

Multi-Functional Cathode Additives for Li-S Battery Technology

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2016 Annual Merit Review

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Project ID # ES281



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Overview

Timeline

- Project start Oct. 2014
- Project end Sept. 2017
- 50% complete

Budget

- Total project funding
 - FY 2015 \$500K
 - FY 2016 \$500K

Barriers

- **Performance:** Low Wh/kg (or L) & W/kg (or L)
- **Cycle life:** Poor cycle life
- **Cost:** High \$/kWh

Partners

- Brookhaven National Laboratory (BNL) (lead)
- Stony Brook University

Relevance and Project Objectives

■ Project Objectives

- Develop high energy Li-S batteries for HEV/PEV/EV applications and reduces the cost associated with batteries.
- Achieve long cycle life of Li-S battery by increasing the sulfur cathode conductivity with transition metal sulfides as multifunctional cathode additives (MFCA).
- Optimize the chemical and physical properties of selected MFCA for high sulfur utilization and long Li-S cell cycle life.

■ Project Relevance

- Our project objectives are aimed at addressing three barriers associated with today's benchmark Li-ion batteries: high cost, lower energy density and short cycle life.
 - Li-S battery technology potentially may double the energy density and lower the battery cost.
 - Success development of MFCA will help to achieve long cycle life for Li-S battery.

Milestones for FY 2015 and 2016

Date	Milestones	Status
December, 2014	Benchmark MFCA coin cells: Achieve > 50% of theoretical capacity of MFCA upon activation	Completed
March, 2015	Benchmark S coin cells: Achieve 1st cycle utilization of cathode comparable to literature report (> 50% of theoretical capacity of Li₂S and S) upon activation	Completed
June, 2015 Go/No-Go	Concept demonstration: Achieve Li₂S or S efficiency > 60% theoretical in the presence of MFCA for hybrid cathode	Completed
September, 2015	Synthesis of the selected MFCA (FeS₂ and TiS₂)	Completed
December, 2015	Lab prepared TiS₂ and FeS₂ testing in hybrid cathode: Achieve equal or better cathode utilization vs. the control with commercial TiS₂ and FeS₂	Completed
March, 2016 Go/No-Go	Obtain MFCA material with different PS and shape and testing in hybrid cathode: Achieve equal or better cathode utilization vs. the control with commercial MFCA.	Completed
June, 2016	Binder selection: Achieve good electrode mechanical integrity with no delamination from Al foil and no loose particles.	On-schedule
September, 2016	Cathode formulation optimization for maximized capacity density: Achieve >500 mAh/g (S + Additive).	On-schedule

Approach/Strategy

Phase I – Material characterization and optimization

Phase II – System optimization

FY 2015				FY 2016			
Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4

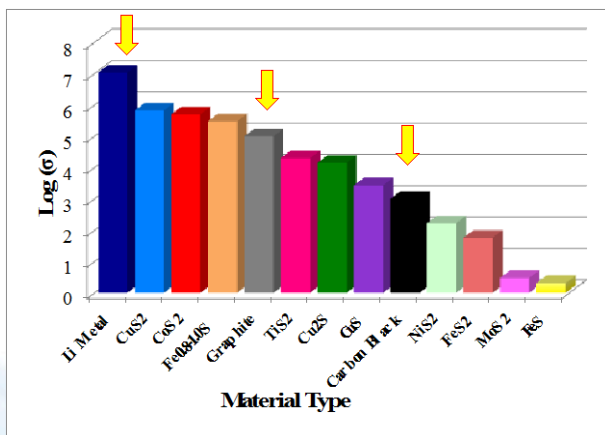
FY 2017

Q3 2015 – Successfully demonstrated sulfur-MFCA interaction

Go/No-Go

Q2 2016 – Improved cell cycling performance achieved for S:TiS₂ hybrid cathode

Go/No-Go



Metal Sulfide Electronic Conductivity

Benchmark Sulfur & MFCA Cells Establishment

Hybrid Cathode Interaction demonstration Go/No-Go

Sulfur – MFCA Interaction Mechanism Understanding

Construct Sample Cells and Characterization

Material, Process, Cell Design Optimization

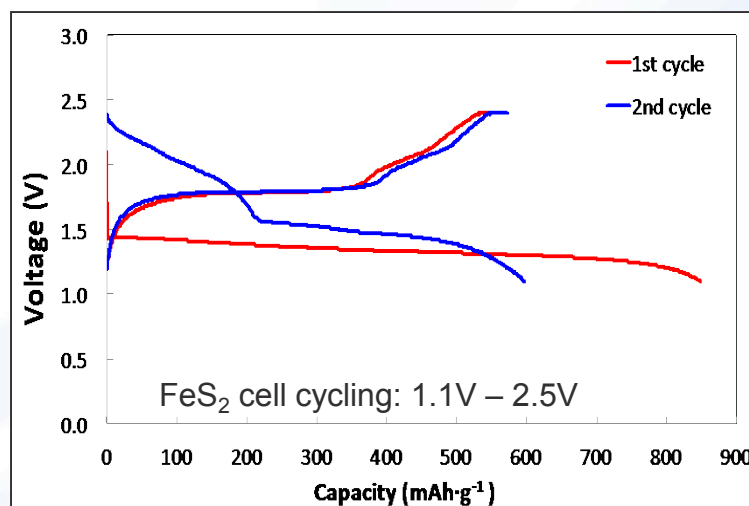
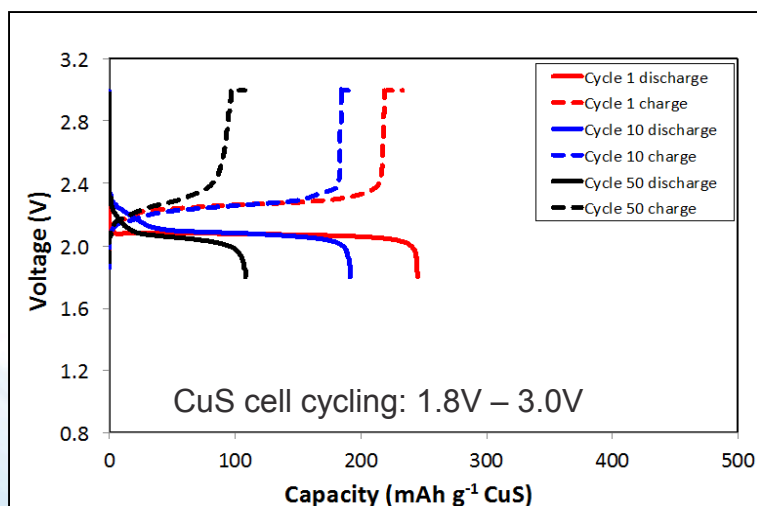
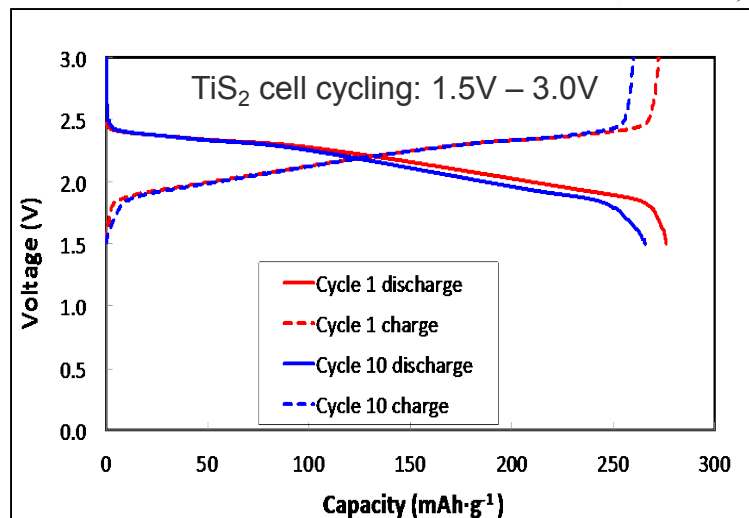
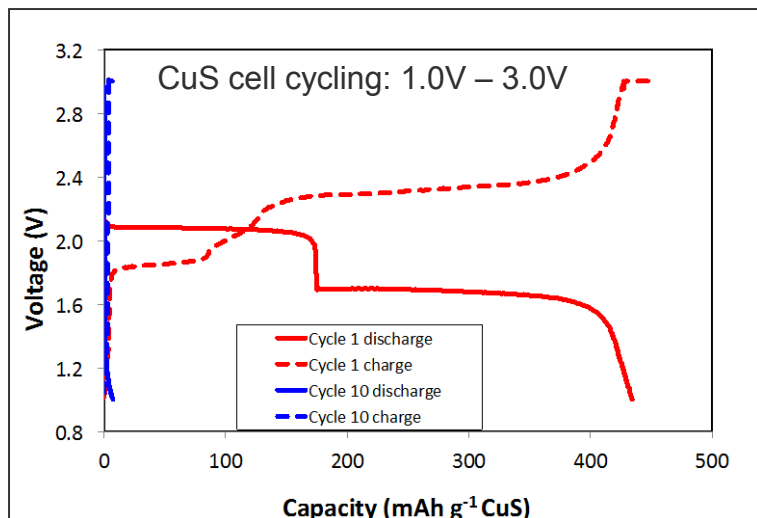
Best MFCA Selection for Optimization Go/No-Go

