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
  - Fundamental research of high-energy materials for Li-S batteries
- Budget
  - $220k FY10
  - $350k FY11
  - $350k FY12
- 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 electronic conductivity of sulfur by using high surface area mesoporous carbon materials
  - Extend the cycle-life Li-S batteries by creating C-S nanocomposites with protective layers
  - Explore electrolyte additive to catalyze the electrochemical reaction of Li_2S
- **Relevance:**
  - Enables high-energy Li-S battery chemistry for EV and PHEV batteries
  - Addresses the cost barriers for automobile batteries

Milestones

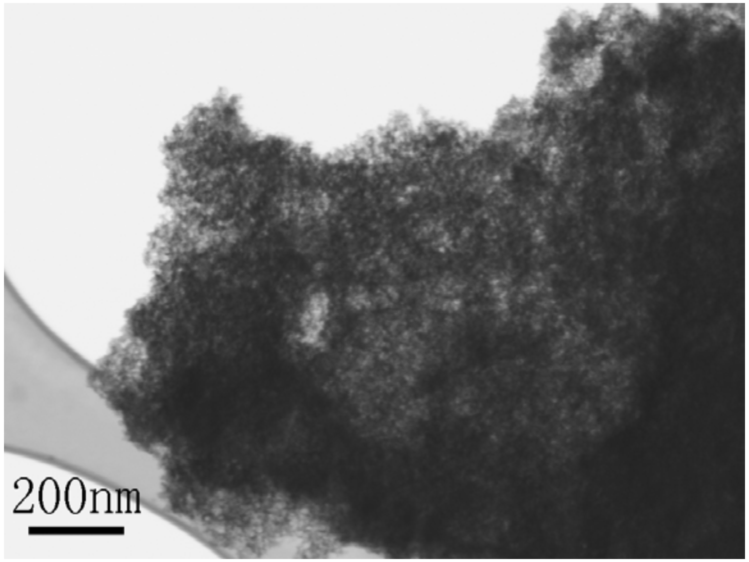
Milestones:	Target:
1. Confirm the earlier observation of long cycle life in half cells and expand the synthesis of sulfur/carbon composite materials of various sulfur loading	Sep, 2010 ✓
2. Compare the performance for different concentrations of additives to the electrolyte	Jan, 2011 ✓
3. Investigate 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 ✓
5. Synthesize novel composite cathodes to improve cyclability	Sep, 2012
6. Explore full cell configuration to minimize excess lithium at the anode	Sep, 2012

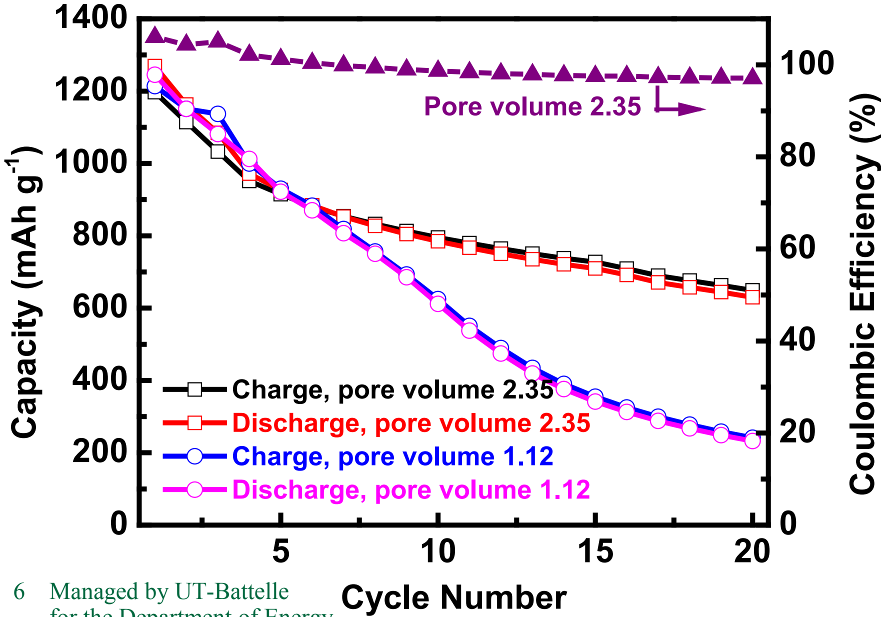
Approach to fundamental research of Li-S batteries.

Goal: Develop advanced materials for Li-S batteries

- **Design novel composite materials for high energy sulfur cathode**
  - C/S composite materials with optimized porous structures
  - Solid electrolyte coatings to retain sulfur at the cathode
- **Tailor electrolytes for Li-S batteries**
  - Reduce the polysulfide shuttle
  - Electrolyte additives to catalyze the electrochemical reactions of Li_2S
- **Explore approaches for anode protection**
  - Suppress dendritic growth for Li-plating
  - Passivation of Li with designed SEI
- **Develop advanced diagnosis tools for the elucidation of battery reaction mechanisms**
  - In situ SEM
  - Air-sensitive-sample handling

Technical Progress – next 11 slides. Porosity is key to capacity retention.



