

Mechanistic Investigation for the Rechargeable Li-Sulfur Batteries

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Overview

Timeline

- ▣ **Start: 10/01/2015**
- ▣ **Finish: 09/30/2016**

Budget

- ▣ **Funding received in FY16**
DOE: \$300k

Barriers addressed

- To enable high energy Li-S battery (A,B,C,D,E)
- Li-S batteries with long calendar and cycle life (C,E)
- Practical high performance cathode material synthesis (A,C,D,E)

Collaborators

- Johnson Controls Inc.
- University of Washington Seattle.
- University of Arkansas
- University of Maryland at College Park
- Pacific Northwest National Laboratory (PNNL)

- Department of Chemistry, Wuhan University
- Department of Chemistry, Wuhan University of Science and Technology
- Beijing Institute of Technology.
- Institute of Physics, Chinese Academy of Sciences

Relevance and Project Objectives

- ✓ *Development of a reliable analytical method for the quantitative and qualitative determination of dissolved elemental sulfur and polysulfide ions in non-aqueous electrolyte, based on High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy(MS).*
- ✓ *Fundamental research on the mechanism of sulfur cathode redox reaction in Li-S batteries (to guide the sulfur cathode material and electrolyte synthesis).*
 - To establish *in-situ* and *ex-situ* electrochemical-HPLC/MS/UV methods.
 - To investigate the distribution of dissolved polysulfide ions during the discharge and recharge of a Li-S battery,
 - To investigate the relationship between the diffusivity of the polysulfide ions and the physical / chemical structure of the porous sulfur cathode.
- ✓ *Investigation of the chemical reaction and equilibrium of dissolved elemental sulfur and polysulfide ions (to reduce the “shuttle effect” and to increase the shelf life, cycleability and charge efficiency).*
 - To search for the electrolyte which is adequate for Li-S batteries.
 - To search for the additives which can form a stable SEI layer on Li anode which can prevent chemical reaction between dissolved sulfur compounds.

Milestones

Month/Year	Milestones	Status
Dec/15	Complete literature review and feasibility study of the methods for polysulfide determination.	Completed
Mar/16	Complete the development of the assay to determine all polysulfide ions	Completed
Jun/16	Complete the design, qualification for an <i>in-situ</i> electrochemical HPLC-MS cell for Li-S investigation.	On schedule
Sep/16	Complete the identification of polysulfide ions formed from elemental sulfur.	On Schedule

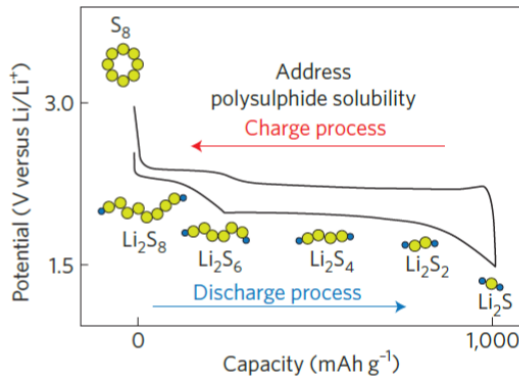
Approaches

- A combination of *High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy(MS)* together with *in situ* electrochemical measurement in a specially designed cell. The electrochemically formed dissolved polysulfide ions can be separated (by HPLC) and determined (by MS).
- *Ex-situ* X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to investigate the surface of sulfur cathode and Li anode to elucidate the surface changes during the Li-S battery operation
- *In-situ* Keyence 3D microscope and electrochemical measurement in a specially designed cell to investigate the surface modification of Li with e.g. various additives and at different stage of charge/discharge.
- Extended collaboration with other US and international academic institutions and US industrial partners.

