Additives and Cathode Materials for High-Energy Lithium Sulfur Batteries

Chengdu Liang

Oak Ridge National Laboratory

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Contributors:
Zhan Lin, Nancy Dudney, and Jane Howe

Project ID: ES105

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Overview

- Timeline
  - Start June, 2010
- Technical barriers for EV and PHEV
  - Very High Energy Li-S Battery (500 Wh/kg) by 2020
  - Poor cycling of Li metal anode
- Budget
  - $220k FY10
  - $350k FY11
  - $350k FY12
  - $350k FY13
- 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 cathode by using high surface area mesoporous carbon materials
  - Block the polysulfide shuttle to extend the cycle-life of Li-S batteries
  - Explore novel battery structure of all-solid Li-S batteries
  - Develop enabling materials for all-solid Li-S batteries
- **Relevance:**
  - Enables high-energy Li-S battery chemistry for EV and PHEV batteries
  - Addresses the cycling problems of Li metal anode

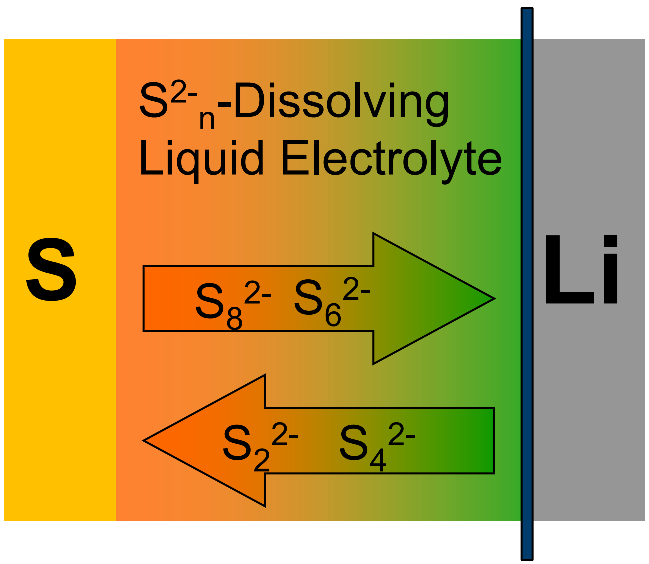
Milestones

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 loadings	Sep, 2010 ✓
2. Compare the performance for different concentrations of additives to the electrolyte	Jan, 2011 ✓
3. Investigate additives to the cathode material, 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 ✓
7. Develop all-solid battery architectures	Sep, 2013 on schedule
8. Identify enabling materials for all-solid Li-S batteries	Sep, 2013 on schedule

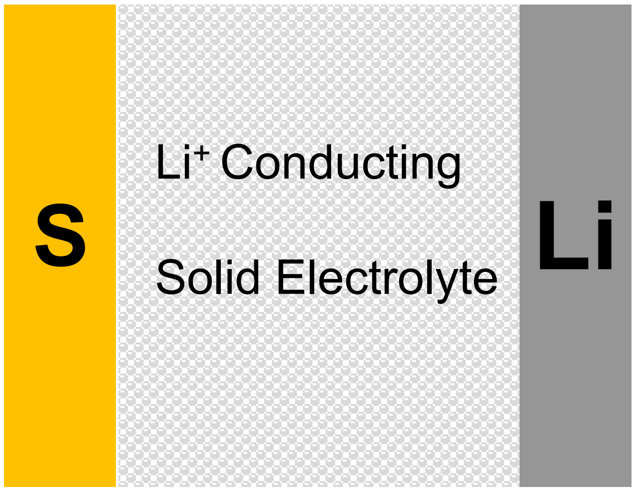
Approaches to Fundamental Research of Li-S Batteries

Goal: Enabling long cycle-life of Li-S batteries by the elimination of the polysulfide shuttle phenomenon

Liquid-Electrolyte Batteries



All-Solid-State Batteries

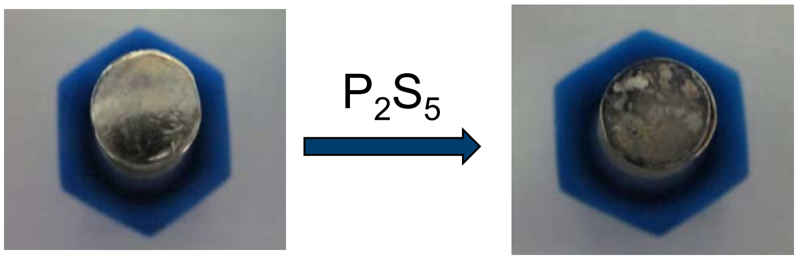


Tailor electrolytes for Li-S batteries
- **Reduce the polysulfide shuttle**
- **Protect metallic lithium anode**

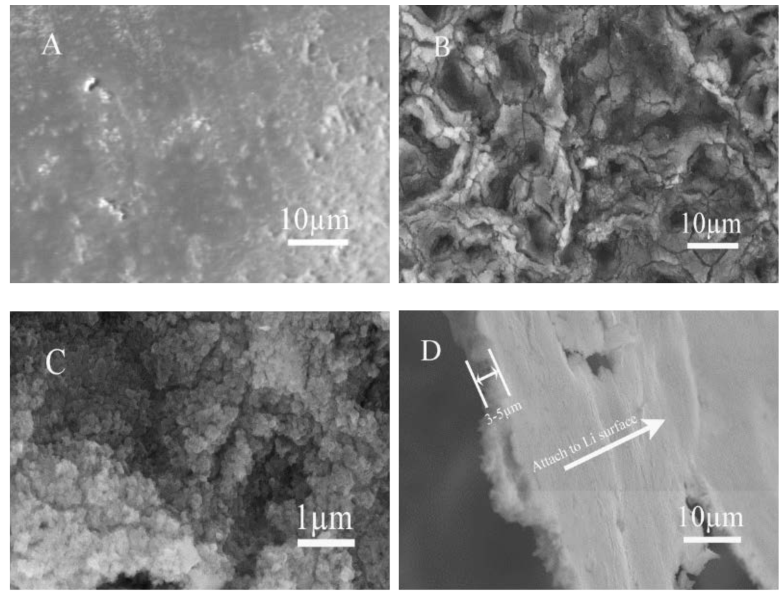
Enable solid-state Li-S batteries
- **Eliminate the polysulfide shuttle**
- **Promote ionic conductivity**

Progress #1: P_2S_5 Additive to Liquid Electrolytes Protects Lithium Anode

fresh protected



protection layer revealed by micrographs



Chemical reaction of P_2S_5 passivation

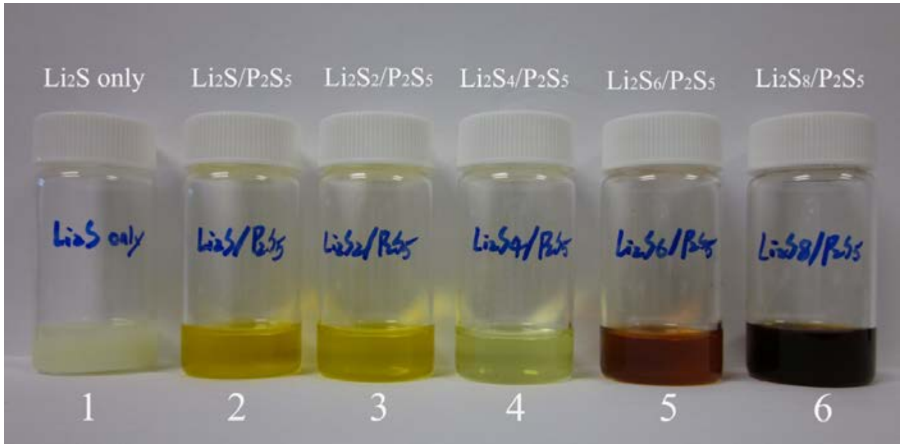
$$P_2S_5 + S^{2-}_n + Li \longrightarrow Li_3PS_4$$

The passivation layer has a chemical composition of Li_3PS_4, which is a ***superionic conductor***!

