Development of High Energy Lithium-Sulfur Batteries

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Pacific Northwest National Laboratory

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Project ID #ES282

Overview

Timeline

- Start date: Oct. 2012
- End date: Sept. 2017
- Percent complete: 80%

Barriers

- Shuttle effect and self discharge
- Low rate at high S loading
- Limited cycling life.

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY15: $400k
- Funding for FY16: $400k

Partners

- Argonne National Laboratory
- Brookhaven National Laboratory
- General Motors
- The University of Western Ontario

Relevance/Objectives

- Study the electrochemical behaviors of thick sulfur electrodes built at relevant scales.

- Advance the fundamental understanding in Li-S batteries through advanced characterizations.

- Decouple lithium metal anode issue from Li-S batteries.

- Project efforts are directly aimed to address the barriers of shuttle effect, low rate capability and limited cycling life.

Milestones

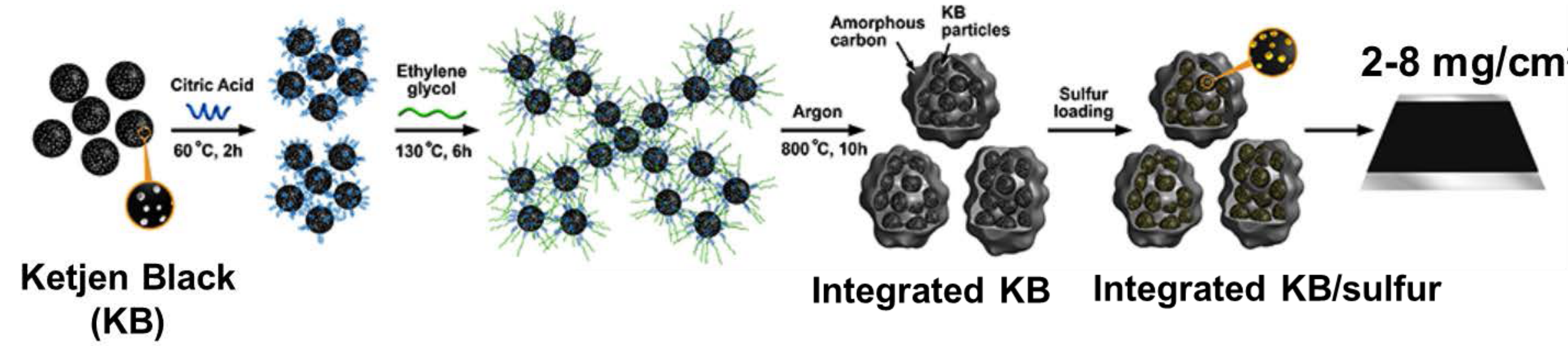
Date	Milestones and Go/No-Go Decisions	Status
December 2015	Complete SEI study on graphite surface in the new EC-free electrolyte.	Completed
March 2016	Demonstrate prototype Li-ion sulfur cells with >95% Coulombic efficiency (no additive) and > 80% capacity retention for 100 cycles.	Completed
June 2016	Identify effective approaches to facilitate electrolyte penetration within thick sulfur cathode (≥ 4mg/cm^2).	On track
September 2016	Complete pouch cell assembly and testing by using optimized electrode and electrolyte.	On track

Approach/strategy

1. Identify key factors in preparation/application of high energy sulfur cathodes in Li-S batteries.
2. Study the electrochemical behaviors of thick sulfur electrodes (3-4 mAh/cm^2).
3. Investigate the reactions between sulfur radicals and different electrolytes.
4. Decouple lithium metal anode problems from the system by using novel electrolyte and graphite anode.

Technical Accomplishments

Integrated Ketjen Black for Low Cost and High-Loading Sulfur Cathode

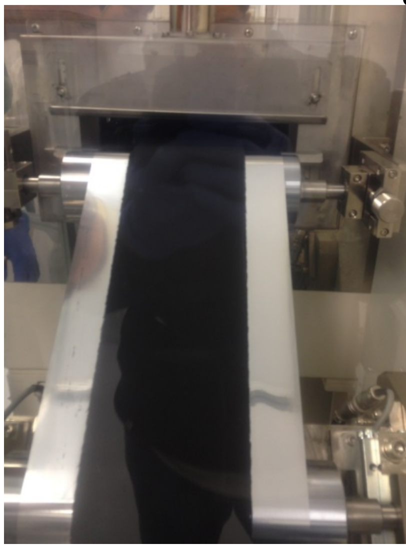


- ✓ Primary particle maintains nanostructures for high utilization of sulfur.
- ✓ Secondary large particles make the coating process readily adaptable by industry and improve the tap density of the electrode material.

