Development of High Energy Lithium-Sulfur Batteries

Jun Liu and Dongping Lu

Pacific Northwest National Laboratory

2018 DOE Vehicle Technologies Program Review
June 18-21, 2018

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Project ID#: bat282

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Overview

Timeline

- Start date: Oct. 2015
- End date: Sept. 2018
- Percent complete: 80%

Barriers

- Low rate at high S loading
- Limited cycling life at low electrolyte/S ratio
- Shuttle effect and self discharge

Budget

- Total project funding-DOE share 100%
- Funding received in FY17: $400k
- Funding for FY18: $400k

Partners

- Brookhaven National Laboratory
- University of Wisconsin–Milwaukee
- General Motors
- Pacific Northwest National Laboratory

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Relevance/Objectives

- Enhance sulfur utilization rate in high loading sulfur cathodes.
- Study the effects of electrode porosity control on cell energy, sulfur utilization, electrolyte/sulfur ratio and cell cycling life.
- Advance the fundamental understanding of electrolyte/additive degradation mechanism in Li-S batteries.
- Mechanism study on sulfur cathode by completely decoupling the interferences from lithium anode.
- Project efforts are directly aimed at barriers of low practical energy density, shuttle effect, low rate capability and limited cycling life of Li-S batteries.

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Milestones

Date	Milestones and Go/No-Go Decisions	Status
December 2017	Study of electrolyte compatibility with different carbon host materials and binders and their effects on reversible sulfur utilization	Completed
March 2018	Design and demonstration of a electrochemical cell by using ceramics Li^+ conductive separator for focused mechanism study on sulfur cathode	Completed
June 2018	Study failure mechanism of Li-S cell under lean amount of liquid electrolyte by decoupling the interference of Li anode using liquid/solid electrolyte hybrid cell	On track
September 2018	Develop functionalized separators to suppress polysulfide shuttle and improve interfacial stability of Li anode	On track

Approach/Strategy

- Develop electrode additives to overcome the electrode wetting problems in high loading sulfur cathodes
- Improve energy density of sulfur cathode through porosity control and effective measures to improve cell performance
- Identify degradation mechanism of $LiNO_3$ and its impact on Li-S batteries
- Remove interferences of Li metal anode for focused study on sulfur cathode through a design of liquid/garnet oxide solid-electrolyte hybrid cell

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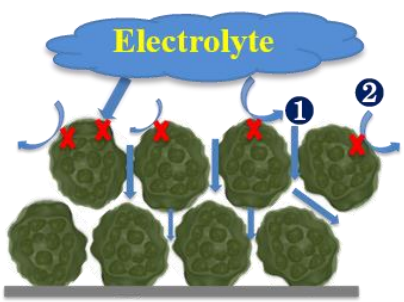
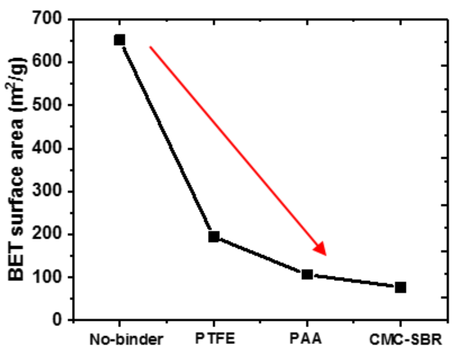
Technical Accomplishments

Identified coating effects of solution-based polymer binders on sulfur cathode

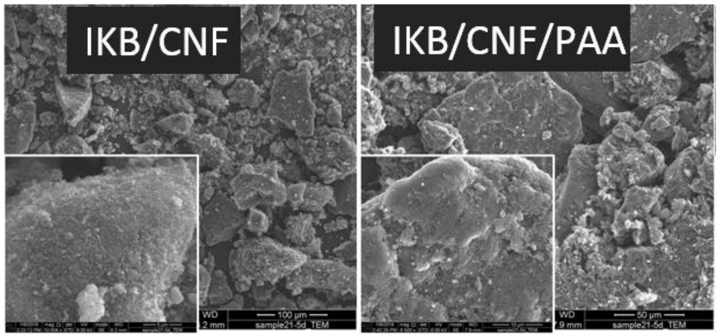
- Significant reduction of both surface area and pore volume is caused by polymer binder coating
- Results in blocked electrolyte penetration