Z. Lin, Z. Liu, W. Fu, N.J. Dudney, and C.D. Liang; "Phosphorous Pentasulfide as a Novel Additive for High-Performance Lithium-Sulfur Batteries," **Advanced Functional Materials**, 2013, 23, 1064-1069

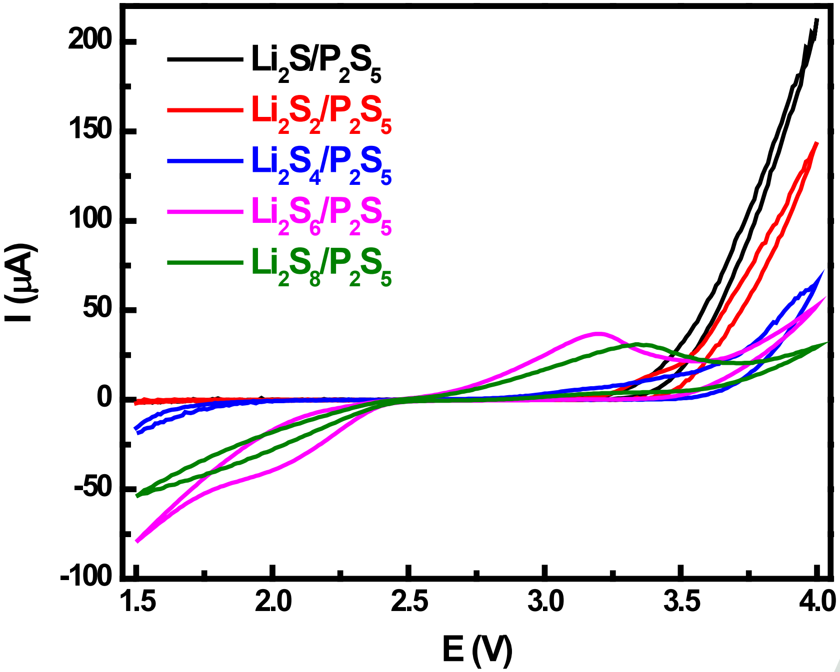
Progress #1: P_2S_5 Additive Facilitates Electrochemical Reaction of Li_2S_n

P_2S_5 forms soluble complexes with Li_2S_n (n, 1-8) in Tetraglyme



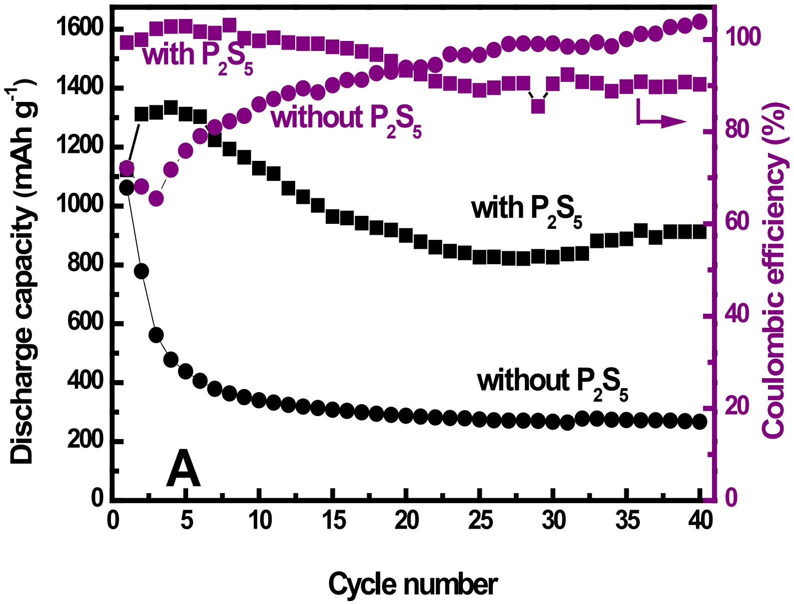
Increase in sulfur number

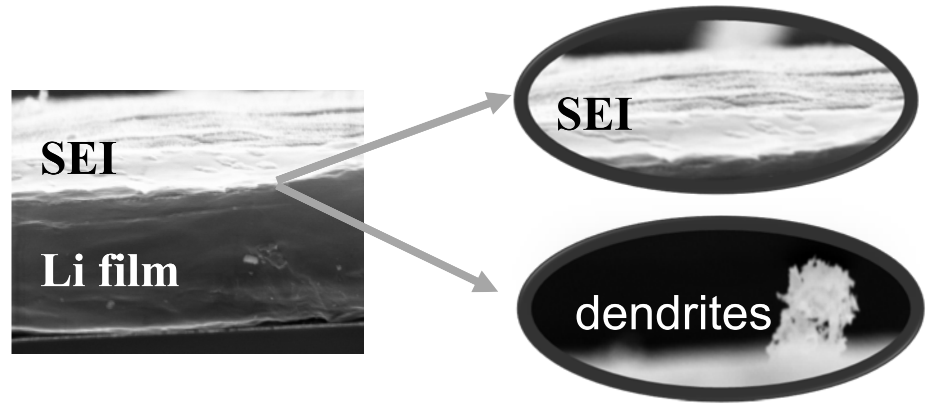
P_2S_5/Li_2S_n complexes are electrochemically active



Z. Lin, Z. Liu, W. Fu, N.J. Dudney, and C.D. Liang; "Phosphorous Pentasulfide as a Novel Additive for High-Performance Lithium-Sulfur Batteries," **Advanced Functional Materials**, 2013, 23, 1064-1069

Progress #1: Good Cycling Achieved but Challenges Remain

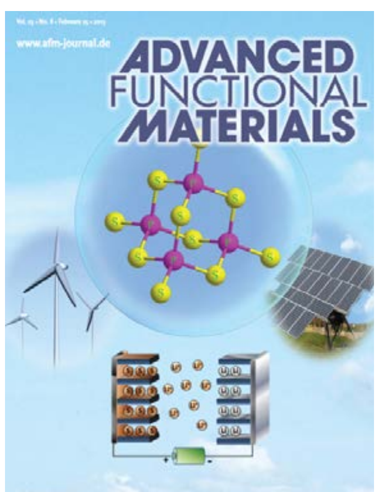




- **Problematic cycling of Li anode**
  - **Dendritic growth of lithium**
  - **SEI formation**
  - **Safety**
- **Dissolution of sulfur cathode**
  - **Loss of active material**
  - **Self discharge**
  - **Low energy efficiency (polysulfide shuttle)**

All-solid Li-S battery configuration eliminates these problems!

