

Carbon/Sulfur Nanocomposites and Additives for High-Energy Lithium Sulfur Batteries

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Overview

- **Timeline**
 - Start June, 2010
- **Technical barriers for EV and PHEV**
 - Low energy density
 - High cost of materials and processing
- **Budget**
 - \$220k FY10
 - \$350k FY11
- **Partners**
 - Oak Ridge National Laboratory
 - Center for Nanophase Materials Sciences, ORNL
 - High Temperature Materials Lab, ORNL
 - In situ SEM

Objectives and Relevance

- **Objectives:**

- Improve the utilization of sulfur active material by creating intimate contact of insulating sulfur with electronic conductors
- Prolong the cycle-life of Li-S batteries based on C-S nanocomposites via retaining the S at the cathode through adsorption
- Explore electrolyte compositions to facilitate the reversibility of Li_2S formation

- **Relevance:**

- Addresses the low energy density and cost barriers for EV and PHEV batteries by enabling the Li-S battery technology

Milestones

Milestones:

Target:

-
- | | |
|---|-------------|
| 1. Confirm the earlier observation of long cycle life in half cells and expand the synthesis of sulfur/carbon composite materials of various sulfur loading | Sep, 2010 ✓ |
| 2. Compare the performance for different concentrations of additives to the electrolyte | Jan, 2011 ✓ |
| 3. Investigate additives to the cathode, including catalysts and alternative sulfur compounds | Sep, 2011 |
| 4. Design new liquid electrolytes, considering both poor/good solvents for Li polysulfides | Sep, 2011 |

Approach to improve performance is three-fold.

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

Retain S at the cathode

C/S composites

Enablers:

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

longevity of
cycle-life

electrolytes
& additives

Li-metal anode

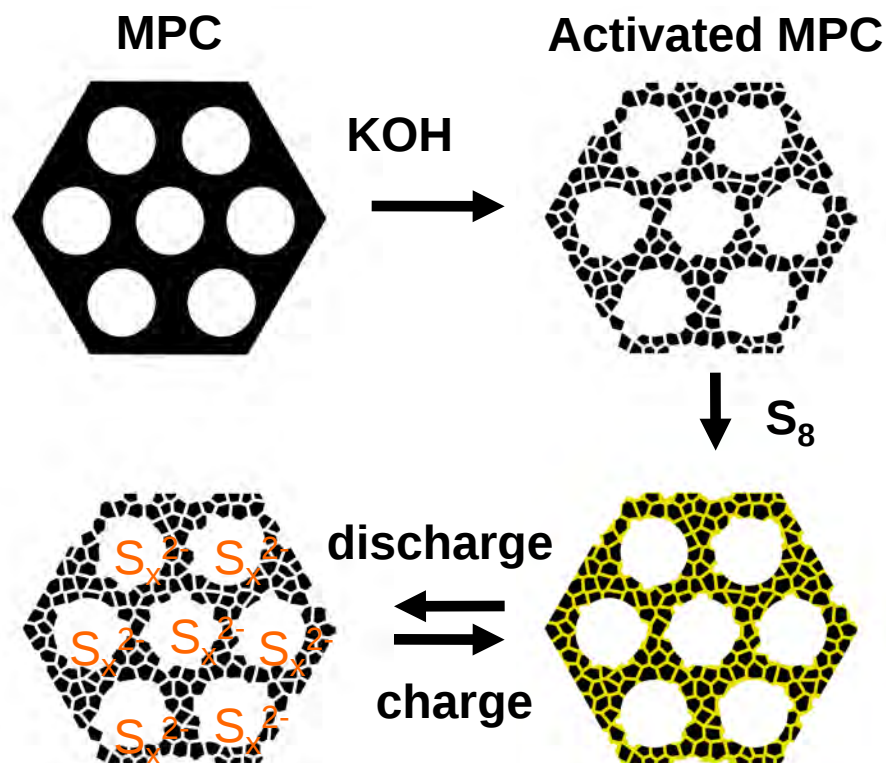
Reverse Li_2S formation

Heal the damaged Li anode

Technical Progress – next 11 slides. Activated templated carbon gives well controlled porosity for sulfur host.

- **C/S composites by using bimodal porous carbon**

- Physical confinement of S in $< 2\text{nm}$ pores
- Electronic contact of S
- Adsorption of polysulfides