Accomplishments and Progress

Benchmark MFCA cell performance and activation

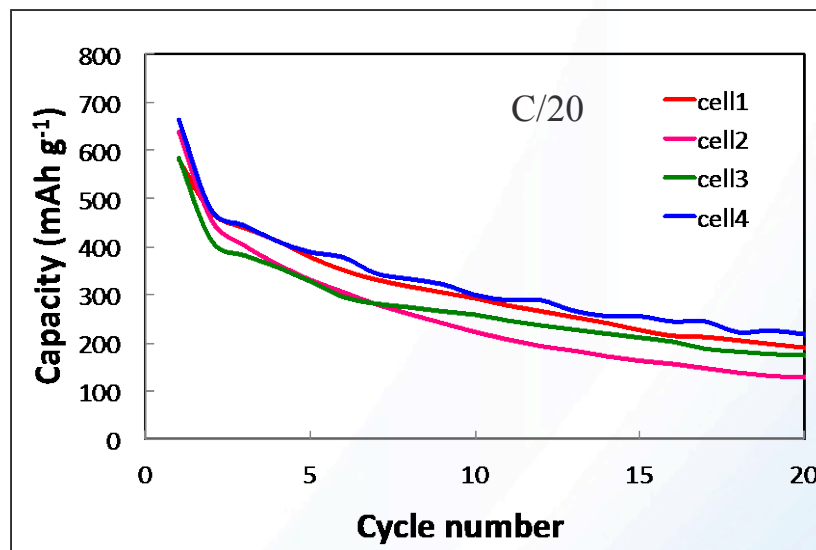
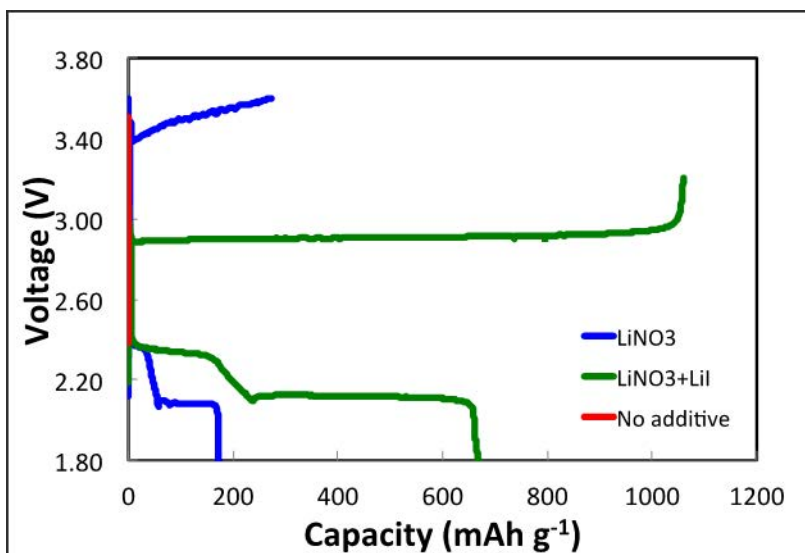


A. Marschilok, K. Takeuchi,
E. Takeuchi, Q. Zhang, C. Cama



Accomplishments and Progress

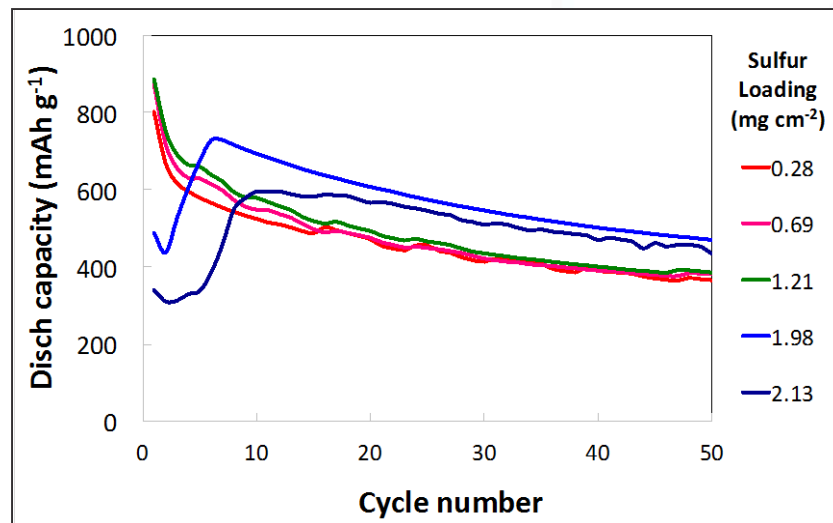
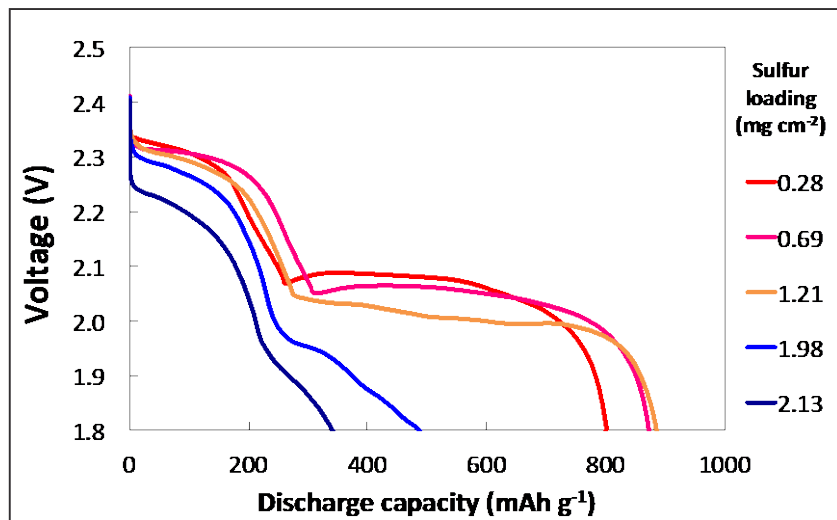
Benchmark Li_2S cell performance



- Li_2S cell activation requires electrolyte additives.
- 50% sulfur utilization in the presence of LiNO_3 and LiI at C/40.
- Fast capacity fade upon cycling at C/20.

Accomplishments and Progress

Benchmark sulfur cell performance – loading effect

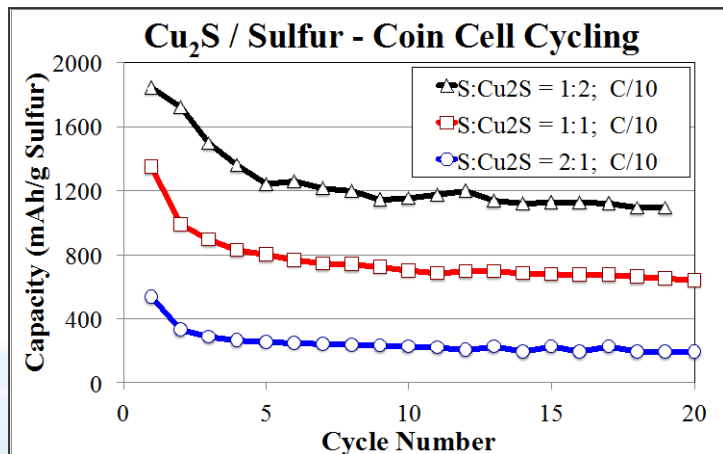
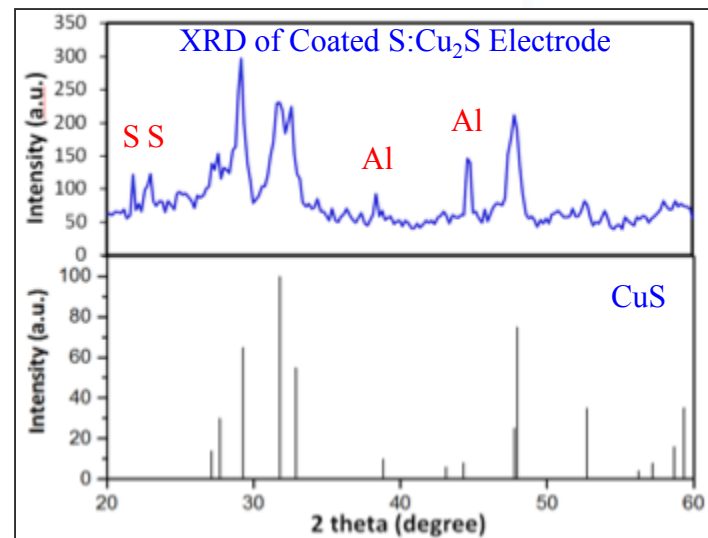
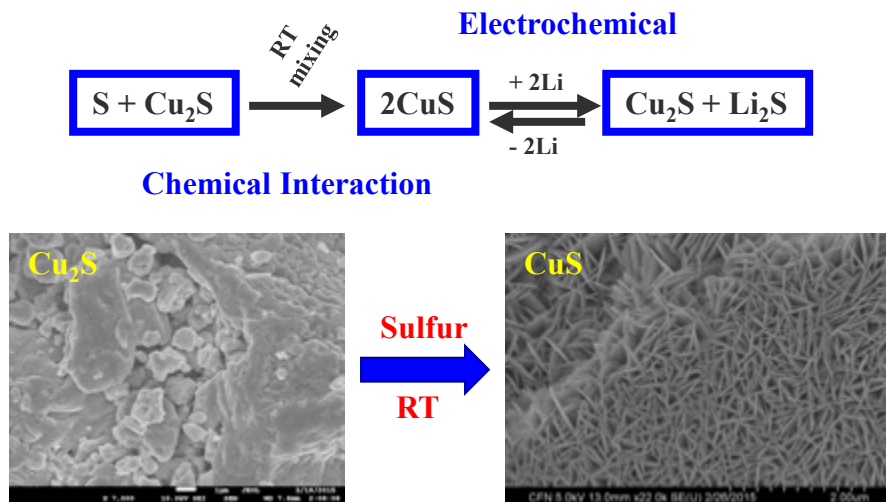


- The initial sulfur utilization is sulfur loading dependent.
- Up to 53% theoretical capacity delivered in the initial discharge (882 mAh g⁻¹ S) for Li-S cells at C/5 rate.
- Activation required for high sulfur loading cells (2+ mg/cm²).

Helen Liu, Ke Sun, Hong Gan, "The effects of carbon type and cathode loading on Li-S battery performance", Poster at 2015 American Institute of Chemical Engineers (AIChE) Annual Meeting, Nov. 8-13, 2015.