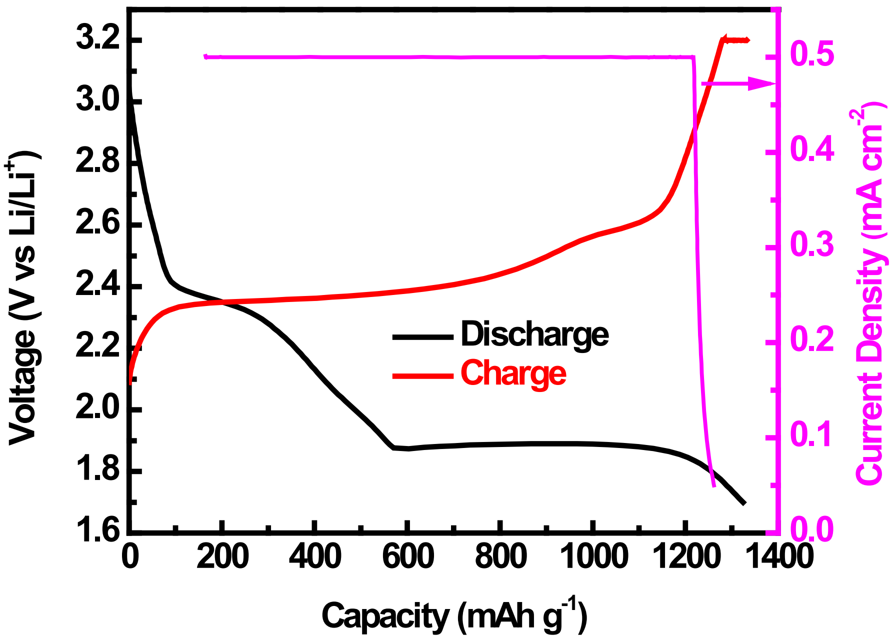


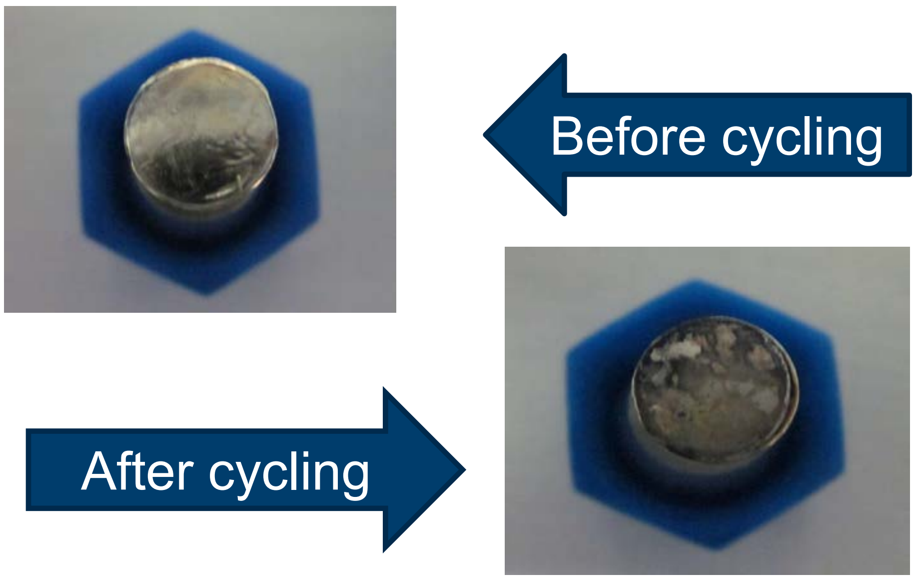
Double templating method has been developed to synthesize porous carbon with controlled porosity:

- Two pore sizes were obtained by using PEO-PPO-PEO based triblock copolymers (7nm) and silica nanospheres (13nm)
- Total porosity was controlled by the ratio of carbon precursors to the templates: two porosities of 1.12 and 2.35 cm^3/g. were demonstrated

The C/S composites with 70 wt.% of sulfur loading showed that the sample with large pore volume has better capacity retention than the one with small pore volume.

Polysulfide shuttle is still the bottle-neck of cycle-life.



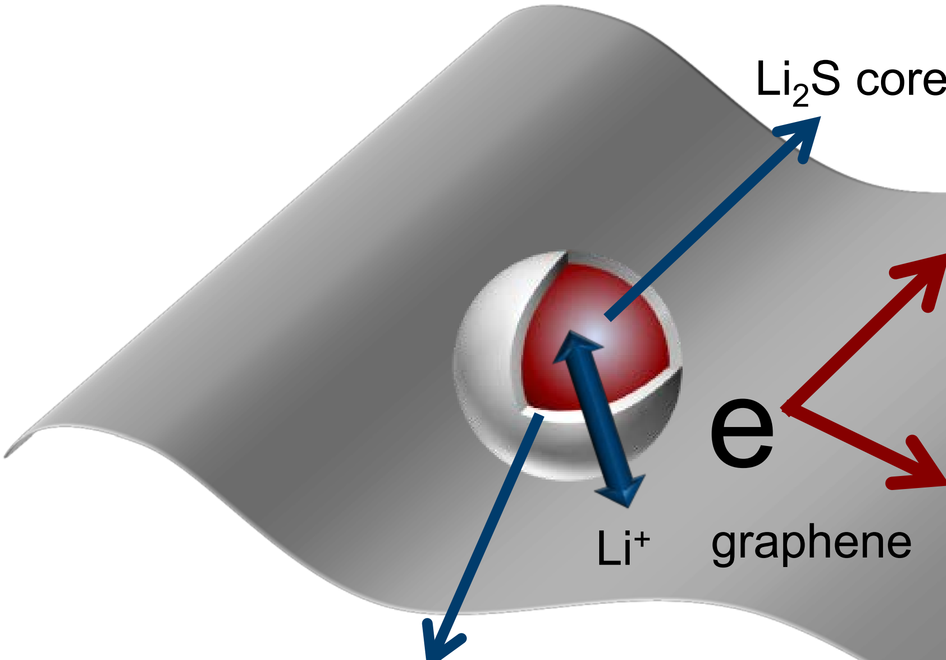


The first charge and discharge curves of the C/S composite electrode with a pore volume of 2.35 cm^3/g. Two plateaus were observed with a ratio of 3:1 of the high to low plateaus. Current tailing at the end of charging indicates possible polysulfide shuttle.

SEM of the lithium anode before and after cycling: lithium sulfide deposition was observed on the lithium anode

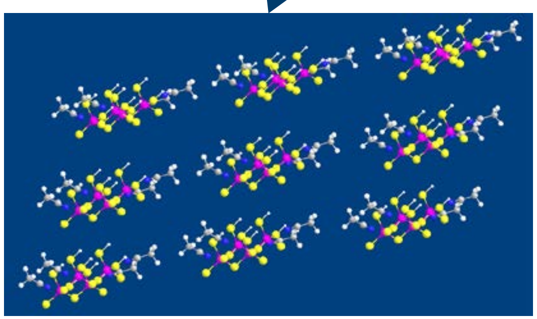
- Polysulfide shuttle still exist in large pore volume C/S composite
- Capacity decay could be linked with sulfur loss through polysulfide shuttle.

Solid electrolyte coated cathode for Li-S batteries.