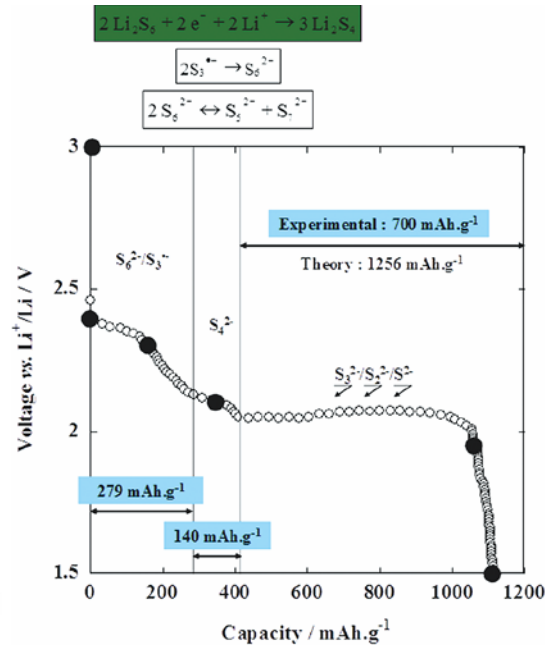
Technical Accomplishments

- Several HPLC/MS/UV essays have been developed and tested for the reliable and accurate analysis of dissolved elemental sulfur and polysulfide ions in the Li-S electrolyte. We believe it is the first (maybe only) method for the accurate determination of polysulfide ions in Li-S electrolytes. It was also proven that the polysulfide itself CANNOT be separated by HPLC and detected by MS, they must be derivatized first.
- The solubility of sulfur in various non-aqueous electrolytes has been determined. The solubility of sulfur was found not only related to the solvent, but also related to the concentration of salt.
- An *in-situ* electrochemical-HPLC experiment provided firm evidence that the polysulfide ions formed during the very initial electron transfer were shorter chain polysulfide ions, not S_8^{2-} as reported in the literature.

Literature Review: Dissolved Polysulfides Play Important Roles



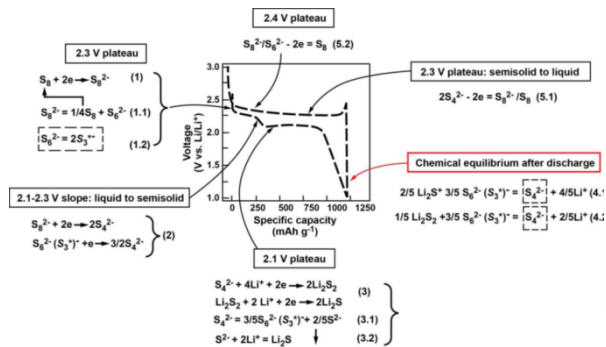
P. Bruce etc. Nat. Mater. 11(2012)19



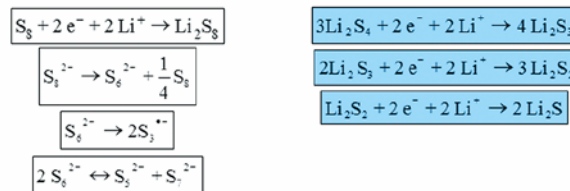
Questions:

1. Multistep multielectron electrochemical process, why are there only two steps in the discharge curve?

2. How to quantitatively and qualitatively measure polysulfide species?



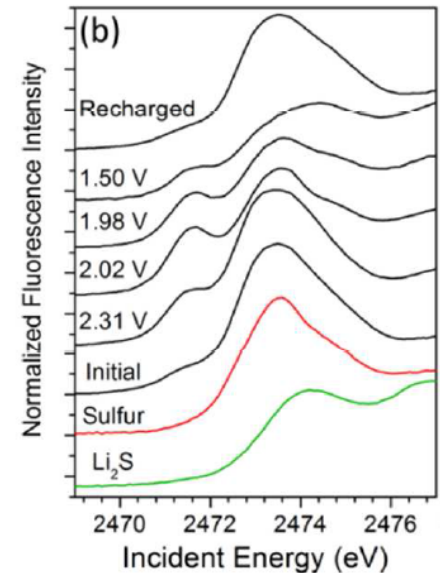
J.Xiao etc. JEC 162(2015)A474



C. Barchase Anal. Chem. 84 2012 3973

Quantitative and Qualitative Determination of Polysulfide Becomes Critical

X-Ray Absorption Near Edge

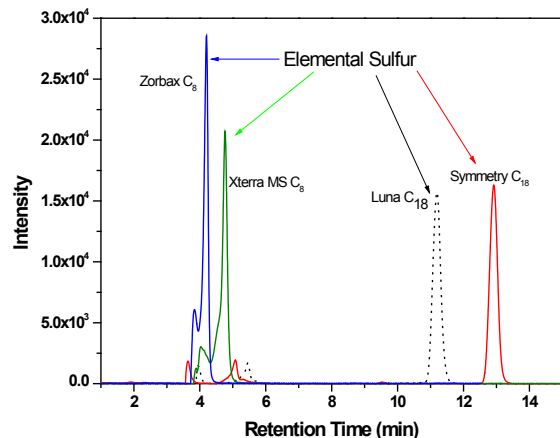


H.D. Abruna etc. RSC Adv. 4(2014)18347

Because it is impossible to make pure polysulfide ion with precise chain length in solution due to the chemical equilibrium and disproportionation.