Accomplishments and Progress

Concept demonstration – Sulfur/CuS interaction

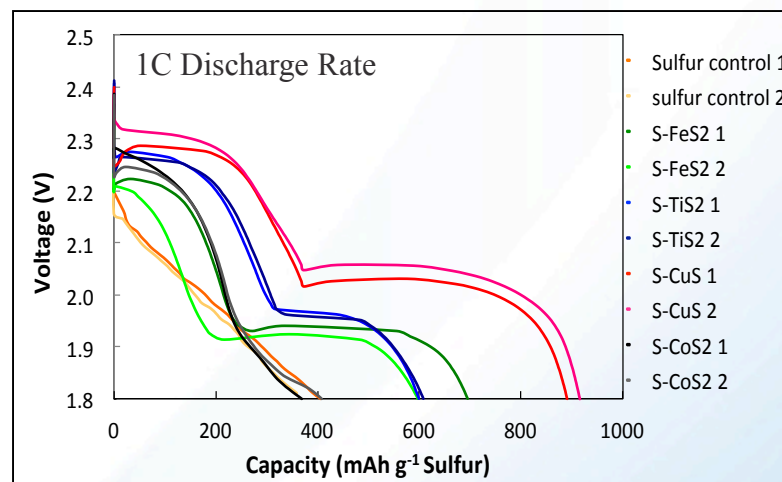
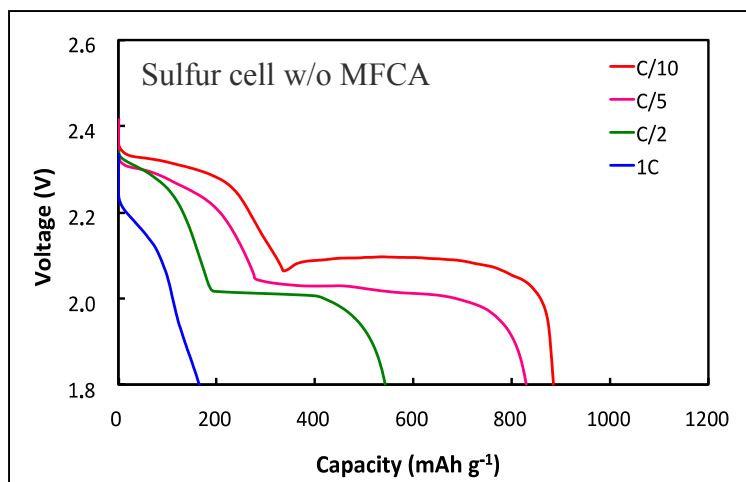


- Sulfur reacts with Cu_2S at RT to form nano-structured flake CuS crystals.
- With excess Cu_2S :S ratio > 1.0 , 100% of sulfur utilization can be achieved (3.0V to 1.8V at C/10 rate).
- Low sulfur utilization observed when Cu_2S :S ratio < 1.0 .

Accomplishments and Progress

Sulfur cell discharge rate and sulfur-MFCA interaction

MFCA	Sulfur%	MFCA%	Carbon%	PVDF%	S Utilization (1C)
None	45	0	45	10	24%
CuS	45	15	30	10	54%
FeS ₂	50	17	25	8	39%
TiS ₂	50	17	25	8	36%
CoS ₂	50	17	25	8	24%



- Transition metal sulfide (CuS, TiS₂, FeS₂, CoS₂) in S:MFCA hybrid cathodes promote initial sulfur cell discharge power capability at 1C rate.

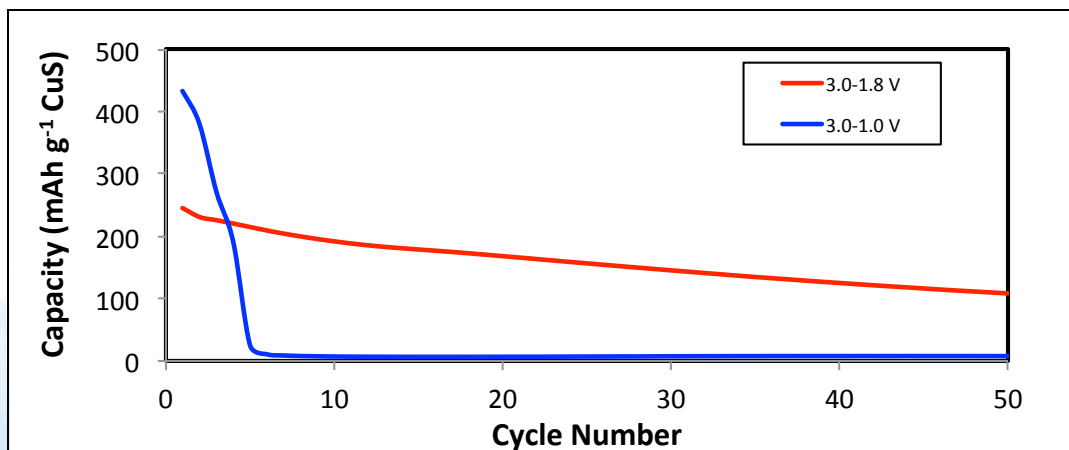
Accomplishments and Progress

CuS additive effect on sulfur cathode - background

- CuS has high theoretical capacity – 560 mAh/g



- CuS is electronically as conductive as carbon black.
- The presence of CuS promote sulfur electrode utilization under high rate discharge.



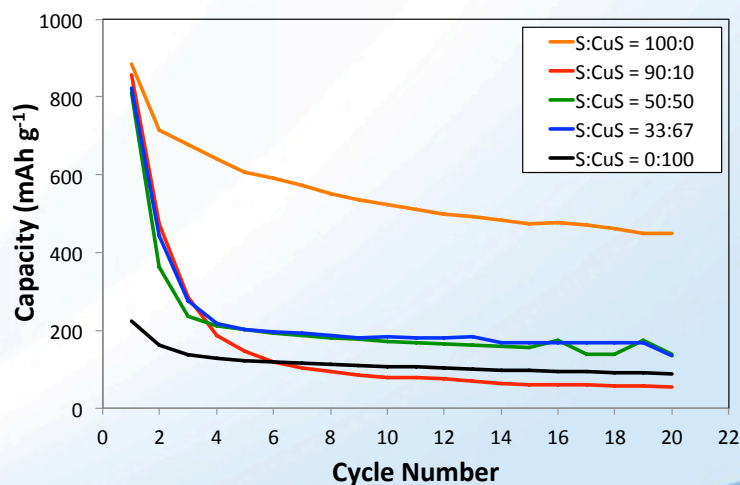
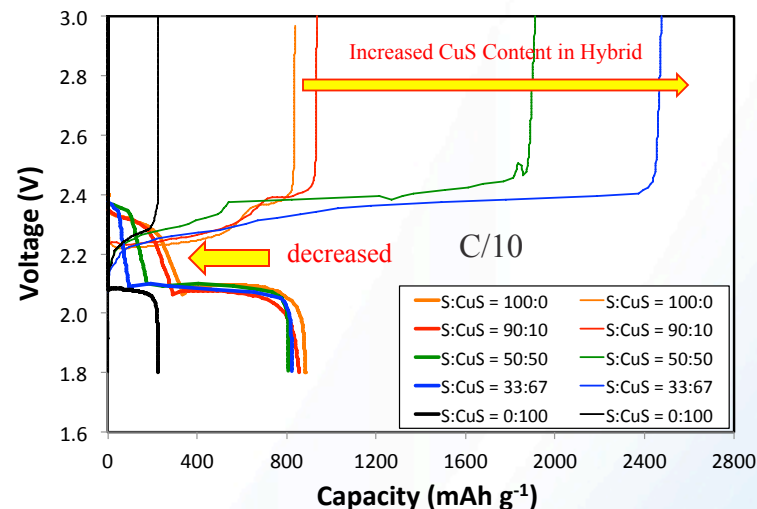
- Reaction 2 is not reversible.
- 1.8V discharge limit for reversible cycles.

Accomplishments and Progress

CuS additive effect on sulfur cathode - electrochemical

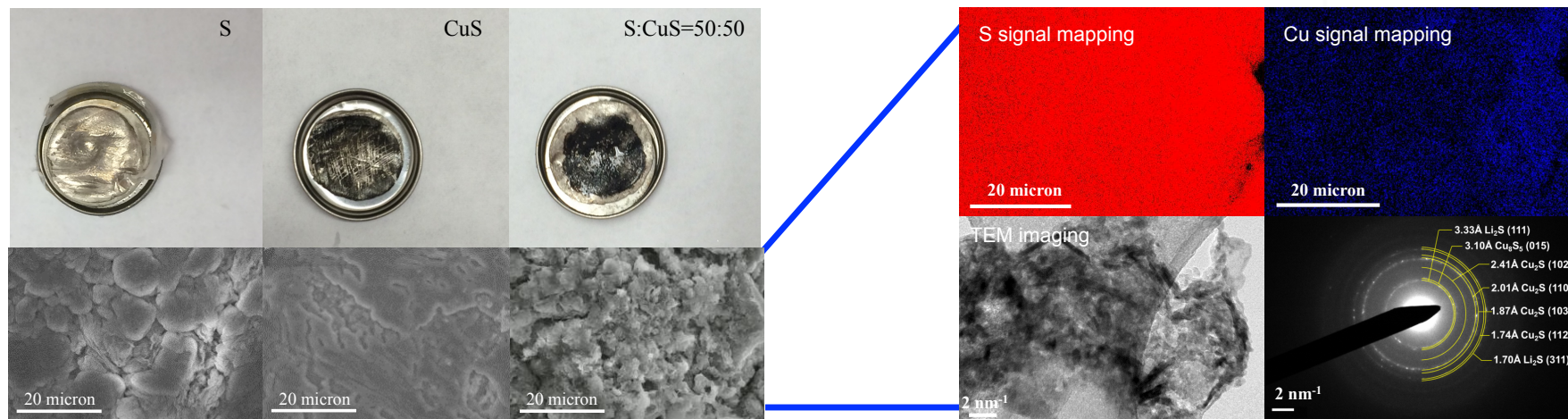
S:CuS Ratio	Mole Ratio	Theoretical Capacity Ratio
S:CuS	100:0	100:0
S:CuS	90:10	95:5
S:CuS	50:50	67:33
S:CuS	33:67	33:67
S:CuS	0:100	0:100

- All hybrid electrode delivered less capacity than the sulfur control.
- Shuttling effect severity proportional to CuS content.
- All hybrid electrode cells showed fast capacity fade within the initial 5 cycles – **why?**

