Advanced Materials for Lithium-Sulfur Batteries

Beyond Lithium-Ion Batteries
Symposium IV

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June 8, 2011

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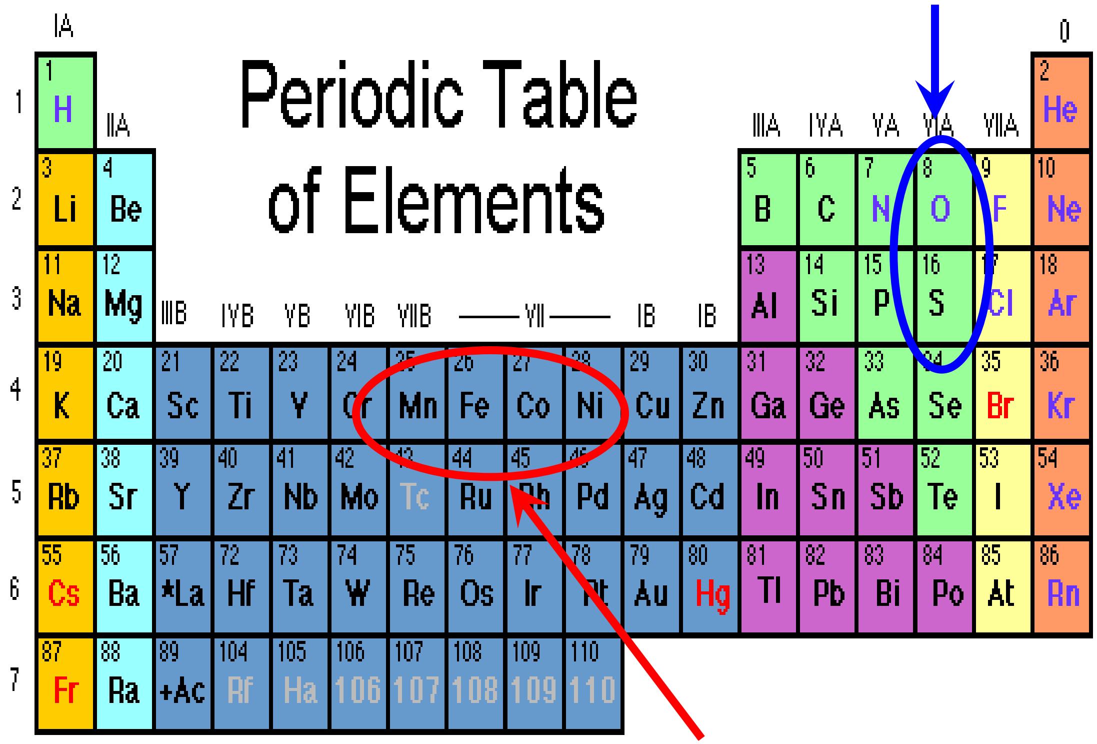
Battery Chemistry: Essential for Innovative Breakthrough for Li-Batteries