HPLC-MS/UV is the technique **NOT** based on standards, but on mass/charge ratio for quantitative and qualitative analysis

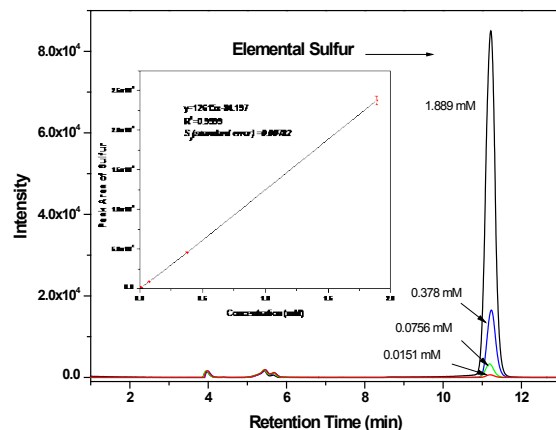
S₈ analysis



- Elemental Sulfur (S₈) can be separated and detected.
- The solubility of S₈ is different in different solvents.
- The solubility of S₈ changes with salt in the same solvent.

Solubility of S₈ in DMSO with different Salts (1M)

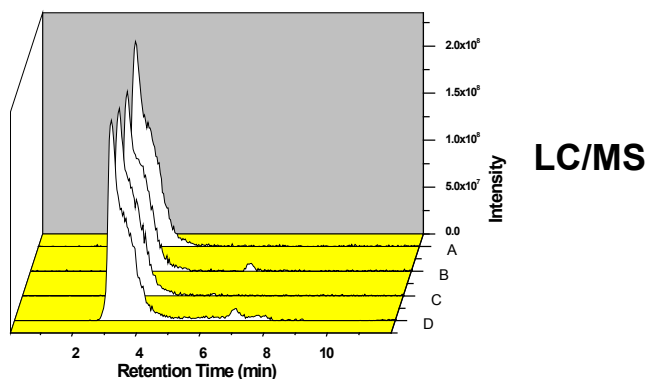
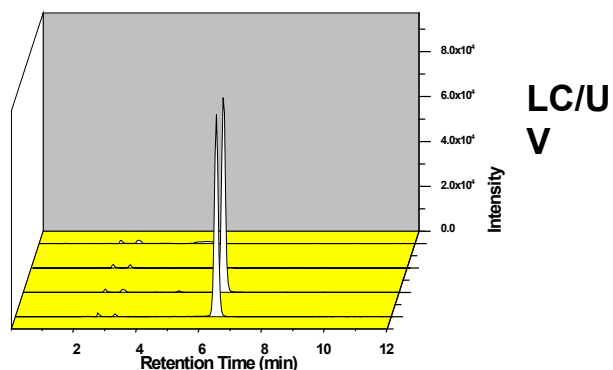
Salt	Solubility (mM)
LiTFSi	1.933
LiClO ₄	2.416
LiBF ₄	1.768
LiCF ₃ SO ₃	2.161
TEABF ₄	2.170