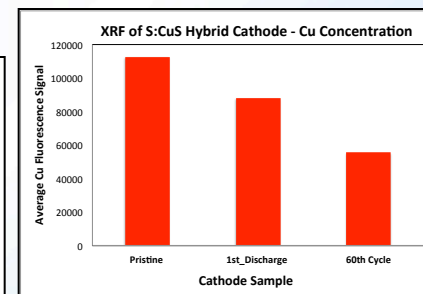
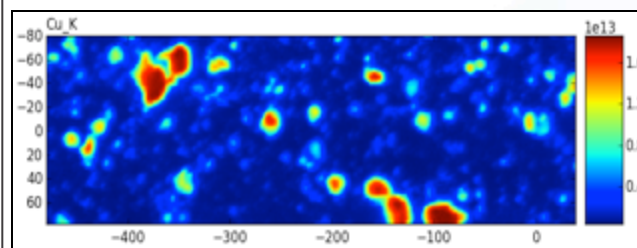
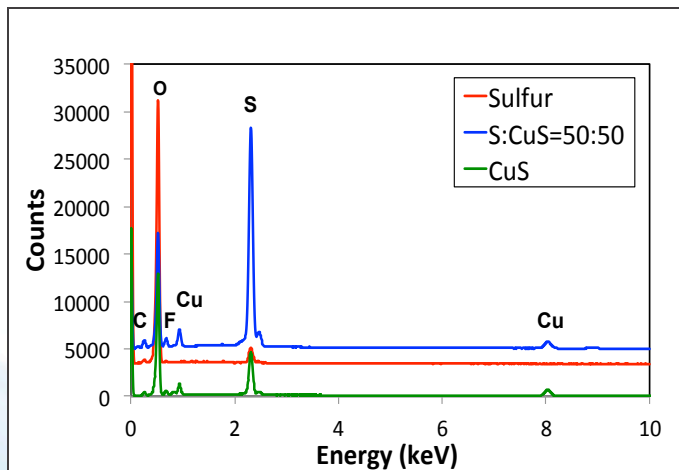


Accomplishments and Progress

CuS additive effect on sulfur cathode – Cu dissolution



Cathode X-Ray Fluorescence Spectroscopy - Cu



- Recovered anode – different discoloration and morphology.
- EDS - more Cu and S on hybrid cell anode surface.
- TEM/ED - Li_2S , Cu_2S , and Cu_8S_5 on hybrid cell anode surface.
- XRF - decreased Cu fluorescence signals from hybrid cathode after cell cycling (pristine vs. cycled hybrid cathode).

Accomplishments and Progress

CuS additive effect on sulfur cathode – Cu dissolution

- Is CuS soluble in electrolyte?
- Do polysulfides catalyze the solubility of CuS?

Copper Concentration Measurement by ICP-OES

Sample #	Sample*	Cu Concentration (ppm)
1	Electrolyte for calibration	0.0
2	Electrolyte + CuS	6.9
3	Li ₂ S ₄ + Electrolyte + CuS	0.0
4	Li ₂ S ₈ + Electrolyte + CuS	0.0

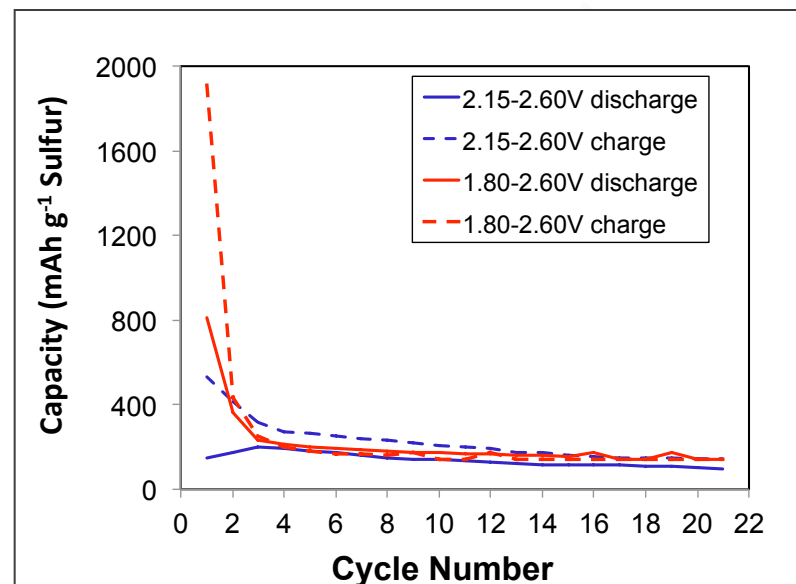
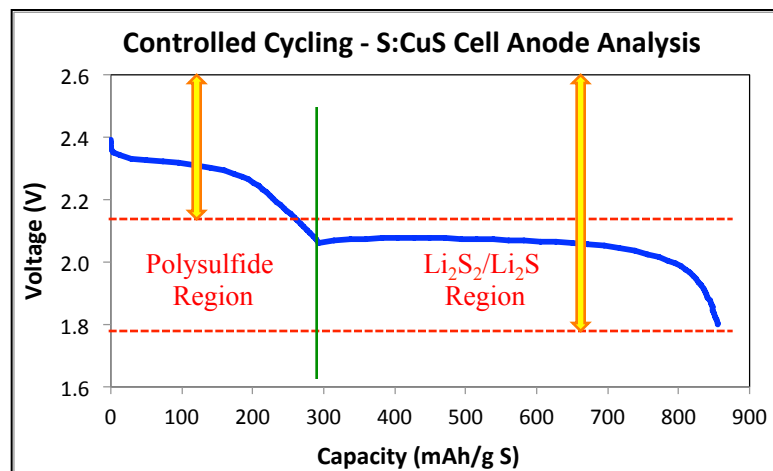
*Electrolyte: 1.0 M LiTFSI / DOL:DME = 1:1 v/v + 1 wt% LiNO₃

Polysulfide concentration = 70 mM

- CuS is only slightly soluble in pure electrolyte.
- CuS is insoluble in electrolyte in the presence of polysulfides.

Accomplishments and Progress

CuS additive effect on sulfur cathode – Cu dissolution



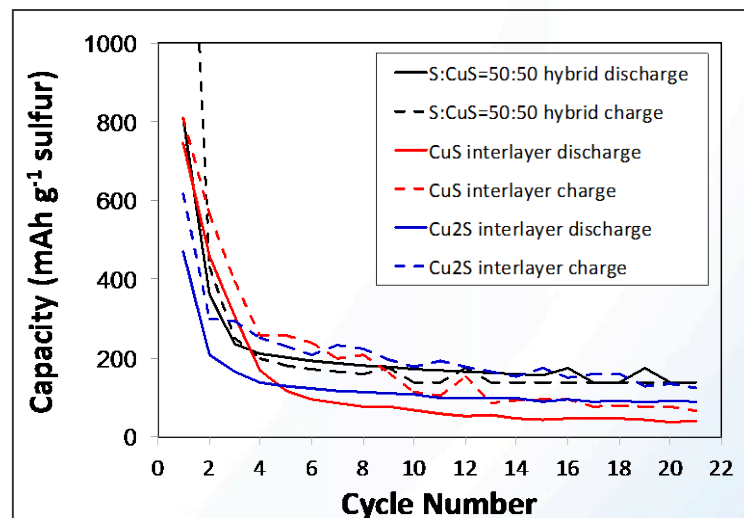
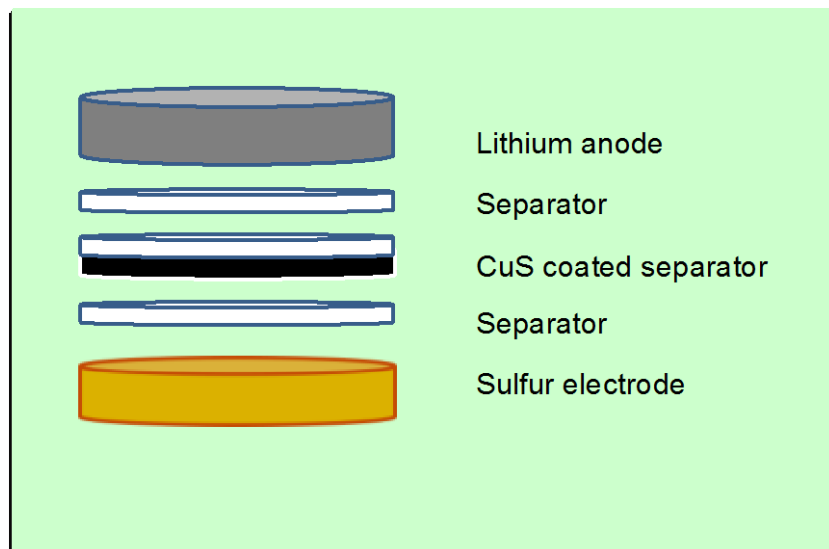
- 2.6V to 2.15V cycling
 - Clean anode surface
- 2.6V to 1.8V cycling
 - Dark anode surface
- Polysulfide (Li_2S_8 and Li_2S_4) is not the cause of CuS dissolution.



Accomplishments and Progress

CuS additive effect on sulfur cathode – Cu dissolution

Can CuS dissolution caused by the insoluble Li_2S_2 or Li_2S ?



- The low ordered soluble polysulfide species (S_3 – either ions or radical) generated at voltages below 2.15V is the cause of CuS dissolution.