A new core-shell structure overcomes the key challenges for Li-S cells:

- Poor ionic and electronic conductivities
  - Low utilization of sulfur
- Sulfur dissolution
  - Polysulfide shuttle
  - Low coulombic efficiency
  - Corrosion of Li anode
- Poor cycling performance
  - Change of microstructure

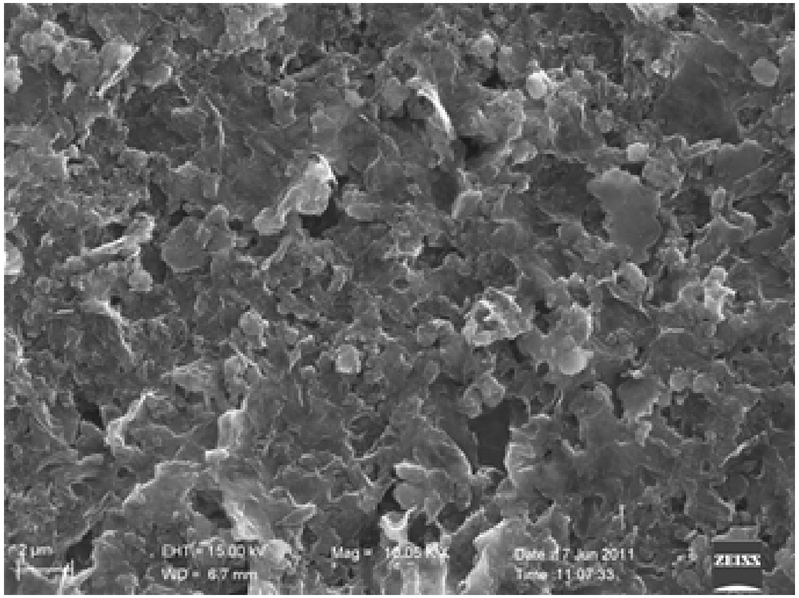


Solid electrolyte shell prevent direct contact of Li_2S_x with liquid electrolyte

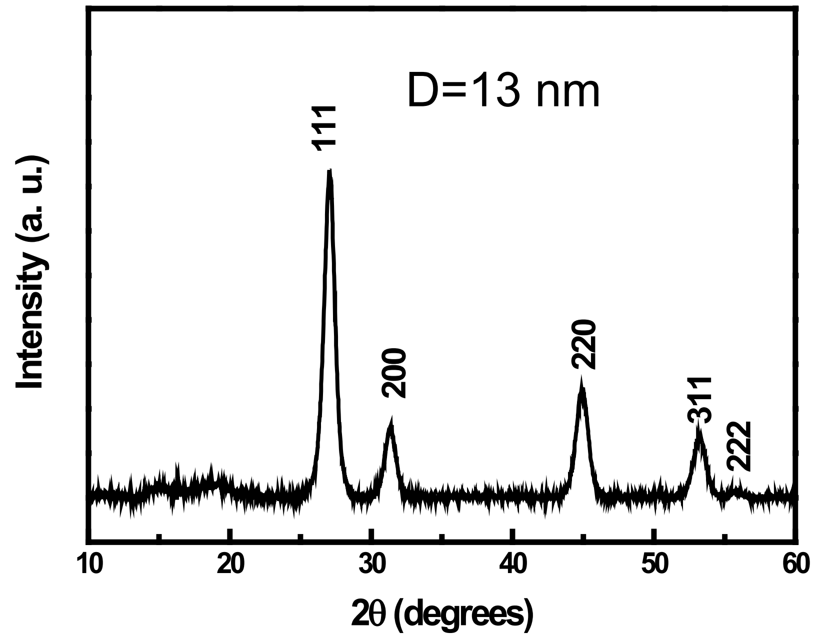
Concept:

- Impart ionic and electronic conductivities to the cathode through intimate contacting with conductors
- Prohibit sulfur dissolution and shuttle phenomenon by solid electrolyte coating

$Li_2S@Li_4P_2S_7$ Core-shell Nanoparticles were synthesized through facile solution chemistry approach.

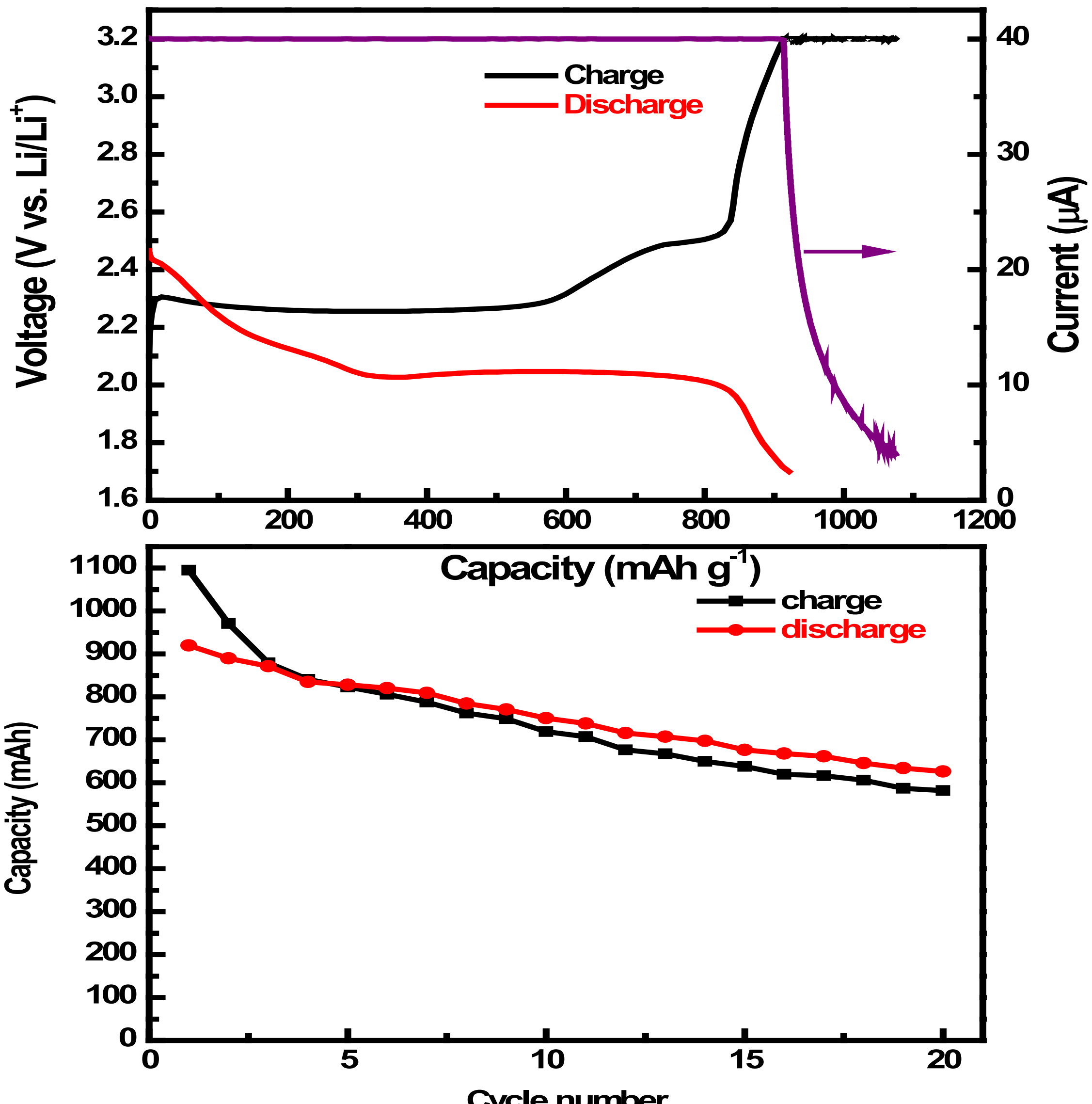


SEM of solid electrolyte coated electrode with a composition of 60 wt.% $Li_4P_2S_7$ coated Li_2S nanoparticles, 30 wt.% carbon black, 10 wt.% PVC