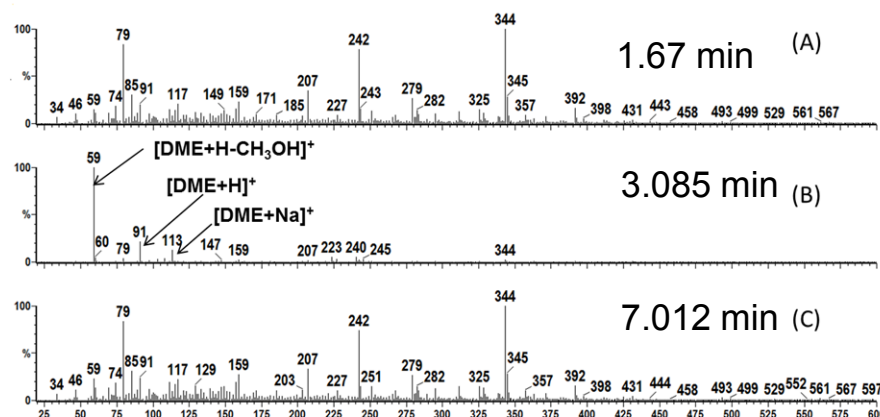
Solubility of S₈ in pure solvent

Solvent	Solubility mM, pure solvent	Solubility (mM), 0.1M electrolyte (LiTFSI)	Solubility (mM), in 1.0M electrolyte
AN	0.610	0.596	0.390
PY	48.046	28.005	15.909
DMF	5.944	5.895	2.603
PC	1.318	1.255	0.633
GBL	3.888	3.366	1.606
DGME	10.259	9.511	3.875
DME	9.957	8.963	3.994
DMSO	3.936	3.845	1.933
BMPTFSi	0.349	0.245	0.216

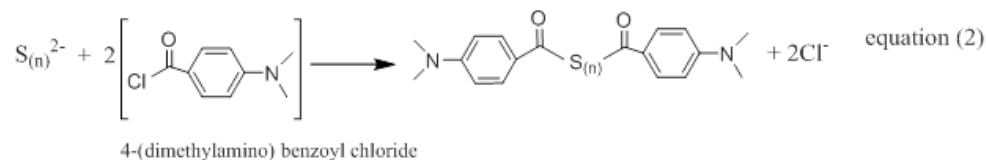
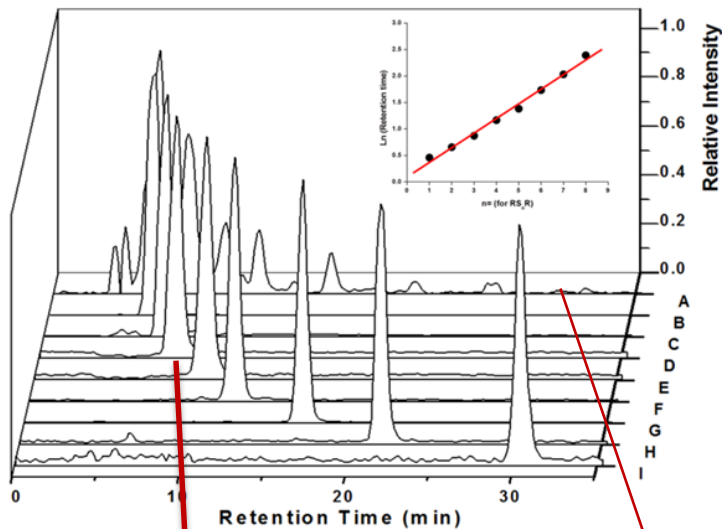
Polysulfides itself cannot be separated in LC column due to the lack of retention in the solid phase



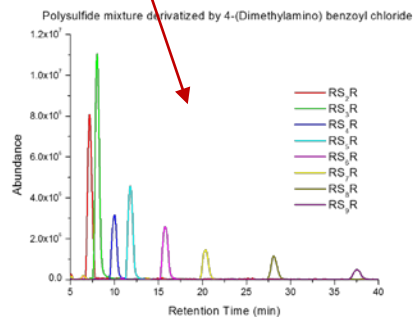
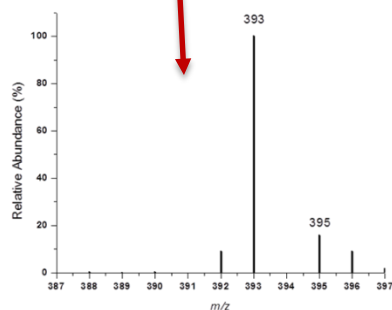
- Solutions:
 - A: pure DME
 - B: Na_2S saturated DME
 - C: S_8 saturated DME
 - D: DME saturated with both S_8 and Na_2S
- Only S_8 can be detected by UV and only DME can be detected by ESI-MS
- Polysulfides cannot be separated due lack of retention mechanism.