Accomplishments and Progress

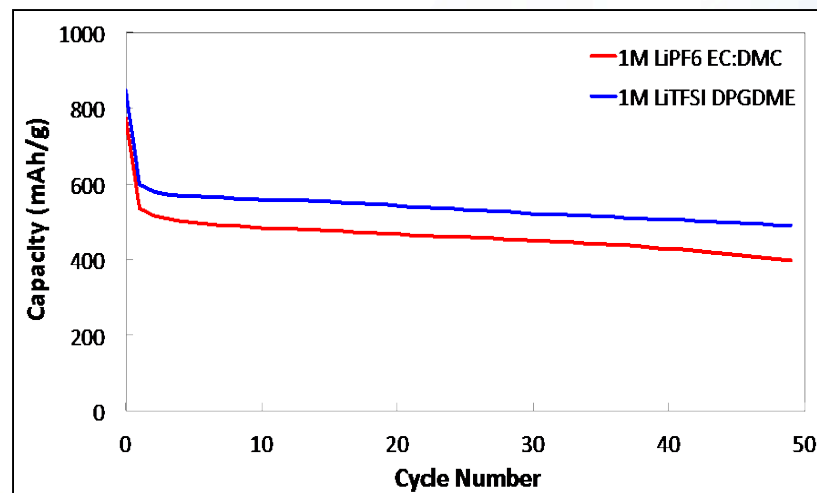
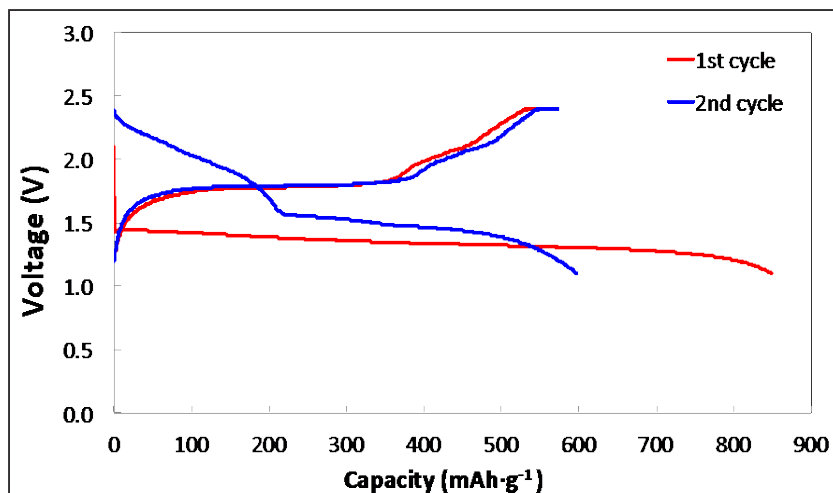
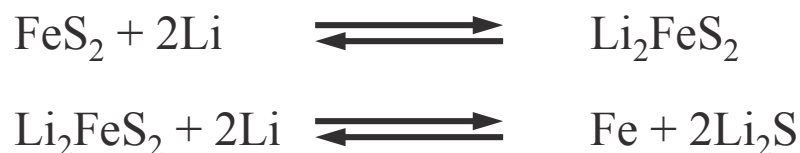
CuS additive effect on sulfur cathode – conclusion

- The presence CuS in hybrid cathode promotes sulfur cell discharge under high rate.
- CuS additive is detrimental to the sulfur cell cycling stability due to CuS dissolution.
 - High ordered polysulfide (Li_2S_n , $n = 4$ to 8) does not cause CuS dissolution.
 - Electrolyte soluble low ordered polysulfide (Li_2S_n , $n = 3$ or less) is responsible for CuS dissolution.
 - Deposition of conductive Cu_2S species on the anode surface catalyze the polysulfide reduction, enhancing shuttling effect and inducing more Li_2S deposition on anode surface.

Accomplishments and Progress

FeS₂ additive effect on sulfur cathode - background

- FeS₂ is conductive (semi-conductor) and used as cathode in thermal lithium batteries - theoretical capacity – 890 mAh/g

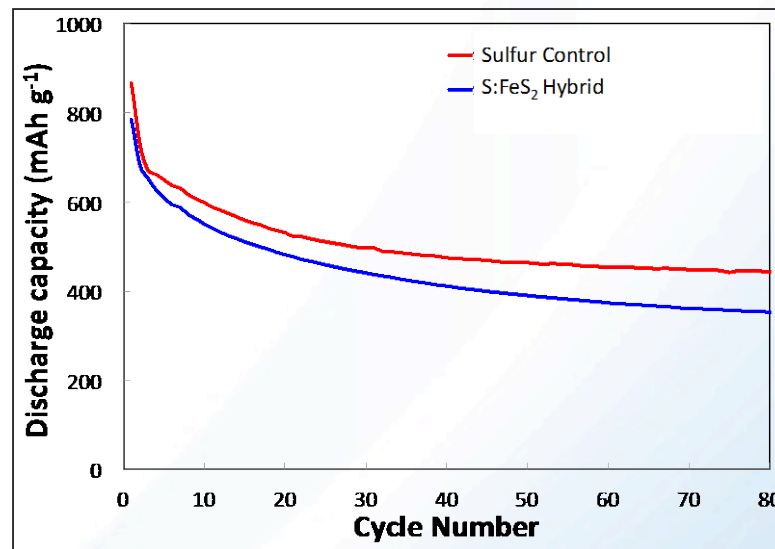
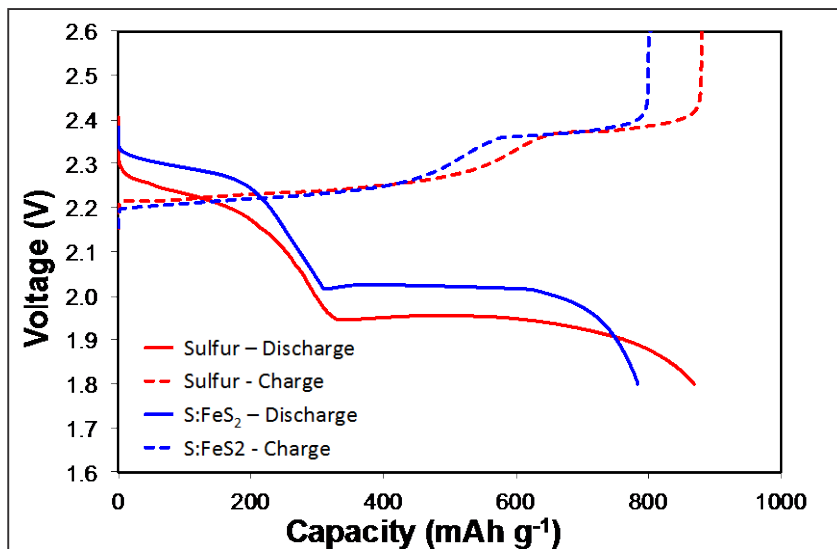


- Phase transition during 1st discharge
 - 1st discharge needs to go down to ~1.0V to activate FeS₂

Accomplishments and Progress

FeS₂ additive effect on sulfur cathode – without activation

Study	Hybrid Formulation	Electrolyte	Cycling Voltage	Discharge Rate	Charge Rate
	S:FeS ₂ :C:PVDF	LiNO ₃	Range		
1	60:0:50:10	Yes	2.6V - 1.8V	1C	C/5 - C/20
2	60:20:30:10	Yes	2.6V - 1.8V	1C	C/5 - C/20

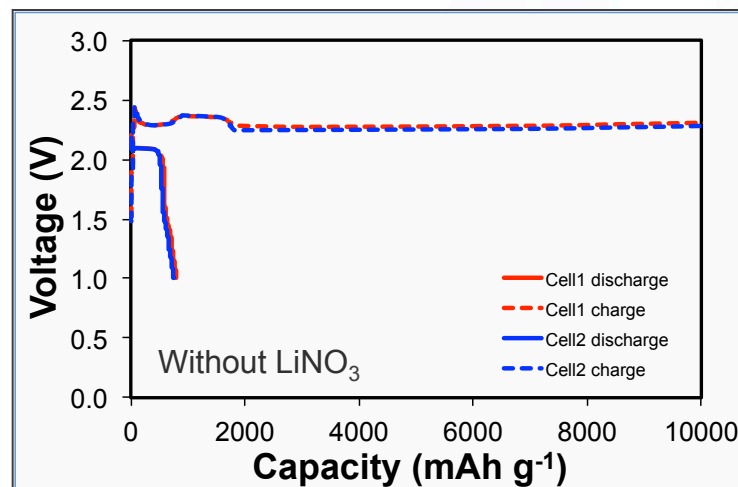
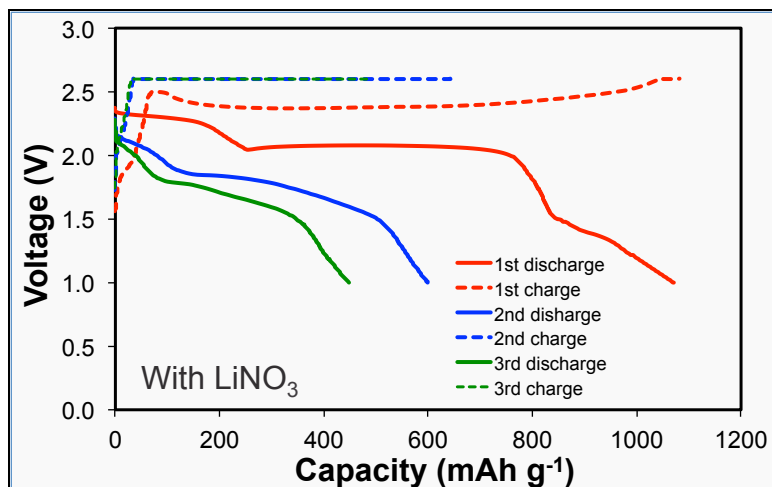


- Cell with FeS₂ exhibited higher voltage relative to control cell.
- Without FeS₂ activation, hybrid electrode cell showed no obvious effect on cycling.