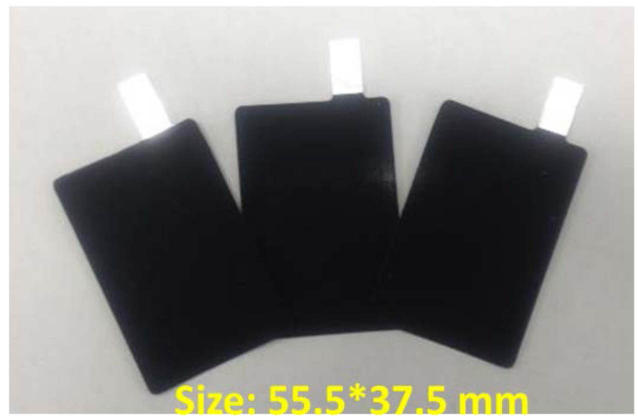
Technical Accomplishments

Continuous and Uniform Slurry Coating of Sulfur Electrode with Adjustable Sulfur Loading

Continuous coating



Double-side coated sulfur cathode



- ✓ Continuous and uniform sulfur electrode coating with Integrated KB/sulfur composite was validated at PNNL pouch cell line.
- ✓ The sulfur cathode with adjustable loadings of 2-8 mg/cm^2 was achieved.

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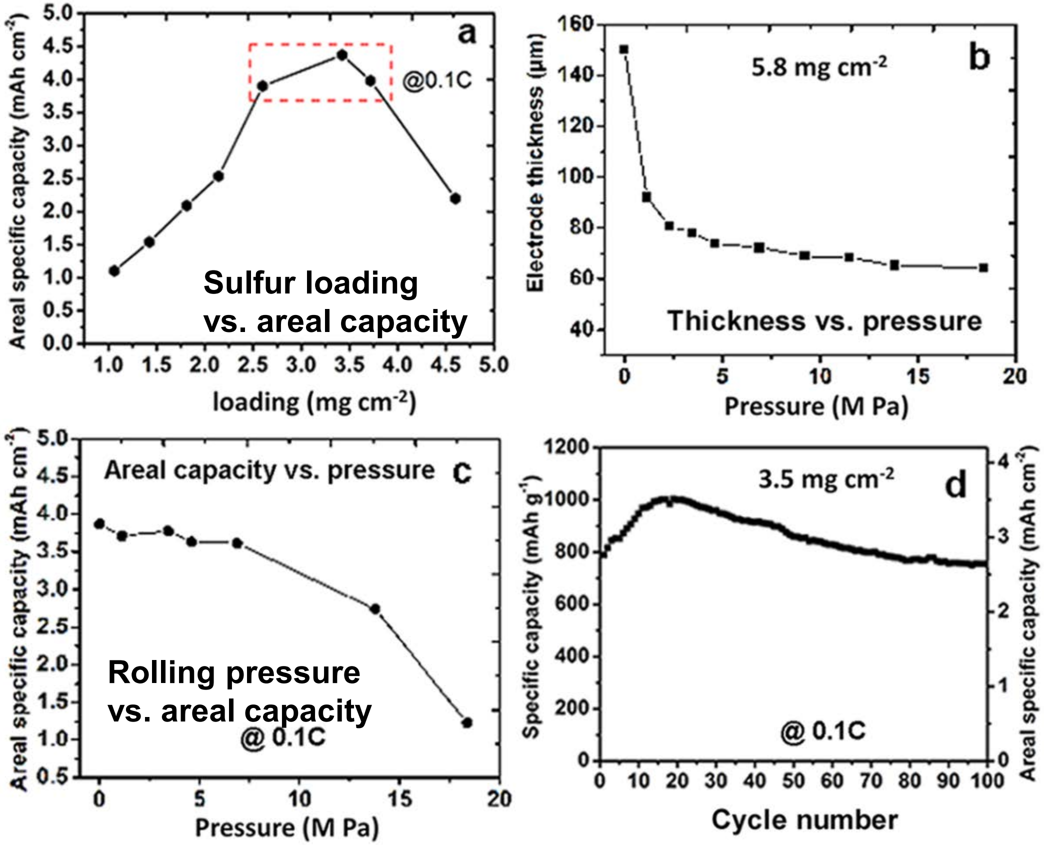
Technical Accomplishments