Polysulfides can be separated and analysis by HPLC-/UV/MS with proper complexation essay

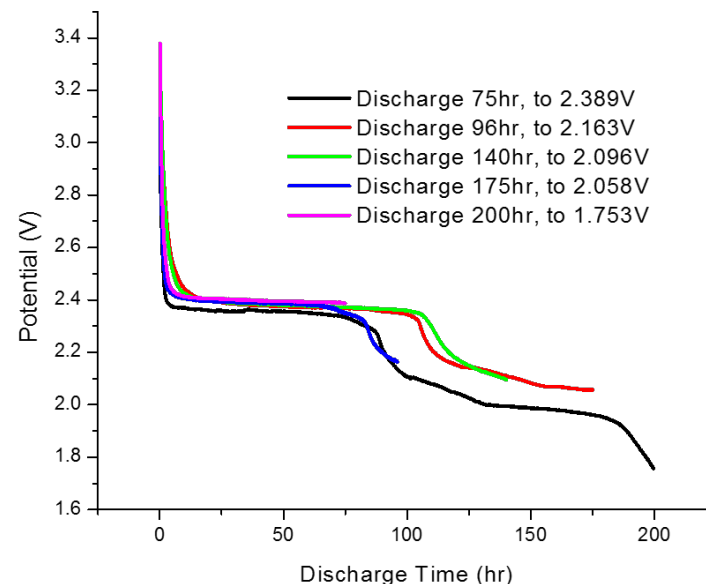
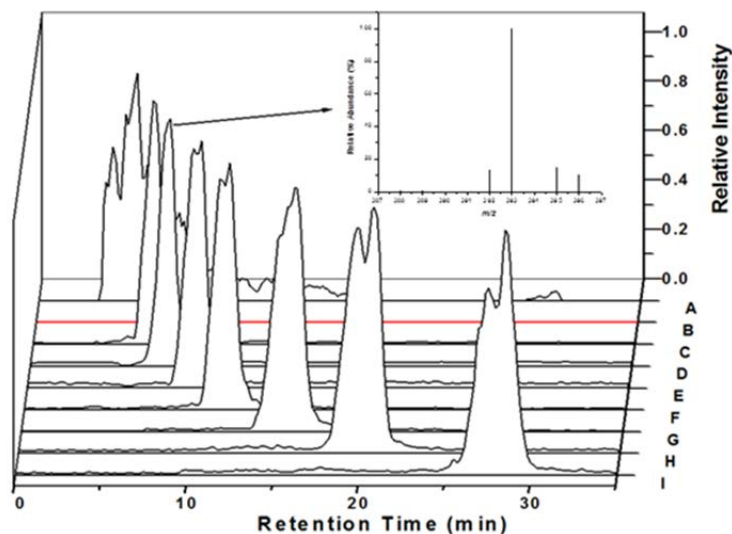


ALL 8 polysulfides are separated and qualitatively analyzed for the first



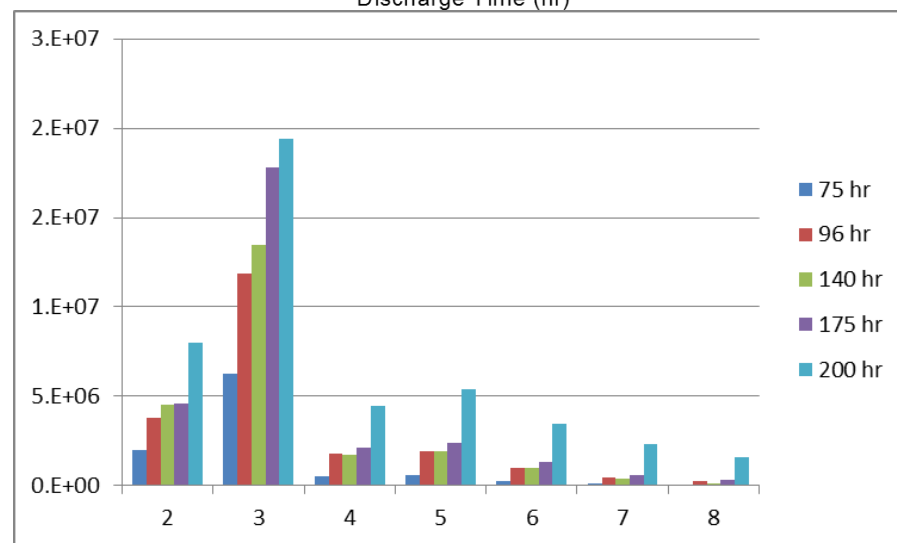
Na_2S and S_8 in acetonitrile, molar ratio of $\text{Na}_2\text{S}:\text{S}$ is 1:3