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

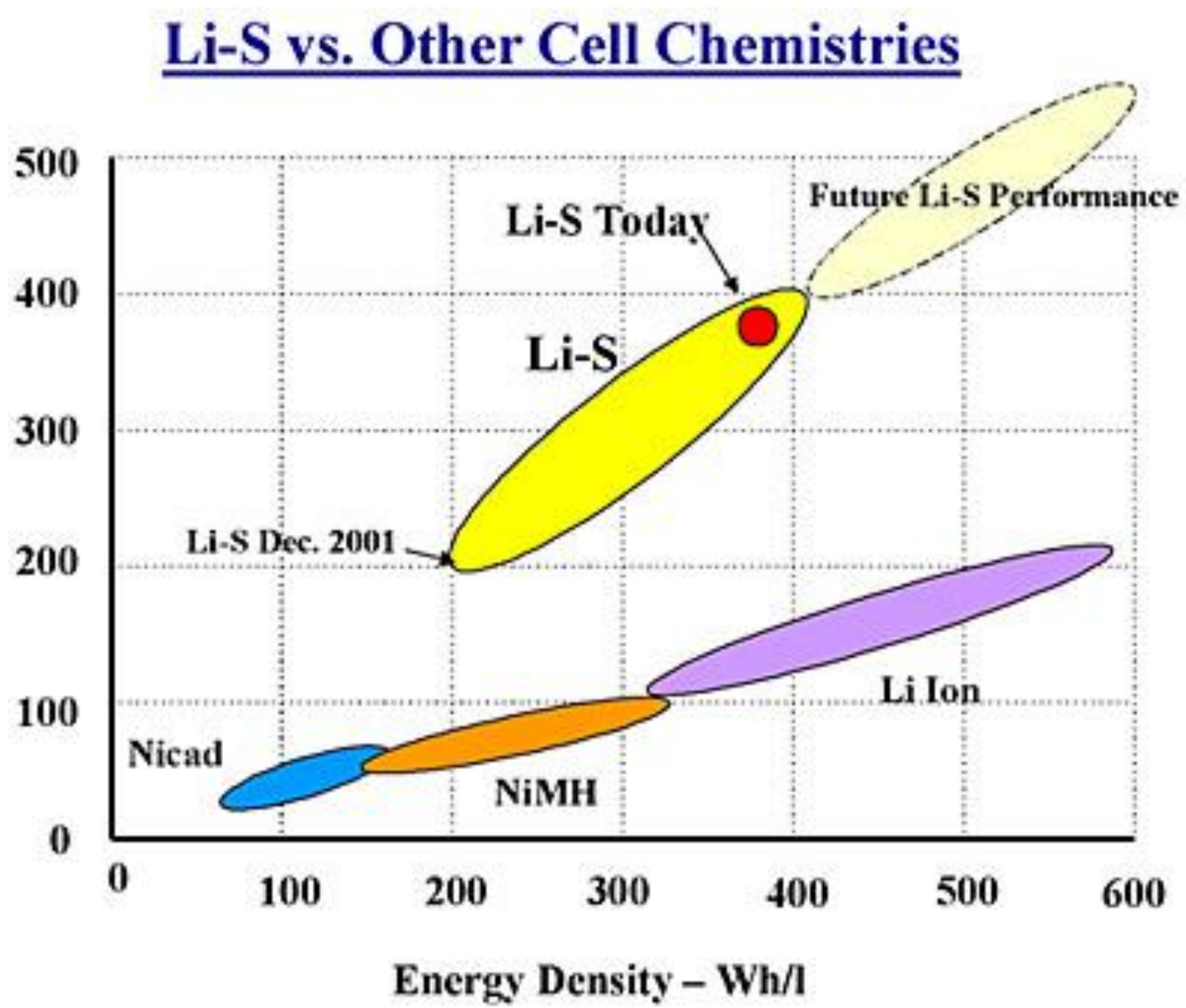


heavy compounds with O, P

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

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



Source: Sion Power

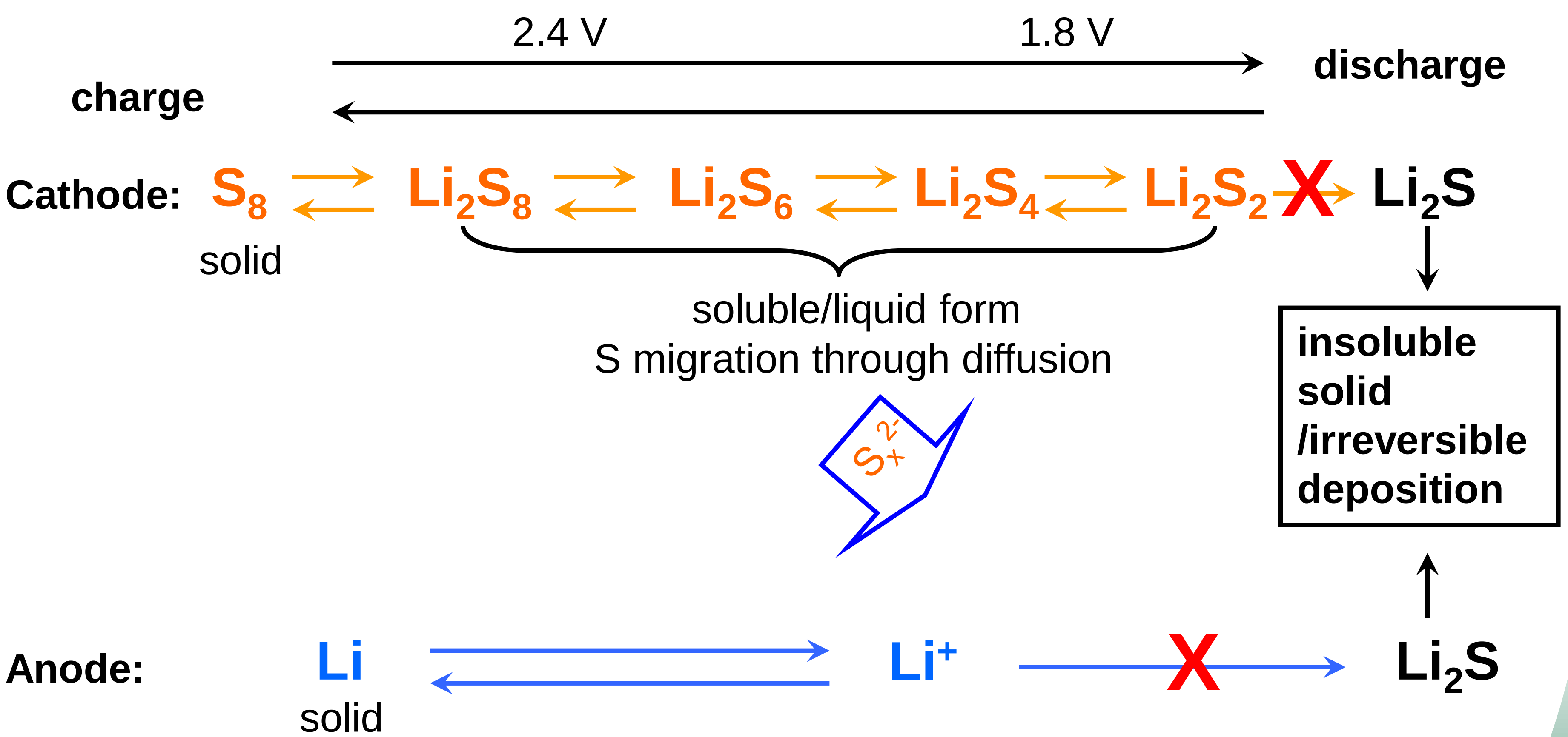
Theoretical Specific Energy

Li/S:
2600 Wh/kg

Features of Li-S

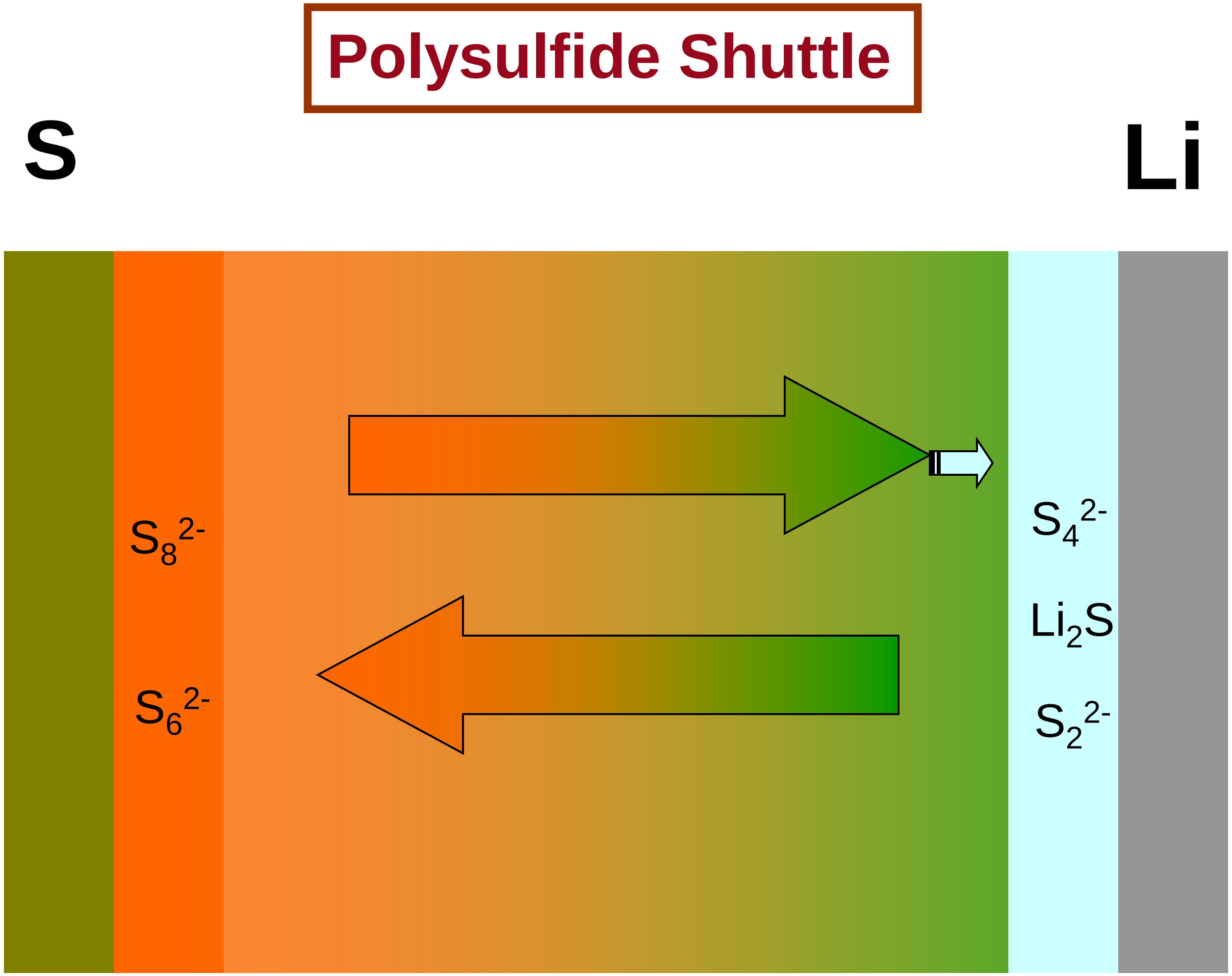
- High Capacity
  - High energy density
- Moderate Voltage
  - Safe
  - Compatibility
- Low Cost
  - High abundance

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?



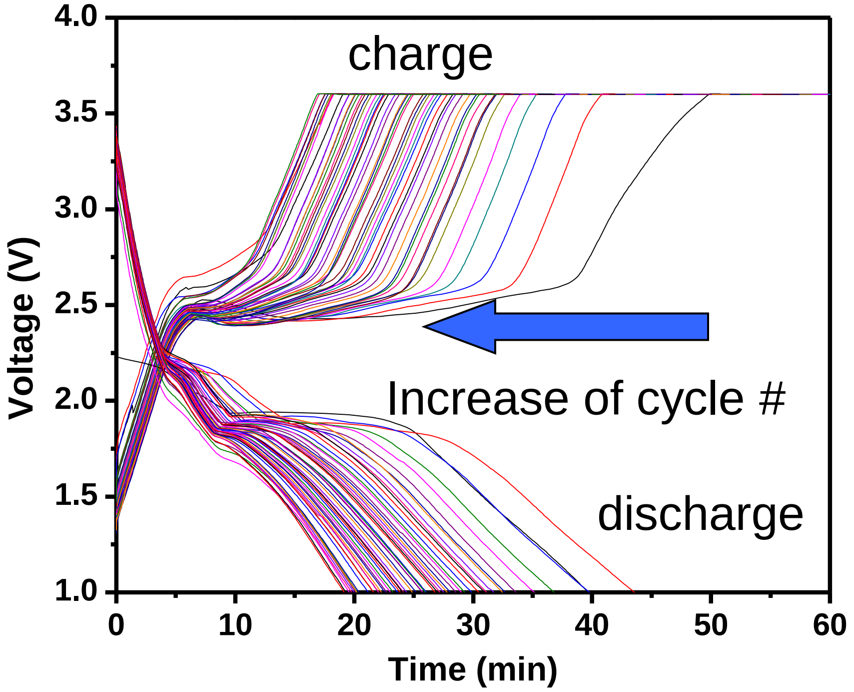
- Self-discharge
- Capacity fading
- Cell resistance increase
- Poor cyclability