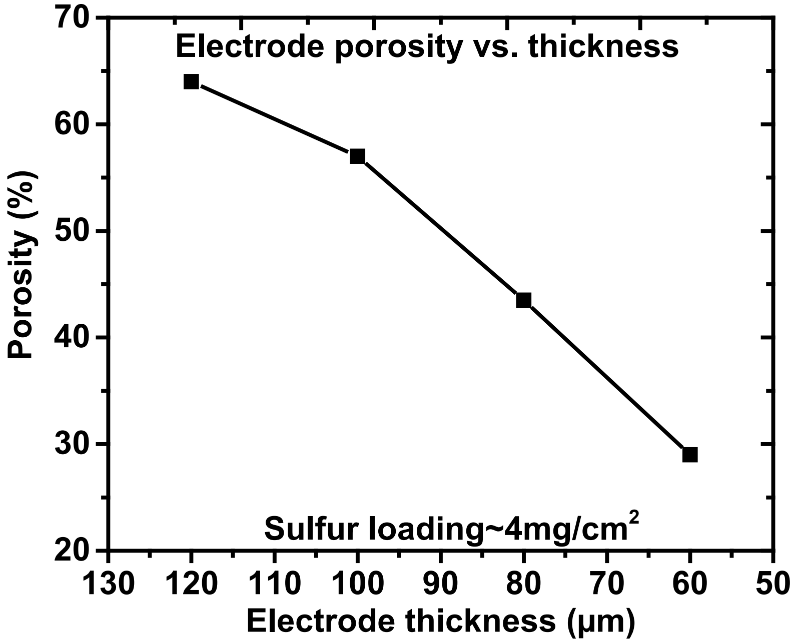
Thick Sulfur Electrodes: Sulfur Loading, Areal Capacity, Rolling Pressure and Cycling

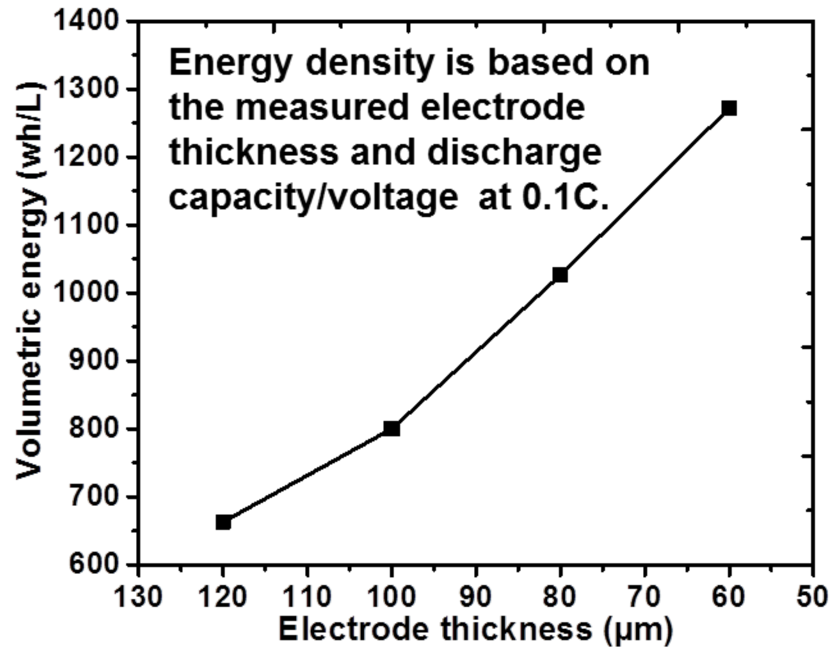


- ✓ A trade-off between sulfur loading and areal capacity.
- ✓ Calendaring under appropriate pressure decreases required electrolyte amount and improves cycling stability.

Technical Accomplishments

Control of Porosity and Energy Density for High-Loading Sulfur Cathode





- ✓ Significantly improved volumetric energy density with reduction of electrode thickness and porosity.