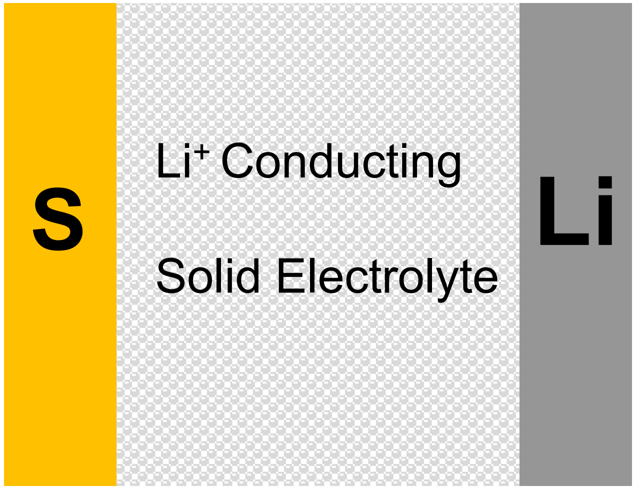
Highlighted as journal cover on Feb. 25, 2013 issue of Advanced Functional Materials



Challenges of All-Solid Li-S Batteries

Sulfur cathode:

- Ionic conductivity
- Electronic conductivity
- Electrochemical reversibility
- Fast kinetics
- Compatibility with solid electrolytes



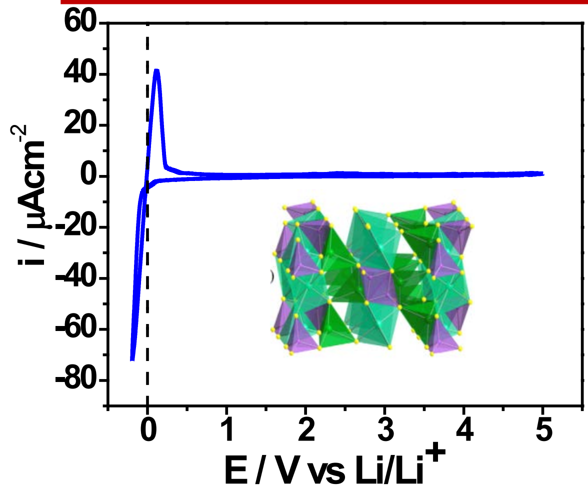
Solid electrolyte:

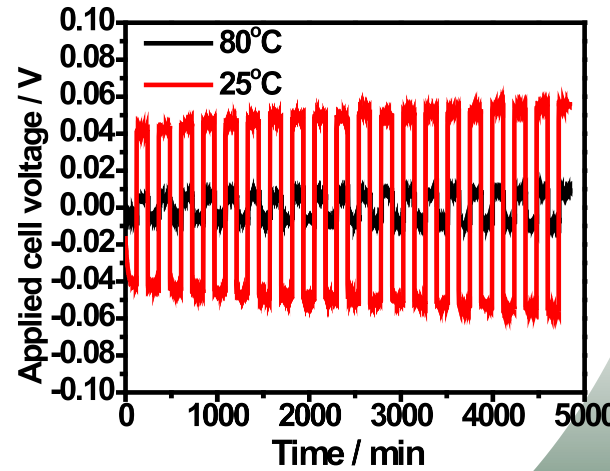
- > 10^{-4} S/cm Ionic conductivity at RT
- Compatible with lithium and sulfur or sulfur compounds
- Low interfacial resistance

Nanostructured Li_3PS_4 meets the requirements for a solid electrolyte.

S/C cathode **Li metal anode**

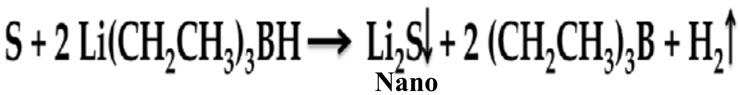
A photo of solid cells

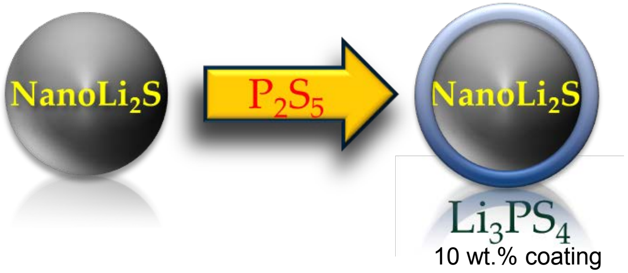




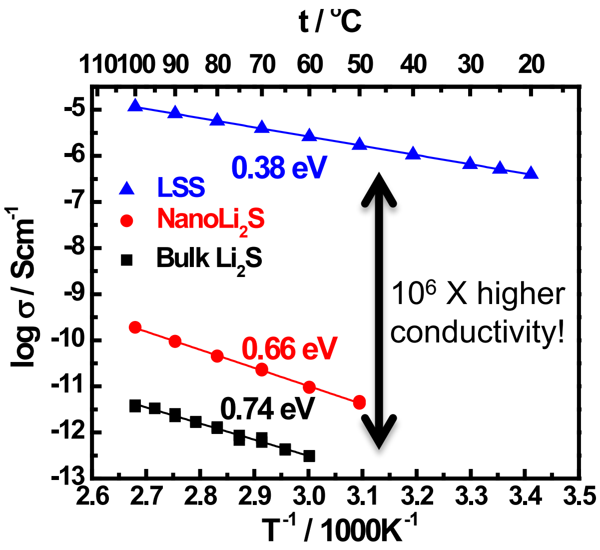
The development of Li_3PS_4 solid electrolyte is a collaboration with a BES project. Liu and Liang *et al*. **JACS**, 2013, **135**, 975-978

Progress #2: $Li_2S@Li_3PS_4$ Core-Shell Nanoparticles Conducts Li^+

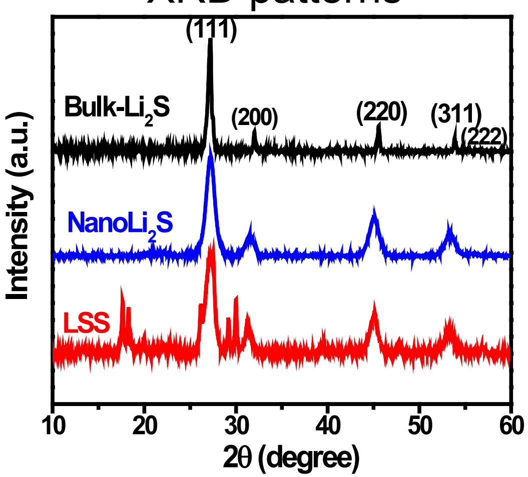




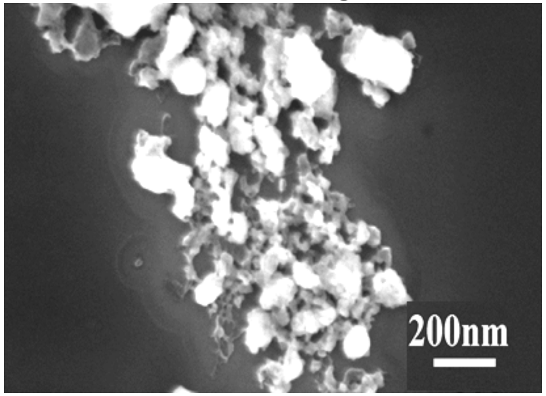
Li_2S nanoparticles mixed with P_2S_5 yields core-shell nanoparticles $Li_2S@Li_3PS_4$ which are designated as LSS (lithium superionic sulfide). The LSS has an excellent ionic conductivity. The core-shell structure was confirmed by XRD, SEM and Raman.