Accomplishments and Progress

FeS₂ additive effect on sulfur cathode – LiNO₃ and activation

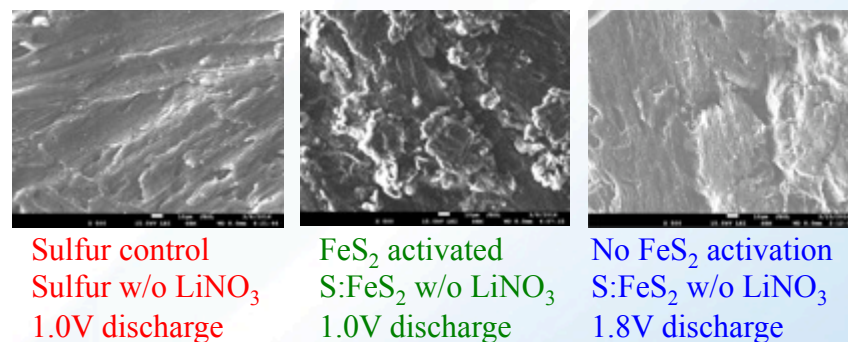
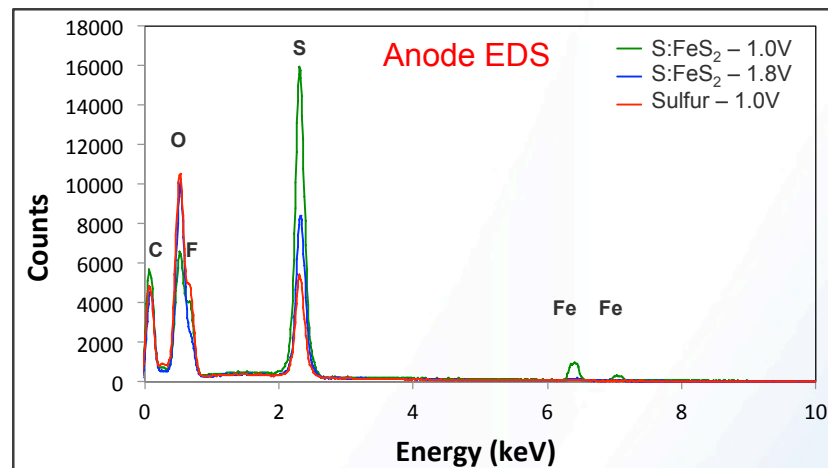
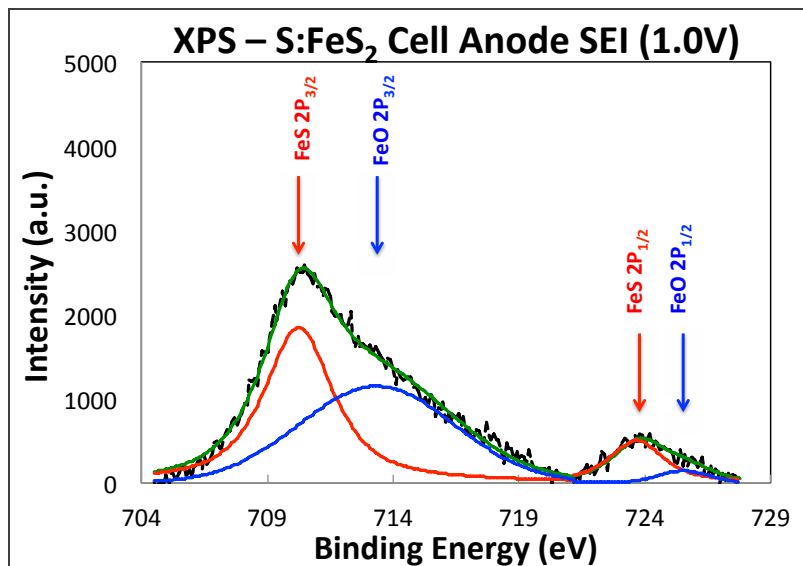
Study	Hybrid Formulation	Electrolyte	Cycling Voltage	Discharge Rate	Charge Rate
	S:FeS ₂ :C:PVDF	LiNO ₃	Range		
1	60:20:30:10	Yes	2.6V - 1.0V	0.2C	C/5 - C/20
2	60:20:30:10	No	2.6V - 1.0V	0.2C	C/5 - C/20



- FeS₂ activation at voltage below 1.5V during 1st discharge.
- With LiNO₃ leads to significant cell impedance growth resulting in polarized cell voltages.
- Without LiNO₃, cells can not be charged due to severe shuttling effect – **Why?**

Accomplishments and Progress

FeS₂ additive effect on sulfur cathode – Fe dissolution



- FeS₂ dissolution observed for the hybrid cathode cell with iron identified on anode surface.
- Severe Fe dissolution happens only for FeS₂ activated (1.0V) hybrid cathode cells
- XPS identified FeS and FeO on the anode surface - correlated to severe shuttling effect.

Accomplishments and Progress

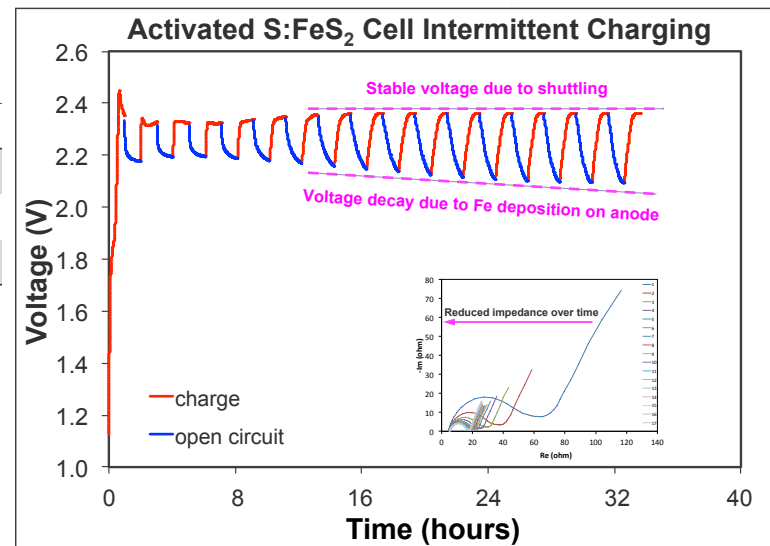
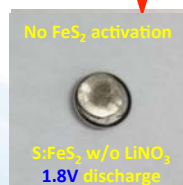
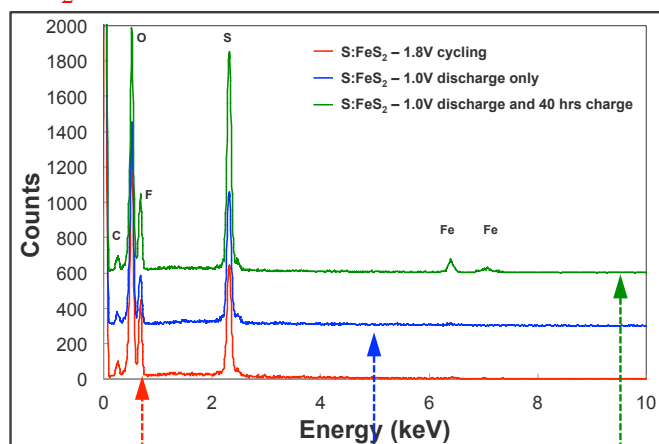
FeS₂ additive effect on sulfur cathode – Fe dissolution

Does polysulfide catalyze the dissolution of FeS₂? – No!

Iron Concentration Measurement by ICP-OES

Sample	Corrected Fe Concentration (ppm)
FeS ₂ in 1:1 DME:DOL	2.6
FeS ₂ + 0.07 M Li ₂ S ₈ in 1:1 DME:DOL	1.8
1:1 DME:DOL only	0.0

Is FeS₂ activation sufficient for iron dissolution? – No!



- Polysulfide does not catalyze FeS₂ dissolution.
- FeS₂ activation only is not sufficient for iron dissolution.
- The charging of FeS₂ activated hybrid cathode leads to Fe dissolution.
- Deposition of FeS on anode surface leading to severe shuttling effect, preventing cells to be fully charged.

Accomplishments and Progress

FeS_2 additive effect on sulfur cathode – conclusion

- Activation of FeS_2 requires cell to be discharged to 1.0V.
- The presence of FeS_2 additive leads to higher sulfur cell discharge voltages.
- Without activation, FeS_2 has no obvious impact on sulfur cell cycling performance.
- The presence of LiNO_3 allows the FeS_2 to be activated and the cell can be cycled, but with the compromised cell impedance growth.
- Elimination of LiNO_3 from the electrolyte also allows the FeS_2 to be activated, but resulting in uncontrollable shuttling effect during charging.
- Significant iron dissolution occurs during charging step of the FeS_2 activated S: FeS_2 hybrid cathode cell.
- FeS and FeO deposition on anode SEI layer catalyzes the polysulfide shuttling effect during cell charging.

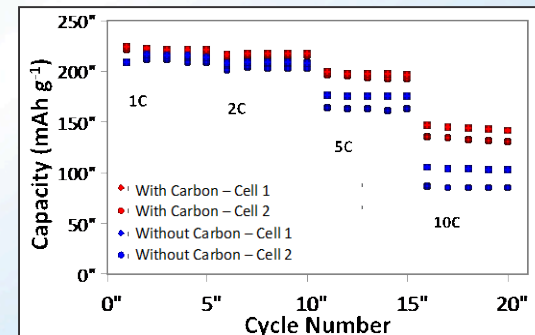
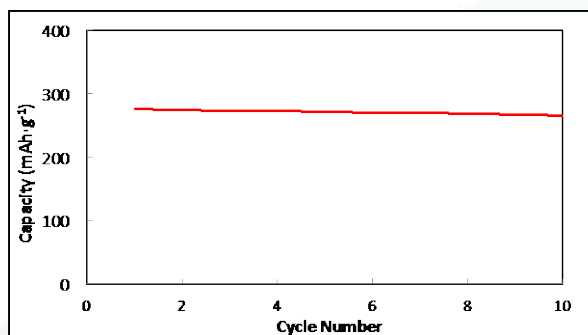
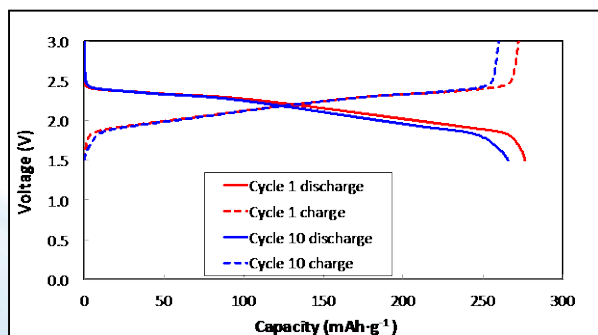
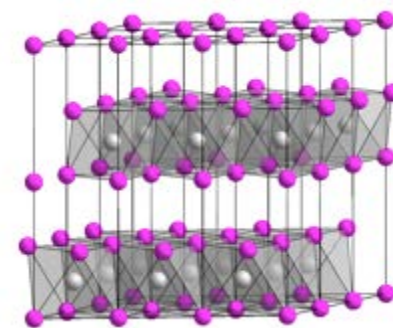
Accomplishments and Progress

TiS₂ additive effect on sulfur cathode - background

- TiS₂ has layered crystal structure and capable of reversible lithium intercalation - theoretical capacity 239 mAh/g.



- TiS₂ can be activated at voltage above 1.5V.
- TiS₂ is electronically more conductive than carbon black.
- TiS₂ cells have high rate capability even without carbon conductive additive.

