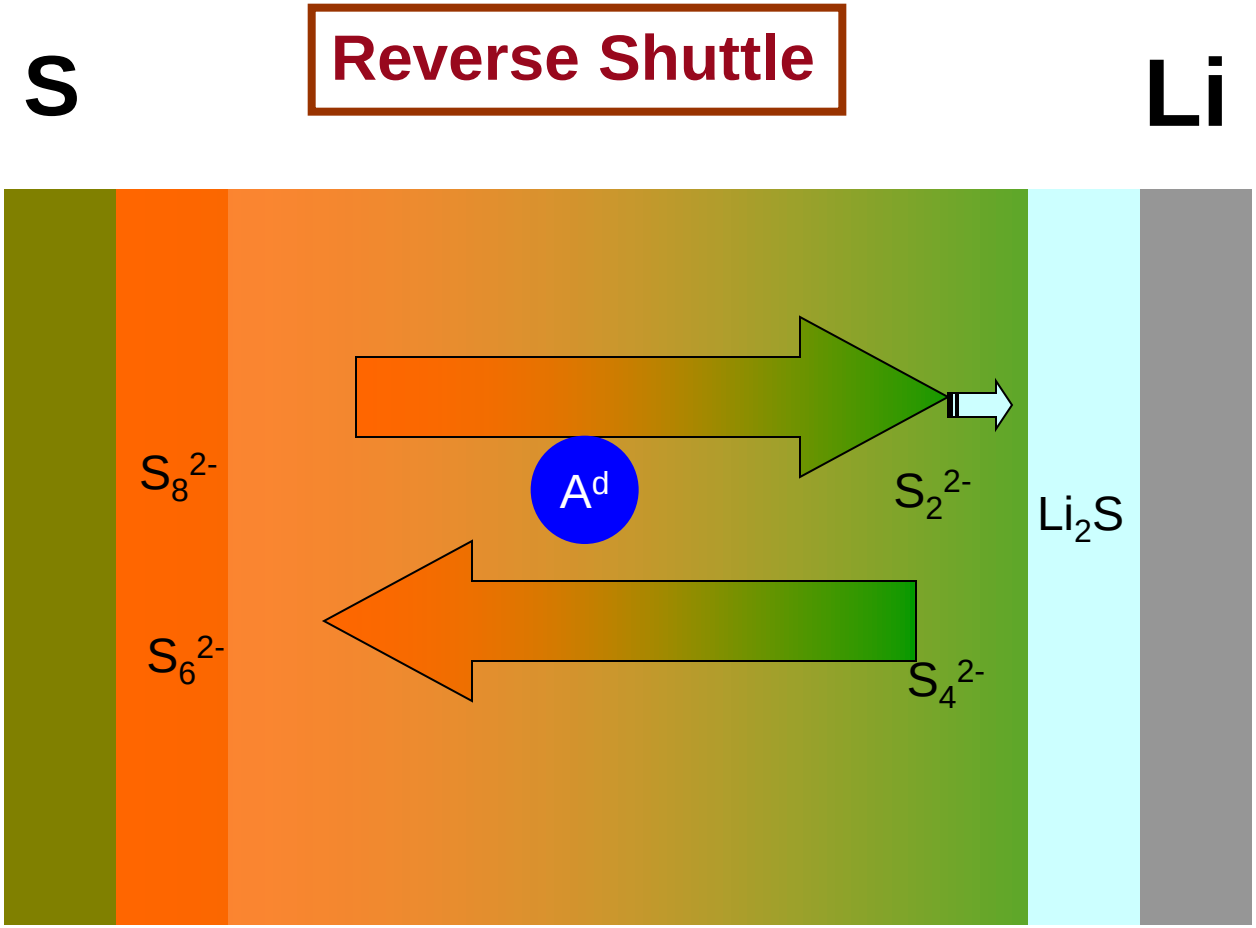
Catalyzed Reversibility of Li_2S Formation Drives S back to Cycling.



Speculation on how the additives function?