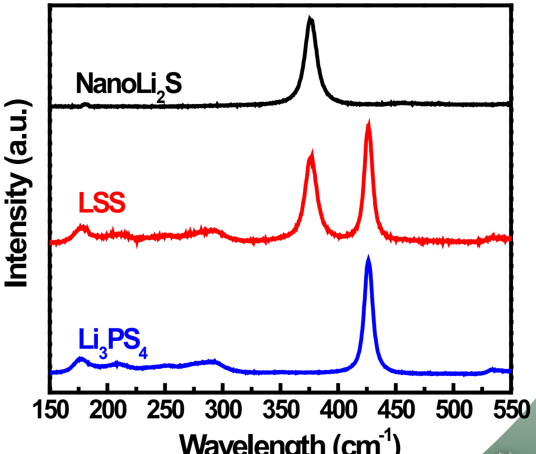
XRD patterns



SEM image

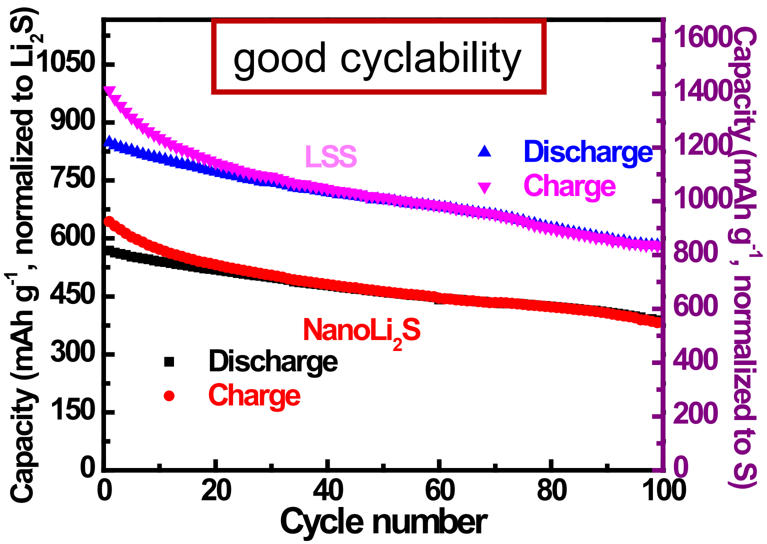


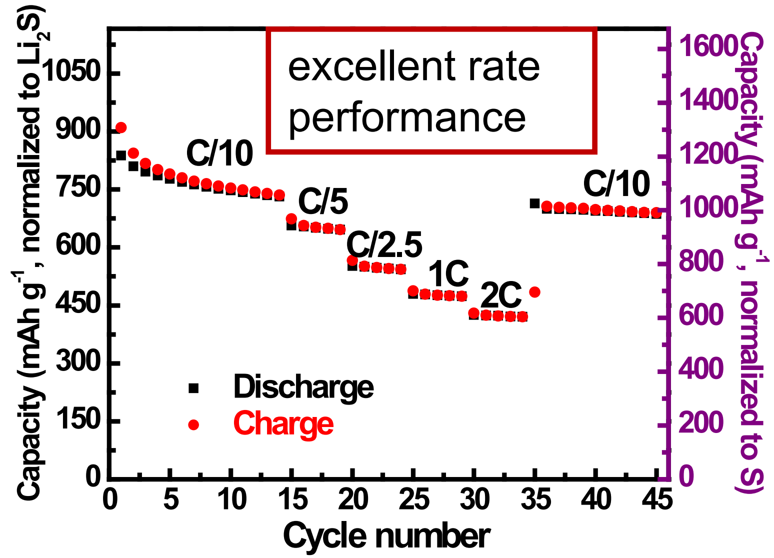
Raman spectra

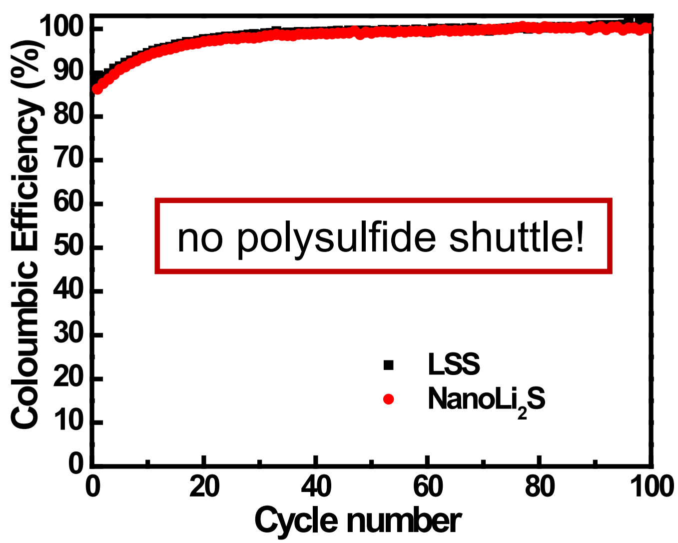


Z. Lin, Z. Liu, N.J. Dudney, and C.D. Liang; "A Lithium Superionic Sulfide Cathode for All-Solid Lithium-Sulfur Batteries," **ACS Nano**, **2013** web-published Feb. 22

