



Electrochemically Stable High Energy Density Lithium-Sulfur Batteries

Prashant N. Kumta

Swanson School of Engineering, University of Pittsburgh, Pittsburgh,
Pennsylvania

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Overview

Timeline

- Project start date:
 - April 1, 2019
- Project end date:
 - September 30, 2021
- Percent complete: 90%

Budget

- Total project funding
 - DOE share: \$800, 000
 - Cost share: \$88, 928
- Funding for FY 2020: \$449, 799
- Funding received in FY 2021: No cost extension

Barriers

- Barriers addressed
 - Limited Cycle life
 - (polysulfide dissolution, shuttling effect)
 - Low coulombic efficiency
 - Low sulfur utilization
 - Poor rate capability
 - (poor electronic and Li ion conductivity)

Partners

- Interactions/collaborations
 - UPitt (D. K. Achary)
 - Malvern Panalytical (S. Speakman)
 - Kurt J. Lesker Co. (KJL)
 - Flex Cellz

Relevance/Objectives

Objectives:

Develop, fabricate, and demonstrate a single layer/multilayer lithium sulfur battery (LSBs) pouch cell of cell capacity > 100 mAh using optimized electrodes ($\geq 6 \text{ mg S/cm}^2$ loading) to achieve areal capacity ($\geq 5 \text{ mAh/cm}^2$), CE ($\geq 99.9\%$), and, ability to exhibit cell energy density $\geq 500 \text{ Wh/kg}$ with cycle life of $\geq 1,000$ and fade in capacity of $\leq 20\%$.

Proposed solution:

- Develop high throughput, high yield commercially inexpensive process for the synthesis of electrochemically stable S infiltrated complex framework materials (CFM-S) based cathode of composition 90 wt.% S
- Synthesize Lithium ion conductor (LIC) and functional electrocatalyst (FEC) dispersed CFM-S to improve the reaction kinetics of high order PS conversion to low order PSs
- Develop dendrite free Li alloy anode exhibiting > 1000 cycles with areal capacity > 5 mAh/cm^2 @ C/2
- Fabricate high loading ($\geq 6 \text{ mg/cm}^2$) sulfur-rich electrodes ($\geq 65 \text{ wt\%}$ sulfur in the electrode) exhibiting $\geq 1000 \text{ mAh/g}$ S capacity @C/3 with excellent life-cycle (>300 cycles) and high >99.9% CE when tested with dendrite-free lithium metal alloy anode (LMAs)
- Fabricate, evaluate performance and optimize $\sim 20 \text{ cm}^2$ pouch cell of cell capacity > 100m Ah and target energy density ($\geq 500 \text{ Wh/kg}$) meeting the DOE-battery500 goals

Impact:

- Development of S infiltrated framework materials along with LICs, and FECs and polysulfides (PSs) trapping agents enabling chemical binding of PSs and catalytic promoters facilitating high order PS to Li_2S conversion using economic precursors ($\sim \$23/\text{kg}$) will likely meet the target of production cost of LSB ($\leq \$80/\text{kWh}$). Pouch cell made of optimized electrodes ($\sim 200\text{-}500 \text{ mAh}$ cell) is expected to achieve energy densities of $\sim 500 \text{ Wh/kg}$ at the University of Pittsburgh.
- Success of the proposed work will result in demonstrating LSB technology as a viable energy storage system for EV.

Milestones for 2020 and 2021

Date	Description	Type	status
February 2020	Synthesis, characterization and performance study of lithium ion conductor (LIC) and functional electrocatalyst (FEC) dispersed S infiltrated highly porous carbon-based CFM	Technical	completed
April 2020	Electrode fabrication and optimization of electrode thickness of achievable areal capacity $\geq 6\text{mAh/cm}^2$, and cycle life ~ 300 cycles; $< 5\%$ fade	Technical	completed
August 2020	Large area electrodes meeting the targeted capacity: $\geq 6\text{mAh/cm}^2$, and cycle life ~ 100 cycles; $< 5\%$ fade	Technical	Completed
December 2020	Pouch cell with optimized electrodes and dendrite free Li-SIA/MCA anodes: areal capacity $\geq 6\text{mAh/cm}^2$, cycle life > 300 cycles, and $< 10\%$ capacity fade	Go/No-Go	Completed
June 2021	Develop $\geq 200\text{mAh}$ pouch cell using high capacity cathode ($\geq 1000\text{mAh/gS}$) coupled with Li-SIA alloy	Technical	Ongoing
September 2021	Performance testing of multilayer pouch cells of large area electrodes with high S loading in lean electrolyte conditions ($E/S \leq 4\text{ }\mu\text{L/mg}$) with respect to targeted porosity ($< 60\%$), S utilization ($> 60\text{ wt.}\%$) meeting the targeted capacity $\geq 6\text{mAh/cm}^2$ exhibiting stable cycle life ~ 1000 cycles.	Technical	ongoing

Any proposed future work is subject to change based on funding levels

Approach

Several approaches outlined below were developed and studied:

- **Generation of novel complex framework materials (CFM) enabling high sulfur loading (> 90 wt.%) and polysulfide (PS) confinement**
- **Interface engineering of CFM-S by homogeneous non-porous high electronic conducting (EC) and Li-ion conducting (LIC), conjugated Li-polymer sulfur containing polymer (CLi-P-SCP) PS dissolution resistant coatings to confine PSs, and improve the cycle life and rate capability.**
- **Identification of functional electrocatalysts (FECs) for rapid conversion of higher order PS to Li_2S_2 / Li_2S and Li_2S to S. Incorporation of FECs during S infiltration to promote PS conversion kinetics to Li_2S and as a result, improve the S utilization and cycle life.**
- **Development of novel 3D architecture electrode using EC and LIC coated CFM-S of targeted capacity ($\geq 6\text{mAh/cm}^2$) using 3D printing to achieve the desired architecture (control porosity, and thickness) guided by computational analysis.**
- **Development of single layer and multilayer ($\sim 20\text{cm}^2$) pouch cell of cell capacity > 100 mAh targeting Batt 500 goals (energy density $\geq 500\text{Wh/kg}$, cycle life ~ 300 cycles), and deliver final full cell meeting the performance and safety standard**