- 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

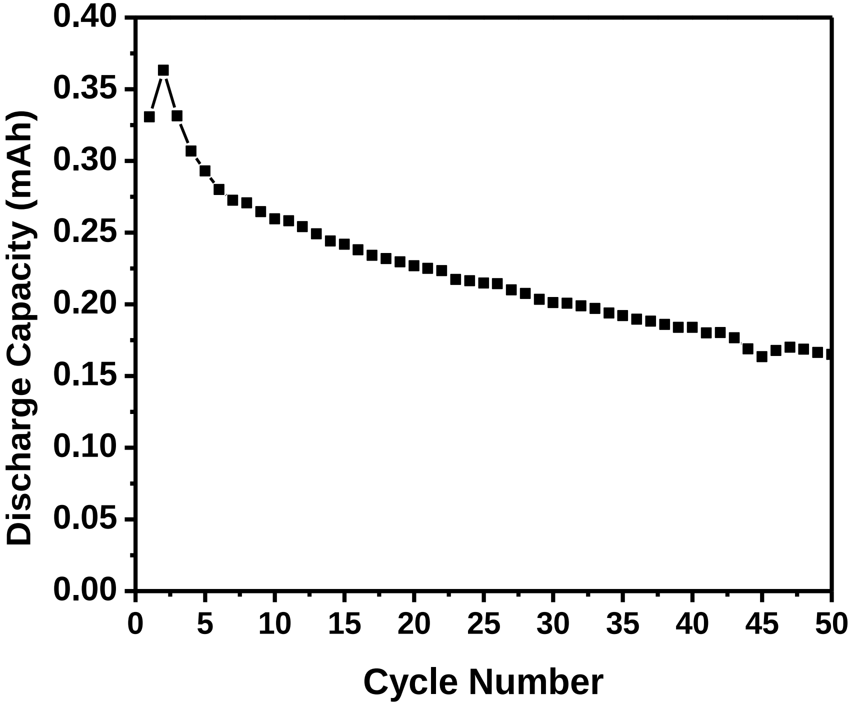
1) Cheon, S. E.; Choi, S. S.; Han, J. S.; Choi, Y. S.; Jung, B. H.; Lim, H. S. *Journal of the Electrochemical Society* 2004, *151*, A2067-A2073. 2)Mikhaylik, Y. V.; Akridge, J. R. *Journal of the Electrochemical Society* 2004, *151*, A1969-A1976.

Li-S Cell Has a Short Cycle-Life.

Charge/discharge curves



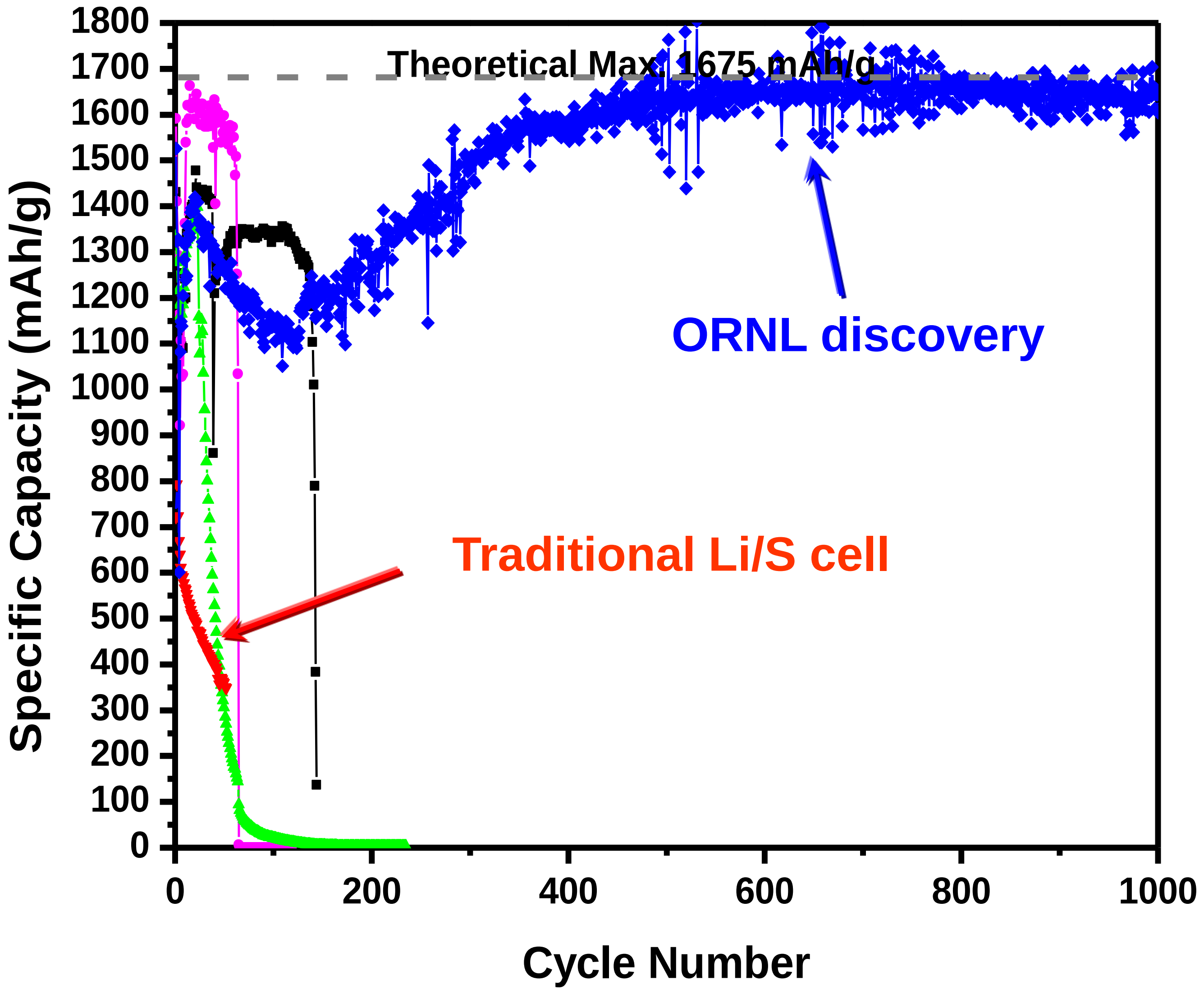
Cycle performance



Detrimental deposition of Li_2S :