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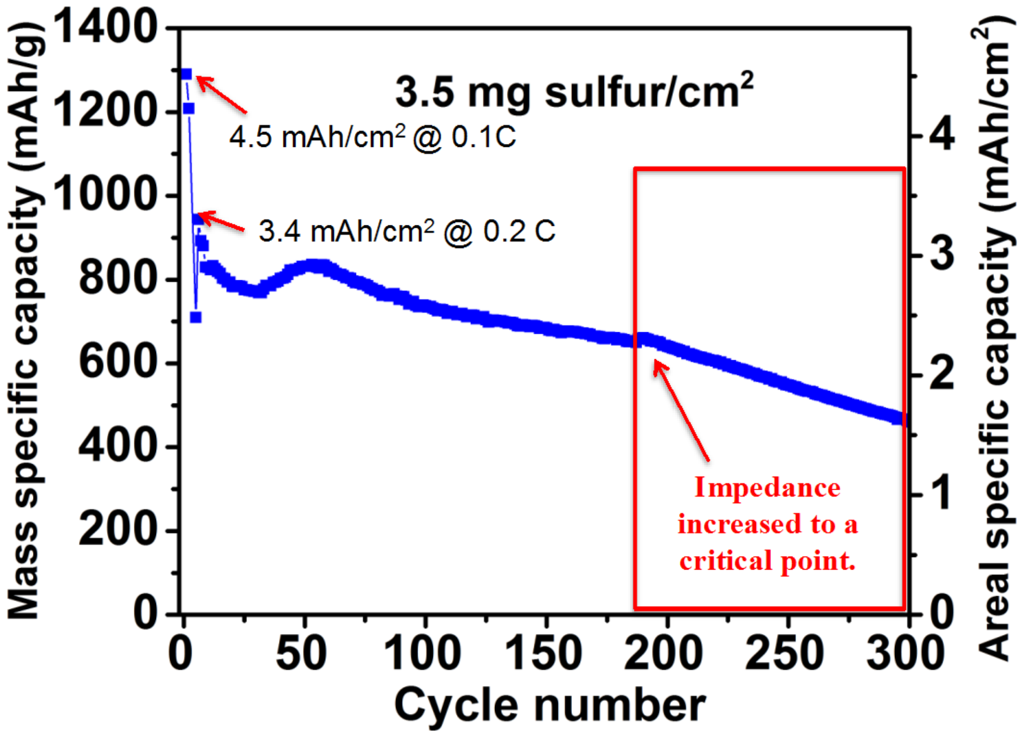
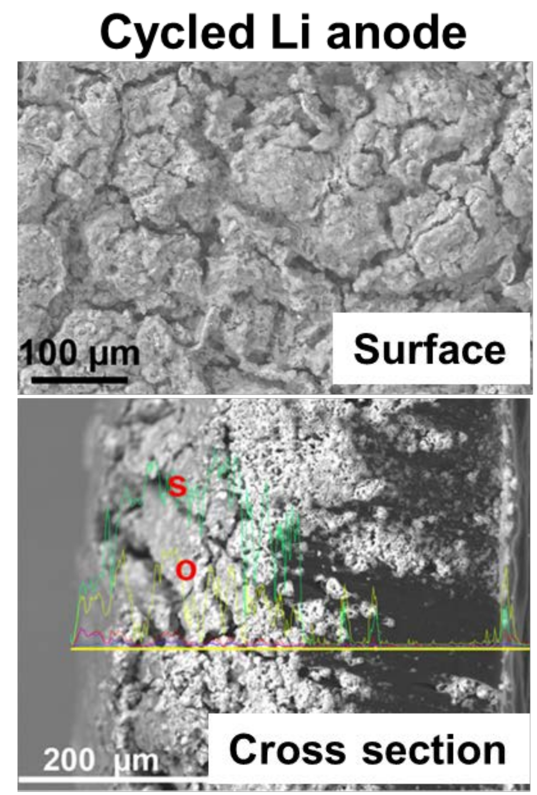
Technical Accomplishments

Thick Interphase Accumulates on Li Metal Side During Cycling

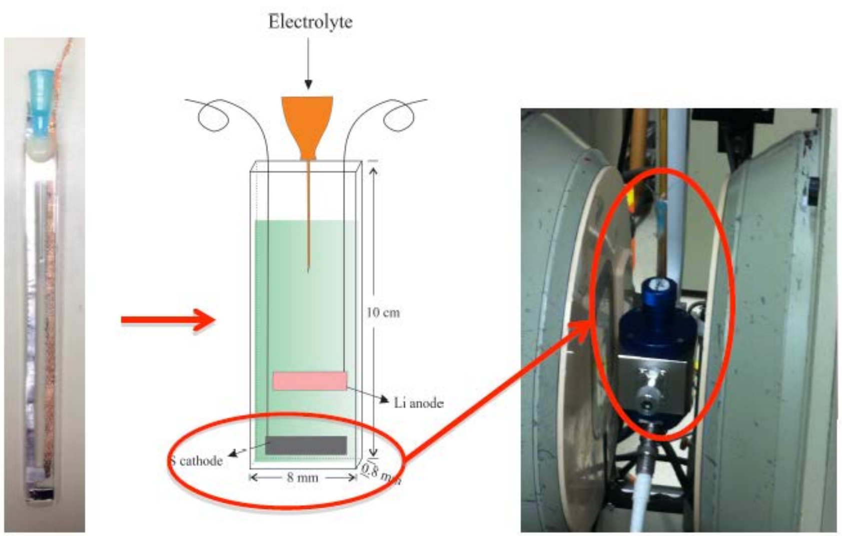


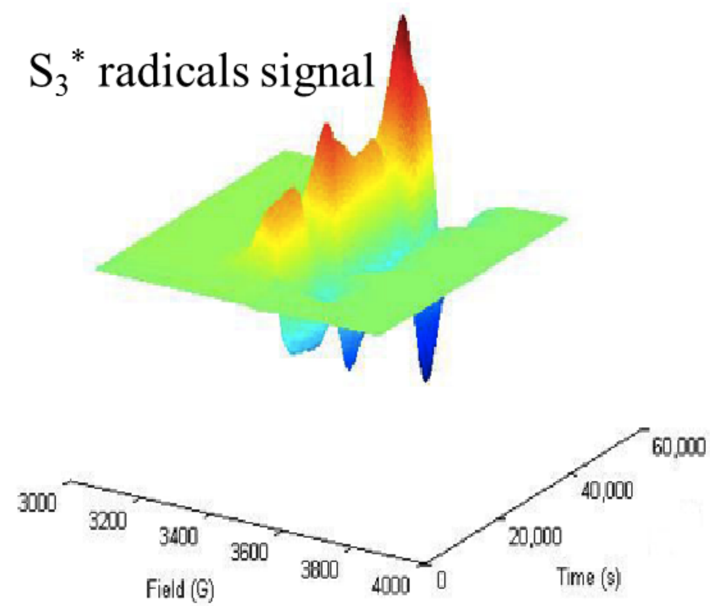


- ✓ Stable cycling (150 cycles) was observed from thick electrodes.
- ✓ Li_2S_x diffusion pathway may be partially blocked in the thick electrodes.
- ✓ Li metal anode becomes the dominant failure factor for extended cycling.