1. **React with Li_2S and free the sulfur back to cycling.**
2. **Regenerate electrochemically at the charge cycle.**

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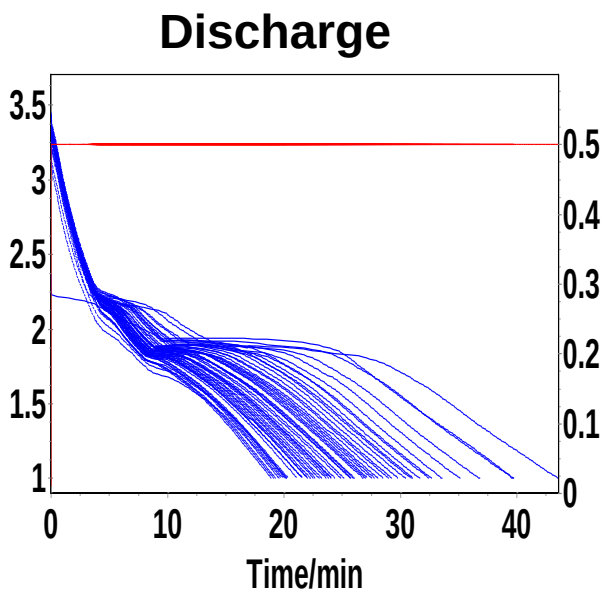
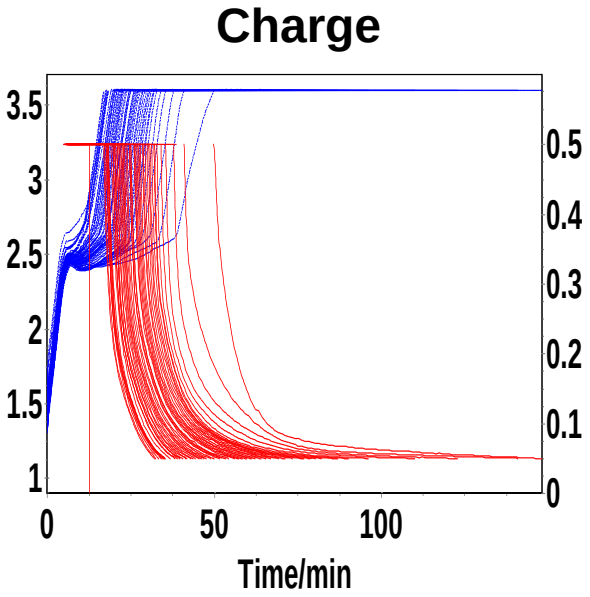
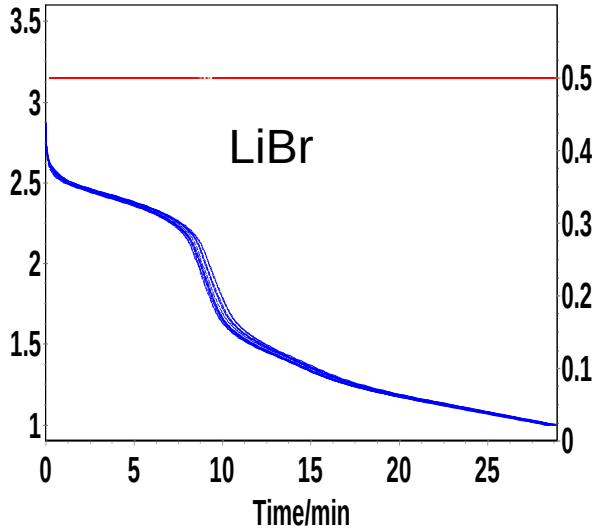
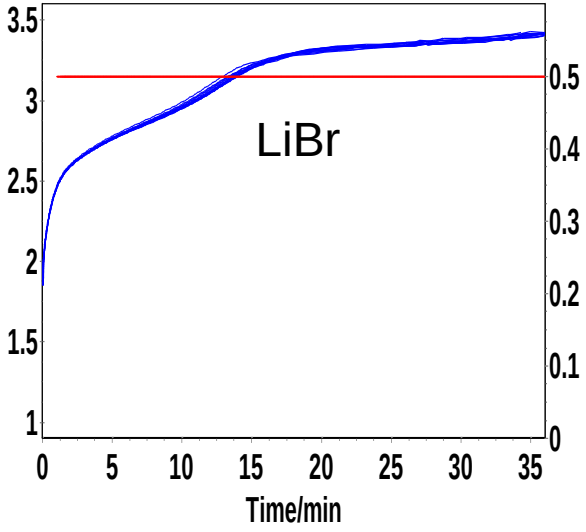
LiBr Additive Alters and Stabilizes Shape of Voltage Curves.