The distribution of polysulfides at various depth of discharge (right) and in a discharged Li-S cell (left)

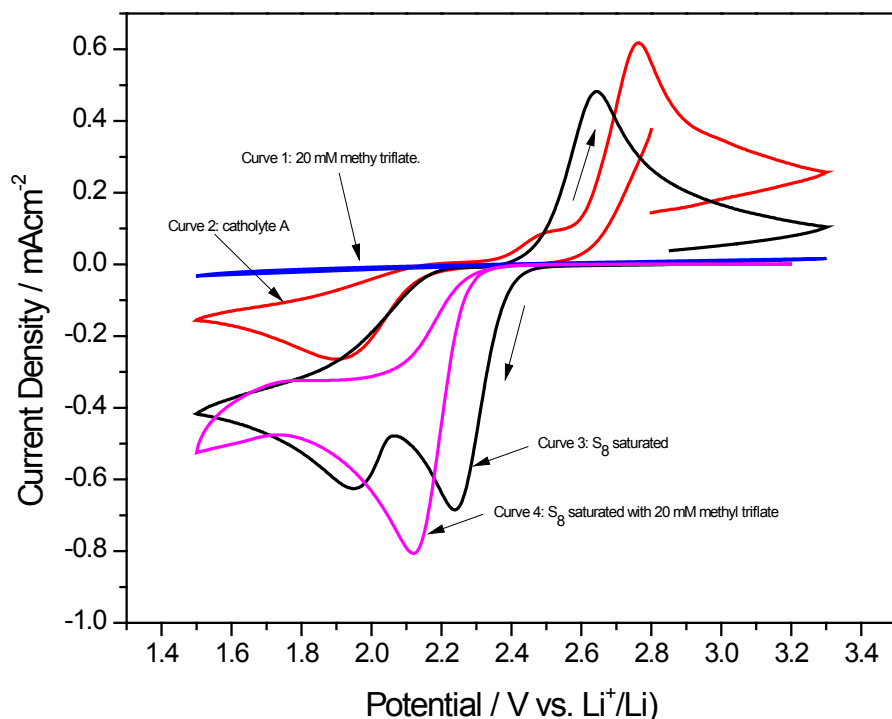
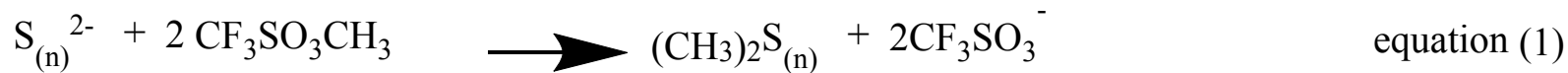


M	$[M+H]^+$	Retention Time	Relative Intensity for the electrolyte
R ₂ S	329	6.19±0.12	0
R ₂ S ₂	361	7.02±0.19	0.352(4.8%)
R ₂ S ₃	393	8.13±0.02	1.000(6.4%)
R ₂ S ₄	425	10.09±0.05	0.229(5.6%)
R ₂ S ₅	457	11.95±0.02	0.278(7.0%)
R ₂ S ₆	489	15.96±0.06	0.181((8.1%)
R ₂ S ₇	521	20.66±0.07	0.121(9.7%)
R ₂ S ₈	553	28.57±0.17	0.081(8.1%)

Rel. Std Dev.