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

1000 Cycle-Life is Possible.



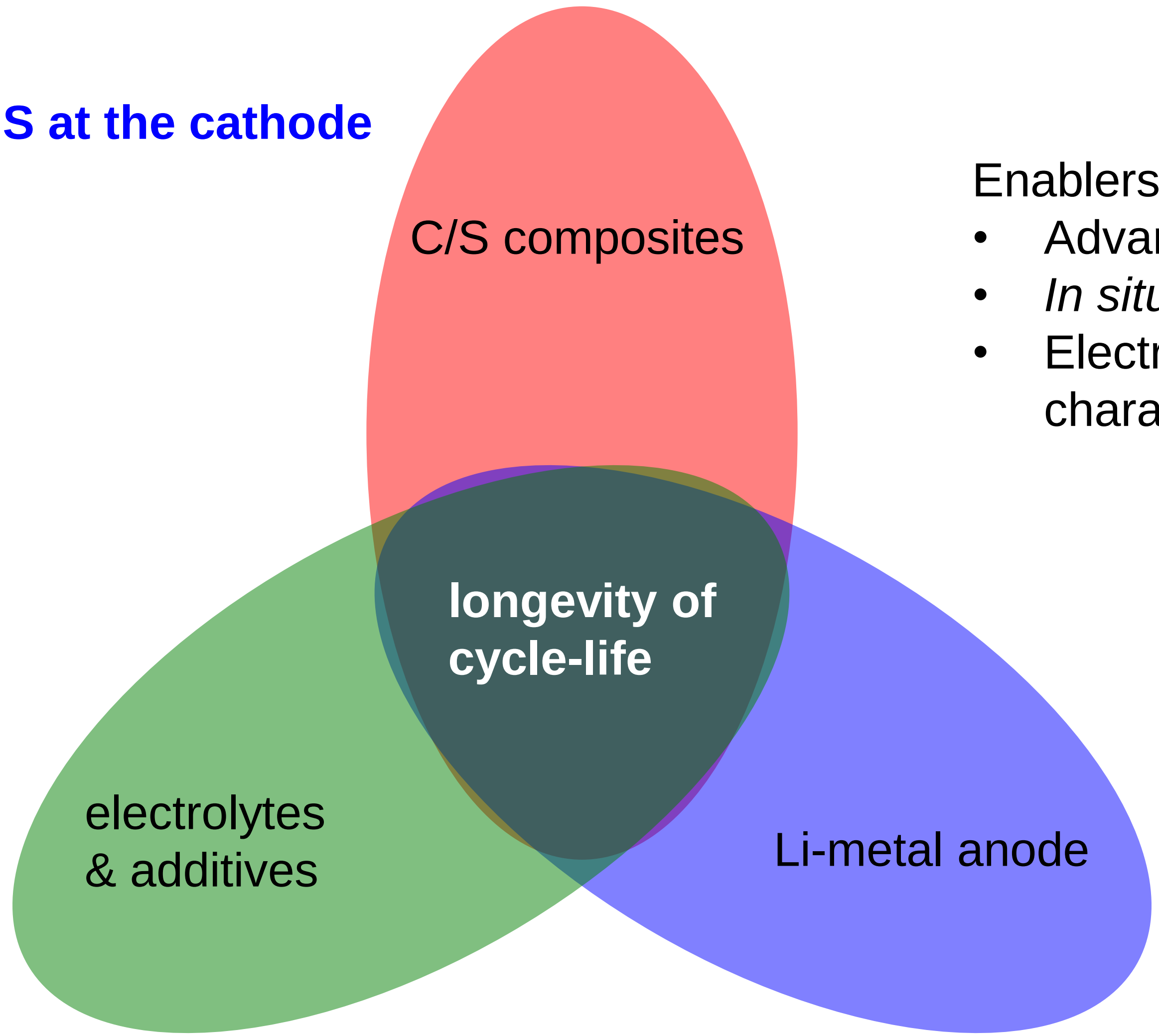
Managed by UT-Battelle
for the Department of Energy

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

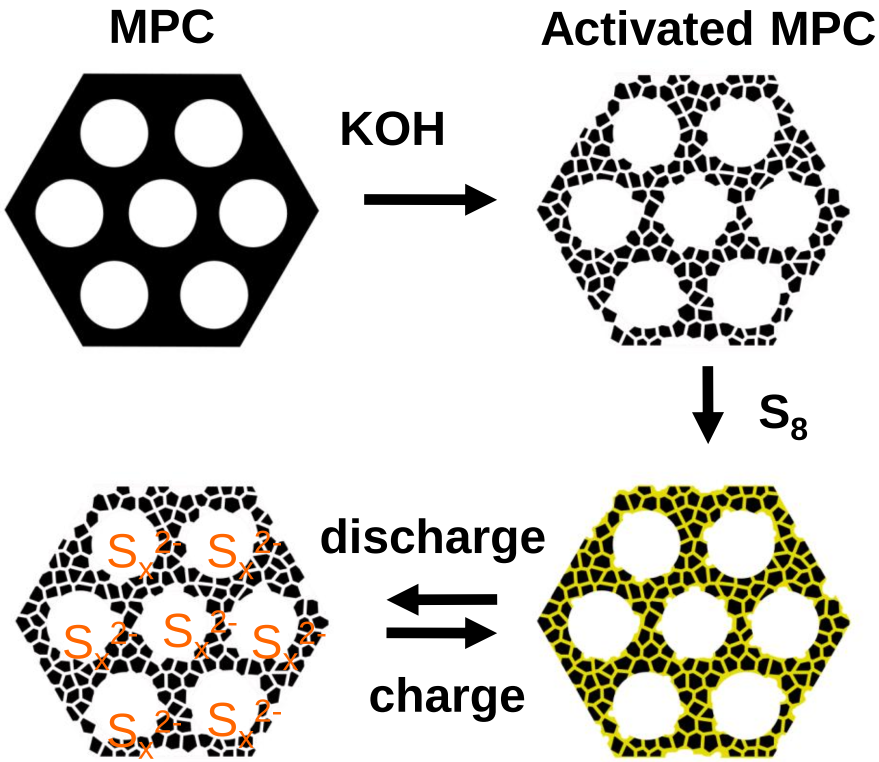


Reverse Li_2S formation

Heal the damaged Li anode

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

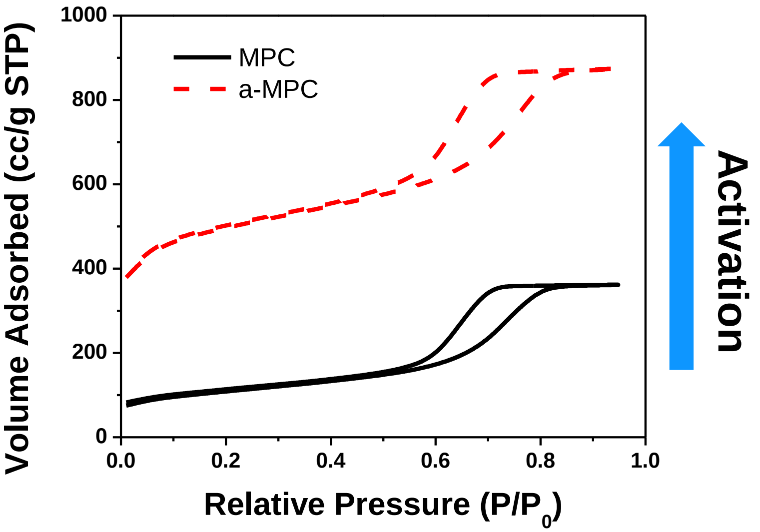


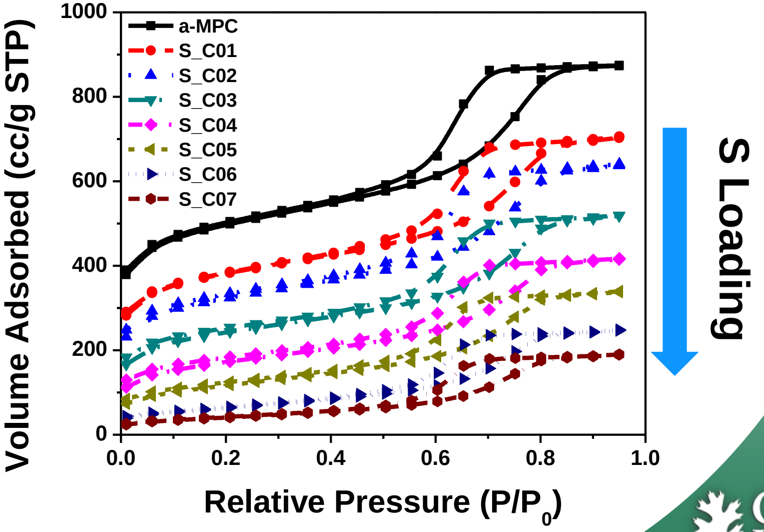
Micropores (<2nm): host sites for S
Mesopores (2-50 nm): path for Li^+ transport

Simple Synthesis Procedure Eases the Preparation.