Blocked electrode wetting in the presence of binders



Reduced BET surface of IKB (integrated Ketjen Black)/CNF in the presence of binders



SEM images

Smooth and covered surface with binder (IKB/CNF, 90%; binders,10%)

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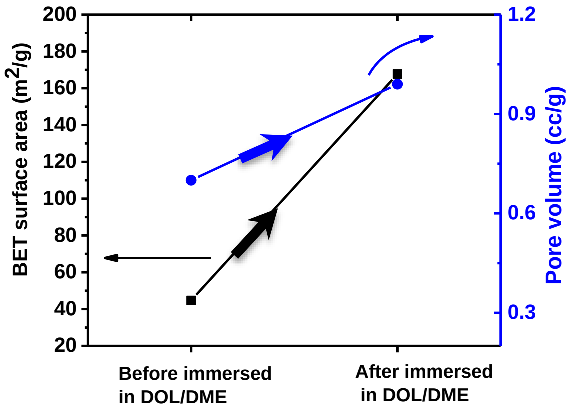
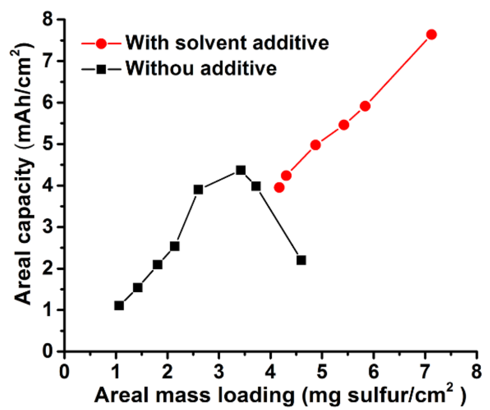
Technical Accomplishments

Electrode additives to overcome wetting issues in high loading sulfur cathodes

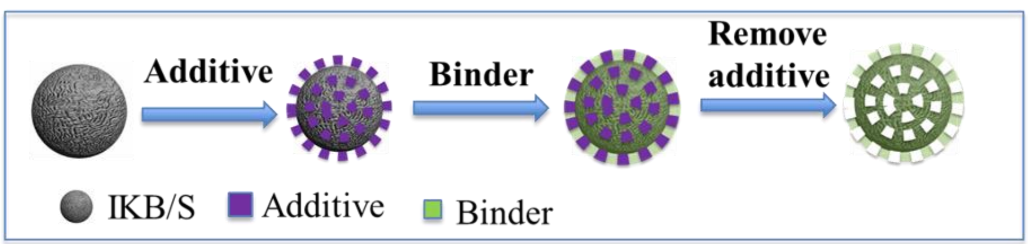
- Electrode additives enable quick electrolyte infiltration and high sulfur utilization rate



BET Surface activation with additive PEGDME



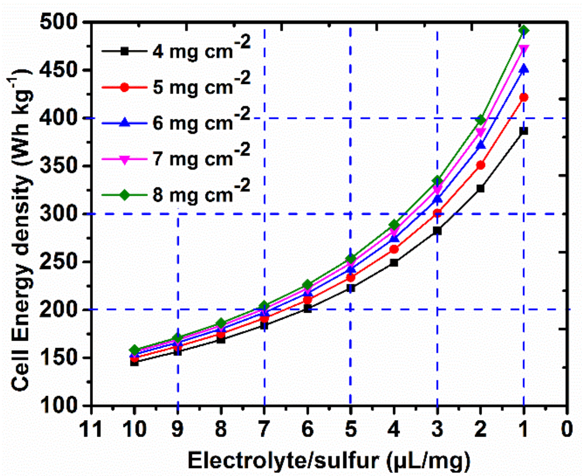
Enhanced sulfur utilization in high loading sulfur cathode by using additive



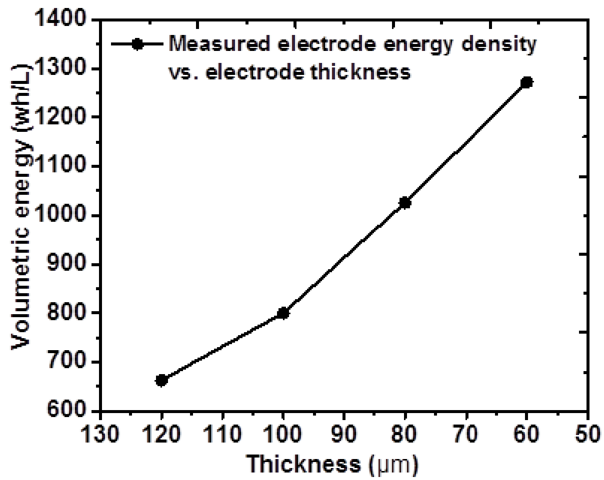
Functional additives for electrode preparation