XRD pattern of $Li_2S@Li_4P_2S_7$ Core-shell Nanoparticles: particle size of Li_2S was 13 nm based on peak width. $Li_4P_2S_7$ coating was confirmed by Raman spectrum. The coating was too thin to show significant XRD peaks

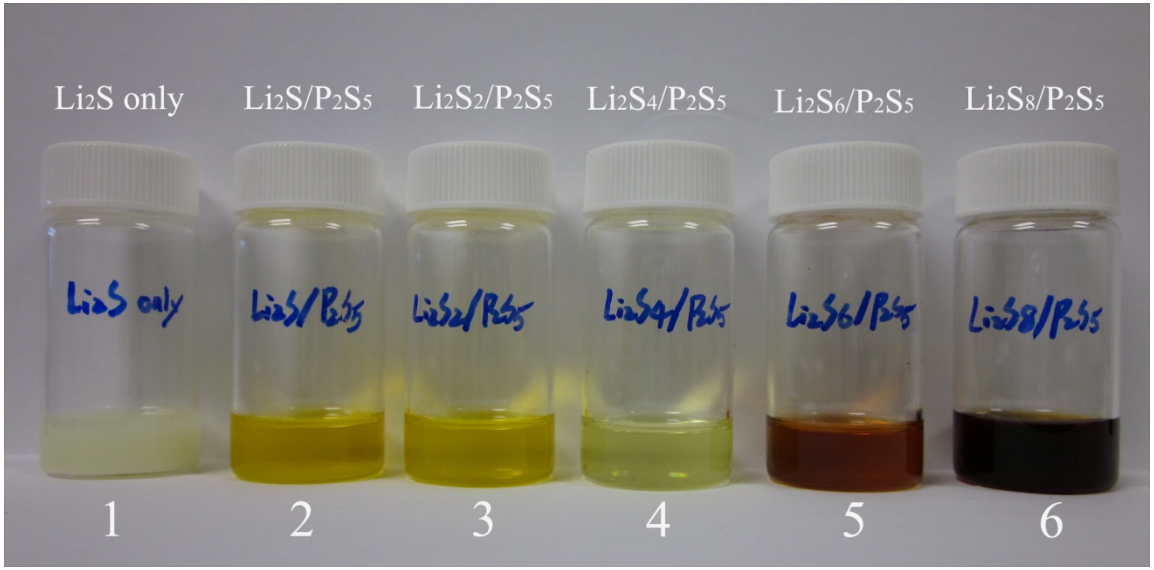
Solid electrolyte coated cathode has superior cycling performance in liquid electrolytes.



- The cathode consisted of pre-lithiated nanoparticles
- No shuttle phenomenon was observed in any cell
- No sulfur dissolution observed in the electrolytes (good solvents, DME, TEGDM)
- Capacity varies with the electrode preparation from 200 mAh/g to 1100 mAh/g
- Close to 100% coulombic efficiency

P_2S_5 as novel electrolyte additive for Li-S batteries.

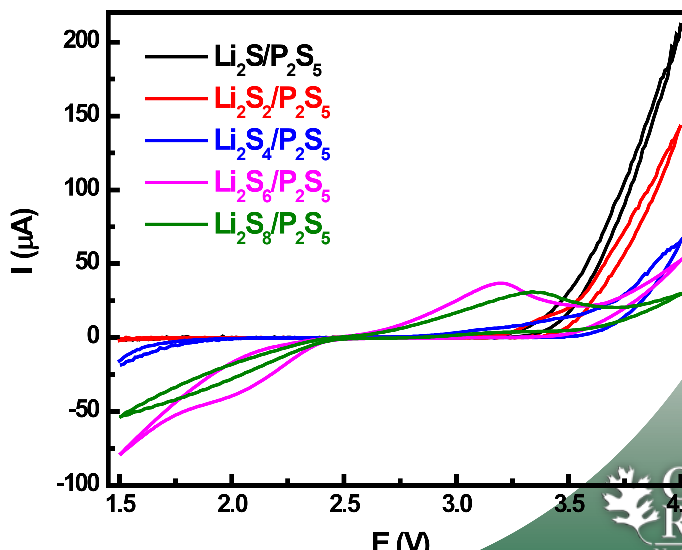
The photo presents the solubility of a series of mixtures of Li_2S_x ($1 \leq x \leq 8$) with and without P_2S_5 in TEGDME



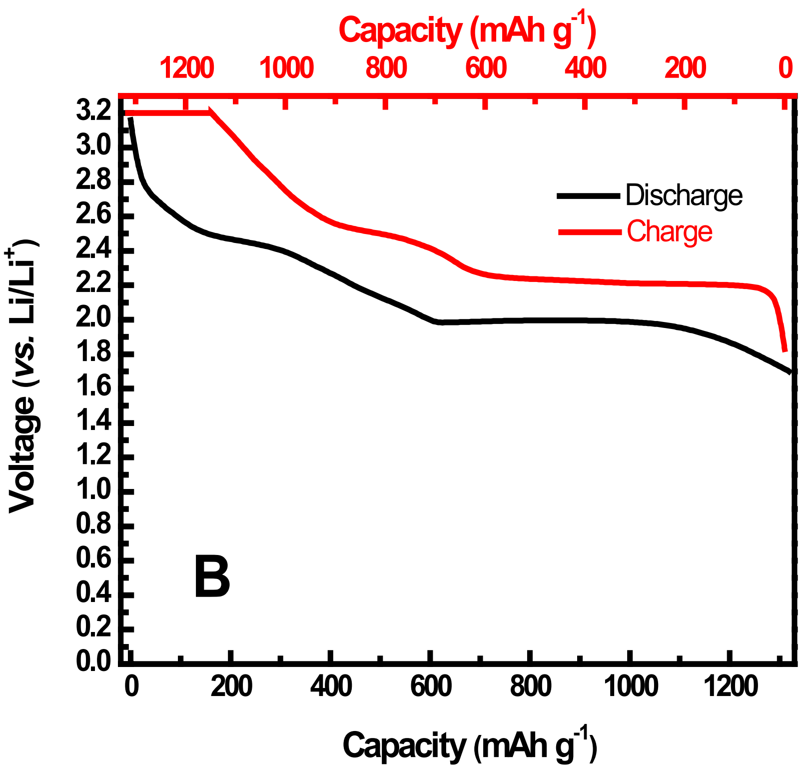
P_2S_5 forms complex with Li_2S_x and facilities the dissolution of lithium sulfide/polysulfides in ether based electrolytes.