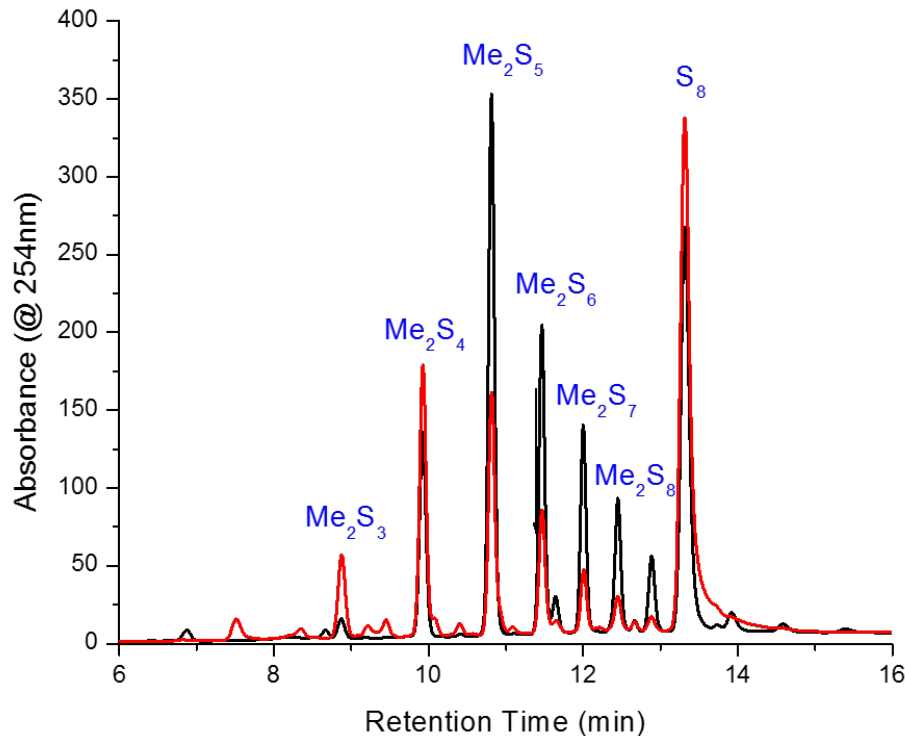
In-situ capture of polysulfide formed during reduction



Catholyte A : 0.0194 g sulfur in 20 mL 1M LiTFSi/DME solution saturated Li₂S. Glass carbon electrode; 30 mV/s

- To investigate the mechanism of sulfur reduction, the polysulfides formed during electrochemical reaction need to be identified before subsequent **CHEMICAL** reaction in the electrolyte.
- When the polysulfide ions are derivatized, the resulting complexes are inert – not participate further chemical reaction nor be electrochemically reduced or oxidized.

Comparison of in-situ and ex-situ detection methods.



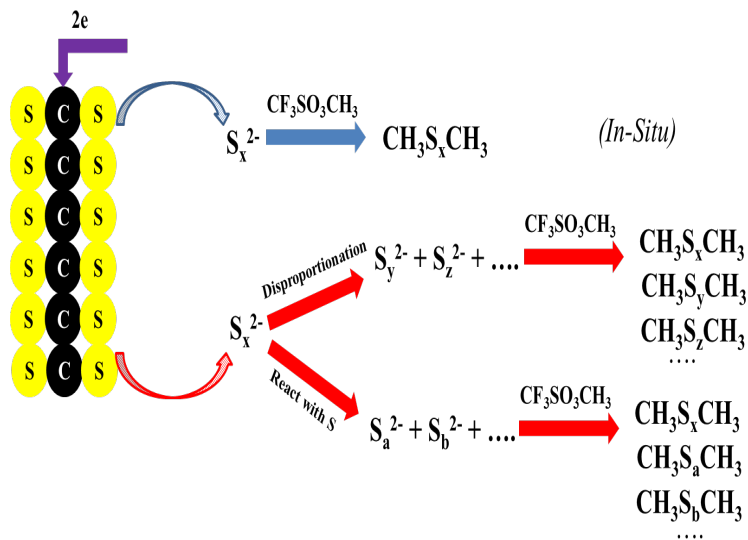
Sulfur saturated in 20 mL 1M LiTFSi/DME, Glass carbon electrode; polarized at 2.3 V vs Li

- The glass carbon electrode was polarized at 2.3 V vs. Li – the first electron transfer (from elemental sulfur to polysulfide).
- **Black:** *ex-situ* (electrolyte was taken out and then derivatized outside)
- **Red:** *in-situ* (derivatizer was added into the catholyte solution)
- ***S₈²⁻ was not the polysulfide form in the electrochemical reduction.***

The electrochemically formed polysulfides react with elemental sulfur chemically

Derivatization method	Discharge capacity at 2.3V (mAh)	Percentage of elemental sulfur left from theoretical calculation based on 2-electron transfer	Percentage of elemental sulfur left from HPLC/UV measurement
In-Situ	1.42	34.0%	37.9%
Ex-Situ	1.43	33.3%	24.9%

Electrochemical reduction of elemental sulfur was not enough to count for all the sulfur consumption in Li-S cell.