Technical Accomplishments

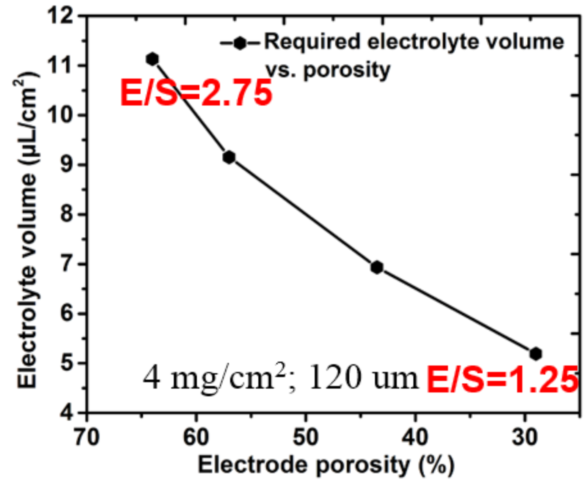
Benefits of electrode porosity control



System energy vs. sulfur loading and electrolyte



Boosted volumetric energy



Reduced electrolyte amount

- High loading cathode and lean electrolyte for high energy
- Low electrode porosity boosts electrode volumetric energy
- Dense electrode reduces electrolyte uptake, improving specific energy density and saving electrolyte for long cycle life

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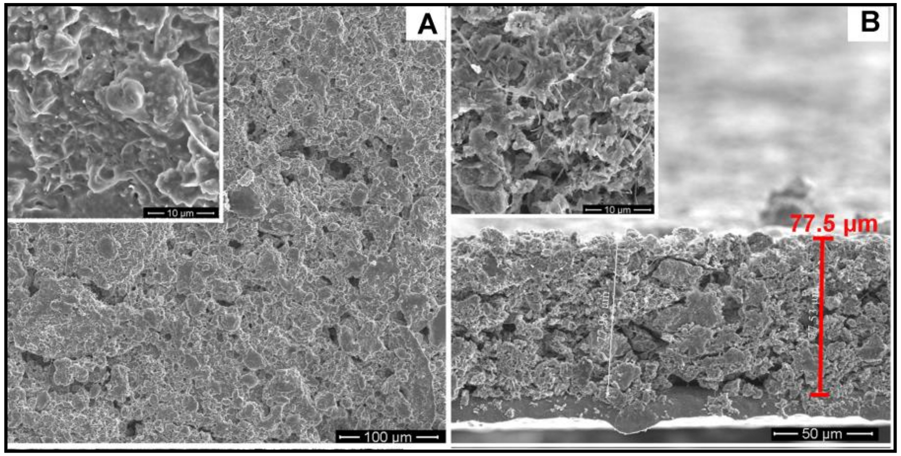
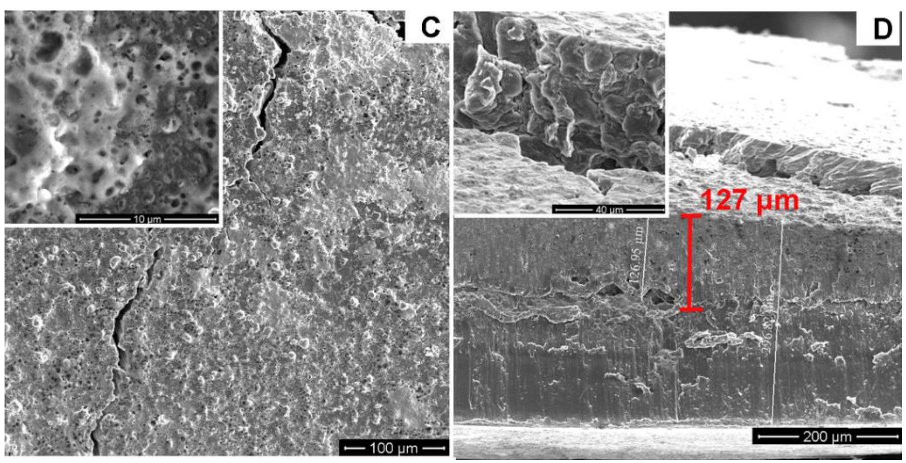
Technical Accomplishments