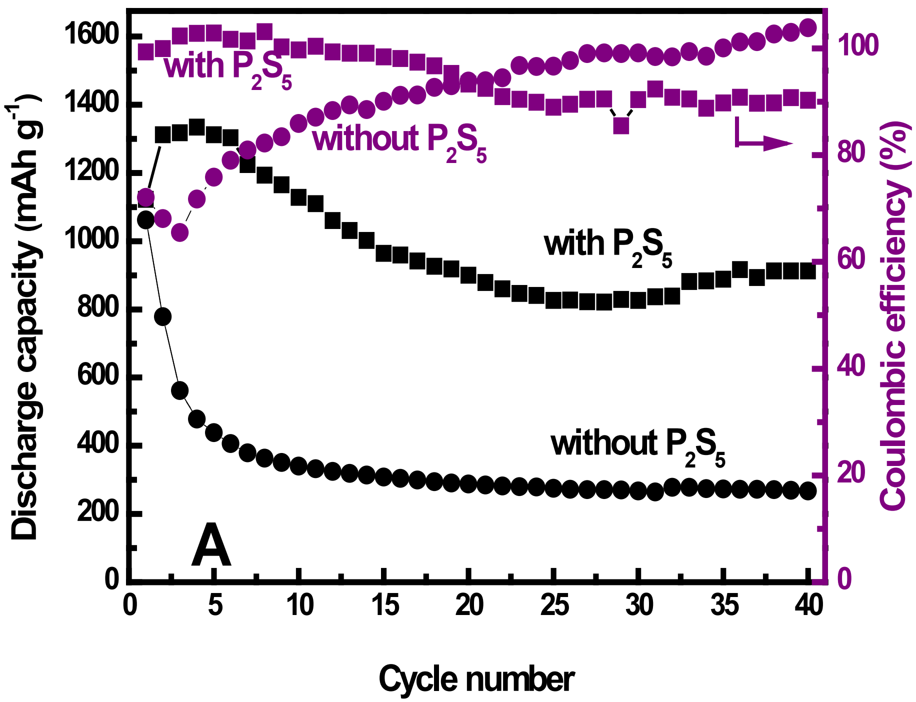
Cyclic voltammograms (CV) of Li_2S_x/P_2S_5 complexes:

- No redox peak was observed in the Li_2S/P_2S_5 complex between 1.7 and 3.2 V. This complex can be reduced at potential below 1.7 V and be oxidized at potentials over 3.2 V.
- Complexes of Li_2S_x/P_2S_5 ($x \geq 2$) have redo peaks between 1.7 and 3.2 V.



P_2S_5 improves cell performance.

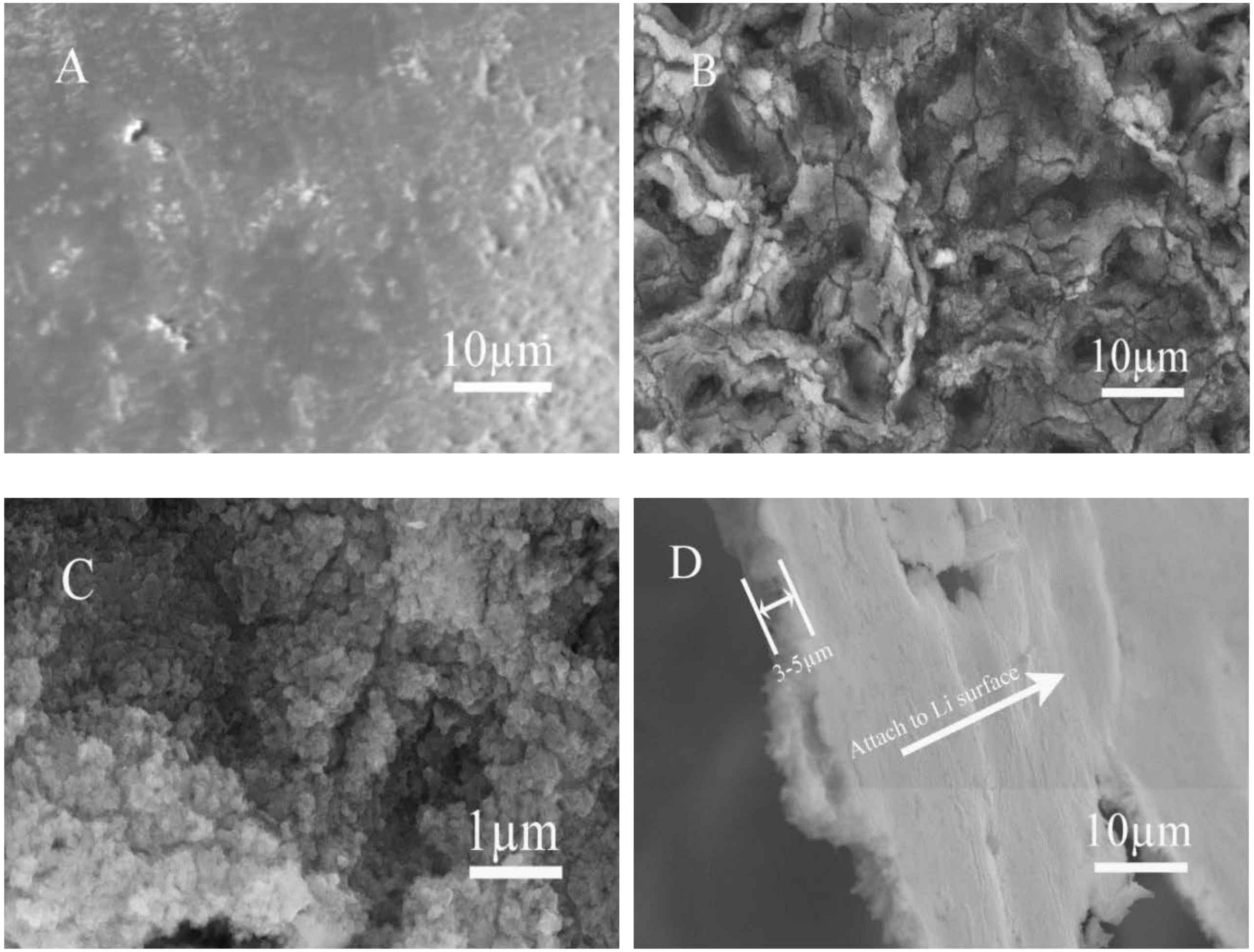




Charge discharge curves showed that the polysuflide shuttle was suppressed: Nonporous carbon was used to demonstrate the efficacy of additive effect.