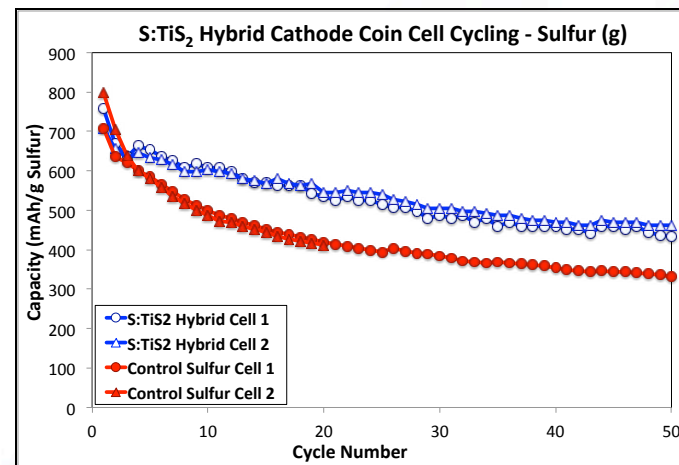
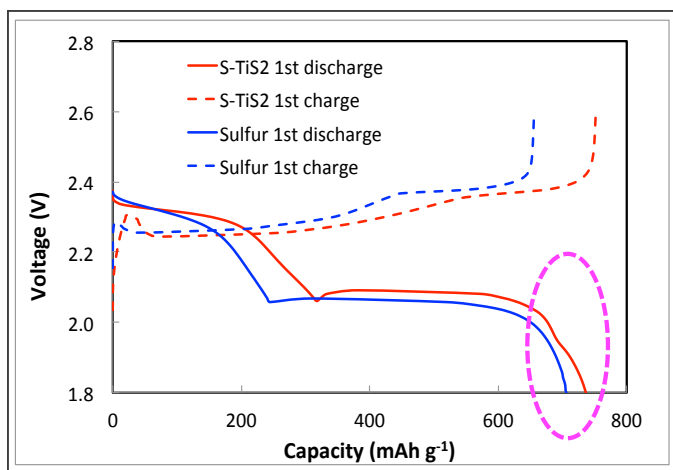


Accomplishments and Progress

TiS_2 additive effect on sulfur cathode

Cell #	Electrode	S:TiS ₂ :C:PVDF	Total Loading (mg/cm ²)	S Loading Capacity (mAh/cm ²)	TiS ₂ Loading Capacity (mAh/cm ²)	Total Loading Capacity (mAh/cm ²)
1	S:TiS ₂	60:20:30:10	1.71	1.43	0.07	1.50
2	S:TiS ₂	60:20:30:10	2.69	2.25	0.11	2.36
3	Sulfur	60:00:30:10	2.58	2.59	0.00	2.59
4	Sulfur	60:00:30:10	2.54	2.55	0.00	2.55

2032 Coin cells; 1.0M LiTFSI/DOL:DME = 1:1 v/v + 1wt% LiNO₃; C/10 rate charge/discharge

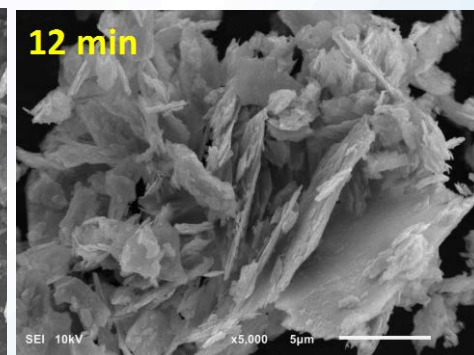
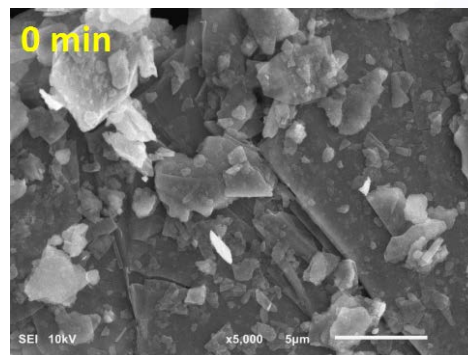
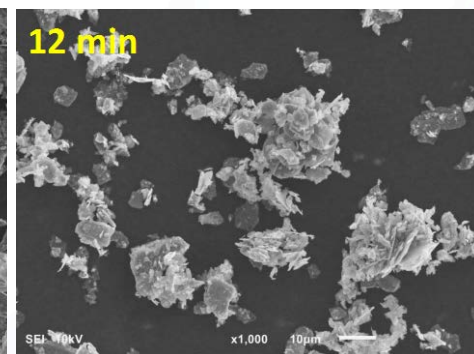
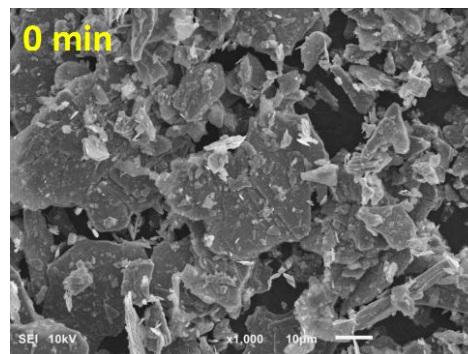
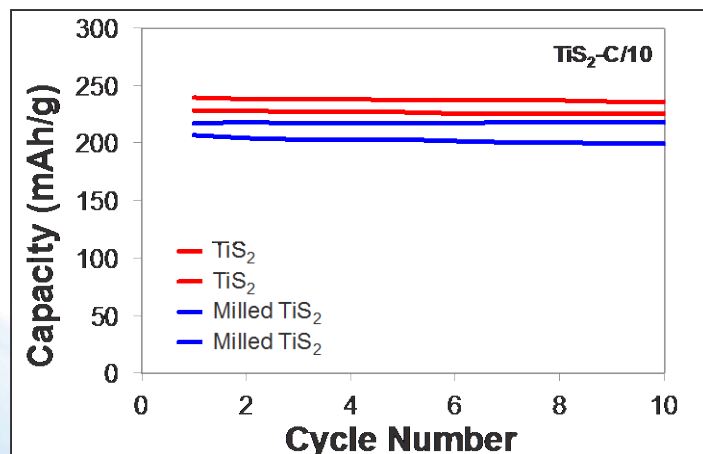
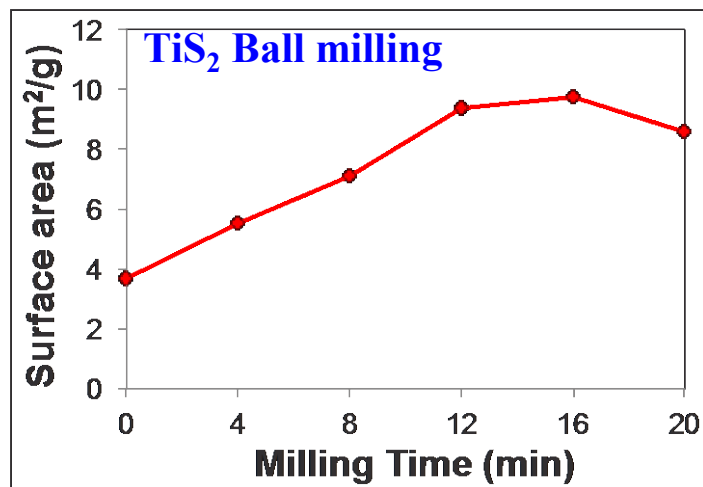


- TiS₂ activated with more sloped voltage profile near the end of discharge.
- Similar initial sulfur utilization observed (based on S only).
- S:TiS₂ hybrid electrode cells exhibited lower capacity fade rate.

Accomplishments and Progress

TiS₂ additive effect on sulfur cathode – BET & particle size

Amy Marschilok, Kenneth Takeuchi,
Esther Takeuchi, Qing Zhang, Jeff Jou

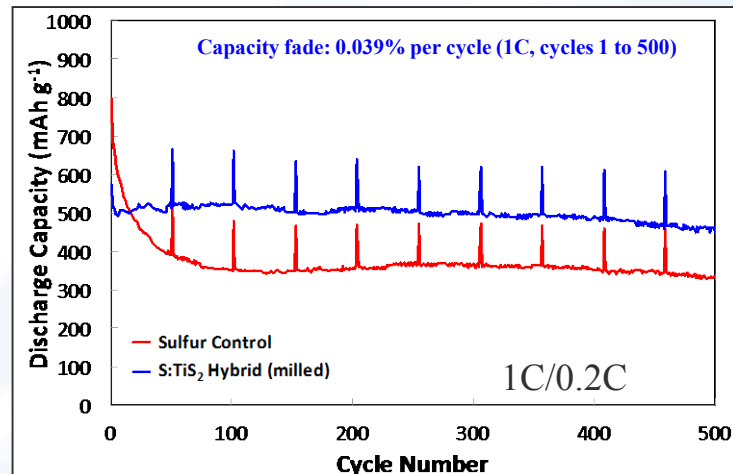
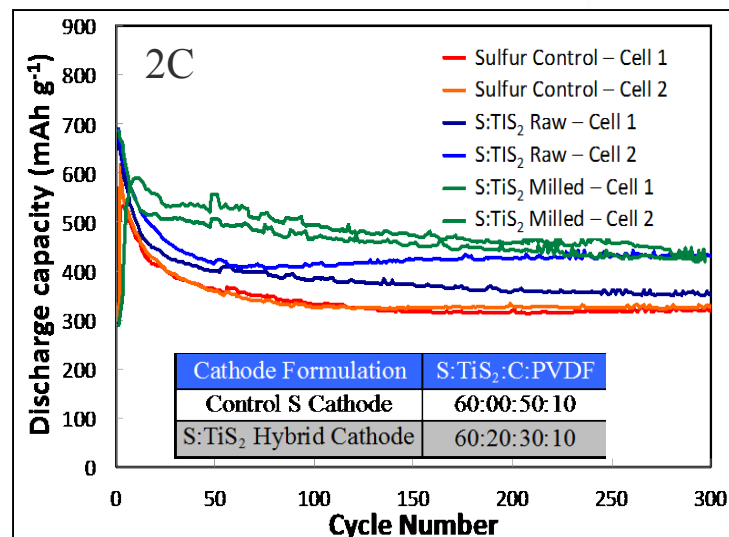
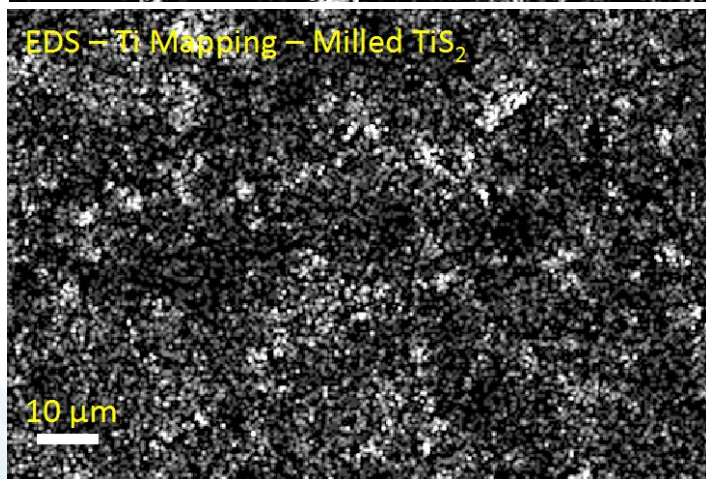
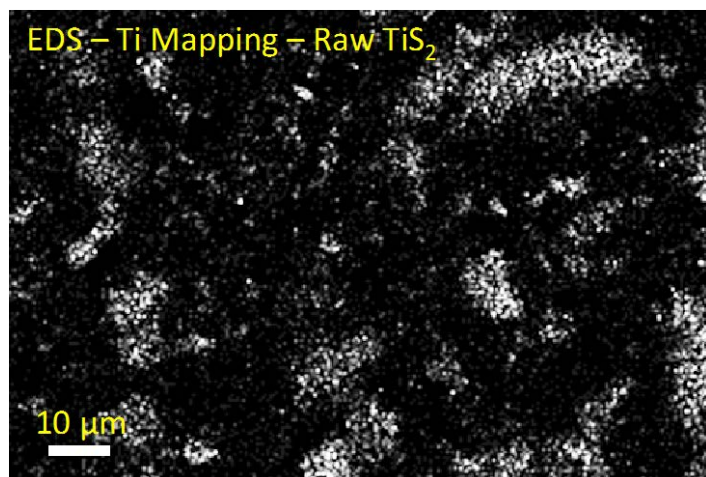