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Possible Mechanism for Reverse Shuttle Reaction

Discharging

$$S_8 \xrightarrow{+e} S_{Hx}^{2-} \xrightarrow{+e} \cdot S_{Lx}^{-}$$

$$\cdot S_{Lx}^{-} \xrightarrow{+e} S_{Lx}^{2-} \xrightarrow{+e} S_{1,2}^{2-}$$

Hx=6,8 Lx=2,3,4

Charging

$$S_{1,2}^{2-} \xrightarrow{-e} S_{Lx}^{2-} \xrightarrow{-e} \cdot S_{Lx}^{-}$$

$$\cdot S_{Lx}^{-} \xrightarrow{-e} S_{Hx}^{2-} \xrightarrow{-e} S_8$$

Hx=6,8 Lx=2,3,4

$$\cdot S_{Lx}^{-} + Br^{-} \longrightarrow S_{Lx}^{2-} + [Br]$$

$$\cdot S_{Lx}^{-} + [Br] \longrightarrow BrS_{Lx}^{-}$$

$$BrS_{Lx}^{-} + [Br] \longrightarrow BrS_{Lx}Br + Br^{-}$$

$$BrS_{Lx}^{-} \xrightarrow{+e} S_{1,2}^{2-} + Br^{-}$$

$$BrS_{Lx}Br \xrightarrow{+e} S_{1,2}^{2-} + Br^{-}$$

$$[Br] \xrightarrow{+e} Br^{-}$$

$$Br^{-} \xrightarrow{-e} [Br]$$

$$S_{1,2}^{2-} + [Br] \longrightarrow \cdot S_{Lx}^{-} + Br^{-}$$

$$\cdot S_{Lx}^{-} + [Br] \longrightarrow BrS_{Lx}^{-}$$

$$BrS_{Lx}^{-} + [Br] \longrightarrow BrS_{Lx}Br + Br^{-}$$

$$BrS_{Lx}^{-} + S_{1,2}^{2-} \longrightarrow S_{Hx}^{2-} + Br^{-}$$

$$BrS_{Lx}Br + S_{1,2}^{2-} \longrightarrow S_8 + Br^{-}$$

Additives create additional reactions that reverse the formations of Li_2S.

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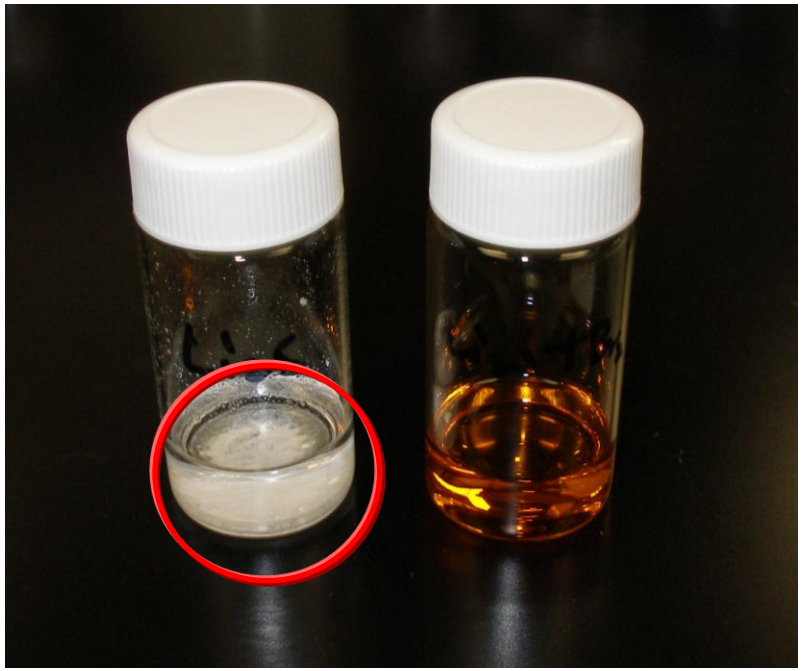
Bench-top Demonstration Gives Further Evidence that LiBr Catalyzes Reversibility of Li_2S Formation.



Images of Li_2S in organic solvents: Left, without Br_2; right, with Br_2

In the charging cycle:

$$LiBr \longrightarrow Br_2 \text{ (cathode)} + Li \text{ (anode)}$$

Electrochemically generated Br_2 proceeds to the following chemical reaction

$$Br_2 \text{ (liquid)} + Li_2S \text{ (solid)} \longrightarrow$$

$$Li_2S_x \text{ (solution)} + LiBr \text{ (solution)}$$

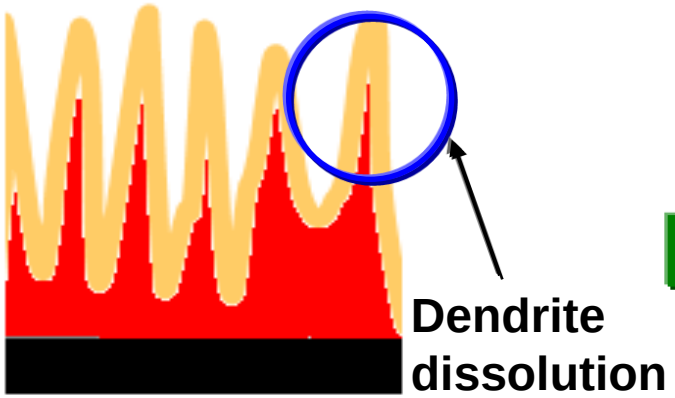
This reaction returns the Li_2S solid back to solution and accelerates the electrochemical reaction, therefore catalyzing the reversibility of Li_2S formation

Shuttles could Possible Heal Damaged Li Anode.

Over charging at the Cathode produces:

Br_2 S_xBr_2 S^{2-}_x

Migration through the electrolyte



Over charging at the anode rebuilds:
Thick lithium metal anode

Li^+

Re-deposition of lithium

Self-healing

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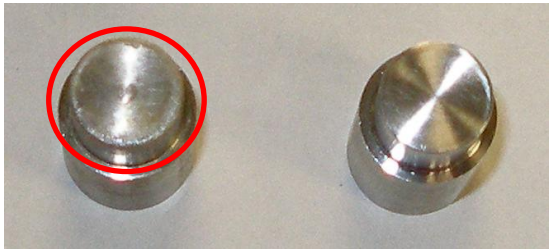
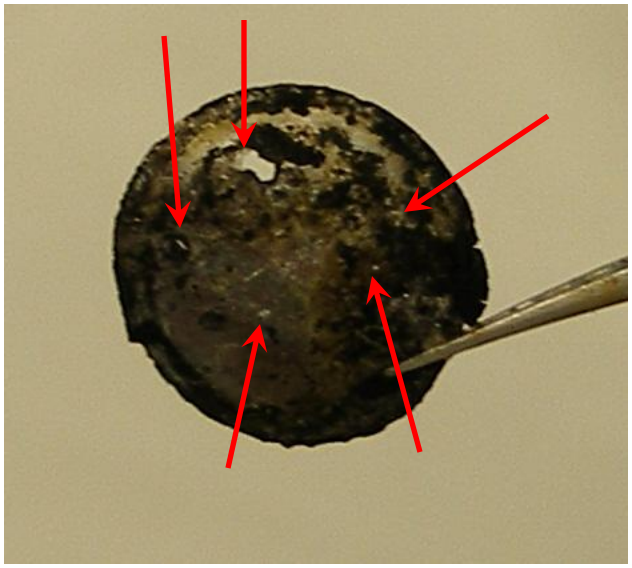
A Major Drawback of LiBr Additive is Severe Corrosion of Cell Parts.