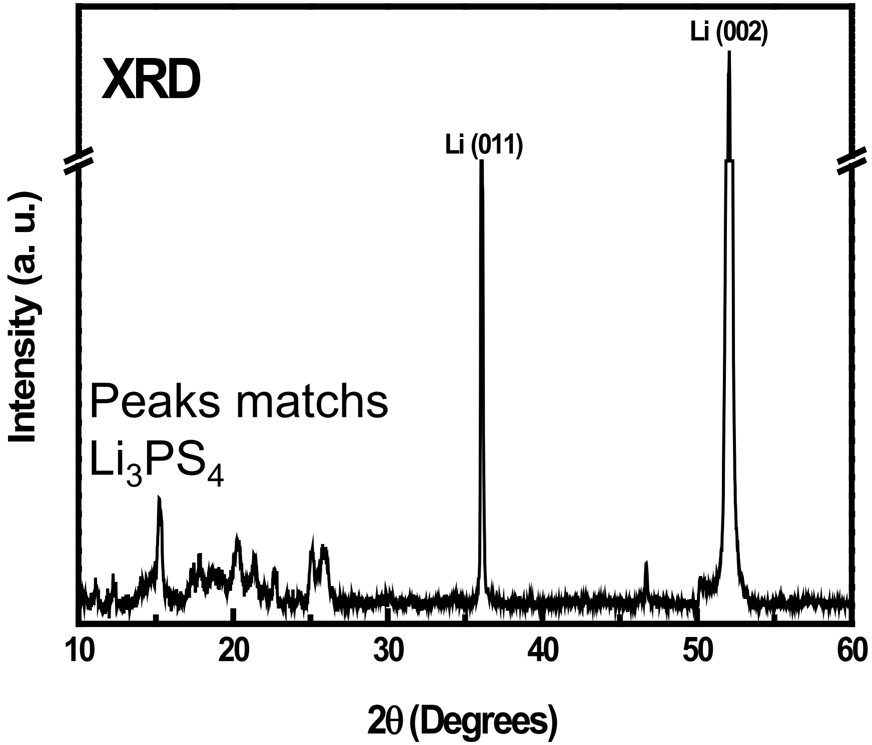
Comparison of cycling performance of cells with/without P_2S_5. Much higher capacity retention was observed in the cell with the additive.

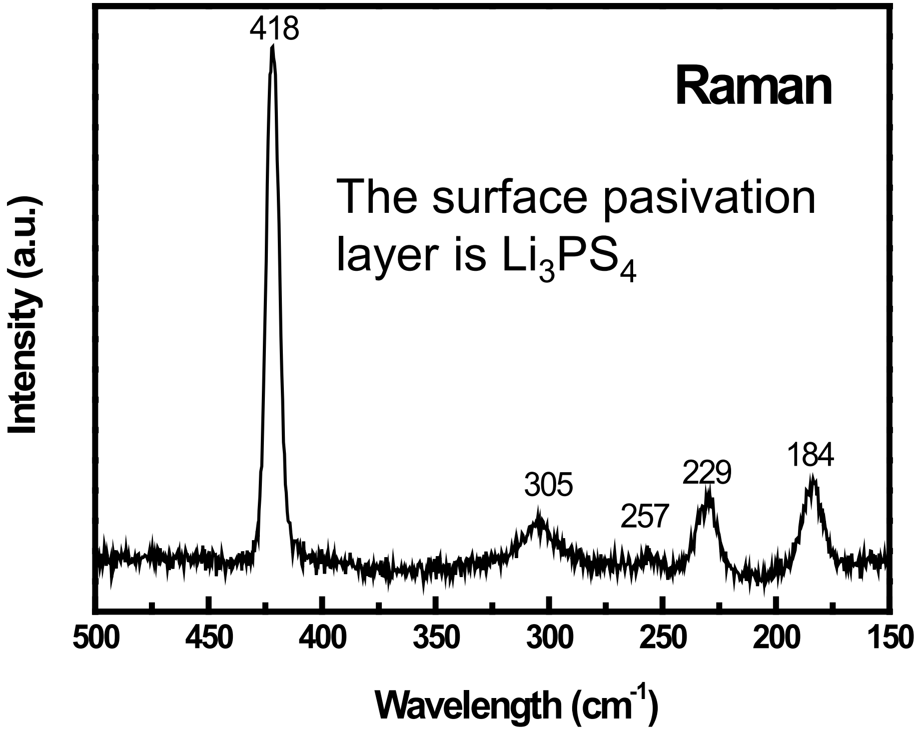
P_2S_5 passivates the surface of Li anode.



SEM images of (A) the surface of pure metallic Li, (B, C) the passivation layer morphologies with different magnifications, and (D) the cross-section of the passivation layer peeled off from Li surface after the 1st cycle when using Li_2S_8/P_2S_5 as the catholyte in 1 m LiTFSI @ TEGDME.

Composition of surface passivation layer on Li anode.