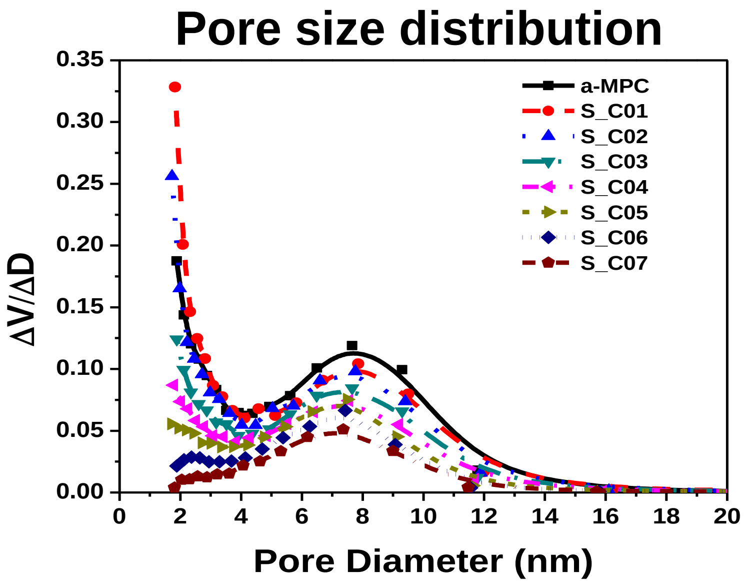
Three-step Synthesis of Carbon/Sulfur Composite

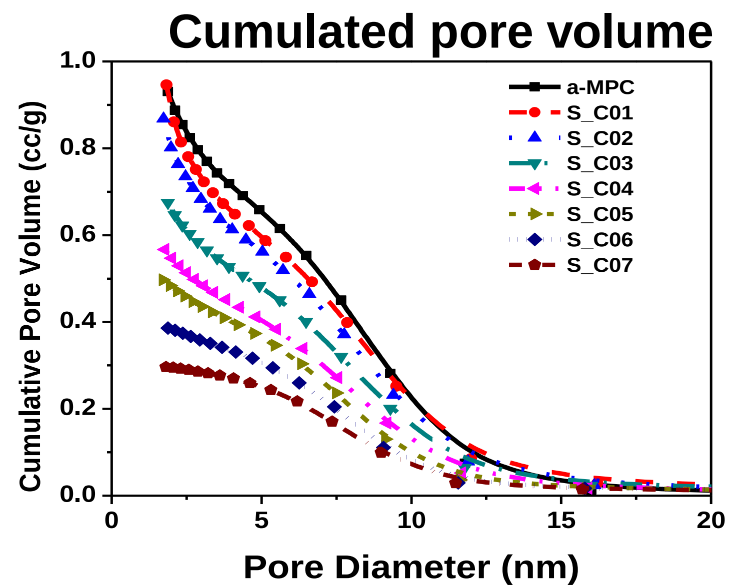
1. Soft-template synthesis of mesoporous carbon
2. KOH activation
3. Sulfur infiltration

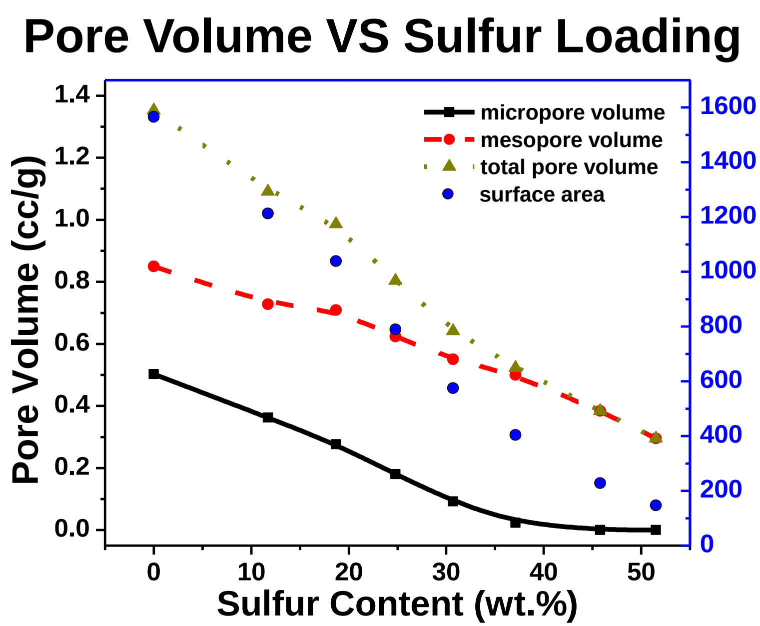




Composite is Tailored with Sulfur Loading.



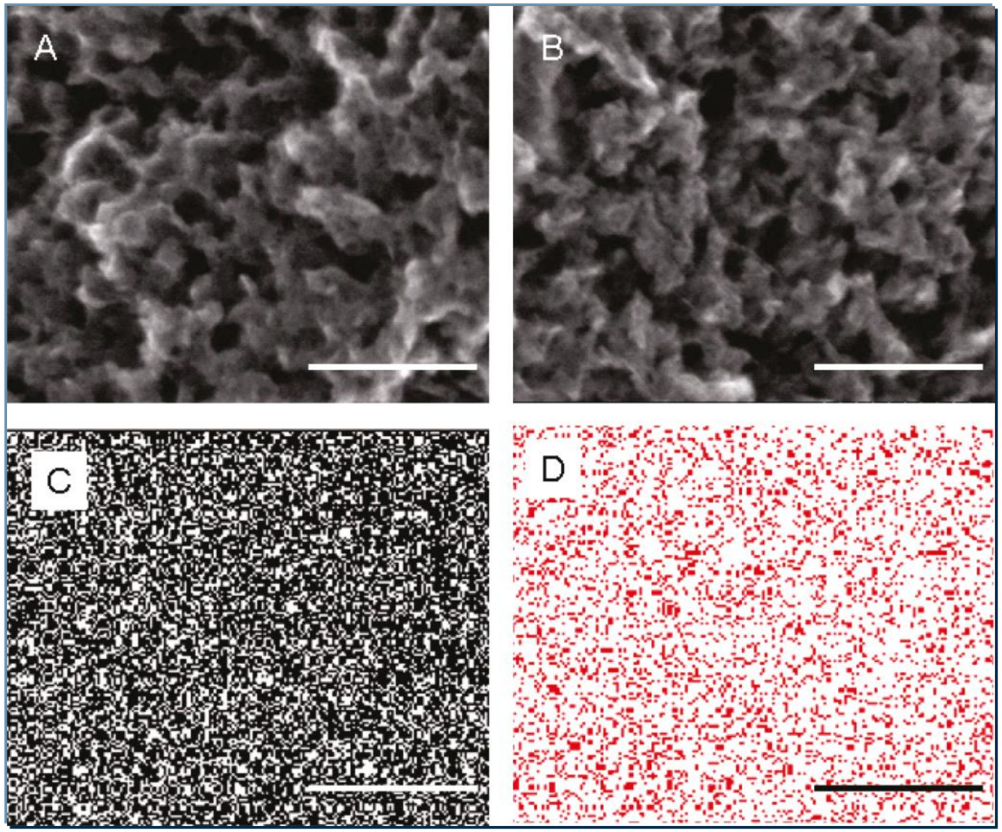




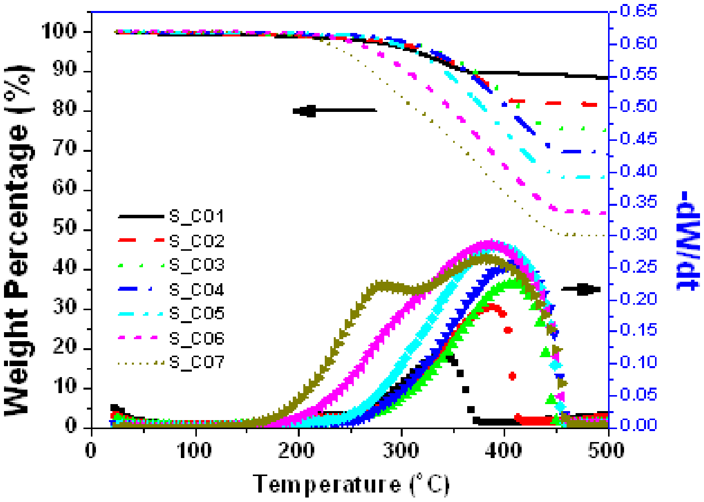
- S preferentially fills the micropores
- Pore Volume is the key parameter for S loading
- Mesopores impart high surface area to the composite

Sulfur Loading is Precisely Positioned.