Benefits of electrode porosity control



Surface and cross-section of dense cathode (60 µm, 4 mg/cm^2) after 200 cycles



Surface and cross-section of Li anode after 200 cycles with dense cathode

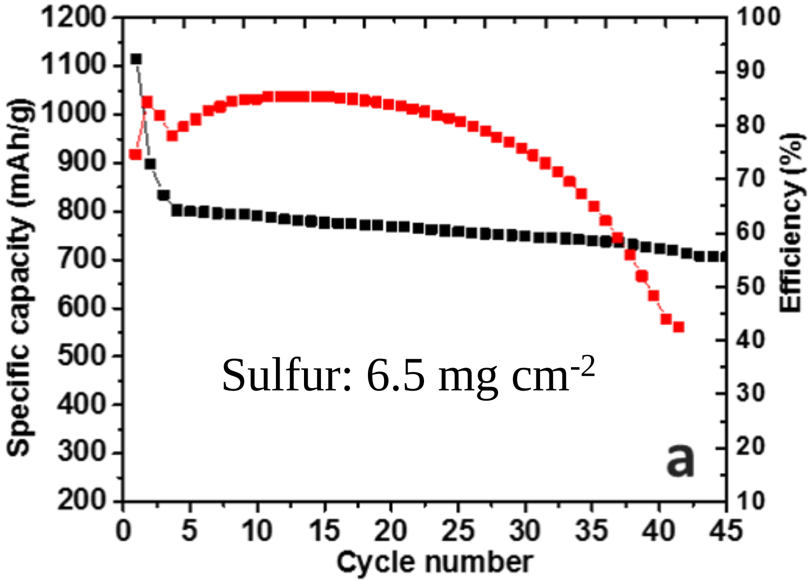
- Dense cathode suppresses free polysulfide diffusion; electrode expands ca. 25% in thickness after 200 deep cycles.

- The quick growth of Li interphase is suppressed due to the maintained internal pressure from dense cathode.

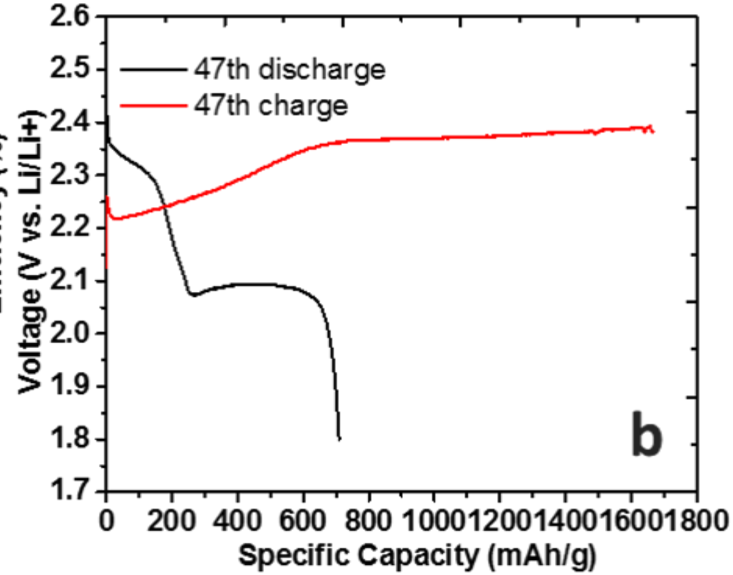
Technical Accomplishments

Low coulombic efficiency issue in high energy sulfur cathodes

- Low Coulombic efficiency, as well as its fast decay, is usually observed in high loading sulfur cathodes
- Indicates quick depletion of $LiNO_3$ additive



(a) Cycling stability and Coulombic efficiency of sulfur electrode



(b) failed charge/discharge profiles (47th cycle)

(Electrolyte:1 M LiTFSI/DOL/DME+0.2 M $LiNO_3$)