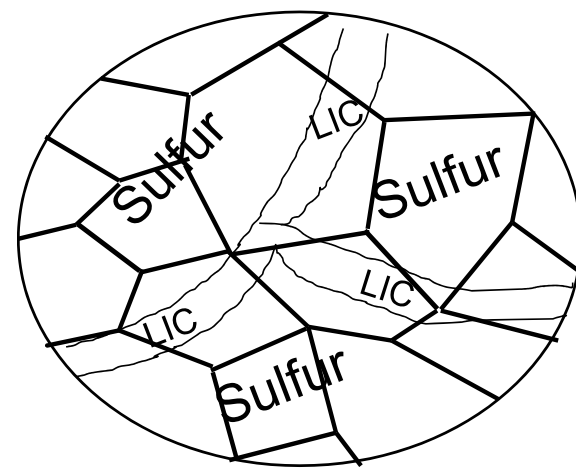
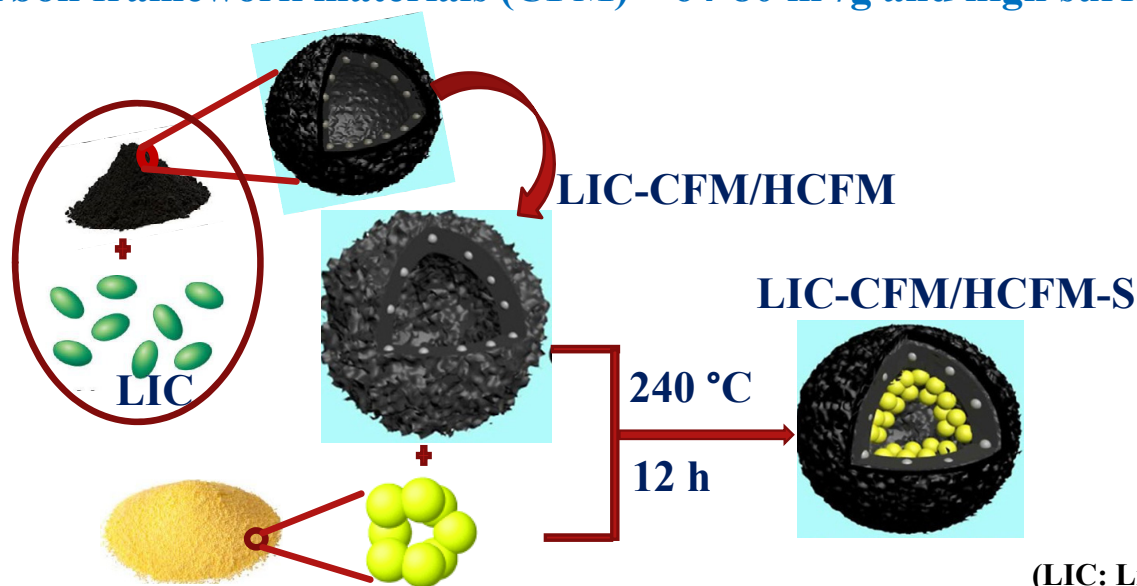
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Technical Accomplishments and Progress

Materials Synthesis: Liquid/Vapor phase sulfur infiltration

❖ Lithium ion conductor-CFM with S (LIC-CFM-S) – Simple Scalable Process

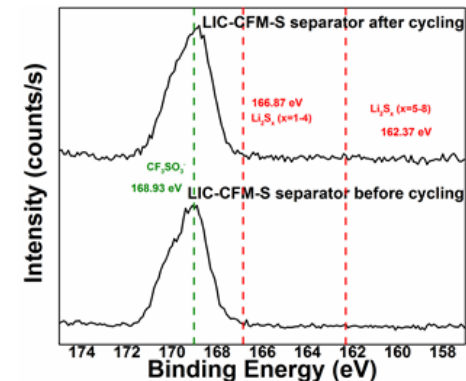
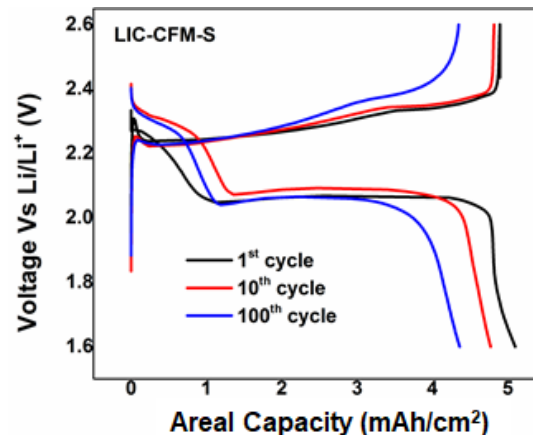
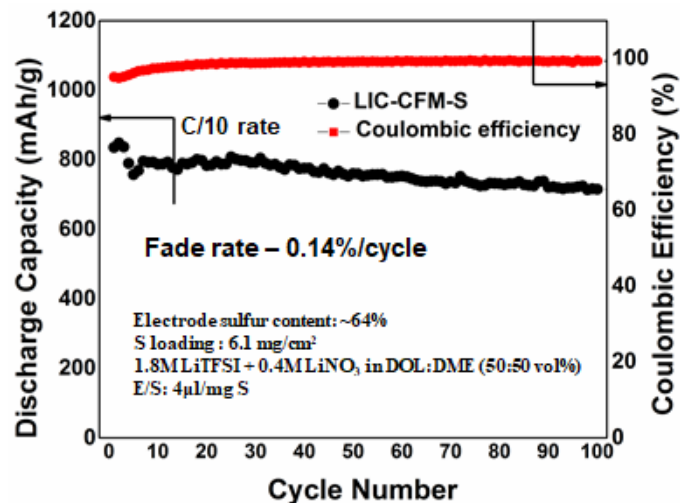
Systems: carbon framework materials (CFM) – 64-80 m²/g and high surface area CFM (HCFM) – 2000 m²/g