Technical Accomplishments

Understanding of Formation and Function Mechanism of Sulfide Radicals During Cell Cycling

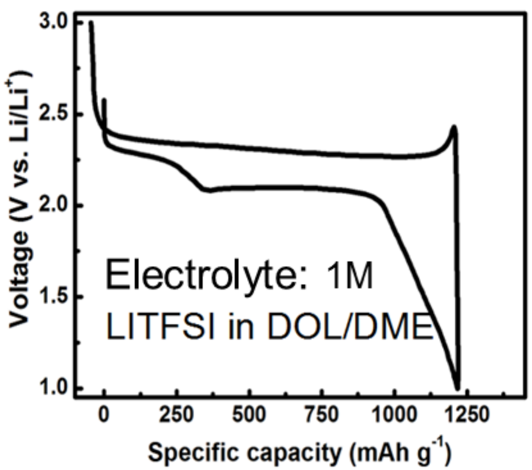


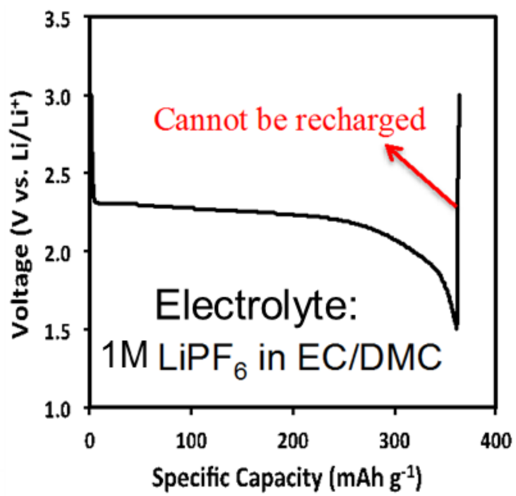


- ✓ Generation and evolution of sulfur radicals during cycling can be monitored directly by in situ EPR technique.
- ✓ S_3^* radical is formed and changes periodically in concentration during the cell cycling.

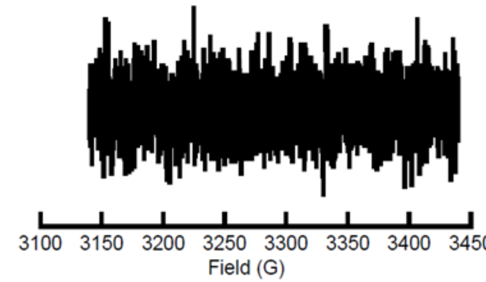
Technical Accomplishments

Interactions between Sulfur Radicals and Different Electrolytes





S_3^* radicals disappear after mixing Li_2S_8 with 1M $LiPF_6$/PC solution.