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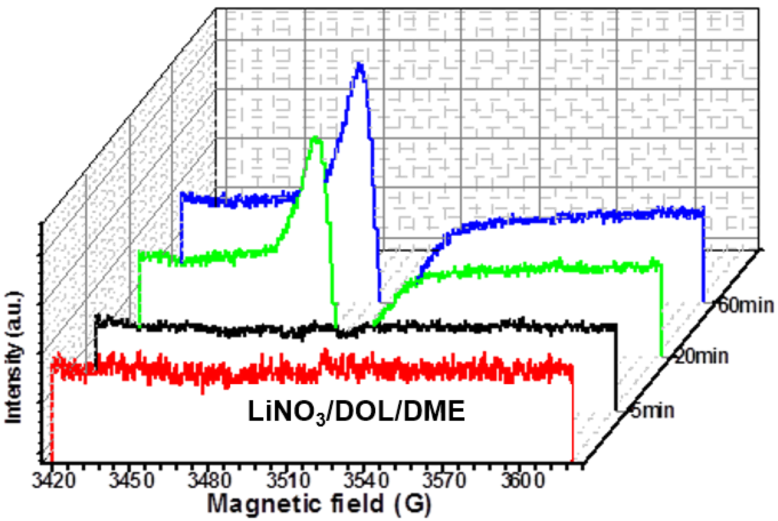
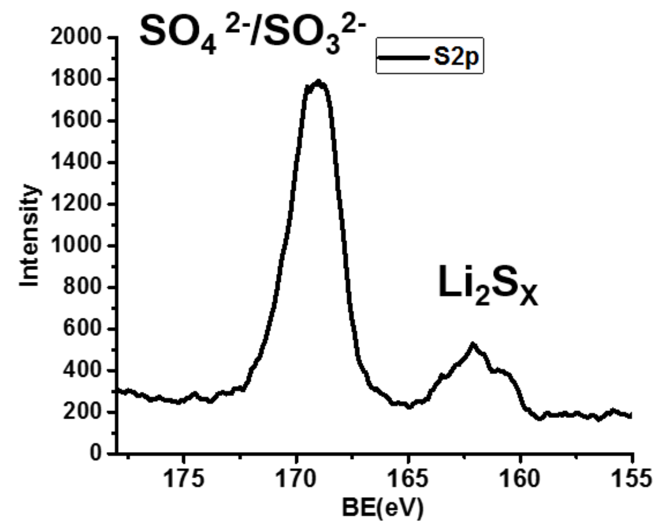
Technical Accomplishments

Identified new degradation mechanism of LiNO3 at sulfur cathodes

- In-situ EPR results indicate chemical reactions of between Li2S and LiNO3
- SO4 2-/SO32- are identified as oxidation products



In-situ EPR (Electron paramagnetic resonance) of Li_2S with $LiNO_3$ contained solution



XPS result of sulfur cathode

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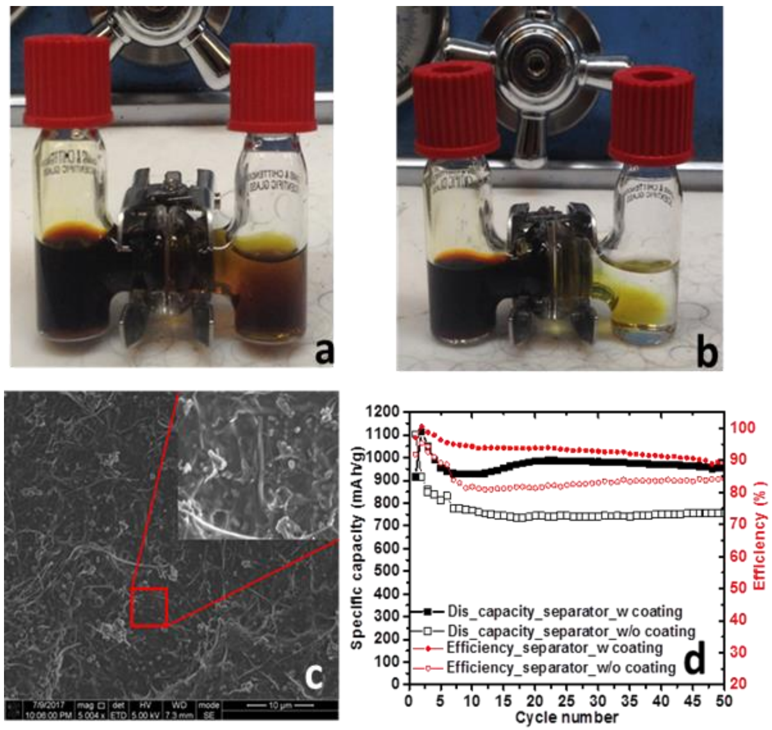
Technical Accomplishments

Functional polymer coated separator to mitigate polysulfide shuttle



Visual comparison of polysulfide diffusion in H-cell using Celgard 2400 separator.