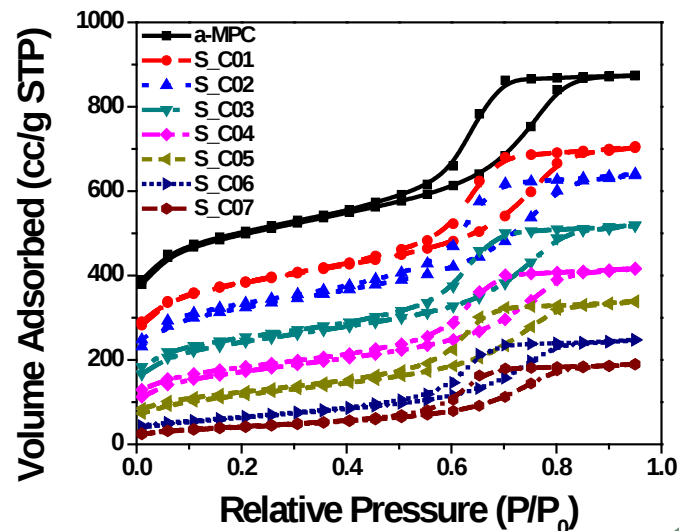
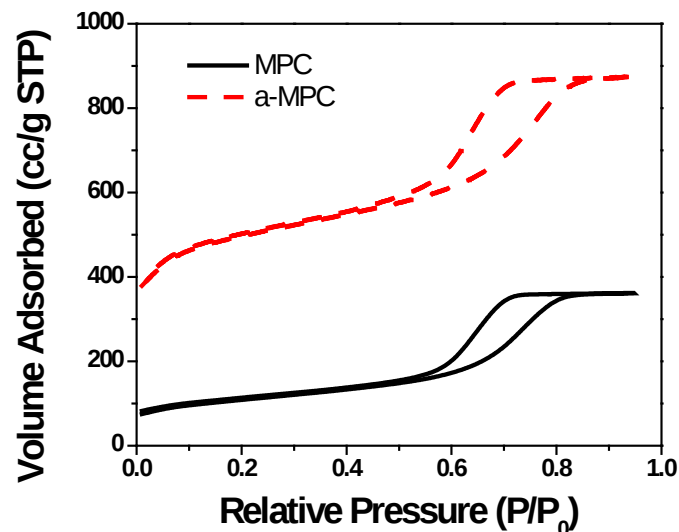
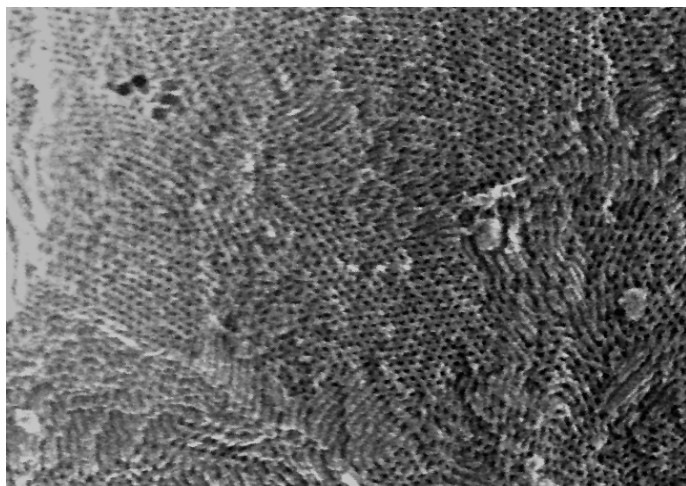
Micropores ($< 2\text{nm}$): host site for S

Mesopores (2-50 nm): path for Li⁺ transport

Sulfur fills microporosity of the templated carbon. Loading can be adjusted.

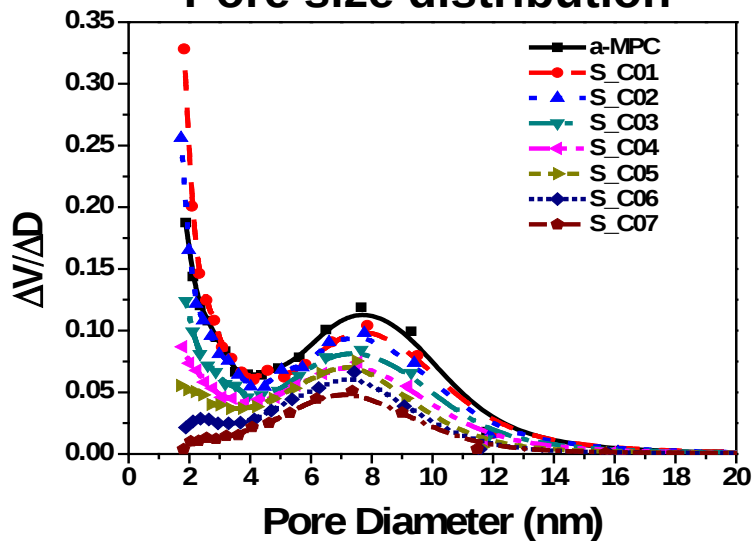
Three-step Synthesis of Carbon/Sulfur Composite

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

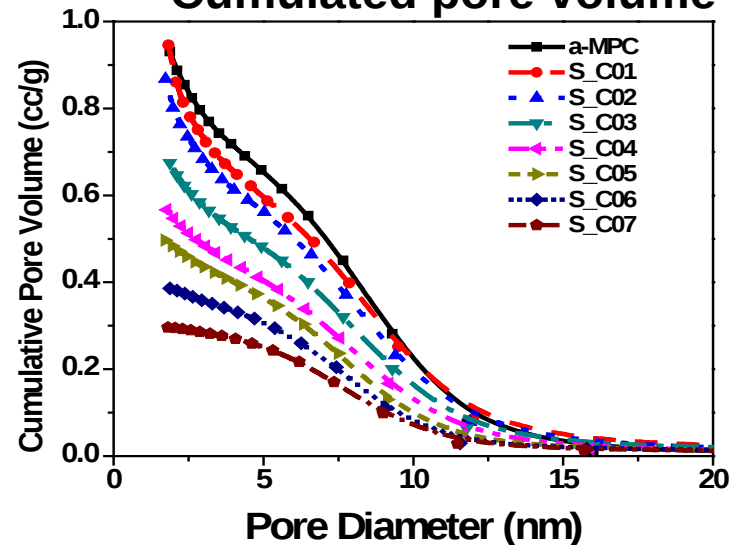


Composite is tailored with sulfur loading.