(LIC: Li-ion conductor; CFM: complex framework materials)

- **Step 1:** LIC coated on CFM (LIC-CFM)
- **Step 2:** Mixing of LIC-CFM and Sulfur with appropriate weight ratio 20: 80 or 10:90 etc.
- **Step 2:** Mixture sealed in a Swagelok cell
- **Step 3:** Mixture kept for 12 h at 240 °C

Lithium ion conductor-CFM-S (LIC-CFM-S)



XPS analysis
: No PS dissolution

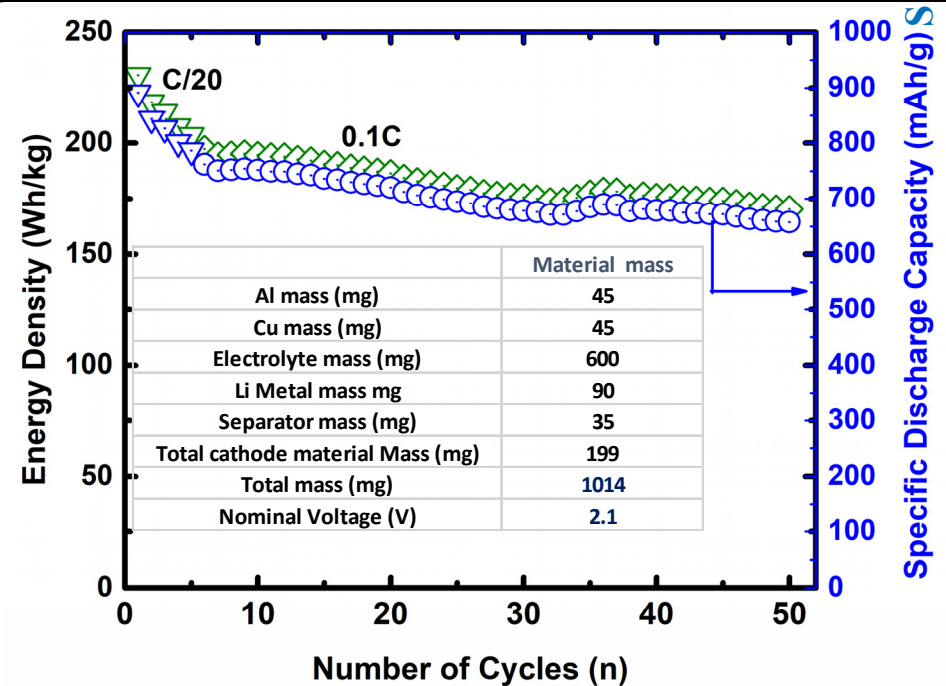
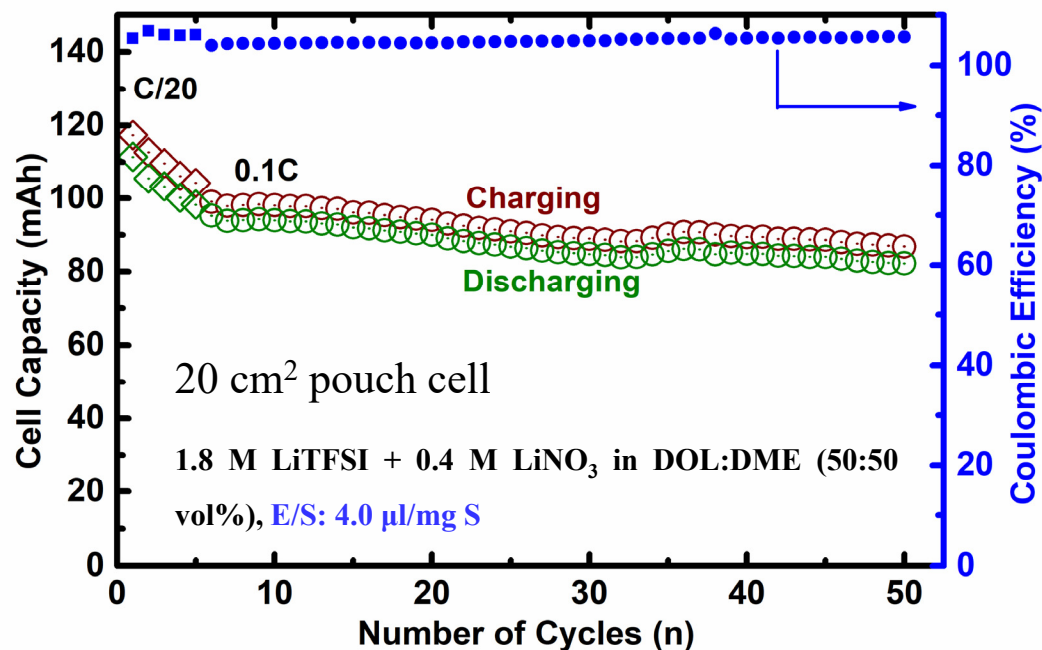
- CFM-S with LIC improves ionic conductivity (3.25×10^{-4} S/cm)
- Expected to maintain ionic conductivity of electrode during long term cycling
- The LIC-CFM-S exhibits high areal capacity of 4.3 mAh/cm² after 100 cycles with fade in capacity ~0.14 % per cycle
- Significant improvement in stability and cyclability observed
- Dual role of LIC and PS trapping achieved by the Li-ion conductive coating

LIC dispersed on nanocrystalline porous architecture of CFM shows excellent ability of trapping PS and maintaining ionic conductivity of the electrode improving the areal capacity and stability.