SEM and Elemental Maps

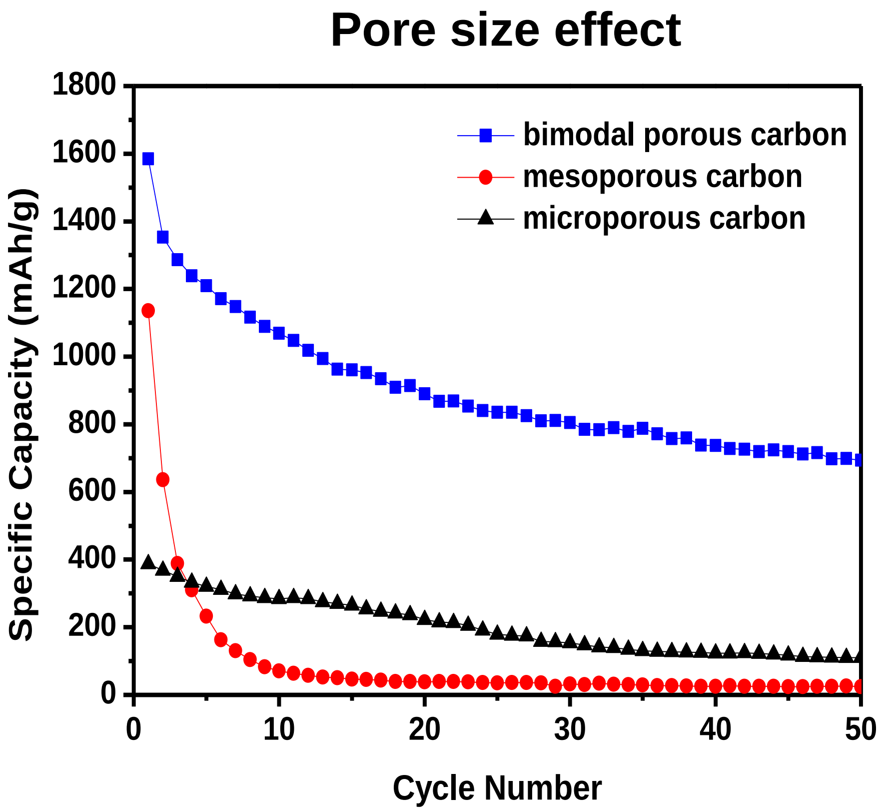


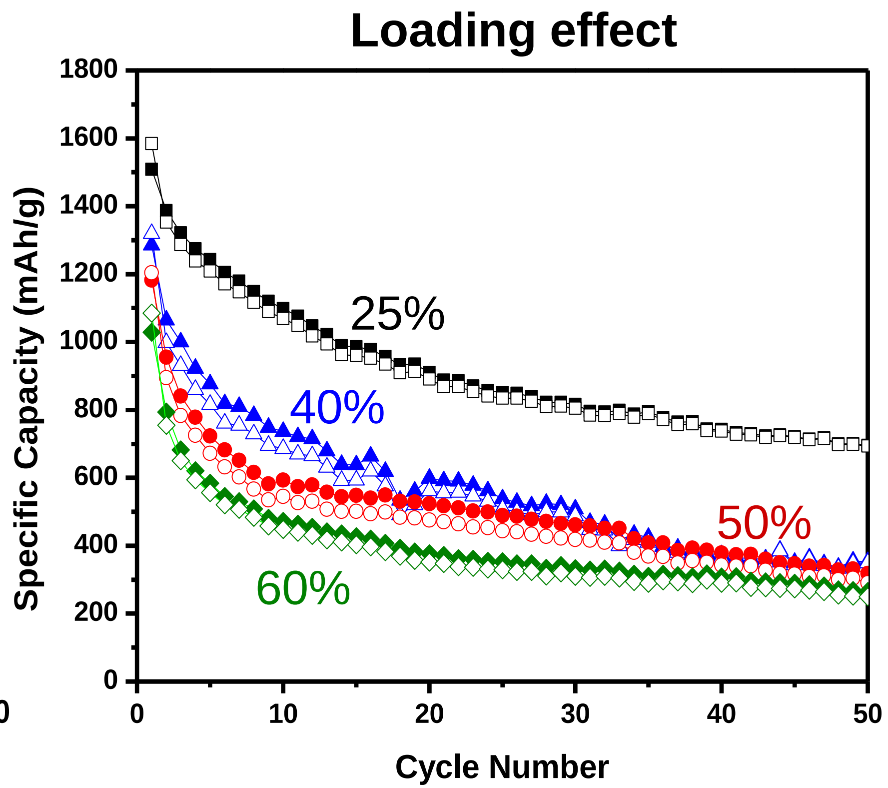
TGA analysis of Sulfur Loading



Elemental S is precisely controlled within the micropores

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



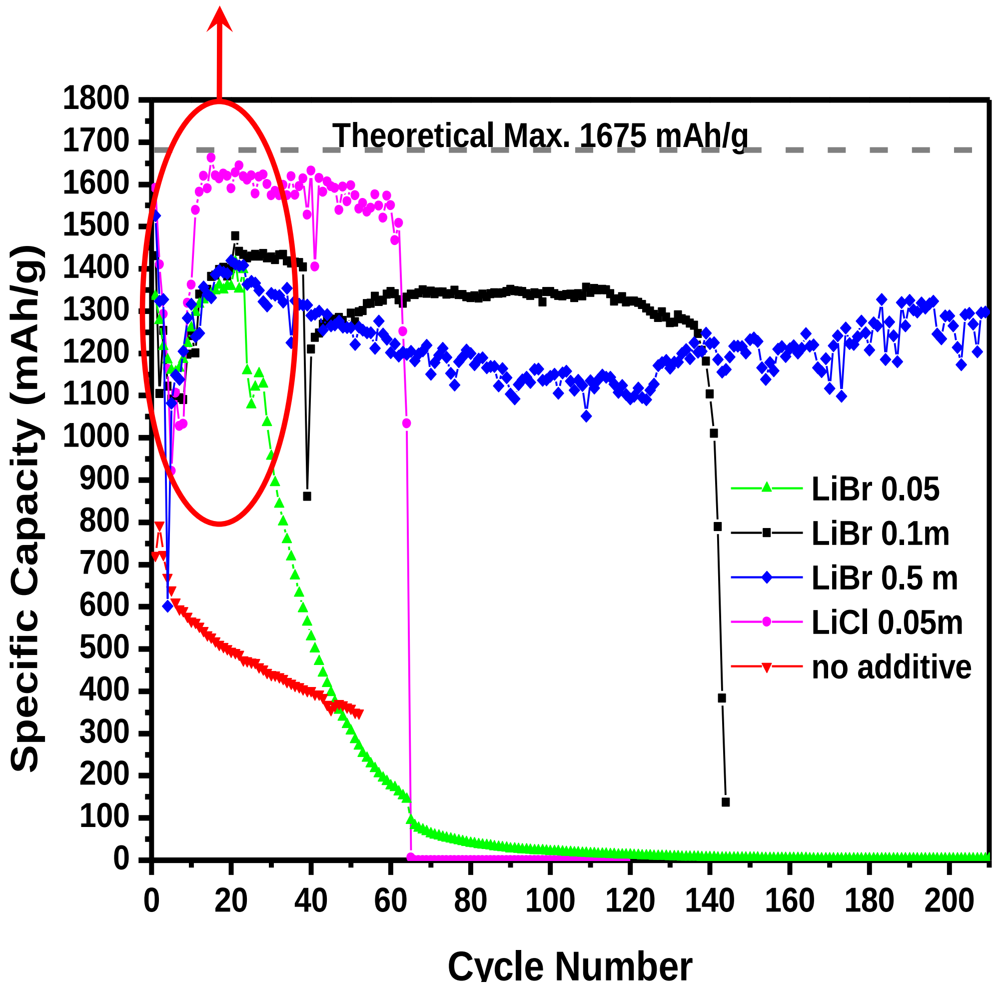


Note: specific capacity is per gram sulfur. Theoretical is 1675 mAh/g.