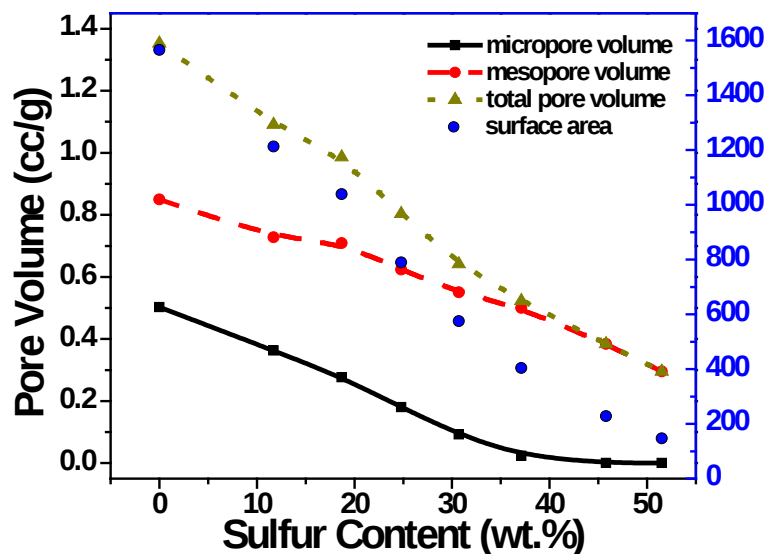
Pore size distribution



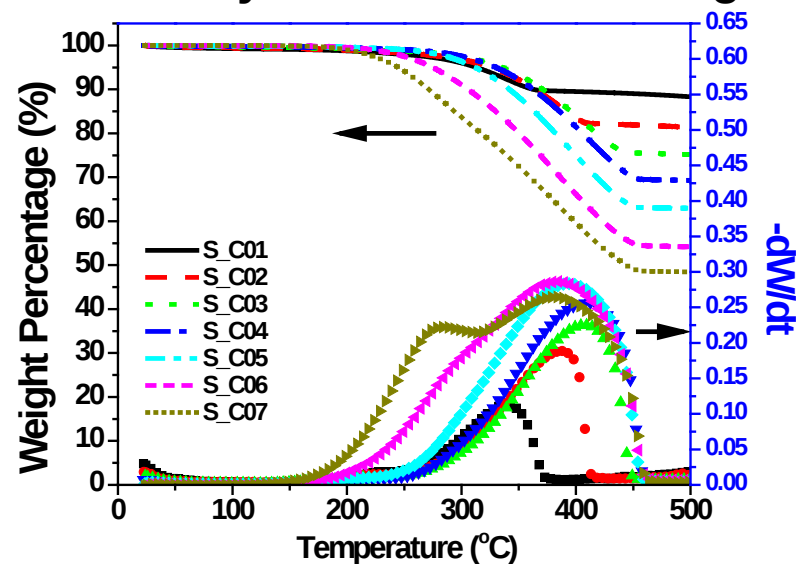
Cumulated pore volume



Pore Volume VS Sulfur Loading

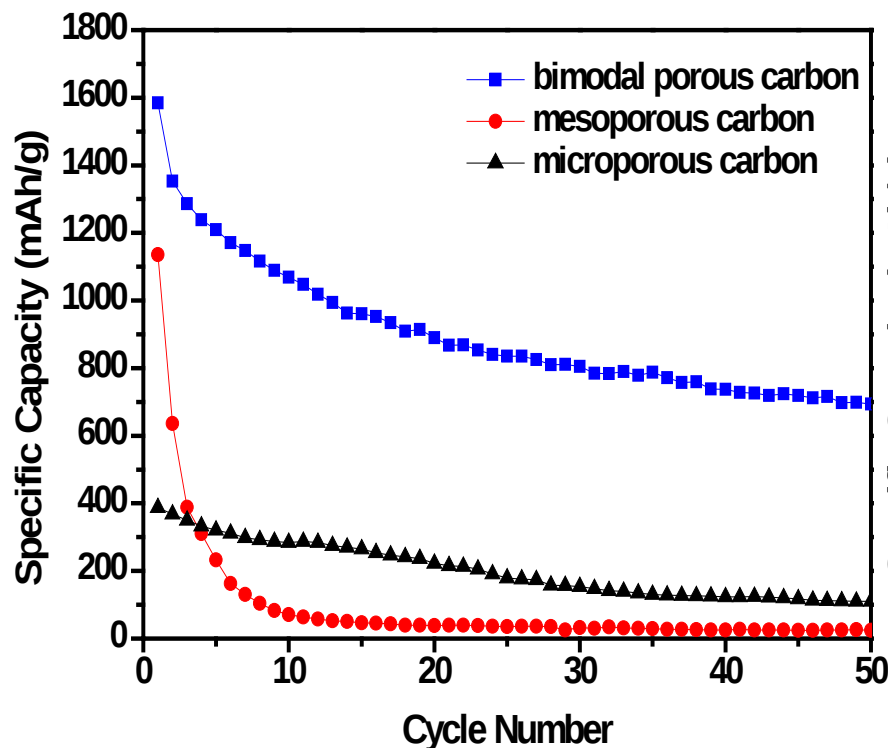


TGA analysis of Sulfur Loading

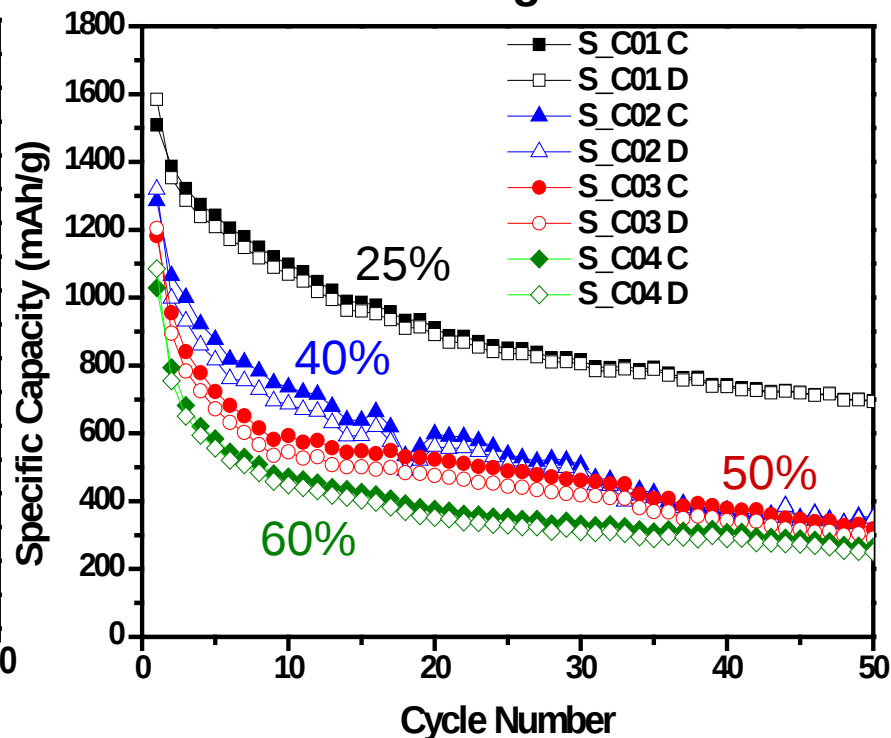


Cycling performance (without electrolytes additives) is greatly improved by nano-engineered carbon host which retains sulfur.