As soon as polysulfide ions are formed electrochemically, they will be captured by derivatization, the subsequent chemical reactions are avoided. The method provides a “snap shoot”.

Response to last year reviewer's comments

Comments from 2015 AMR

Response

Project was not reviewed in 2015AMR

Project was not reviewed in 2015AMR

Collaborations with other institutions and companies

- **Johnson Controls Inc.**
Optimization of sulfur cathode fabrication.
- **University of Washington Seattle**
Solid state synthesis of sulfur cathode materials.
- **University of Arkansas**
Material synthesis and sulfur loading.
- **University of Maryland at College Park**
Dissolve polysulfide investigation (electrolyte)
- **Pacific Northwest National Laboratory (PNNL)**
Sulfur loaded carbon cloth electrodes

- **Department of Chemistry, Wuhan University**
In situ electrochemistry – spectroscopy technique development.
- **Department of Chemistry, Wuhan University of Science and Technology**
Synthesis of nano particle size sulfur materials
- **Beijing Institute of Technology**
Sulfur material synthesis
- **Institute of Physics, Chinese Academy of Sciences**
Electrode structure analysis

Remaining Challenges and Barriers

- The *in-situ* technique developed can only applied to the very first electron transfer without altering the redox mechanism of the sulfur cathode. Because in a practical system, polysulfide ions will experience the subsequent homogeneous reactions.
- It remains a challenge of searching adequate and effective electrolyte additives which can form more stable SEI layer preventing continuous reaction between polysulfide, sulfur and Li anode.
- To limit the diffusivity of dissolved sulfur and polysulfide ions beyond the surface coating and encapsulation.
- Sulfur containing electrode with high sulfur loading and decent conductivity.

Proposed Future Work for *FY 2016* and *FY2017*

■ FY2016 Q3 Milestone:

Complete the design, qualification for an *in-situ* electrochemical HPLC-MS cell for Li-S investigation.

■ FY2016 Q4 Milestone:

Complete the identification of polysulfide ions formed from elemental sulfur.

FY2017 work:

- Investigating the mechanism of sulfur redox reaction by means of in-situ and ex-situ electrochemistry-HPLC/MS/UV techniques.
- *In-situ* Keyence 3D microscope and electrochemical techniques will be used to study the surface conditions of both sulfur cathode and Li anode using the in-situ optical cell.
- Investigating the relationship between the diffusivity of the dissolved sulfur compounds with the porous structure of the sulfur cathode.
- Synthesis sulfur cathode material for performance improvement.
- Continuing and enhancing the collaborative research with academic research institutions and industrial partners.

Summary

■ Relevance

- ✓ *Development of a reliable analytical method for the quantitative and qualitative determination of dissolved elemental sulfur and polysulfide ions in a non-aqueous electrolyte, based on High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy(MS).*
- ✓ *Fundamental research on the mechanism of sulfur cathode redox reaction in Li-S batteries (to guide the sulfur cathode material and electrolyte synthesis).*
- ✓ *Investigation of the chemical reaction and equilibrium of dissolved elemental sulfur and polysulfide ions (to reduce the “shuttle effect” and to increase the shelf life, cycleability and charge efficiency).*

■ Approaches

- ✓ *In-situ electrochemistry-HPLC)/MS/UV.*
- ✓ *Ex-situ X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).*

■ Technical Accomplishments

- ✓ *Developed HPLC/MS essays for the reliable determination of dissolved polysulfide ions.*
- ✓ *Determination of the solubility of sulfur in various electrolytes*
- ✓ *In-situ and ex-situ determination of dissolved polysulfide ions during the charge and discharge of Li-S batteries.*

■ Proposed Future work

- ✓ *in-situ and ex-situ electrochemistry-HPLC/MS/UV for sulfur redox mechanism study.*
- ✓ *In-situ Keyence 3D microscope and electrochemical techniques for the cathode and anode surface studies.*
- ✓ *Investigating and synthesis porous sulfur cathode for performance improvements.*