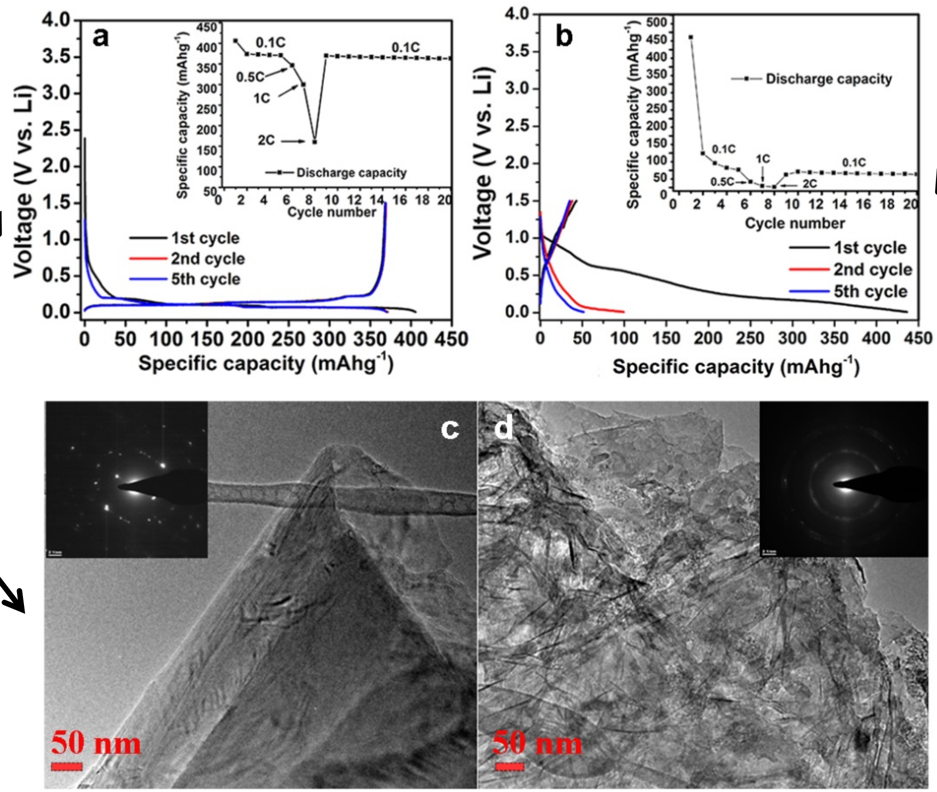


- ✓ Identified incompatibility between polysulfide radicals and carbonate based solvents (e.g. EC), which can't be used in sulfur batteries as electrolyte components.
- ✓ Potential interactions between polysulfide radicals and ether based solvents should be carefully considered for long-term cycling of Li-S batteries.

Technical Accomplishments

Cycling Stability of Graphite Electrode in Ether Based Electrolyte Without EC Additive

In 5M LiTFSI/DOL

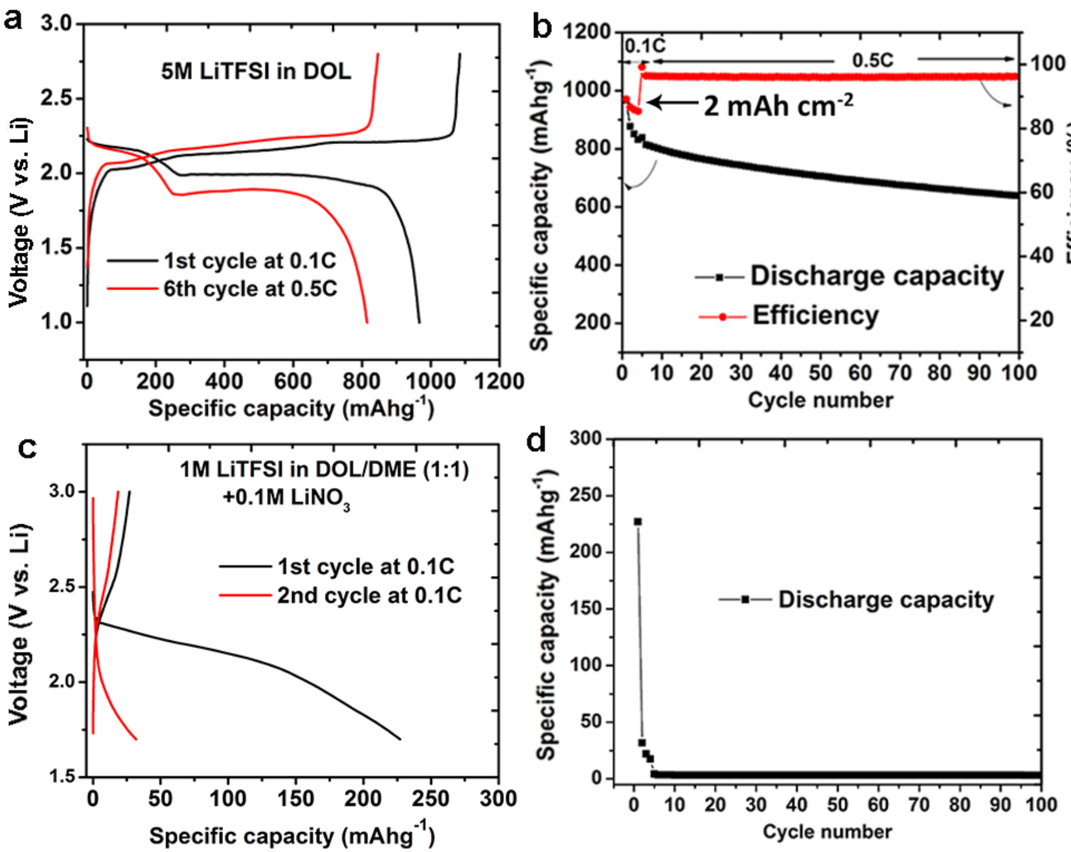


In 1M LiTFSI/DOL/DME

- Graphite electrode is exfoliated quickly in conventional 1M LiTFSI/DOL/DME electrolyte BUT exhibits high reversibility and rate capability in 5M LiTFSI/DOL electrolyte.