Pore size effect



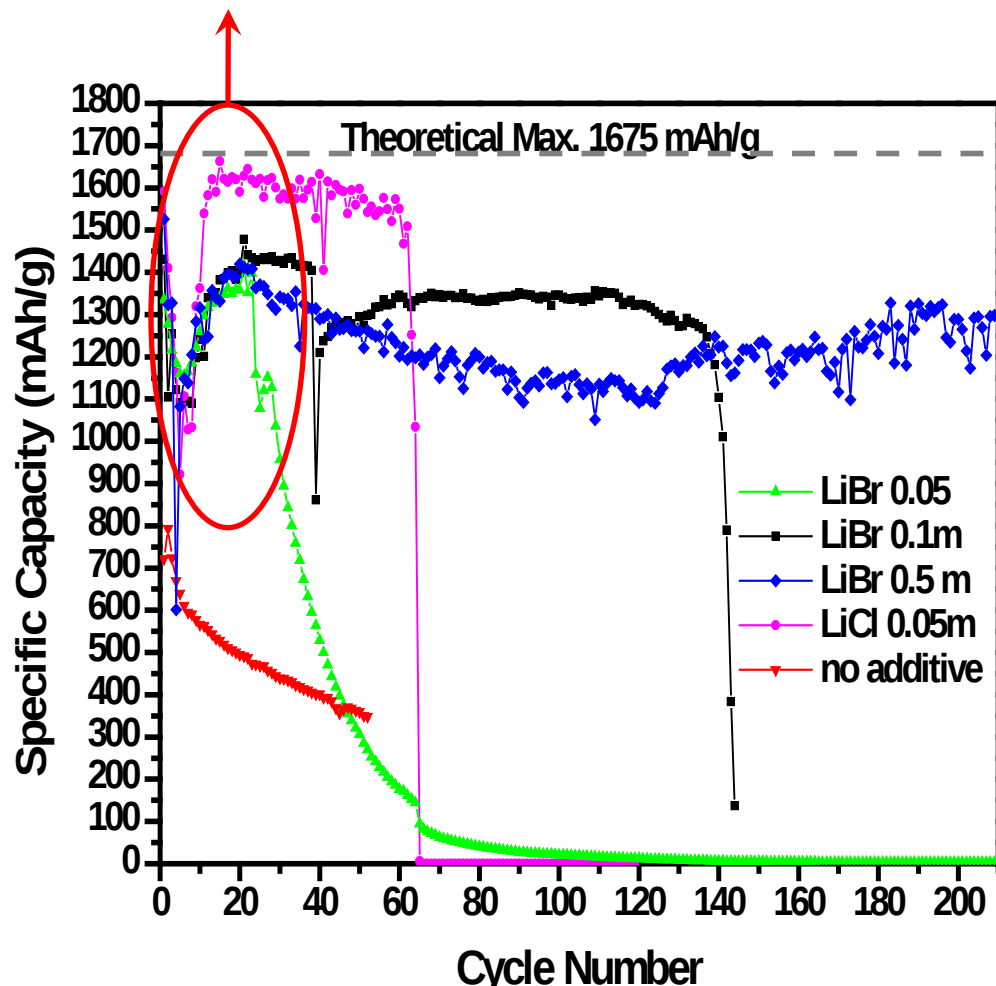
Loading effect



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

Electrolyte additives can reverse Li_2S formation, improving cycle life of Li/S half-cells.

Polymerization of electrolytes after 10 cycles



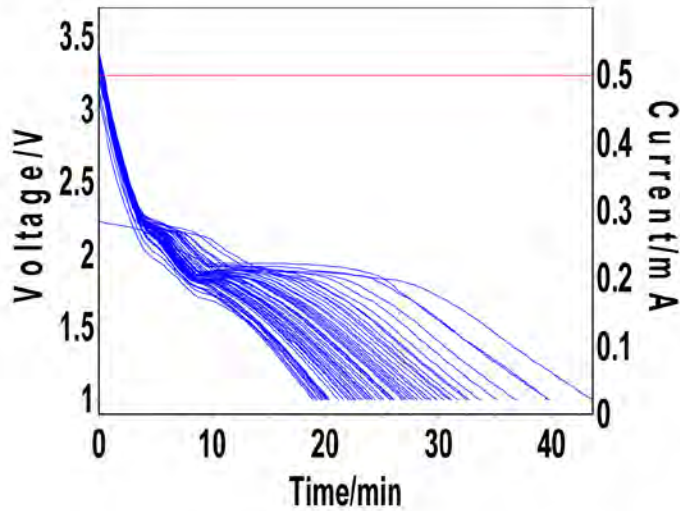
Traditional approach:
Avoid the formation of Li_2S