OAK RIDGE
National Laboratory

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

Polymerization of electrolytes after 10 cycles

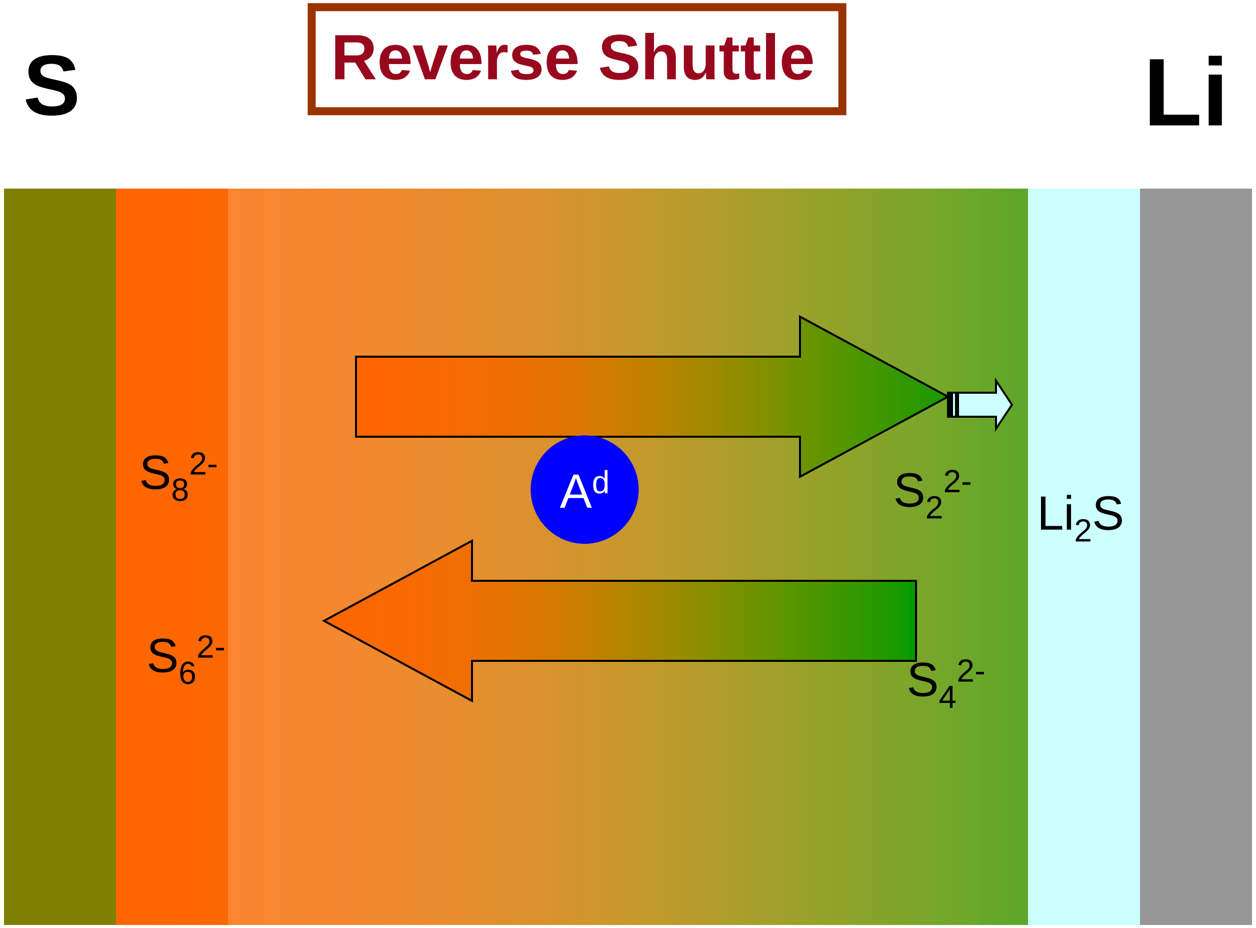


Traditional approach:
Avoid the formation of Li_2S

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

Catalyzed Reversibility of Li_2S Formation Drives S back to Cycling.



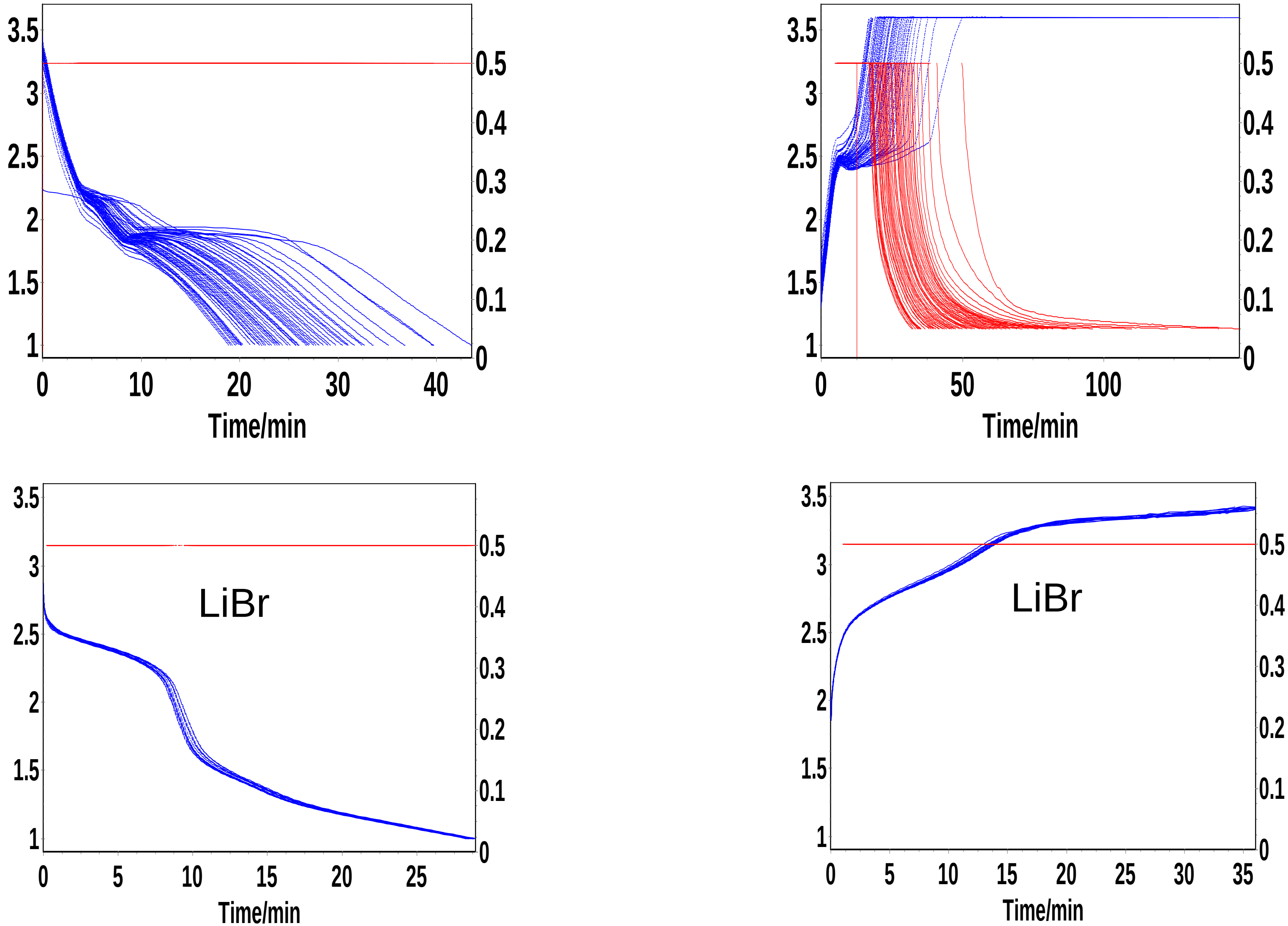
Speculation on how the additives function?

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

LiBr Additive Alters and Stabilizes Shape of Voltage Curves.

Discharge

Charge



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

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

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

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

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

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

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

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

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

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

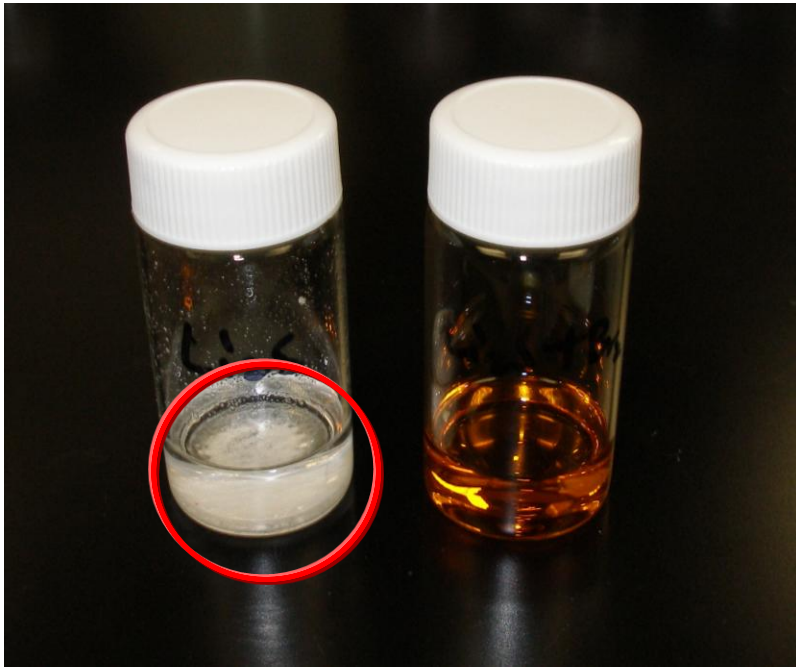
$$BrS_{Lx}^{-} + [Br] \longrightarrow BrS_{Lx}Br + Br^{-}$$

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

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

Additives create additional reactions that reverse the formations of Li_2S.