Further optimization to achieve higher capacity > 1000 mAh/g S is ongoing exploring dispersion of FECs. Addition of electrolyte additives to explore formation of stable SEI and CEI at anode and cathode is also ongoing

Any proposed future work is subject to change based on funding levels

LIC-CFM-S: Li-S Single layer Pouch Cell (~100 mAh)



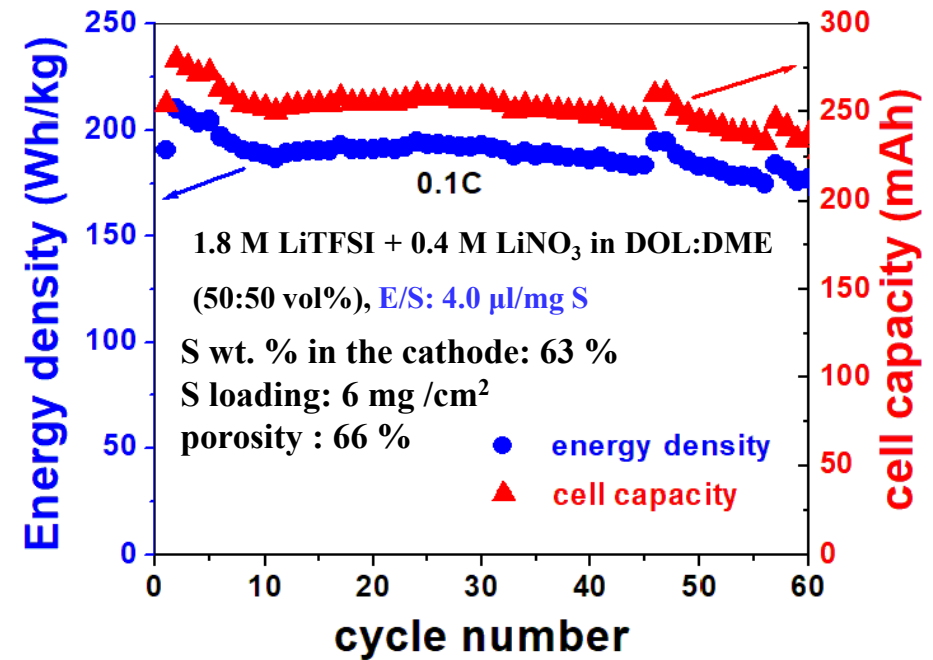
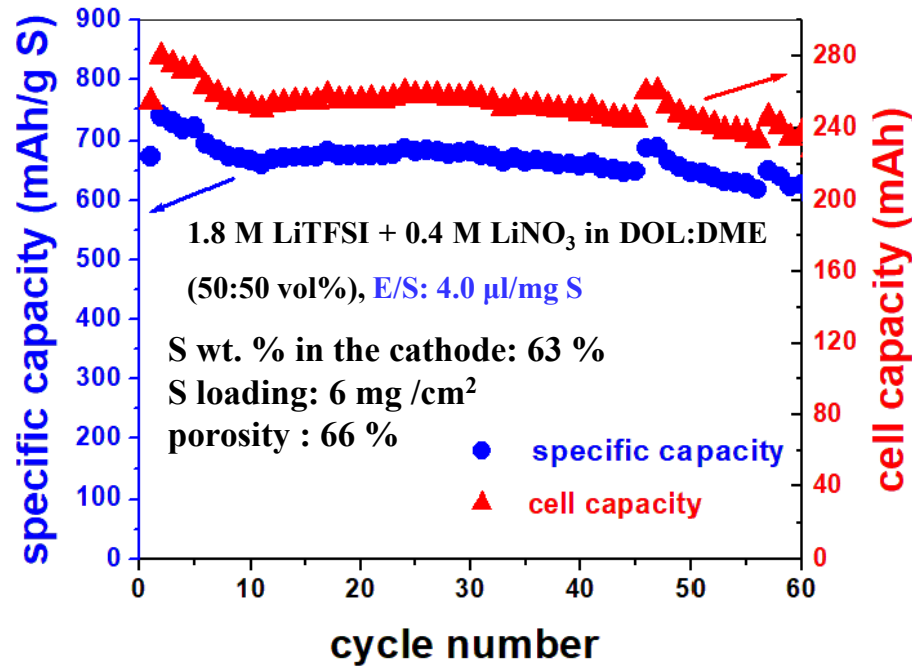
- S wt. % in the cathode: 63 %; S loading: 6.26 mg /cm²
- thickness : 150 μm; porosity : 66 %
- First five cycles at C/20 after first two formation cycles
- **Areal Capacity : 4.6 – 4.2 mAh/cm² at 0.1C**
- Capacity fade : 0.28% per cycle at 0.1C
- Promising initial cycles with capacity fade after 60 cycles

Strategies for further improvement

- reduce inactive mass
- **Improve reaction kinetics**
- **Higher S utilization by microstructure engineering**
- Use of FECs and microstructure control
- Effective PS trapping for higher S loading for improved cycle life

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LIC-CFM-S: Li-S 4 layer Pouch Cell (~250 mAh)