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

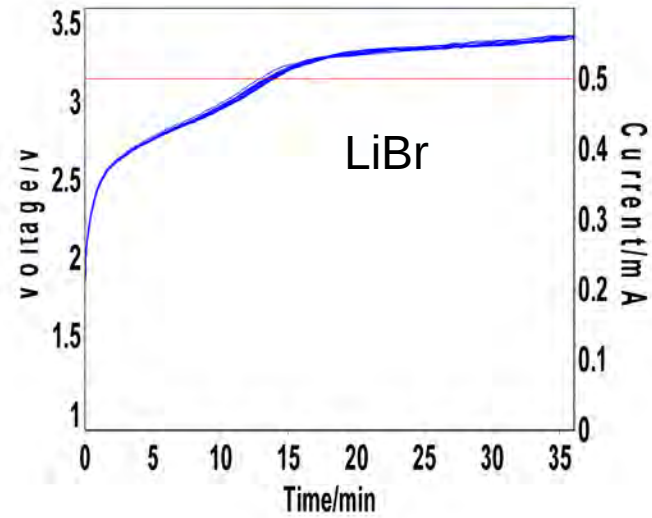
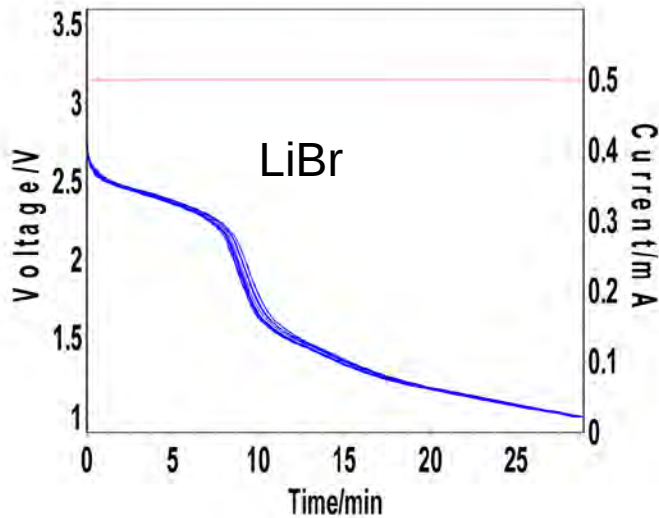
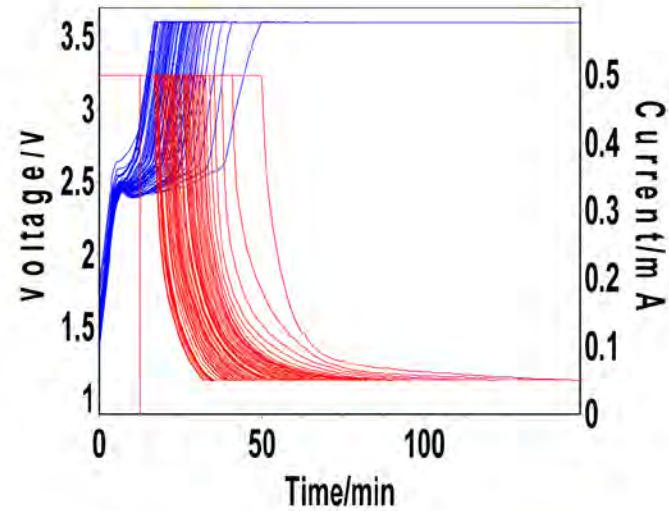
- Additives improve the reversibility of Li_2S formation
- The polymerization of the electrolytes plays an important role on the cyclability of Li-S cells

LiBr additive alters and stabilizes shape of voltage curves.

Discharge

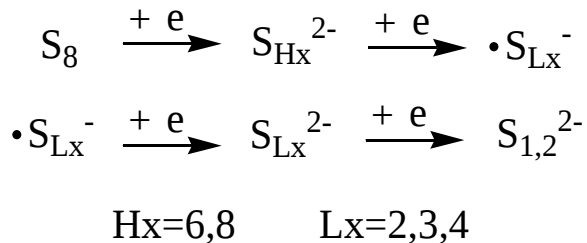


Charge

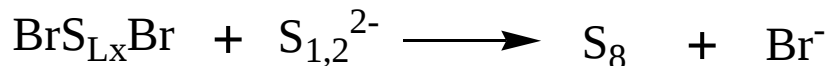
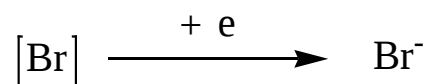
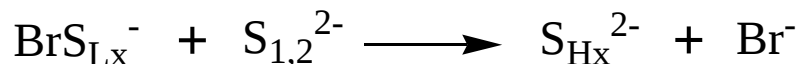
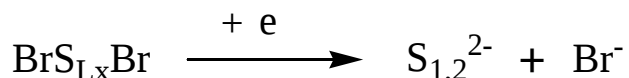
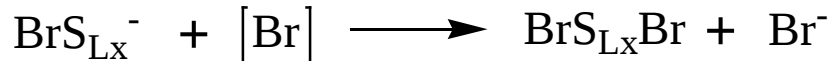
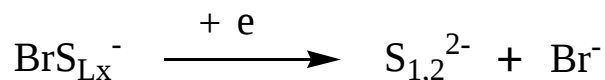
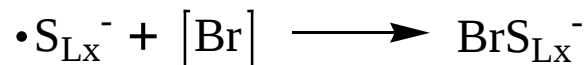
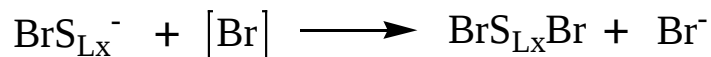
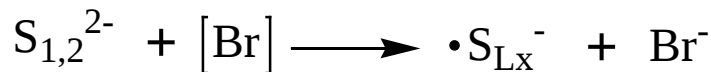
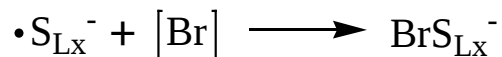
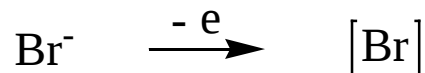
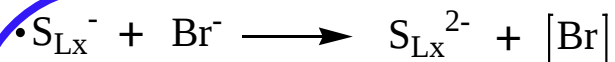
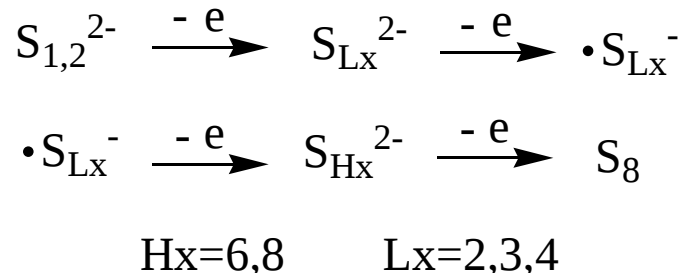