Technical Accomplishments

Development of Novel Graphite/sulfur Battery with Concentrated Electrolyte

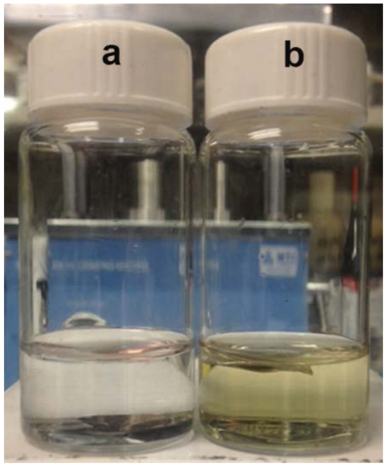


- High capacity retention and Columbic efficiency were achieved for sulfur electrode with loading > 2 mg/cm^2.
- Decoupled negative effects of Li metal anode to simplify the study of sulfur cathode.

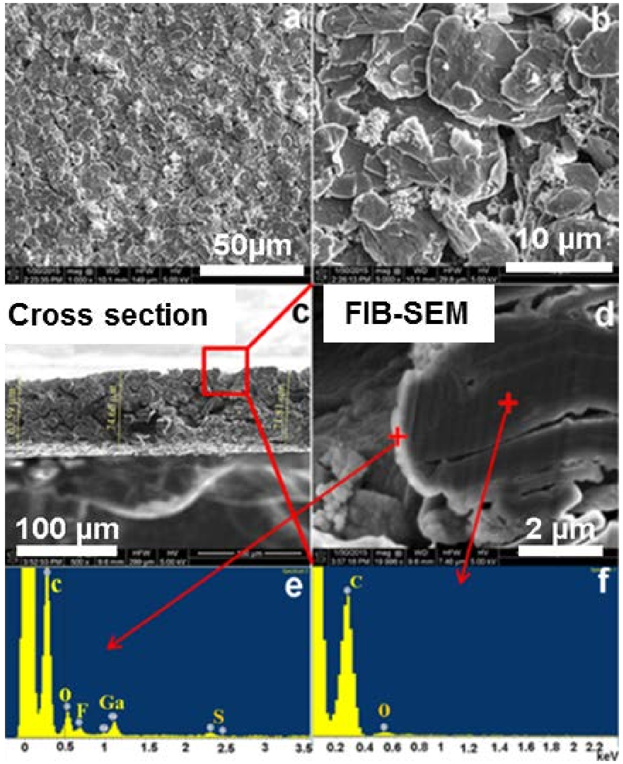
Pre-lithiated graphite was used as the anode and coupled with sulfur cathode

Technical Accomplishments

Characterization of Graphite Electrode after Cycling in Graphite/Sulfur Battery



a. Cycled graphite anode in Gr/S cell
b. Cycled Li anode in Gr/S cell

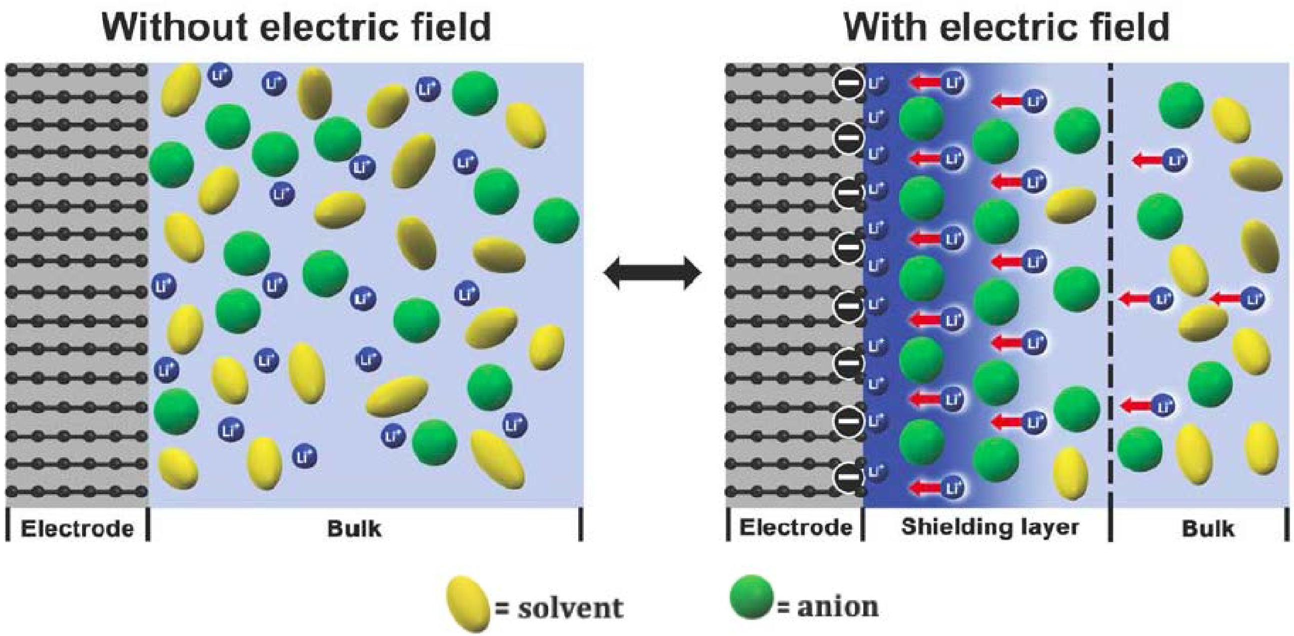


SEM/EDS of graphite electrode after cycled in graphite/sulfur battery.