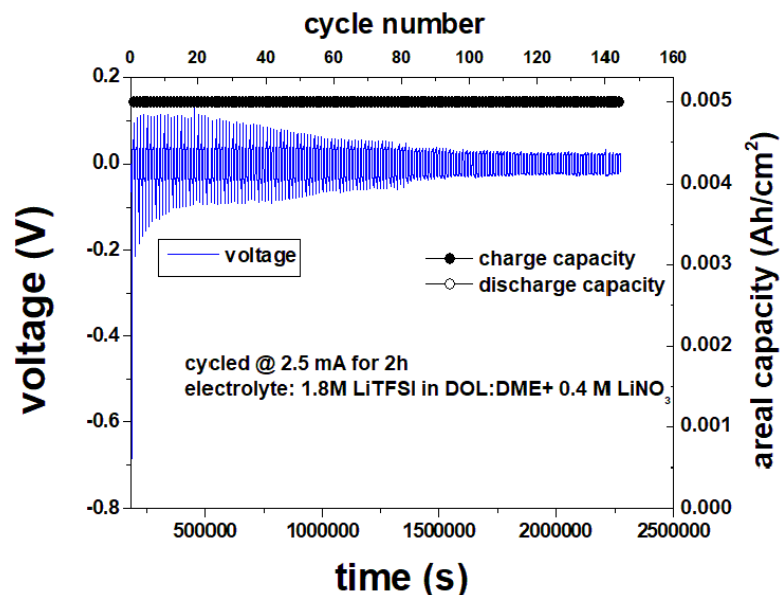
- First five cycles at C/20 after first two formation cycles
- Areal Capacity : 3.5 mAh/cm² at 0.1C
- Successful generation of multilayer pouch cells matching single layer performance

Strategies for further improvement

- Improve reaction kinetics and sulfur utilization by microstructure engineering
- Use of FECs and microstructure control
- Effective PS trapping for higher S loading

Al mass (mg)	135
Cu mass (mg)	90
Electrolyte (mg)	1511
Li metal (mg)	360
Separator (mg)	105
Cathode (mg)	599
Total mass (mg)	2800

Dendrite free Li-SIA anode: areal capacity ≥ 5 mAh/cm² @C/2



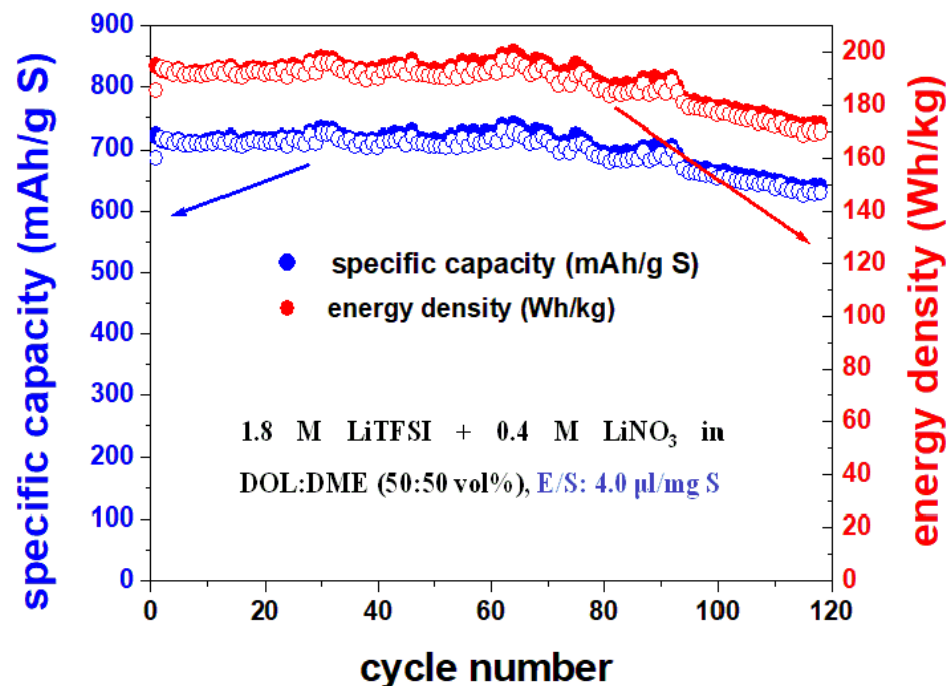
- **V-t cycling of symmetrical Li- SIA anode**
- No significant change of growth potential up to 145 cycles
- **No dendrite formation cycled @2.5 mA for 2h (5 mAh/cm²)**
- Dealloying < 1V
- Suitable Li-SIA alloy anode for Li-S battery
- Similar crystal structure to Li metal
- Density of Li-SIA alloys ($\rho \sim 1.1$ g/cm³ much lighter than copper ($\rho \sim 8.92$ g/cm³))

1.8 M LiTFSI + 0.4 M LiNO₃ in DOL:DME (50:50 vol%), E/S: 4.0 μ l/mg S

- Dendrite free Li metal anode enabling long cycle life
- No significant volume change of anode
- Li metal will not be exposed to electrolyte
- Opportunities to further improve the system using alloying elements to improve alloying kinetics
- Electrolyte additives to form stable SEI