Possible mechanism for reverse shuttle reaction.

Discharging



Charging



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

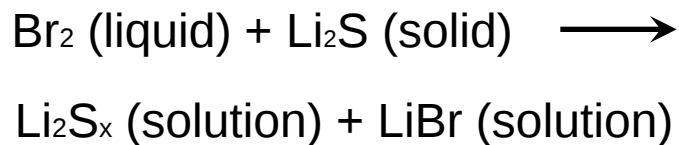


Images of Li_2S in organic solvents:
Left, without Br_2 ; right, with Br_2

In the charging cycle:

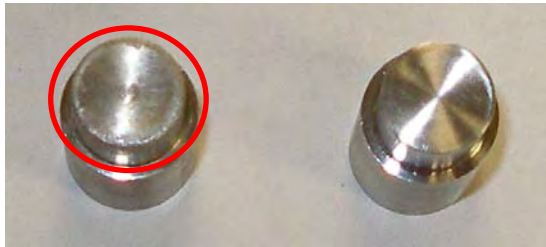


Electrochemically generated Br_2 proceeds to the following chemical reaction



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

A major drawback of LiBr additive is severe corrosion of cell parts.



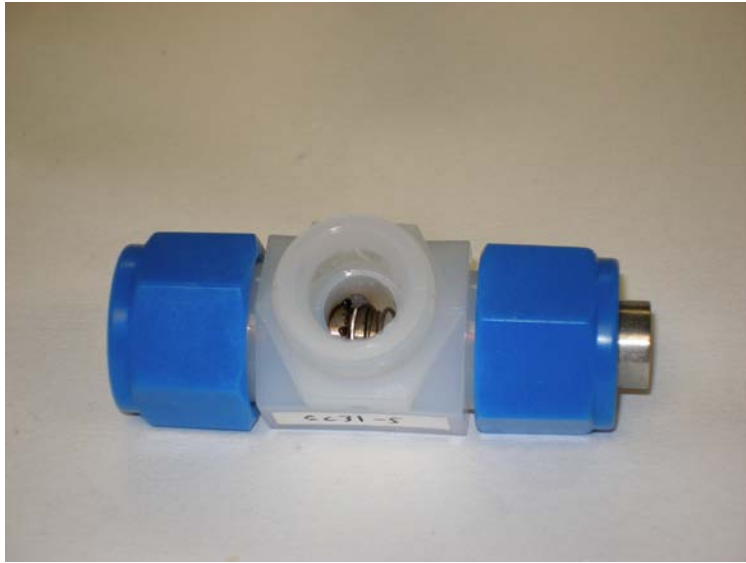
Corrosion of stainless steel parts



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.

Future work

- **Explore other electrolyte additives and compositions to catalyze the reversible formation of Li_2S**
- **Optimize the carbon/sulfur composites to retain sulfur at the cathode**
- **Develop a mechanism to heal the damaged Li metal anode**
- **Seek alternative solutions for stable anode in the Li/S system**

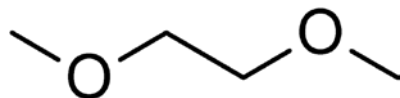
Summary

- **Relevance:** Enabling Li-S battery chemistry has the potential to improve the energy density and reduce the material cost for EV and PHEV batteries
- **Approach:**
 - carbon-sulfur nano-composites retain sulfur during the battery cycling while imparting a high electronic conductivity to the insulating sulfur.
 - electrolyte additives improve the cyclability of Li-S batteries via a new reverse shuttle mechanism
- **Accomplishment and progress:**
 - Synthesis of hierarchically porous carbon for composite electrode
 - Carbon-sulfur composites with various sulfur loading and cycling
 - Electrolyte additives reverse the formation of Li_2S
 - Corrosion issues with electrolyte additives have been identified
- **Future work:**
 - Optimize the carbon-sulfur composites for good utilization and long cycle life
 - Explore battery chemistry for less corrosive electrolyte additives
 - Investigate possible anode materials that match the sulfur cathode

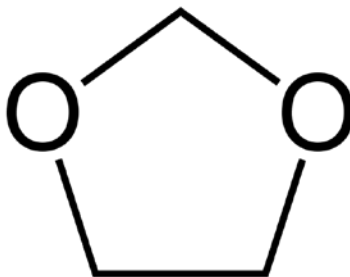
Technical Back-Up slides

Solvents

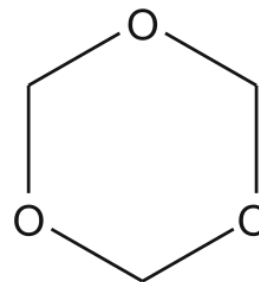
solvents



Dimethoxyethane (DME)