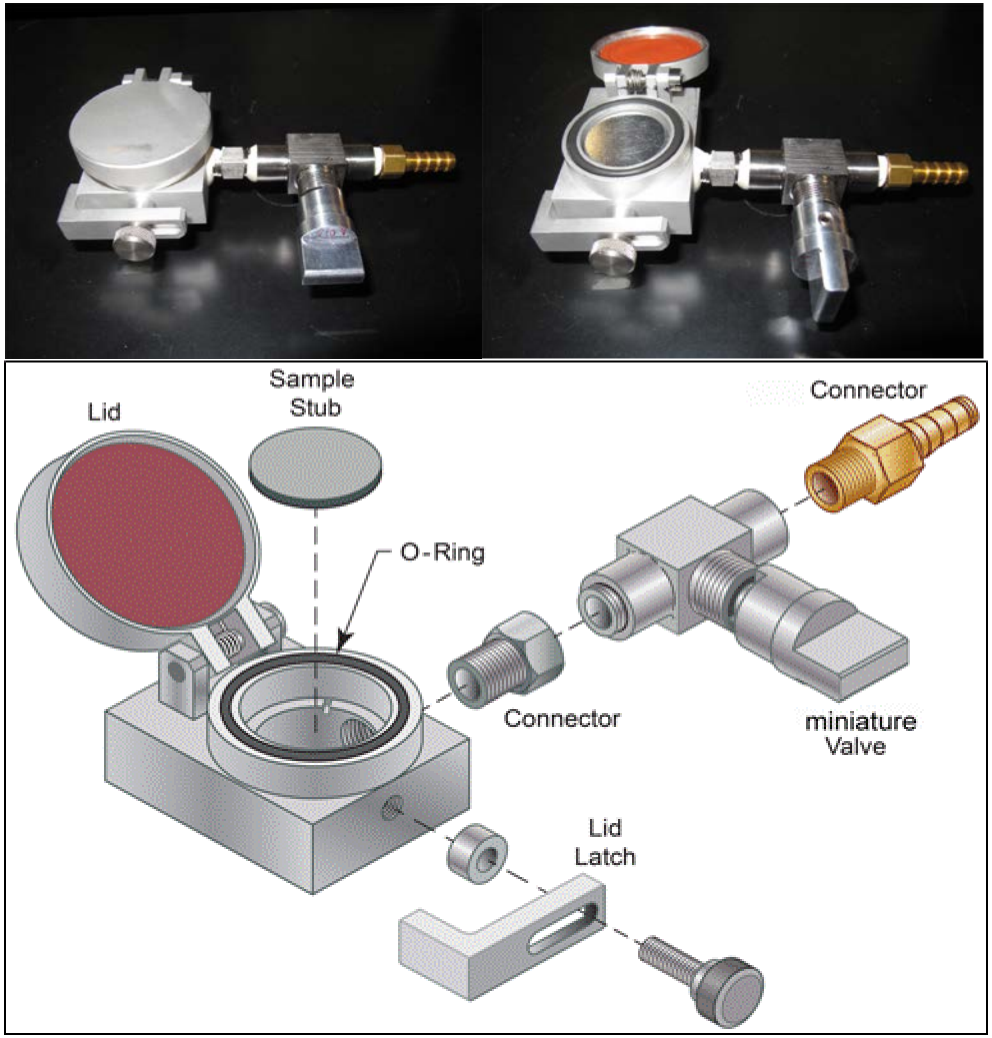




The function of the additive is two-fold:

- P_2S_5 promotes the dissolution of Li_2S and alleviates the loss of capacity caused by the precipitation of Li_2S; and
- P_2S_5 passivates the surface of lithium metal and therefore eliminates the polysulfide shuttle phenomenon.

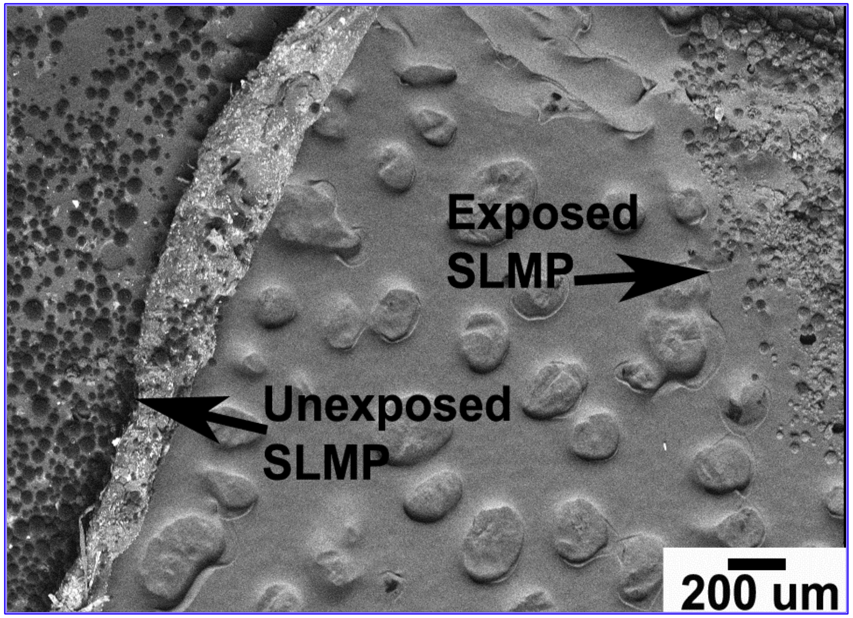
Air-transfer sample holder for cell diagnosis.

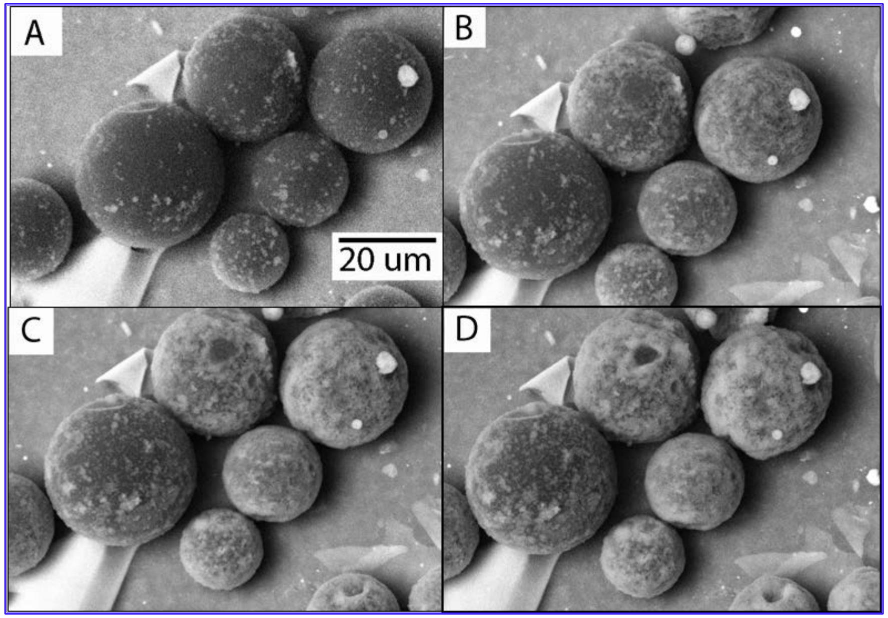


The vacuum chamber transfer stage with the lid in (a) a closed and (b) open position; and (c) Exploded view showing the O-ring seal and hinged lid.