Progress #2: LSS Enables All-Solid Li-S Battery Cycling at 60 ºC





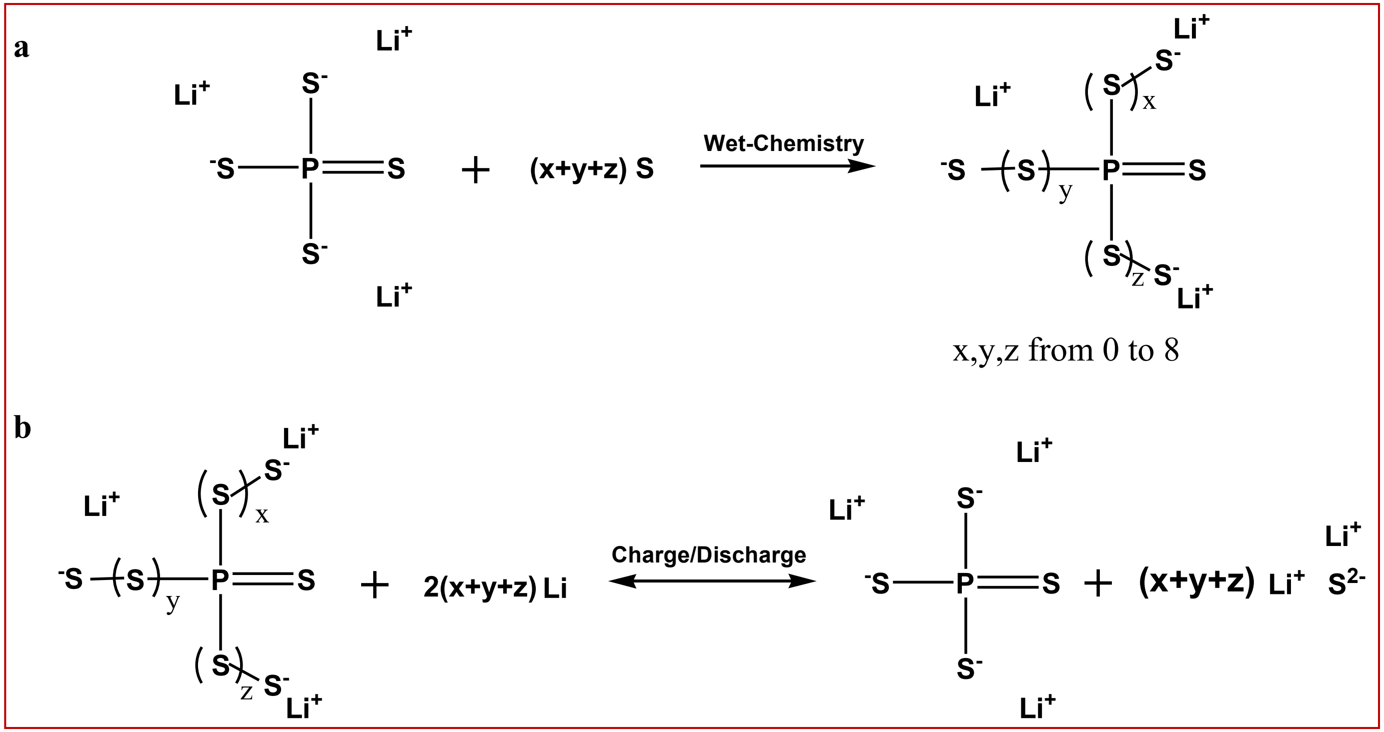


- LSS functions as a pre-lithiated cathode: no lithium metal is required for battery assembly
- Good cyclability has been achieved in an all-solid Li-S battery configuration
- Excellent rate performance has been obtained at 60 ºC
- No polysulfide shuttle observed

Z. Lin, Z. Liu, N.J. Dudney, and C.D. Liang; "A Lithium Superionic Sulfide Cathode for All-Solid Lithium-Sulfur Batteries," **ACS Nano**, **2013** web-published Feb. 22

Progress #3: Overcome the Poor Ionic Conductivity of S Cathode through Chemical Reactions

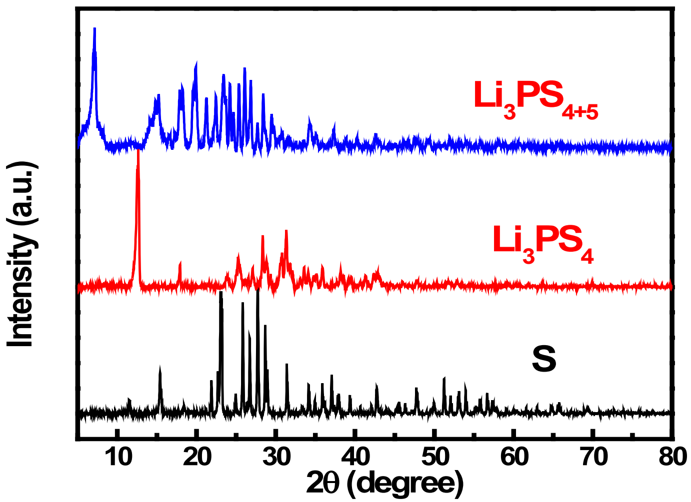
Key problem for S cathode: Poor ionic conductivities of S and its discharge products

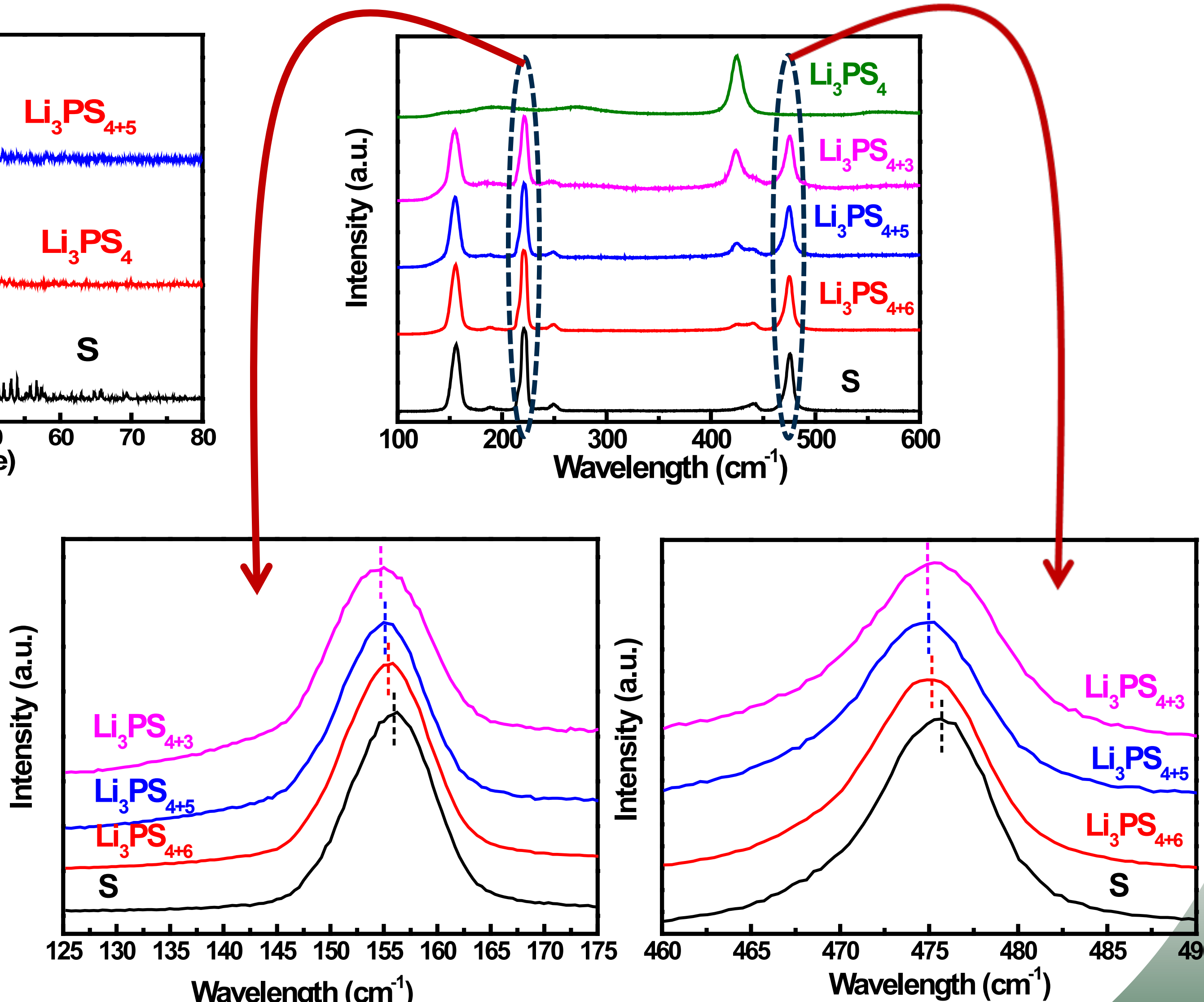


- Lithium polysulfidophosphates were discovered by reacting Li_3PS_4 with elemental sulfur
- This new family of sulfur rich compounds are able to be discharged and charged through reversible cession and formation of S-S single bond

(a) Lin and Liang patent pending
(b) Z. Lin, Z. Liu, W. Fu, N.J. Dudney, and C.D. Liang, "Lithium Polysulfidophosphates: A Family of Lithium-Conducting Sulfur-Rich Compounds for Lithium-Sulfur Batteries," **Angew. Chem.-Int. Ed.** (under review)