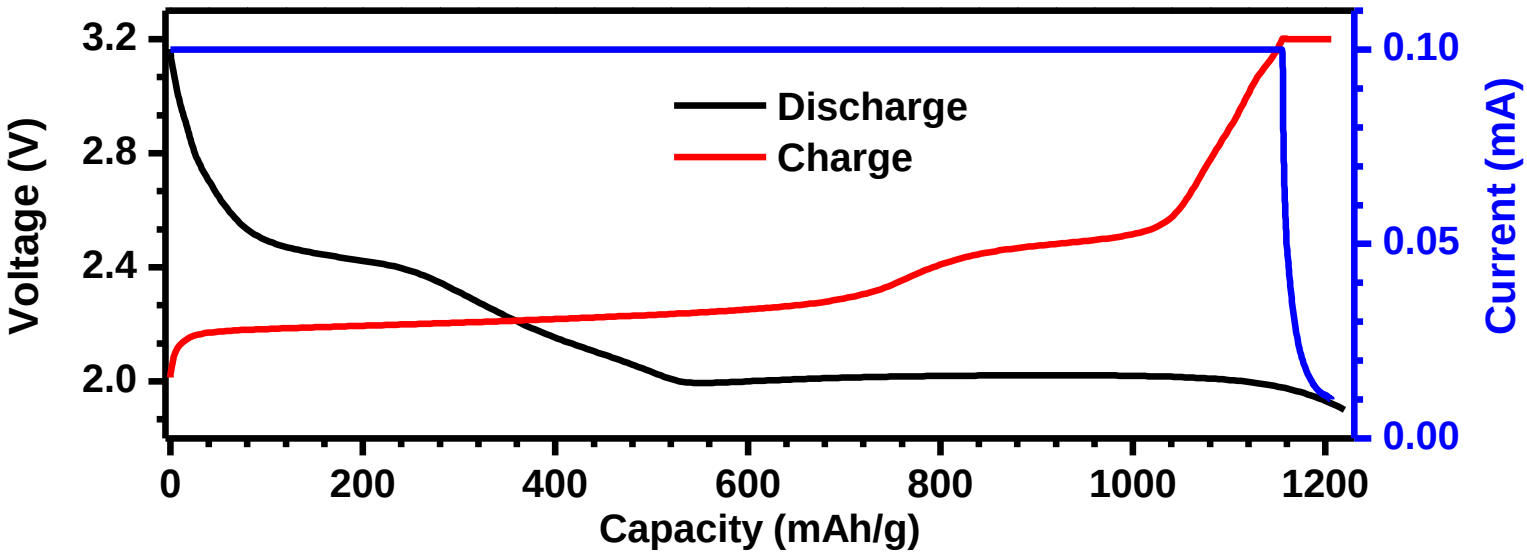
Corrosion of stainless steel parts

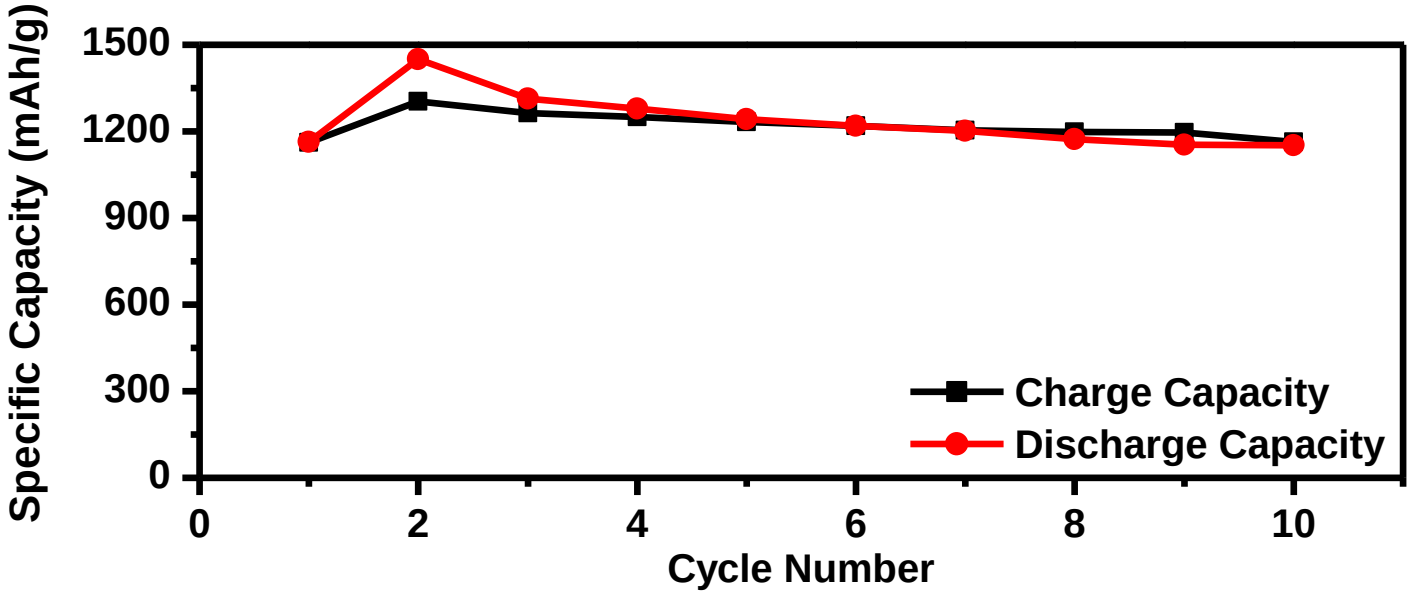


Corrosion of aluminum current collector

Use carbon to replace all metal parts could be the solution.

Novel Electrolyte Additive Addresses the Shuttle Problem





Conclusions

- **Li-S chemistry is promising for next generation of batteries**
  - **High energy density**
  - **Low cost**
  - **Environmental benignity**
- **Advances in material development are essential**
  - **Enhance electronic and ionic conductivities**
  - **Inhibit the migration of sulfur species**
  - **Reverse the formation of Li_2S**
- **Key challenges still remain**
  - **Lithium metal anode could be the limiting electrode**
  - **Improve the compatibility of electrolytes with cell components**

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Acknowledgements

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BES

User Facilities