(a) with and (b) without C-PAA coating after 1 hour rest

(c) SEM image of C-PAA/CNF coated separator.

(d) capacity and coulombic efficiency of Li-S cells using separators with and without C-PAA coating.

- Cross-linked polyacrylic acid (C-PAA)/carbon nanofiber coating can effectively mitigate polysulfide crossover
- Significantly improved reversible capacity and Coulombic efficiency

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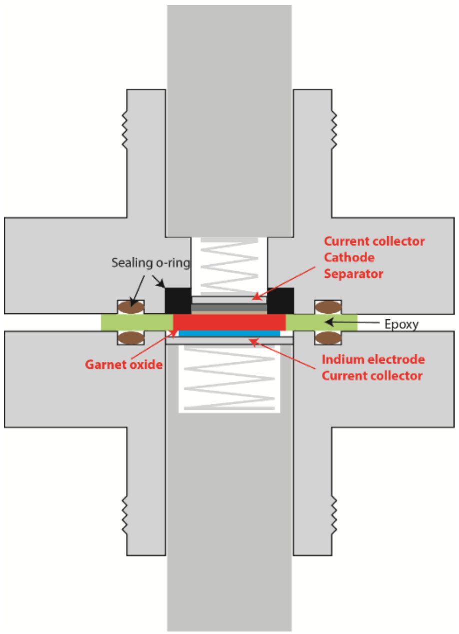
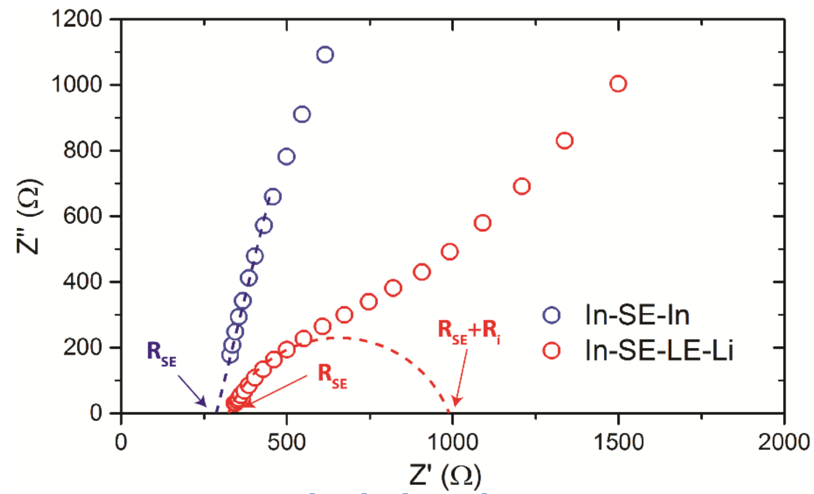
Technical Accomplishments

Hybrid cell design to decouple the interferences of Li for focused studies of sulfur cathodes



Section view of the hybrid cell design



Ideal situation

Electrochemical impedance of In-SE-In and In-SE-LE-Li (5 mv, 10^5-10^{-1} Hz)

- Completely separated two electrodes by garnet oxide membrane
- Sealing mechanism and meticulously designed sealing parts ensures stable electrochemical operation outside the glovebox