Progress #3: XRD and Raman Spectra Confirm the Reaction of Sulfur with Li_3PS_4



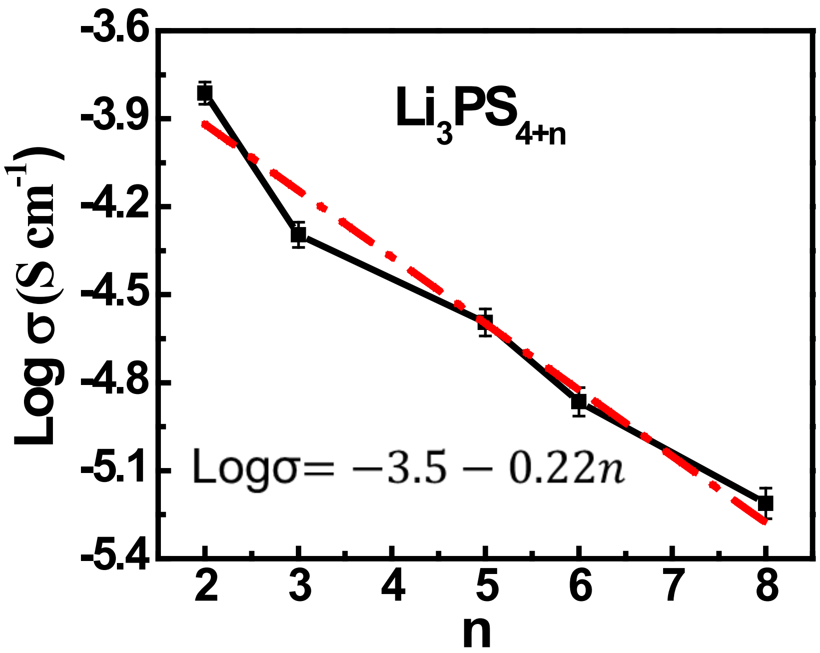


Peaks related to S-S bond

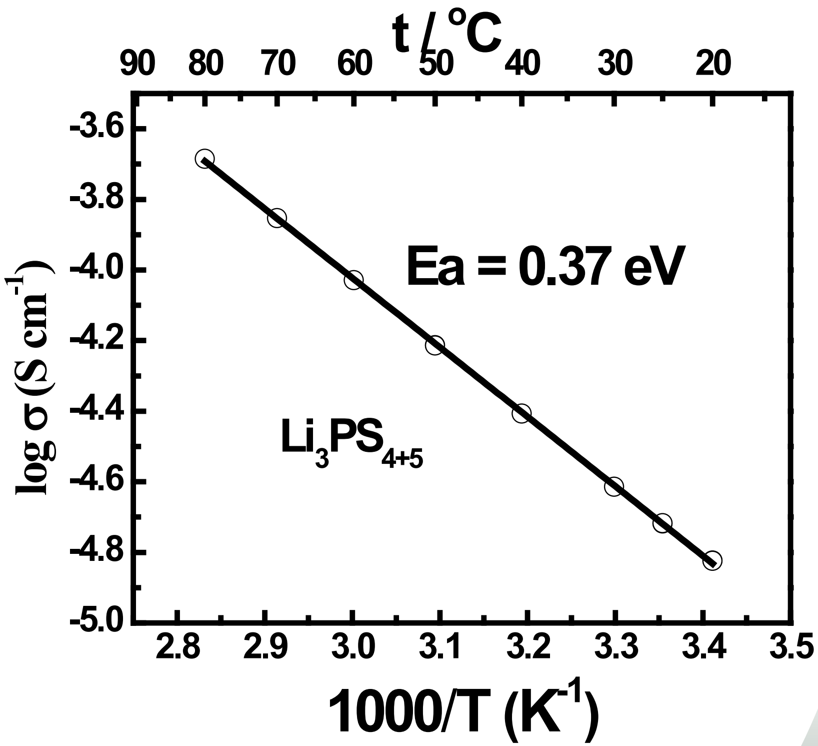
- XRD confirms the formation of new materials
- Raman reveals the polysulfide chains of the lithium polysulfidophosphate

Progress #3: Ionic Conductivity of the Cathode is a Function of Sulfur to Li_3PS_4 Ratio

Room temperature ionic conductivity of Li_3PS_{4+5} is 10^7 times higher than that of Li_2S!