A new sample transfer stage has been developed for taking samples from glovebox to a scanning electron microscope (SEM) without exposure to air and moisture. The transfer stage operates by the difference of pressure inside and outside the SEM chamber: when a sample is loaded in a glovebox and pumped at mild vacuum, the atmosphere pressure pushes the lid against the o-ring seal. The sample is protected by the transfer stage when it is transferred in air. After the sample stage is loaded inside the SEM chamber, the lid pops open when the SEM chamber is pumping down to a lower vacuum for imaging. This is a useful tool for imaging air-sensitive materials used in Li-S batteries and other lithium-ion batteries.

Air-sensitive sample holder enables imaging of lithium anode materials.





SEM image of stabilized lithium metal powder (SLMP) with/without exposure of air. The contrast shows the difference by surface reaction with moisture in air.

SEM of SLMP in contact with moisture at different duration: (A) 0 min, (B) 15 min, (C) 30 min, and (D) 45 min. The contrast of the SEM images indicates the extent of reaction.

Future work

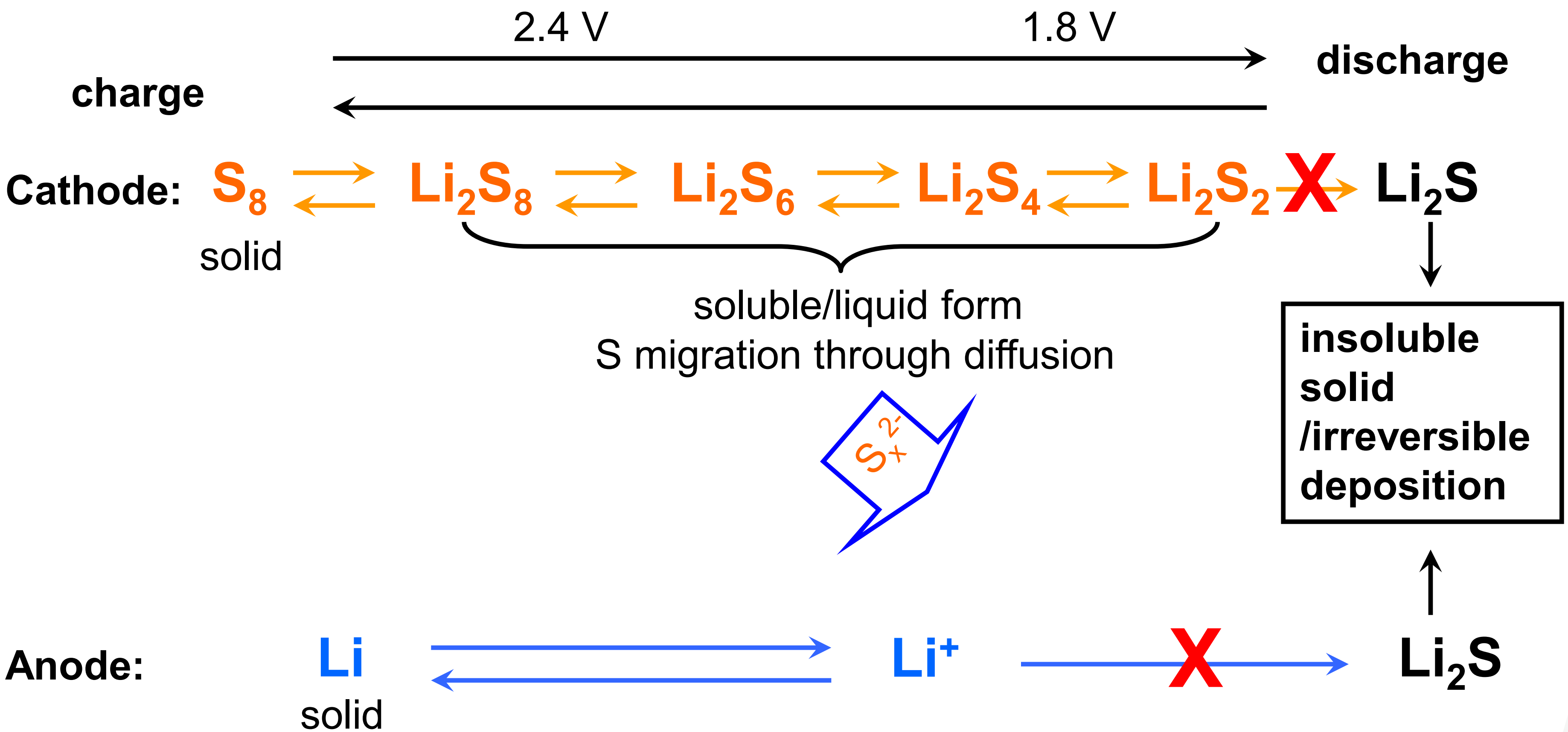
- Develop solid electrolyte coating on cathode to prevent the dissolution of polysulfides in liquid electrolytes
- Explore other electrolyte additives and solvents that are compatible with P_2S_5 to optimize the additive effect
- Optimize the electrolyte composition to form rigid SEI for lithium anode
- Investigate solid electrolyte coatings on lithium metal anode for Li-S batteries
- Evaluate the full cell performance of Li-S batteries with limited usage of solvents and lithium metal

Summary

- **Relevance: Exploratory research of Li-S battery chemistry leads to discoveries of advanced materials for high-energy batteries with potential use in EVs and PHEVs.**
- **Approach:**
  - **Carbon-sulfur nano-composites with optimized porosity retains sulfur at the cathode**
  - **Electrolyte additives facilitate the electrochemical cycling of Li_2S**
  - **Solid electrolyte coating on the Li_2S cathode surface mitigates the dissolution of sulfur during battery cycling**
  - **Surface passivation on lithium anode improves the cycle performance of Li-S batteries**
- **Accomplishment and progress:**
  - **Optimized the porosity of C/S composite electrode**
  - **Discovered new electrolyte additive of P_2S_5 and elucidated the mechanism of additive effect of P_2S_5 on cell performance**
  - **Synthesized a solid electrolyte coated Li_2S cathode for Li-S batteries.**
  - **Developed a novel sample transfer stage for the diagnoses of Li-S batteries**
  - **Understood the importance of lithium protection by SEI**
- **Future work:**
  - **Optimize the electrolyte composition to facilitate electrochemical reaction of Li_2S.**
  - **Explore solid electrolyte coatings for the protection of both cathode and anode**
  - **Evaluate the full cell performance of Li-S batteries with optimized cell components**

Technical Back-Up slides

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**