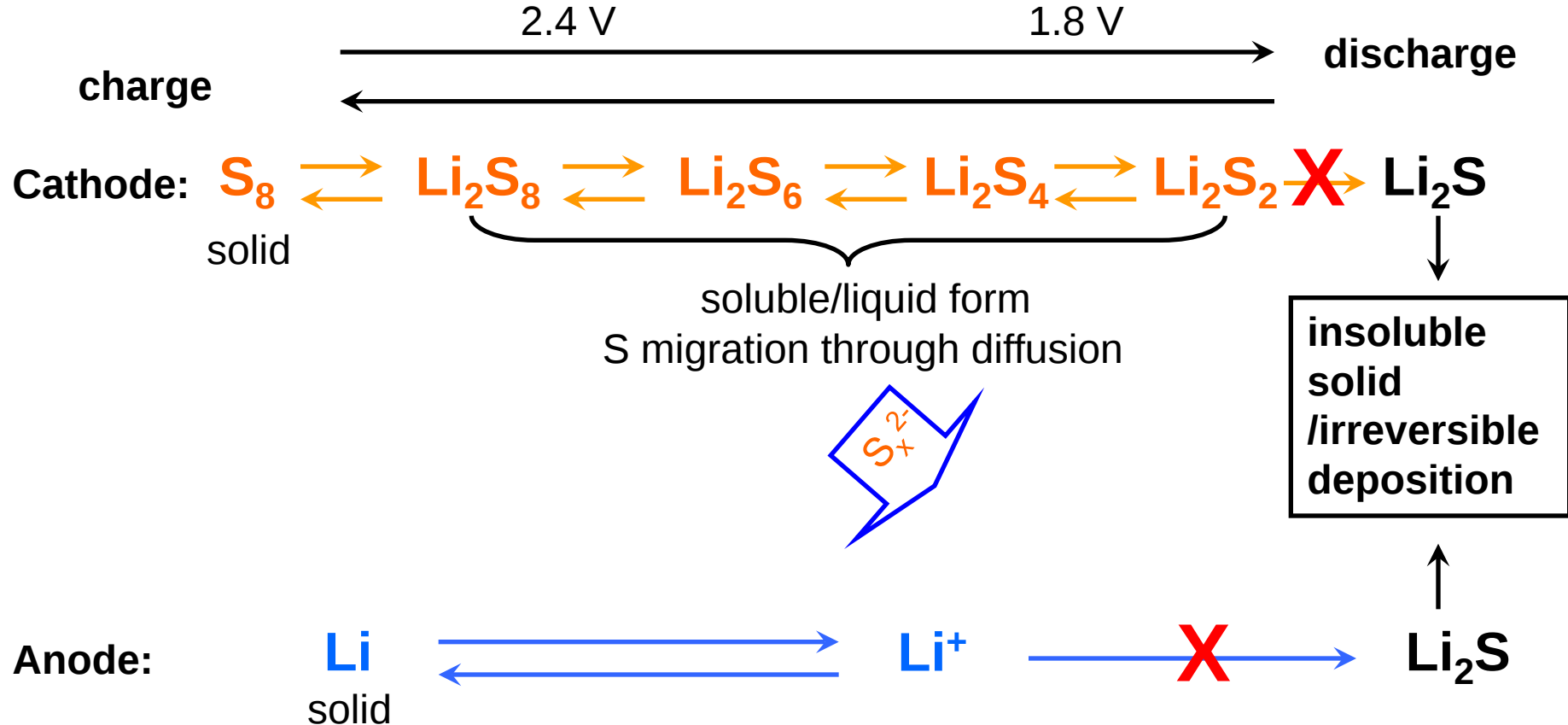


1,3-dioxolane (DOL)