Room temperature conductivity as a function of sulfur in SE

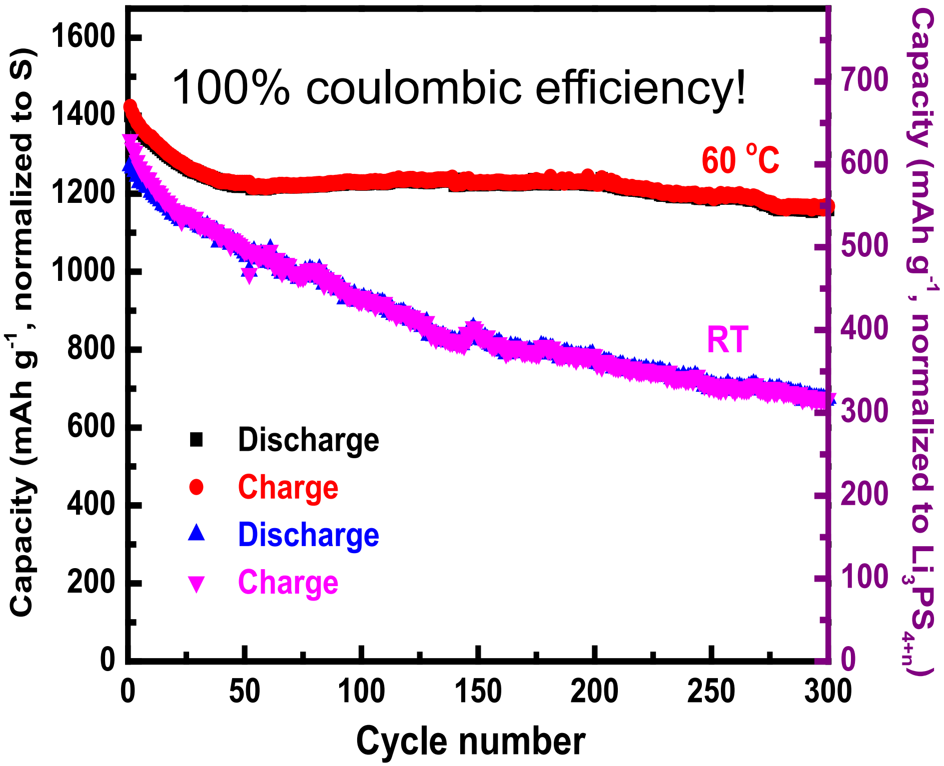


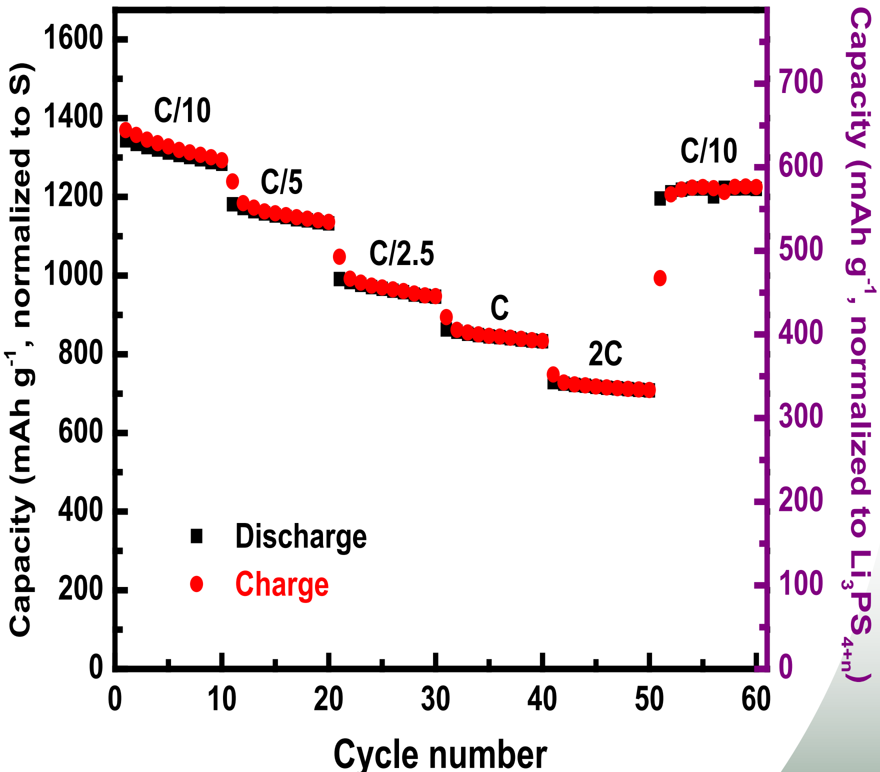
Arrhenius plot

$$\sigma = A_0 e^{-\frac{E_a}{RT}}$$

Progress #3: All-solid Li-S Batteries Have Excellent Cyclability and Rate Performance

All-solid Li-S cells can be cycled at room temperature with better performance at elevated temperatures





Z. Lin, Z. Liu, W. Fu, N.J. Dudney, and C.D. Liang, "Lithium Polysulfidophosphates: A Family of Lithium-Conducting Sulfur-Rich Compounds for Lithium-Sulfur Batteries," **Angew. Chem.-Int. Ed.** (under review)

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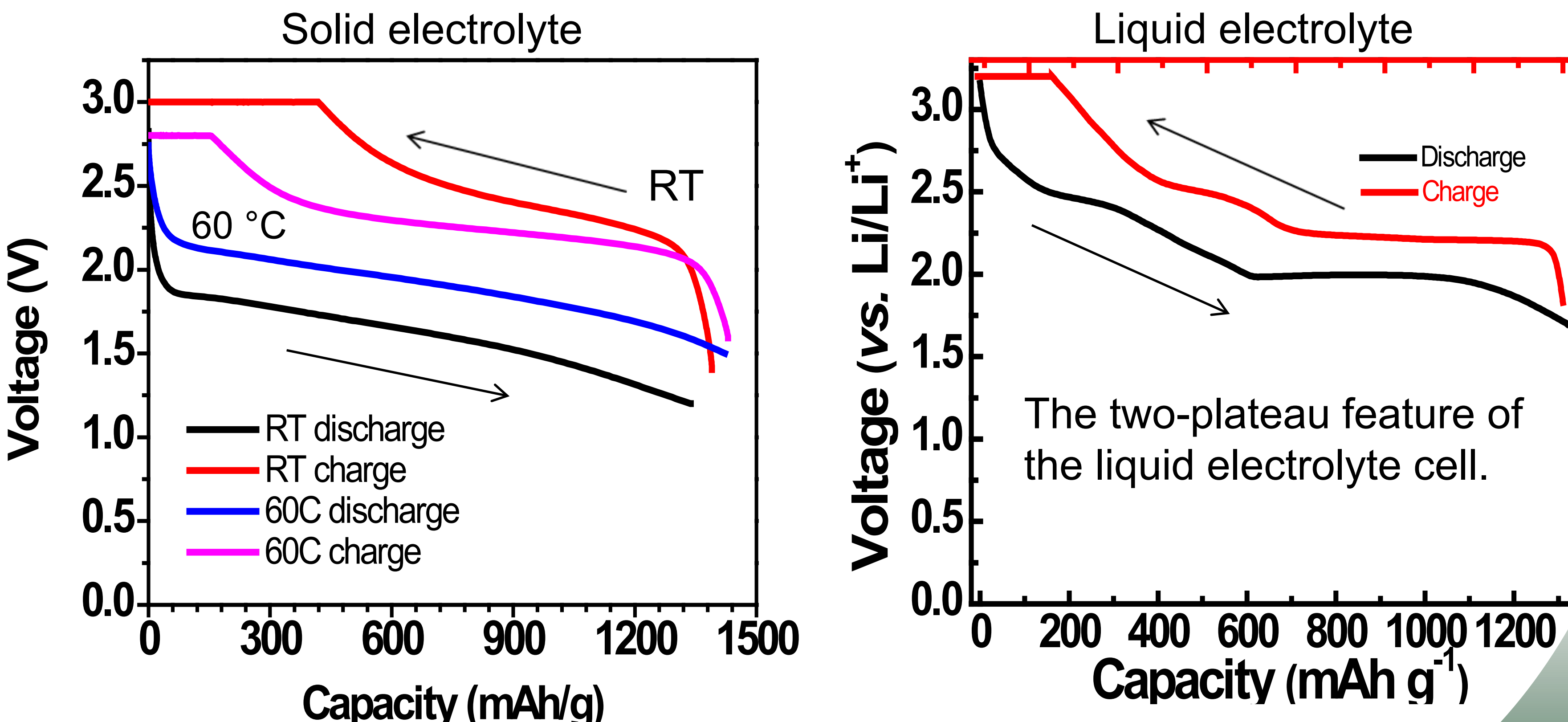
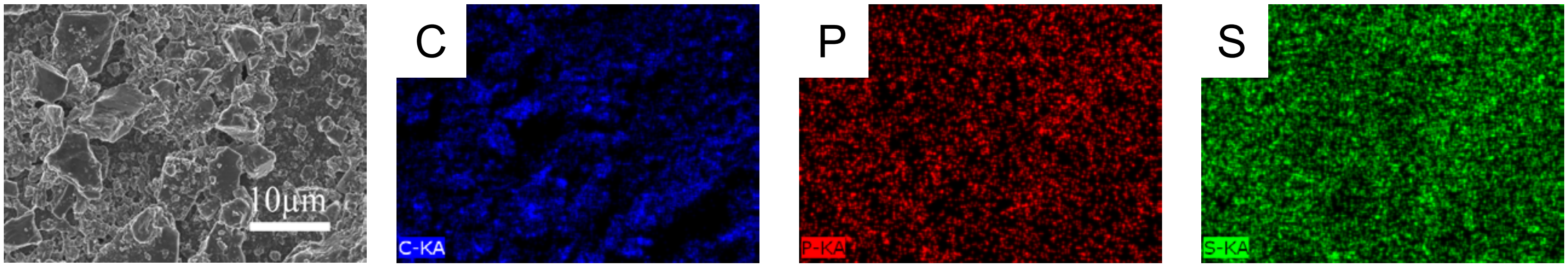
Progress #3: All-solid Li-S Batteries Have a Different Electrochemical Reaction Path