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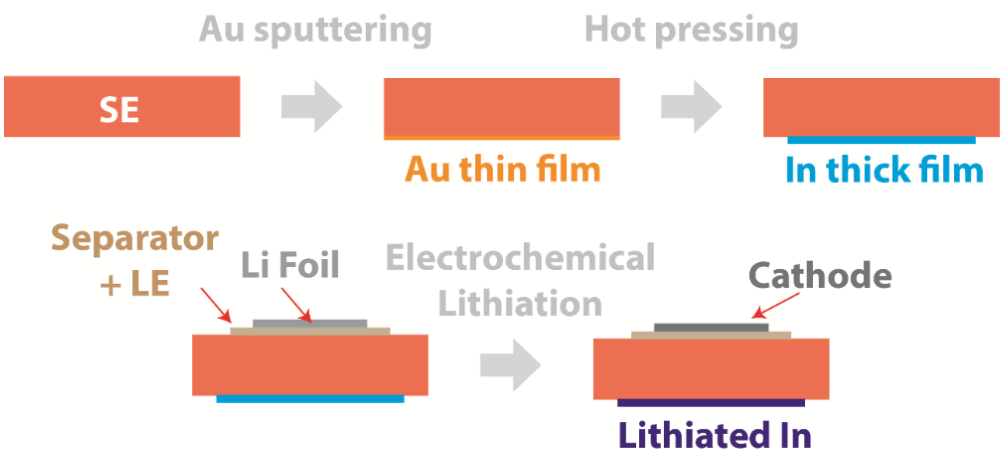
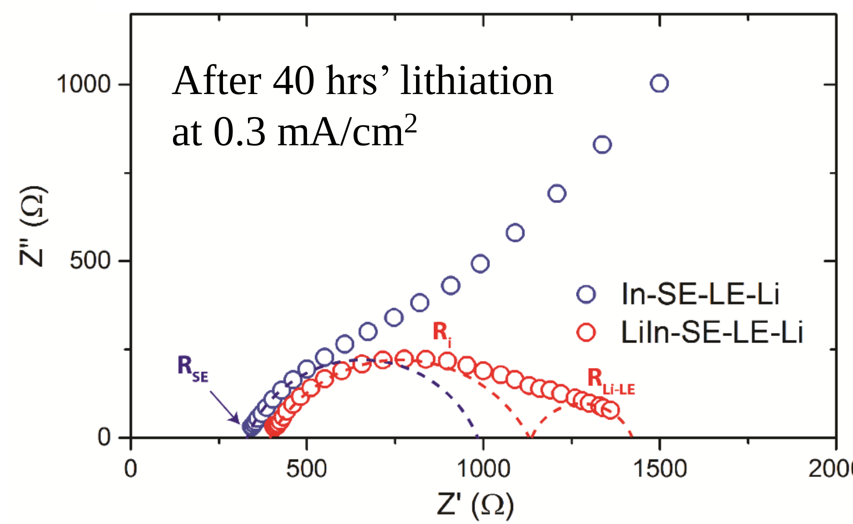
Technical Accomplishments

Stabilized garnet/Li interface for high current density operation



- LiIn anode and Au interlayer coating enable stable anode/garnet interface thus operation of the hybrid cell at high current densities without short circuit.



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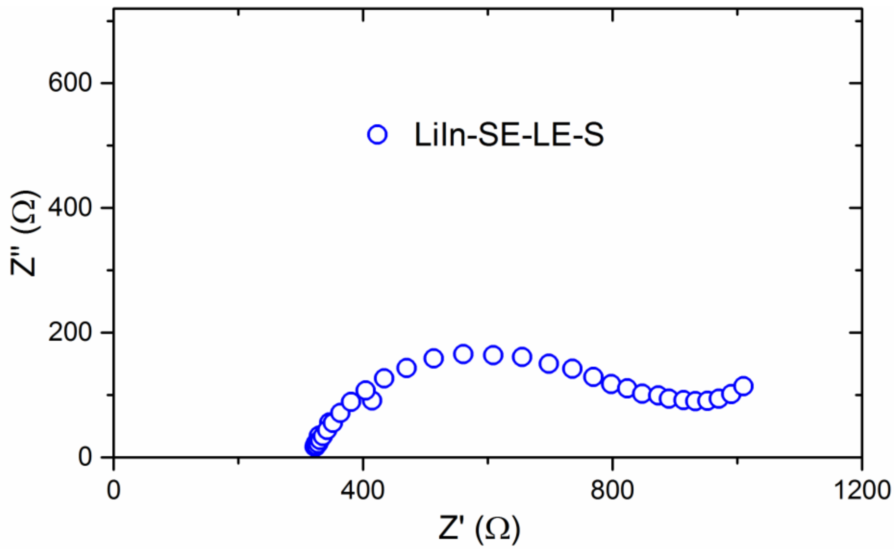
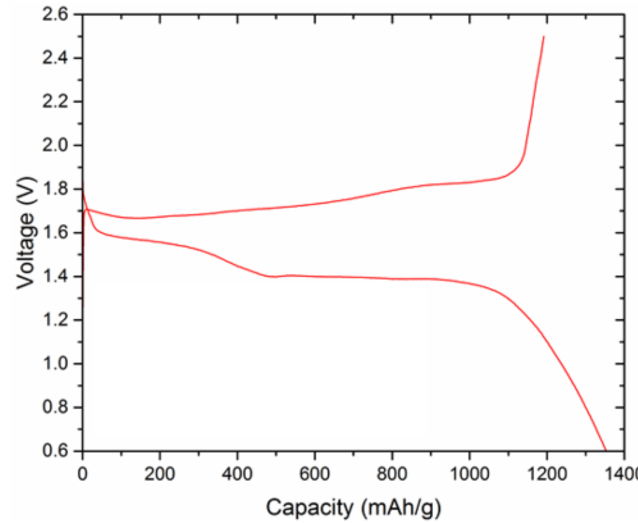
Technical Accomplishments