Trioxane

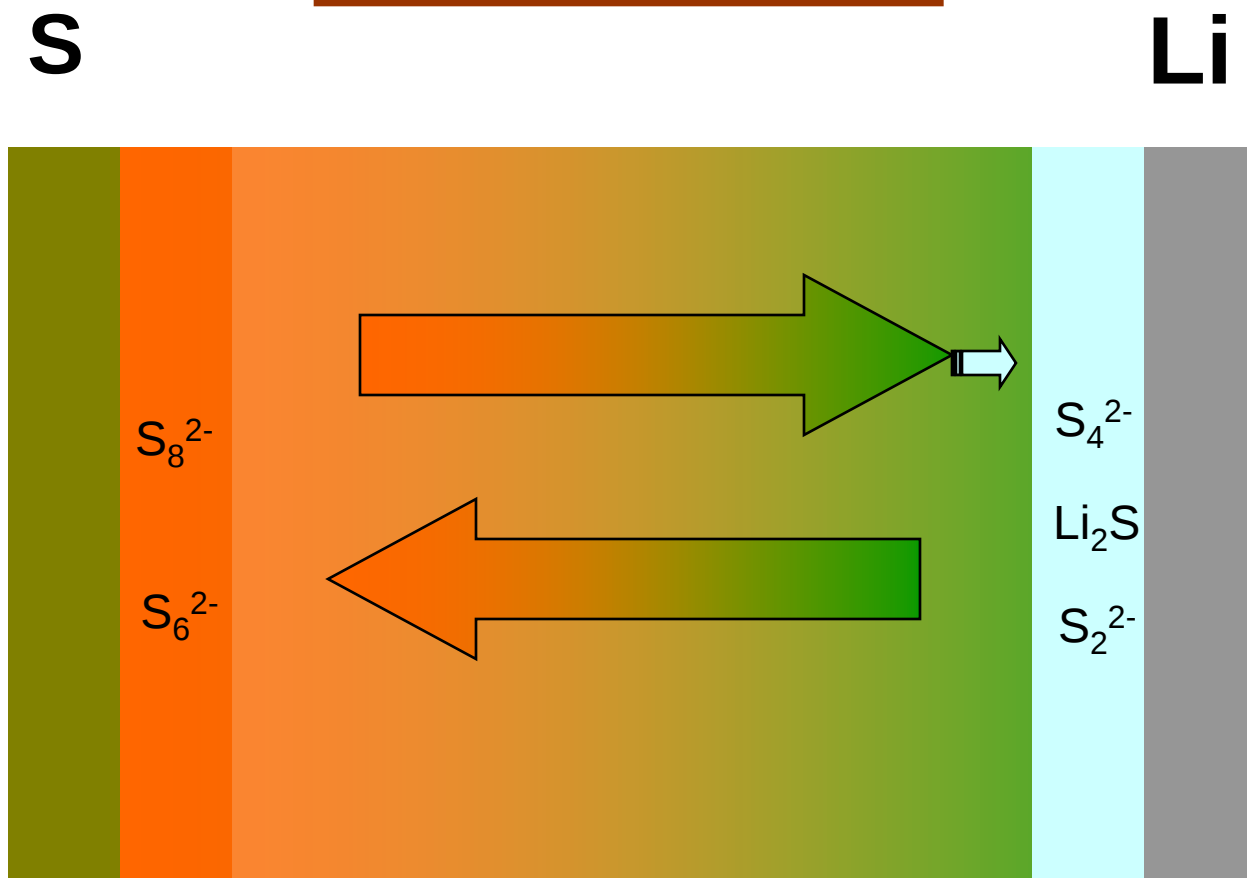
Challenges for Li-S Battery



- 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 can't 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

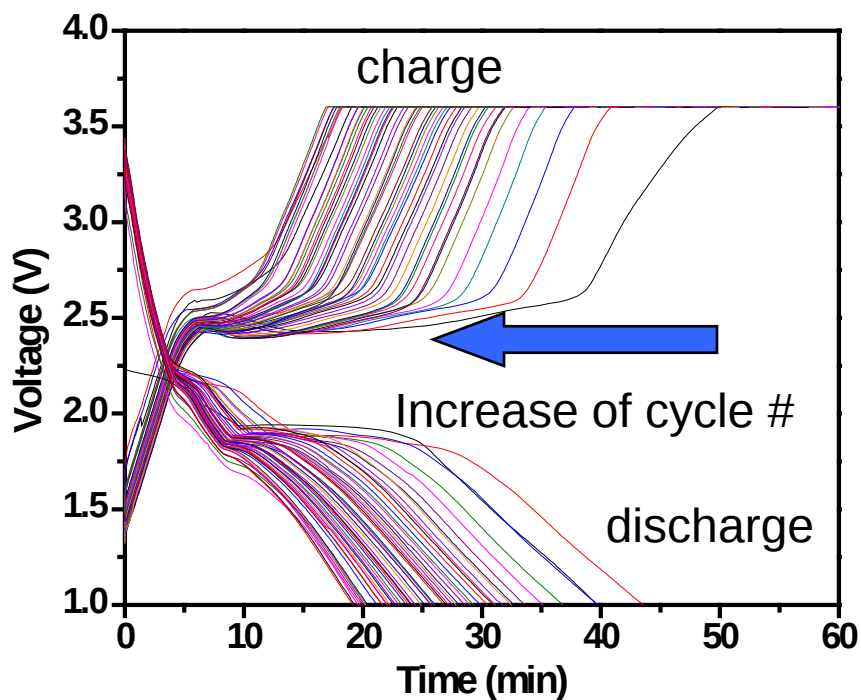
- Chemically immobilize S

- S-polymers
- S-salts

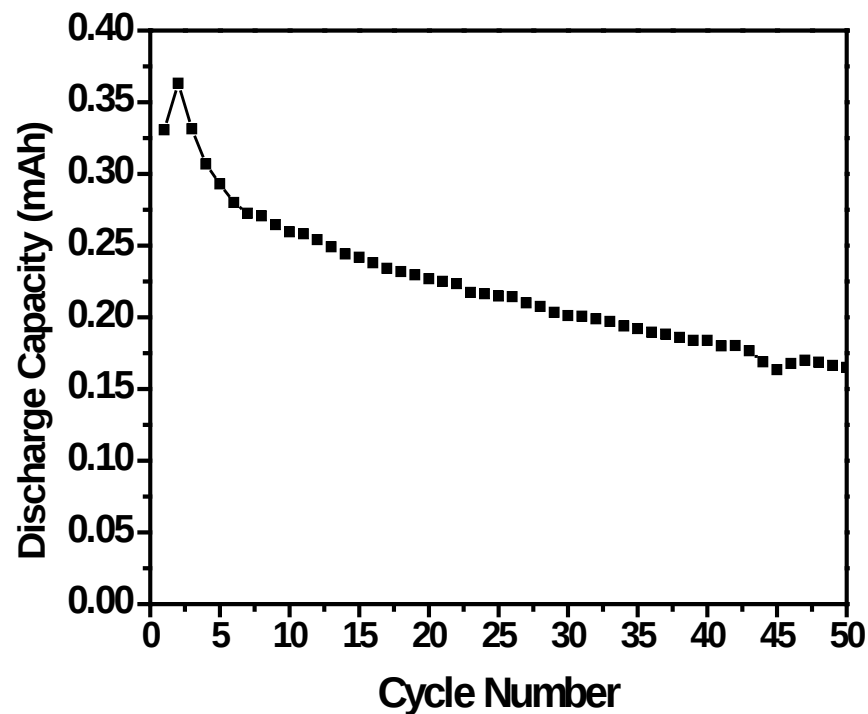
1) Cheon, S. E.; Choi, S. S.; Han, J. S.; Choi, Y. S.; Jung, B. H.; Lim, H. S. *Journal of the Electrochemical Society* 2004, 151, A2067-A2073. 2) Mikhaylik, Y. V.; Akridge, J. R. *Journal of the Electrochemical Society* 2004, 151, A1969-A1976.

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