- No polysulfide plateau presents in the all-solid cell
- Over 85% energy efficiency at 60 ºC

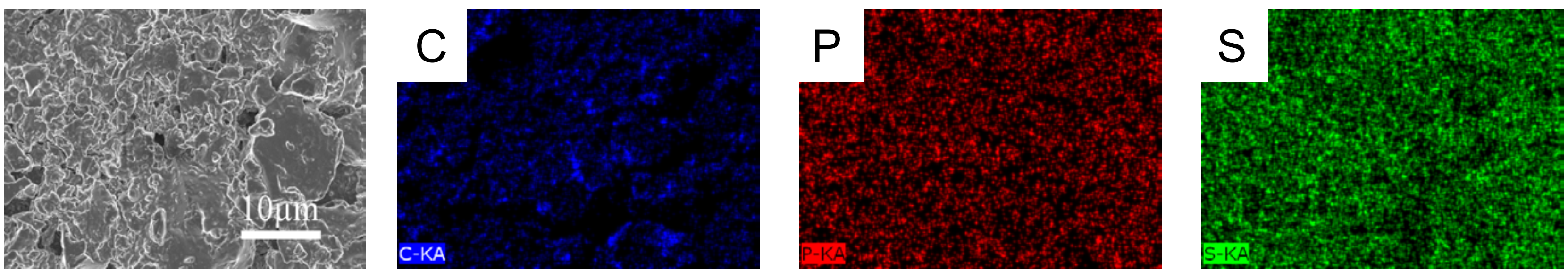


Cathode Structure Preserved after Intensive Cycling

SEM and elemental maps before cycling



SEM and elemental maps after 300 cycles at 60 °C



Images prove the advantages of all-solid Li-S:

- No structural change of the cathode after intensive cycling
- No sulfur migration was observed

Future work

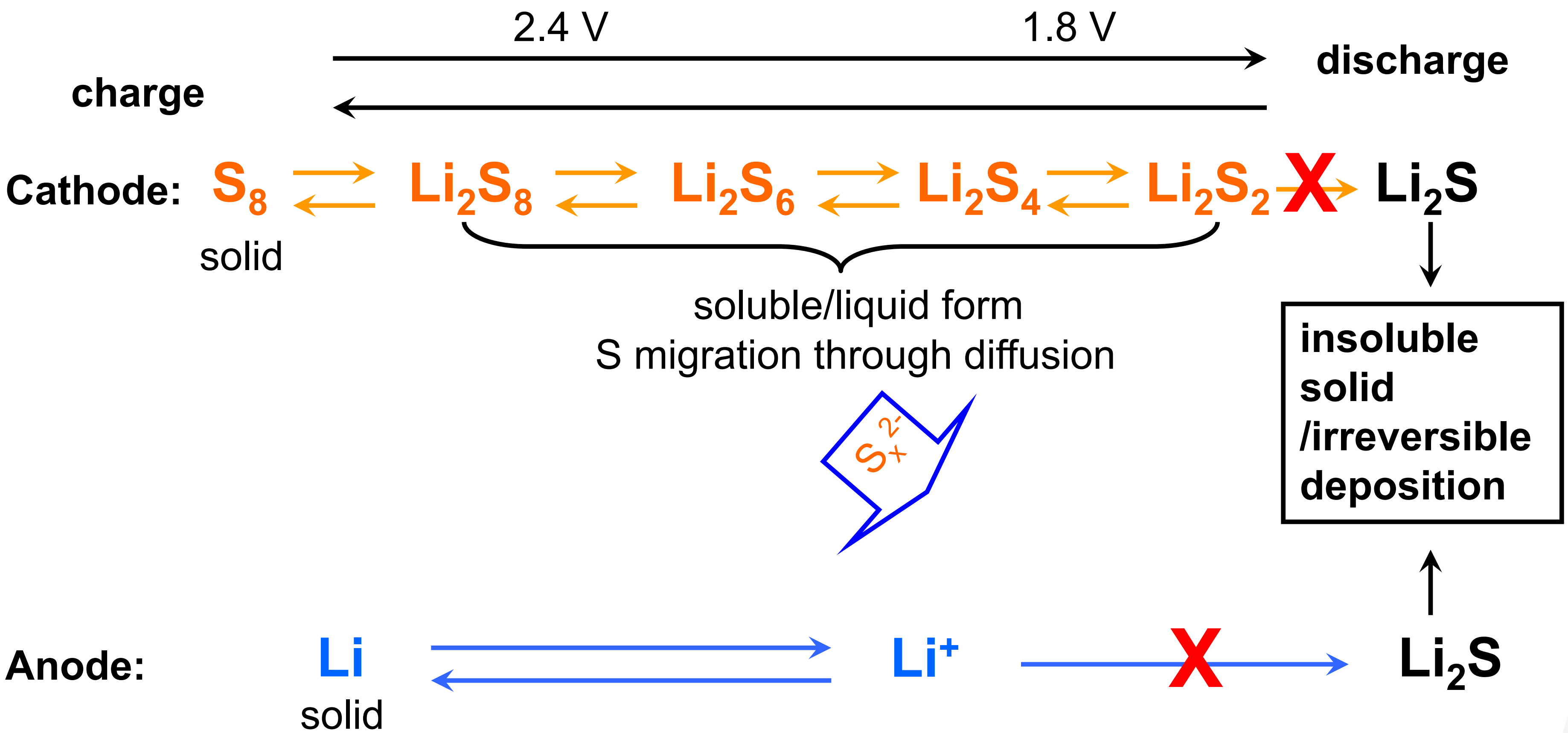
- **Develop new sulfur-rich compounds with ionic conductivity greater than 10^{-5} S/cm**
  - Reduce cell resistance
  - Boost room temperature performance
  - Enable high rate cycling
- **Investigate charge-discharge mechanism of sulfur-rich compounds in the all-solid battery configuration**
  - Guide materials discovery
- **Explore solid electrolytes of high ionic conductivity and low interfacial resistance**
  - Increase energy efficiency
- **Optimize the electrode structure to achieve homogeneous mixing of active materials with electronic conductors**
  - Reduce cell resistance
- **Evaluate the full cell performance of Li-S batteries with optimized thickness of the solid electrolyte layer**
  - Develop practical batteries

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:**
  - **Electrolyte additives facilitate the electrochemical cycling of Li_2S and protect the metallic lithium anode**
  - **All-solid battery structure completely eliminates the polysulfide shuttle phenomenon**
  - **Solid electrolyte membrane prevents the migration of sulfur**
  - **Li^+-conductive cathode materials enable the cycling of all-solid Li-S batteries**
- **Accomplishments and progress:**
  - **Discovered new electrolyte additive of P_2S_5 for conventional Li-S batteries with a liquid electrolyte**
  - **Demonstrated the success of cycling all-solid Li-S batteries**
  - **Developed $Li_2S@Li_3PS_4$ Core-Shell nanoparticles as pre-lithiated cathode material for all-solid Li-S batteries**
  - **Discovered a new family of sulfur-rich ionic conductors as the cathode materials for all-solid Li-S batteries**
- **Future work:**
  - **Optimize the electrode structure to facilitate electrochemical cycling of all-solid Li_2S batteries**
  - **Explore solid electrolyte with high ionic conductivity**
  - **Evaluate the full cell performance of all-solid Li-S batteries with optimized cell components**

Technical Back-Up slides

Challenges for Li-S Battery with Liquid Electrolytes



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