Blocked liquid electrolyte crossover and stable anode for focused sulfur cathode study



Impedance of Sulfur/SSE/ LiIn cell at OCV



Charge/discharge curves of sulfur electrode

- Demonstrated Sulfur/SSE/LiIn cell with high sulfur utilization
- Provide a generic cell design for sulfur cathode study without any interferences of Li anode

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Collaboration and Coordination with Other Institutions

Partners:

- Brookhaven National Laboratory (BNL): sulfur reaction mechanism study
- General Motors: material/electrode test
- University of Wisconsin–Milwaukee: electrolyte/additive study
- Environmental Molecular Sciences Laboratory (EMSL)/ Pacific Northwest National Laboratory (PNNL): in situ EPR study of electrolyte and in situ AFM study on electrode interface

Remaining Challenges and Barriers

- Long-term cycling stability of Li-S battery with high loading sulfur cathodes and lean amount of electrolyte
- Lack of effective and durable electrolyte additives for high Coulombic efficiency cycling
- Instability of Li metal anode interface and electrolyte depletion

Future Work - FY2018-19

- New cathode additives, electrode preparation method, rational electrode architectures to enable high sulfur utilization (>1100 mAh/g) under conditions of high loading (>6 mg/cm^2) and dense electrodes (>1 g/cc)

- Fundamental understandings of electrode wetting, sulfur reaction and electrolyte/additive degradation at the sulfur cathode side by using the hybrid cell setup

- Comprehensive approaches of new electrolyte/additives, electrode/separator coating, and Li protection to enable long cycle life of high energy sulfur cathodes

Summary

1. Identified coating effects of solution based polymer binders in sulfur cathode, which results in blocked electrolyte penetration and loss of electrode active sites.
2. Electrode additives including soluble polymer or inorganic salts are effective to enhance electrode wetting and sulfur utilization in high loading sulfur cathodes.
3. Electrode porosity control boosts electrode energy density and reduces electrolyte uptake, which significantly improves cell specific energy.
4. Through advanced characterization, direct chemical reactions between $LiNO_3$ and Li_2S/Li_2S_x are identified, which lead to quick depletion of $LiNO_3$ in high loading sulfur cathodes.
5. A generic hybrid cell with completely separated electrode chambers by garnet oxide was designed and demonstrated after solving mechanical management, sealing, stable anode, electrolyte compatibility problems.

Acknowledgments

Support from the DOE/OVT/BMR program is greatly appreciated

Team Members: Yuxing Wang, Jie Xiao, and Ji-Guang Zhang

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Technical Backup Slides

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Technical Accomplishments

Parameters for Li-S pouch cell specific energy estimation

Cell component		Unit	values
Electrode dimension		mm*mm	55.5*37.5
Anode/cathode ratio		mAh/mAh	2:1
Layer			10
Sulfur cathode	**Sulfur specific capacity**	mAh/g	1000
	Sulfur fraction in cathode	%	64
	Cathode Density	g/cc	0.67
	Al foil thickness	μm	10
	Sulfur areal loading	mg/cm^2	4-8
	Area capacity	mAh/cm^2	4-8
Anode (Lithium)	**Discharge capacity**	mAh/g	3800
	Li fraction	%	100
	Li density	g/cc	0.534
	Cu foil thickness	μm	6
	Li thickness	μm	104
	Area loading	mg/cm^2	2.6
	Area capacity	mAh/cm^2	8-16
Separator		μm	11
Electrolyte weight		g	E/S=10-1 μL/mg
Packing foil thickness		μm	86
Discharge average voltage		V	2.1