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:

$LiBr \longrightarrow Br_2$ (cathode) + Li (anode)

Electrochemically generated Br_2 proceeds to the following chemical reaction

Br_2 (liquid) + Li_2S (solid) $\longrightarrow$

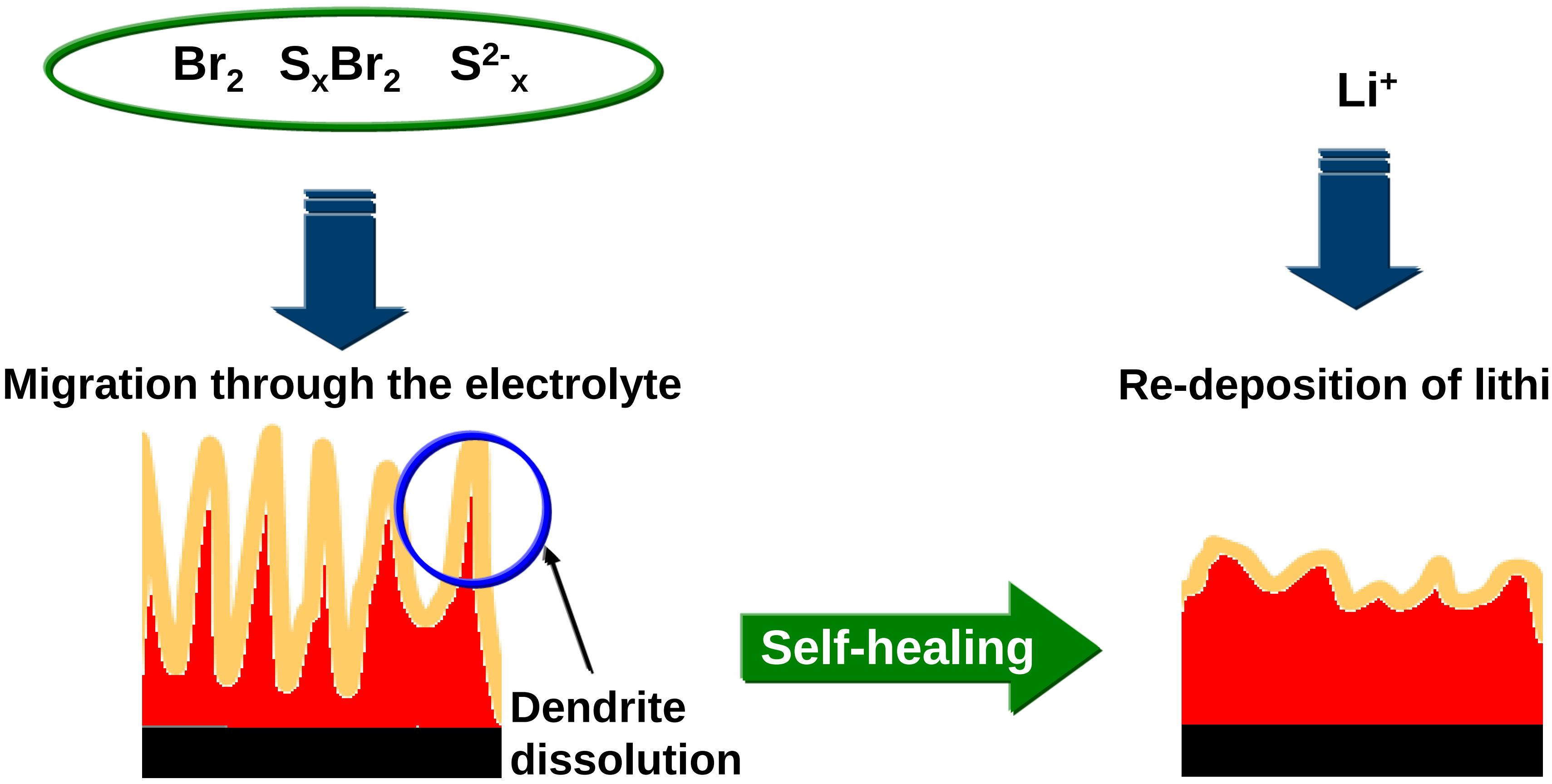
Li_2S_x (solution) + LiBr (solution)

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.

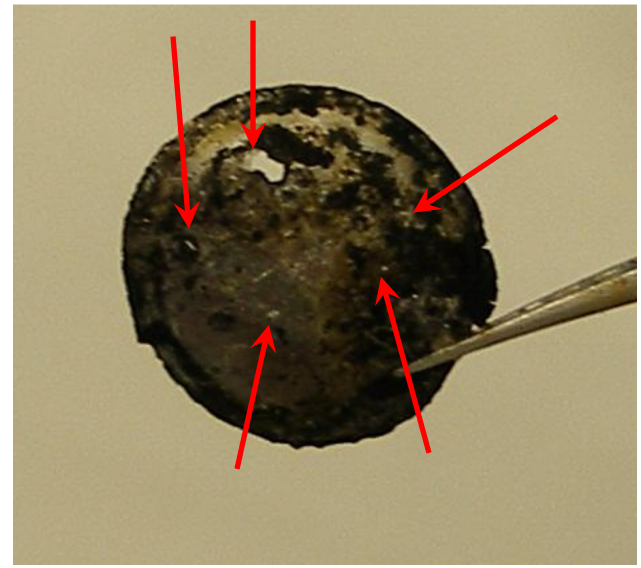
Over charging at the Cathode produces:

Over charging at the anode rebuilds: Thick lithium metal anode



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

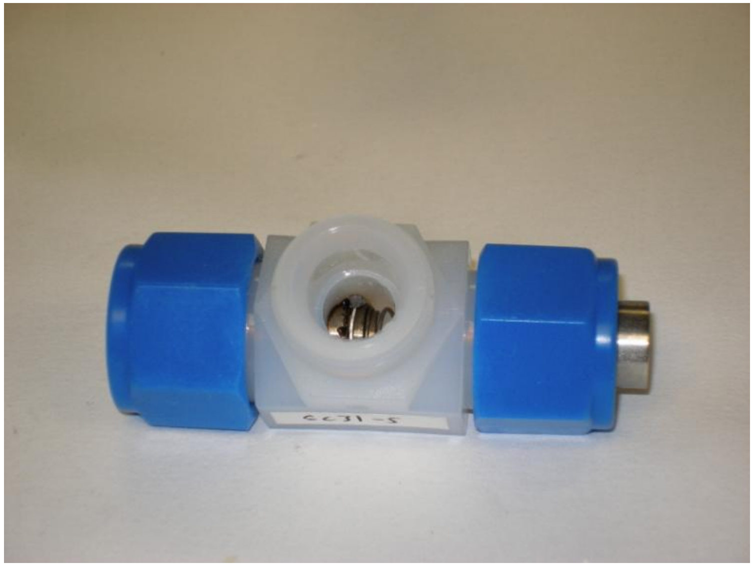
Corrosion of stainless steel parts



Corrosion of aluminum current collector

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

Emerging Concerns of Electrolyte Compatibility Need to be Addressed



Polymerization and the carbonization of electrolyte could cause problems for long-term cyclability .

Need further investigation of electrolyte composition.

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**
  - Block the polysulfide shuttle completely
  - Improve the compatibility of electrolytes with cell components

Acknowledgements

Funding support

Oak Ridge National Laboratory

LDRD

U.S. Department of Energy | Energy Efficiency & Renewable Energy

VT program

U.S. Department of Energy | Office of Science

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