Any proposed future work is subject to change based on funding levels

LIC-HCFM-S and Li-SIA: Single layer Pouch Cell



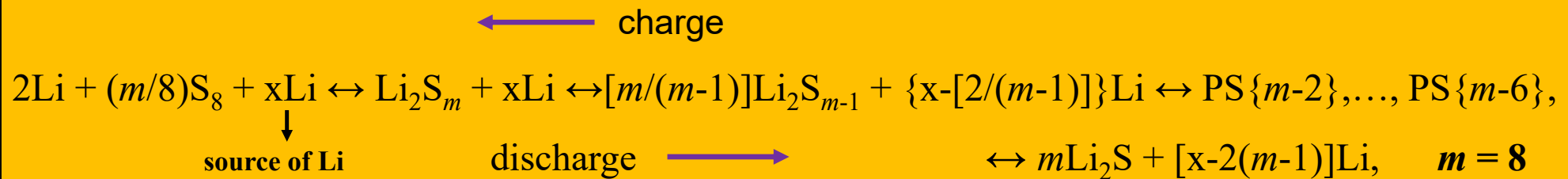
- ✓ Pouch cell: single layer
- ✓ Slurry- 72:18:10 (wt.%)
- ✓ S (wt.%) in cathode : 62 %
- ✓ Cathode Area: 20 cm²
- ✓ Thickness: 103 μm (No calendaring)
- ✓ Porosity: 61%
- ✓ E/S ratio: 4 μl/mg
- ✓ S loading : 5.10 mg/ cm²
- ✓ Anode: Li-SIA alloy
- ✓ Total S: 110.00 mg

- Preliminary results are encouraging in both coin cell and pouch cells
- Room for further optimization studies
- Opportunities to further improve the system by adding electrolyte additives

Any proposed future work is subject to change based on funding levels

Computational Identification of Functional Catalysts for rapid conversion of PSs to Li_2S and elemental $\text{Li}+\text{S}$

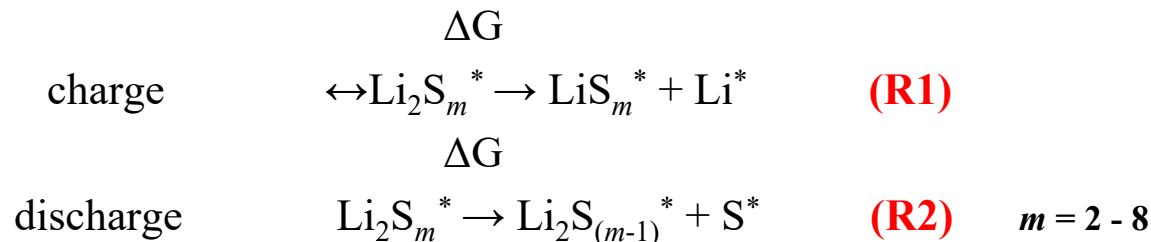
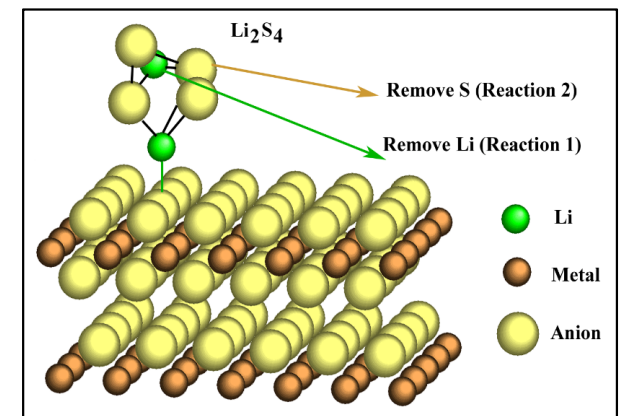
Accelerate the PSs conversion reaction in the forward direction to form Li_2S and backward direction to form pure Li and S
 There is a need to identify a suitable catalyst material for facilitating the following two forward and backward reactions:

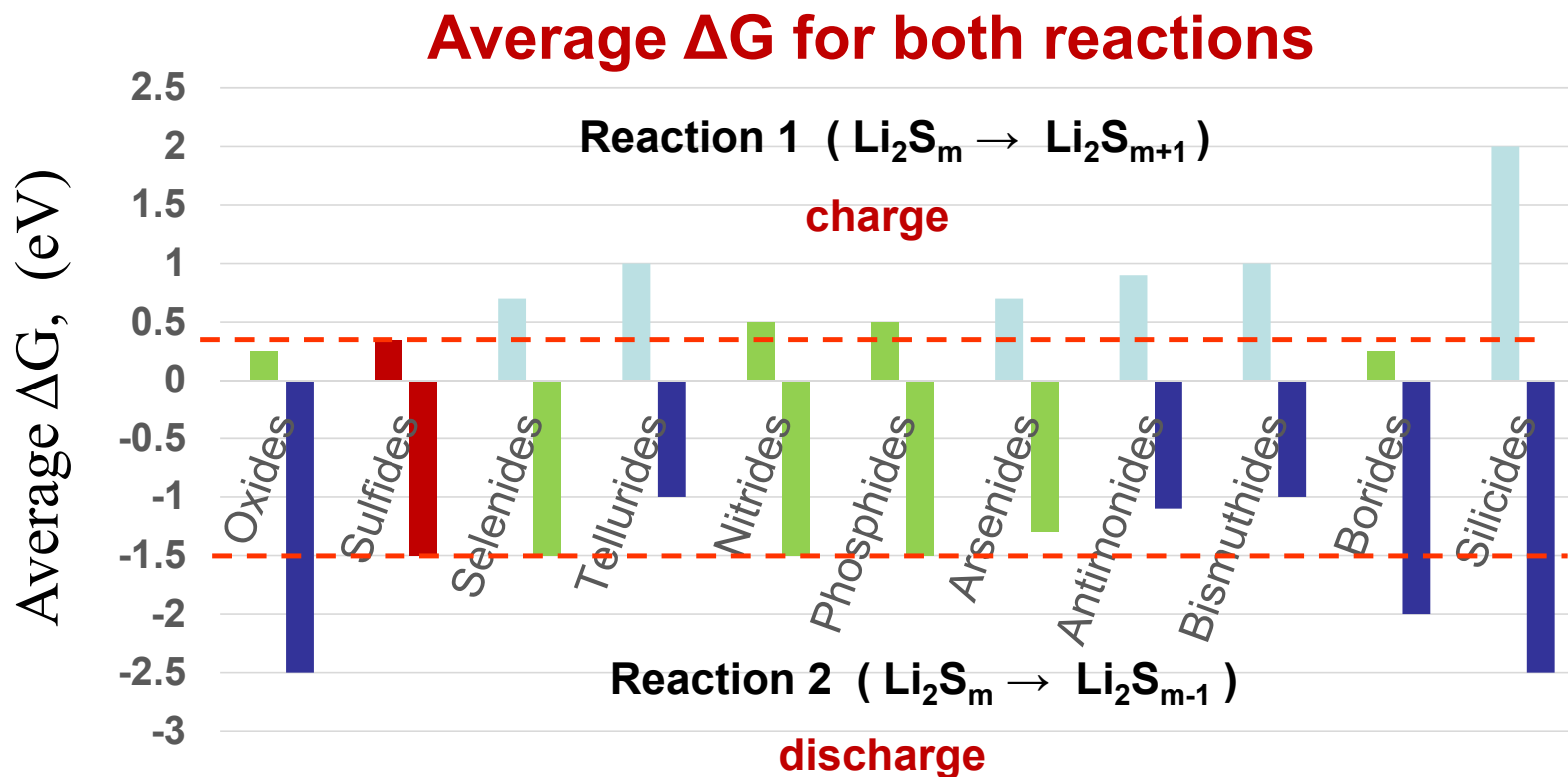


Facilitating these reactions will help significantly decrease or even completely eliminate PSs dissolution

These multistep reactions could be reduced to the following forward and backward elementary steps and may serve as the catalytic activity descriptors of the potential functional electrocatalysts (FECs):

Schematic illustration of PSs decomposition





Using metal sulfides as a benchmark, suggested functional electrocatalysts from this computational study would be:

- ☐ **Reaction 1:** Metal Oxides and Metal Borides
- ☐ **Reaction 2:** Metal Selenides and Metal Arsenides
- ☐ **Both Reactions:** Metal Nitrides and Metal Phosphides

Responses to Previous Year Reviewers' Comments

Q-1: What is the thickness of the sulfur electrodes and their porosity number?

A: The electrode thickness has been maintained $\sim 100\text{ }\mu\text{m}$ for $5\text{mg}/\text{cm}^2$ S loading and porosity has been maintained $< 60\%$.

Q-2. How much volume the sulfur electrode will take?

A: based on the $\sim 100\text{ }\mu\text{m}$ thickness of $5\text{mg-S}/\text{cm}^2$ loading, the volume of the electrode maintained $\sim 0.02\text{ cm}^3/\text{g S}$.

Q-3: Why big hexagonal holes of the sulfur cathode as shown in slide 6.

A: The 3D printed sulfur cathode shows a clear grid structure with the hexagonal pores (holes) coated on the Al foil. The hexagonal pores serve as Li^+ transport channels as well as provide enough volume for accommodation of electrolyte in the sulfur cathode. Additionally, these hexagonal pores can anchor the well-located polysulfides in the cathode, thus relieving the shuttling effect and improve the cycling stability.

Collaboration and Coordination with Other Institutions

Dr. D. Krishnan Achary (University of Pittsburgh): Solid-state nuclear magnetic resonance (MAS-NMR) characterization to study the failure mechanisms

Malvern Panalytical: Materials and phase evolution characterization using in-situ XRD

Kurt J. Lesker Company (KJL): Thin film deposition and vacuum instrumentation

Flex Cellz: Technology Licensing Partner

Nanomaterials for Energy Conversion Storage Technology (NECST) Laboratory–Energy Innovation Center, Pittsburgh: Development of modified coin cell testing and carbon nanoarchitectures, development of pouch cell testing

Remaining Challenges and Barriers

➤ Challenges

- Overcome low coulombic efficiency by controlling the SEI and CEI layer formation in surface engineered and scaled up electrodes by identifying suitable electrolyte additives.
- **Fabrication of single layer/multilayer ($\sim 20\text{cm}^2$) pouch cell of cell capacity $>500\text{ mAh}$ targeting Batt 500 goals (energy density $\geq 500\text{Wh/kg}$, cycle life ~ 1000 cycles)**

➤ Barriers

- Formation of stable SEI and CEI at the electrode surface
- Matching performance of multilayer ($\sim 500\text{ mAh}$) pouch cell configuration with single layer pouch cell and coin cell results with lean electrolyte condition

Future Work

- **Fabrication of single layer pouch cell (~20cm², targeted capacity: ~100 mAh cell) with optimized S electrodes, nano-filler containing CPE as separator and in-house synthesized Li metal alloy anodes (~100μm) to achieve the Batt 500 targeted goals in pouch cell configuration.**
 - ☐ Formation cycle and cell balancing of the optimized system.
 - ☐ Constant current-constant voltage (CCCV) test protocol to determine nominal discharge capacity at 100% state of charge (SOC).
 - ☐ Constant current-constant voltage (CCCV) test protocol to determine nominal discharge capacity at 100% state of charge (SOC).
- **Design and testing of 500 mAh (0.5 Ah) multi-layer pouch cells with initial targeted energy density > 500 Wh/kg**
- **Safety field test will be performed on ~100mAh single layer pouch cell (≥500Wh/kg) using MIL-STD-810G and IEC62133 safety standards in collaboration with PNNL and industry partner. 12 test cells meeting the performance and safety standard will be delivered to DOE.**