- 12 minutes ball milling sample selected for hybrid cathode study

Accomplishments and Progress

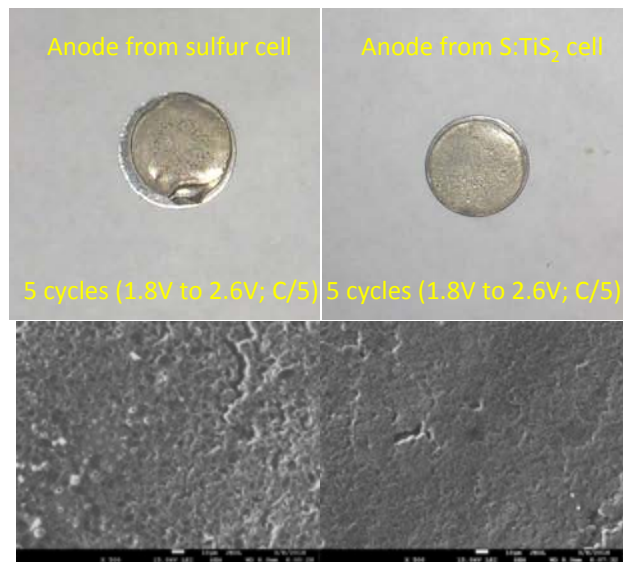
TiS_2 additive effect on sulfur cathode – particle size effect

TiS_2 distribution in coated cathode

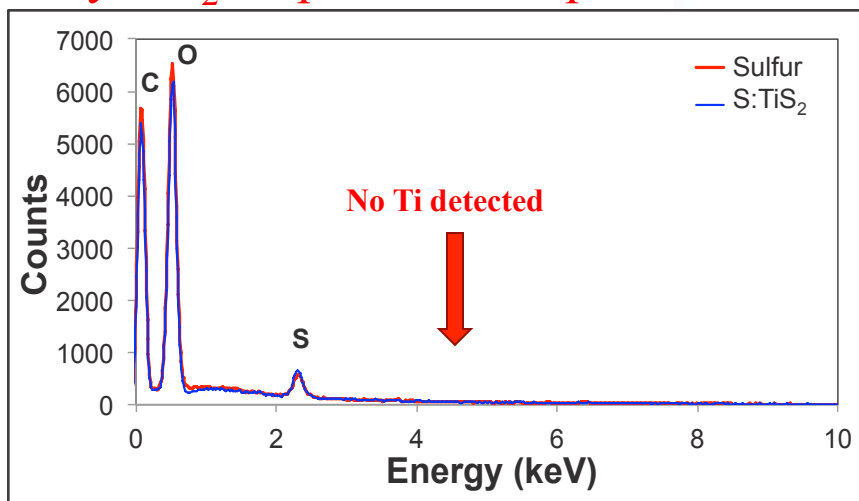


Accomplishments and Progress

TiS₂ additive effect on sulfur cathode - mechanism

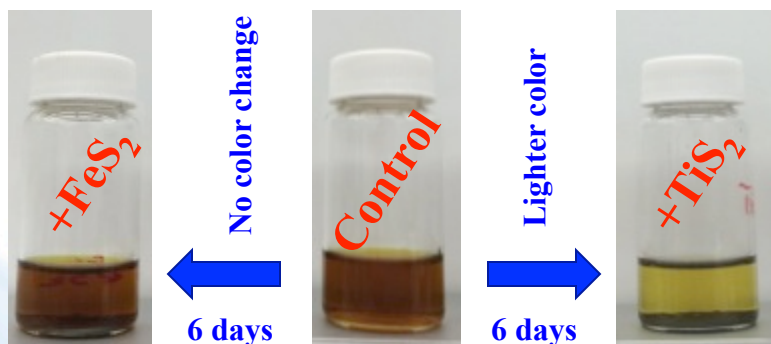


Why TiS₂ help sulfur cell performance?



■ TiS₂ additive benefit

- No TiS₂ dissolution
 - Smooth and clean anode surface.
 - EDS detect no Ti on anode surface.
- Polysulfide adsorption by TiS₂
 - Decreased polysulfide solution coloration vs. control.



Li₂S₈ 5 mM in DOL:DME = 1:1

Accomplishments and Progress

TiS_2 additive effect on sulfur cathode - conclusion

- TiS_2 can be reversibly cycled at up to 10C rate with good capacity retention.
- TiS_2 additive promotes sulfur electrode high rate discharge with improved cycling life.
- Adsorption of polysulfide by TiS_2 contributes to the better cell electrochemical behavior.
- Smaller TiS_2 particle size and uniform TiS_2 distribution are beneficial for S: TiS_2 hybrid cell cycle life.
- Sulfur cells with TiS_2 additive achieved 500 cycles at 1C discharge rate with $< 0.04\%$ capacity fade per cycle.

Responses to Previous Year Reviewers' Comments

- This project is a new start and was not reviewed last year.

Partners / Collaborations

- **Brookhaven National Laboratory (BNL)**
 - Dr. Hong Gan (PI) – Project coordination
 - Dr. Ke Sun – Project execution
- **Stony Brook University**
 - Prof. Esther Takeuchi (Co-PI), Prof. Amy Marschilok, Prof. Kenneth Takeuchi – Transition metal sulfide cathode testing, transition metal sulfide synthesis and sample preparation for particle size study, ICP dissolution studies
- **Center of Functional Nanomaterials (CFN), BNL**
 - Dr. Dong Su – TEM/ED, SEM morphology and structural characterization
 - Dr. Xiao Tong – XPS analysis on anode SEI from S:FeS₂ cycled cells
- **National Synchrotron Light Source II, (NSLS II) BNL**
 - Dr. Yu-chen Karen Chen-Wiegart – XRF on CuS dissolution studies
- **Columbia University**
 - Prof. Simon Billinge – PDF structural characterization on S:FeS interaction

Remaining Challenges and Barriers

- It is challenging to resolve Li-S cell performance issues at just cathode level. Strong interactions between cathode, anode and electrolyte at the system level need to be addressed.
- Decreased sulfur utilization with high sulfur cathode mass loading (>2 mg/cm²) impedes the achievement of low cost, high energy density Li-S batteries.
- Low energy density at the electrode and cell levels due to the low active sulfur % in electrode formulation and low sulfur utilization.
- Dissolution of metal sulfides (CuS and FeS₂) in the conventional electrolyte system limits our choice of MFCA to TiS₂.
- Polysulfide dissolution is still a major challenge for Li-S cell to achieve high energy efficiency and long cycle life.
- Fast capacity fade during the initial cycles needs to be mitigated.
- Anode passivation by LiNO₃ limit the discharge voltage cut off to 1.8V.

Proposed Future Work

- Understand the mechanism that governs the beneficial interaction between sulfur/TiS₂ and continue modify TiS₂ properties for optimized sulfur cell performance.
- Optimize the S:TiS₂ electrode mechanical and electrochemical properties by selecting the appropriate electrode binders and conductive carbons, as well as the electrode preparation process.
- Optimize sulfur cathode formulation and achieve high areal sulfur mass loading of $> 2 \text{ mg/cm}^2$ for high cathode energy density.
- Develop method for cell activation with high sulfur loading.
- Evaluate electrode and cell design factors, such as interlayer cathode structure, to promote sulfur utilization and maximize cell cycle life.
- Reduce polysulfide dissolution by developing new electrolyte systems and revisit some promising MFCA additives.
- Anode surface protection to minimize or prevent side reactions between polysulfide and lithium metal anode.

Summary

- MFCA improves sulfur cathode discharge power capability.
- MFCA activation is highly dependent on metal types (CuS, FeS₂, TiS₂) with unique characteristics for each candidate.
- Dissolution of CuS and FeS₂ is the leading cause for poor cycling performance in cells with hybrid sulfur cathode.
- TiS₂ additive improves sulfur cell high rate cycle life and contributes to the delivered cell capacity.
- Smaller TiS₂ particle size and uniform TiS₂ particle distribution within the S:TiS₂ hybrid cathode are beneficial for improved sulfur cell cycle life.
- Hybrid S:TiS₂ cathode exhibits no Ti dissolution with strong adsorption interaction between TiS₂ and polysulfide.