- ✓ Graphite electrode (bulk and interface) is very stable after cycling in sulfur battery.
- ✓ Much less sulfur loss was observed on cycled graphite anode compared to cycled Li metal anode.

Technical Accomplishments

Function Mechanism of Concentrated Electrolyte for Graphite Electrode



- ✓ With electric field, competition of solvent decomposition and Li salt precipitation happens at the electrode/concentrated electrolyte interface.
- ✓ Electrochemical in situ AFM results indicate that electrical field induces the fast precipitation of Li salt (partially solvated), substantially decreasing solvent decomposition and preventing graphite from exfoliation.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory (ANL): graphite electrode preparation.
- Brookhaven National Laboratory (BNL): sulfur reaction mechanism study.
- General Motors (material test).
- The University of Western Ontario, Canada (electrode surface treatment)
- Environmental Molecular Sciences Laboratory (EMSL)/ Pacific Northwest National Laboratory (PNNL): in situ EPR study on polysulfide radical 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.
- Electrolyte penetration in high loading sulfur cathode particularly with controlled thickness/porosity and/or in the case of concentrated electrolyte.
- Loss of electrolyte for long-term cycling of Li-S battery.
- Instability of Li metal anode interface.

Future Work - FY2016-17

- Continue to modify high loading sulfur cathode preparation procedure in terms of materials synthesis, electrode composition and coating parameters.
- Address electrolyte amount and penetration issues in high loading sulfur electrode ($\geq$ 4 mg/cm^2).
- Investigate electrolyte/additive degradation/depletion mechanism in Li-S battery with high loading sulfur electrode.
- Use graphite/sulfur battery as a platform to fully understand sulfur cathode without interference from Li metal anode side.

Summary

1. Identified the key factors in preparation/application of high loading sulfur cathode
   - Integrated Ketjen Black particles in micron size have been synthesized and utilized as sulfur host for preparation of high loading sulfur electrode.
   - Uniform and crack-free electrode coating with sulfur loading of 2–8 mg cm^{-2} have been achieved with controlled electrode thickness/porosity.
2. Investigated the reactions between sulfur radicals and different electrolytes.
   - The generation and evolution of sulfur radicals during cycling can be directly monitored by electrochemical in situ EPR technique.
   - The S3* radical exists throughout the cell cycling and acts as an effective media for the interplay between chemical and electrochemical reactions of polysulfides.
3. Decoupled lithium metal anode problems from the system by using novel electrolyte and graphite anode.
   - High reversibility and rate capability were achieved on graphite electrode with 5M LiTFSI/DOL electrolyte.
   - High capacity retention and Coulombic efficiency were achieved in graphite/S cells with sulfur loading > 2 mg/cm^2.

Acknowledgments

- ✓ Support from the DOE/OVT/BMR program is greatly appreciated.
- ✓ Team Members: Jie Xiao, Jian Liu, Qiuyan Li, Seth Ferrara, Qiang Wang, Jianming Zheng, Wesley Henderson, Pengfei Yan, Chongmin Wang, Gordon L. Graff, Ji-Guang Zhang.

Technical Backup Slides

Technical Accomplishments

Pouch cell design of 3Ah Graphite/sulfur battery.

Pouch cell parameters						
Width (mm)	Length (mm)	Layers	Cell weight (g)	Cell capacity (mAh)	Voltage	Energy density (Wh/kg)
41.5	75	10	24.76	3009	2.1	255

Cell design information				
Electrode			Quantity	Weight(g)
Anode	Capacity (mAh/g)	360.0	10 (double- layer coating)	9.32
	Loading	95.5%		
	Length (mm)	68.5		
	Width (mm)	37.50		
	Area Weight (mg/cm^2)	18.14		
	Area capacity (mAh/cm^2)	6.24		
Cu foil	Thickness (mm)	0.008	10	1.87
Anode tab	/	/	1	0.13
Cathode	Capacity (mAh/g)	1000.7	10 (double- layer coating)	4.7
	Loading	64.0%		
	Length (mm)	67.0		
	Width (mm)	36.00		
	Area Weight (mg/cm^2)	9.74		
	Area capacity (mAh/cm^2)	6.24		
Al foil	Thickness (mm)	0.012	11	0.86
Cathode tab	/	/	1	0.04
Packing foil	Thickness (µm)	86	1	0.97
Electrolyte	/	/		6.32
Separator	Thickness (µm)	11		0.54
Sealant	/	/	1	0.01