Any proposed future work is subject to change based on funding levels

Summary: Sulfur Cathodes

Technical Accomplishments

- Successful demonstration of lab-scale synthesis of modified CFM-S hybrid composite exhibiting high areal capacity of $\sim 5 \text{mAh/cm}^2$ and excellent cyclability (>100 cycles)
- CFM-S with PS trapping agent exhibiting excellent cycle life with specific capacity $> 800 \text{mAh/gS}$ @ C/10-C/3 rate
- Successful demonstration of LIC-CFM-S with and sans functional electrocatalyst exhibiting high areal capacity ($\sim > 4 \text{mAh/cm}^2$) and excellent cyclability (>100 cycles) of high S loaded electrode
- Successful design validation of single and multilayer Li-S pouch cells and demonstrated pouch cells with energy density $> 200 \text{Wh/kg}$ (dead mass: tabs and pouch case)
- Successful demonstration of dendrite free Li alloy anode as suitable anode for Li-S batteries in both coin cell and pouch cell configurations

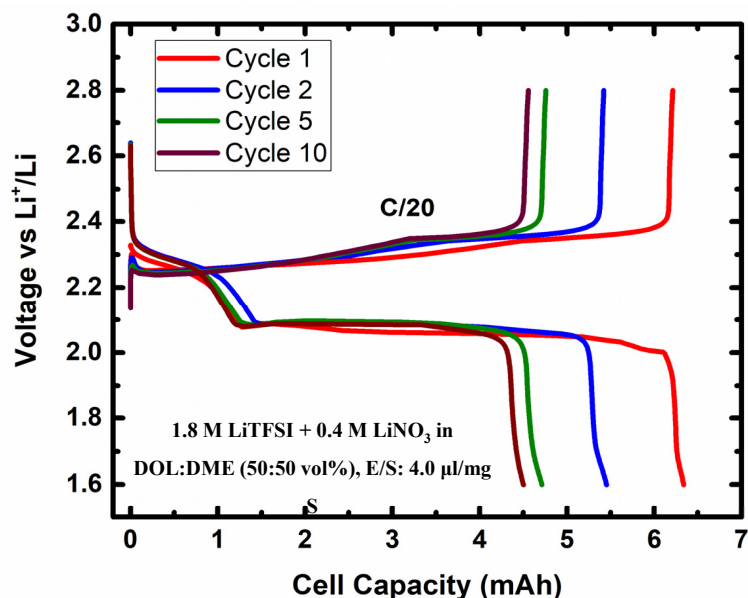
Technical Back-Up Slides

Any proposed future work is subject to change based on funding levels

Battery500 Testing Protocol for Li-S cells

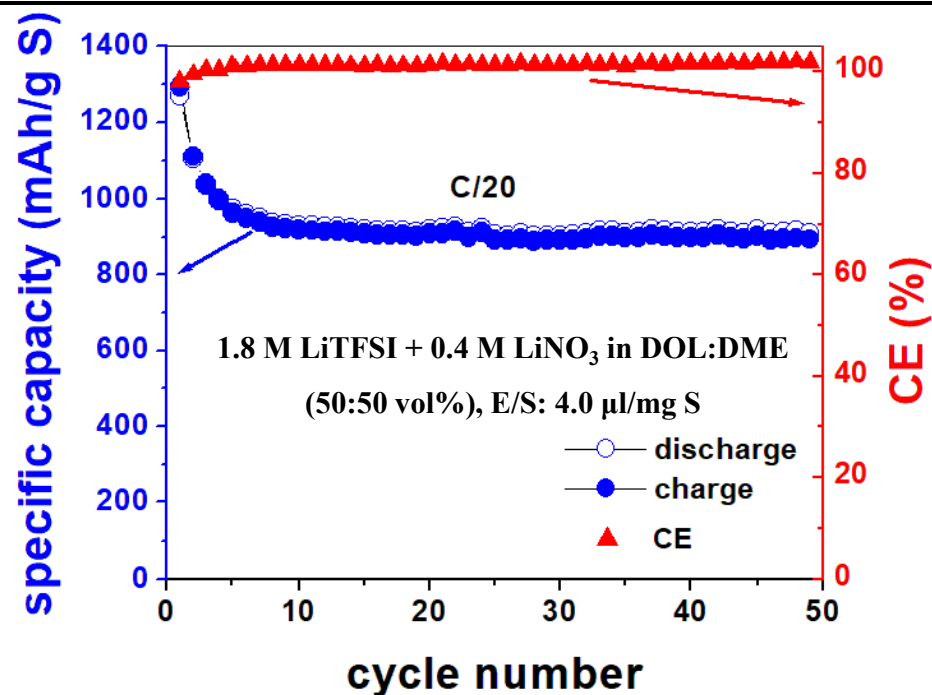
Coin Cell Testing Protocol for Li/S (for FY20 350 Wh/kg milestone)	
Minimum areal capacity	4.6 mAh/cm ² (~6mg/cm ² loading)
Coin cell assembly	CR2032 coin cell kits Sulfur cathode disk, 1 piece PE separator, 20 mm thick, 3/4" diameter, 1 piece
Baseline electrolyte: 1M LiTFSI-DOL/DME(1:1) +2% LiNO ₃	1. Electrolyte amount: Excessive amount of electrolyte for initial evaluation of sulfur cathode 2. Final testing: Lean electrolyte with electrolyte/capacity ratio = 3 g/Ah
Li metal foil: 1.56 cm diameter (1 piece)	1. Initial testing: 250 μm Li metal foil 2. Final testing: 50 μm Li (N/P = 2.2)
Testing protocols	1. Testing temperature: 25 °C 2. Voltage range: 1.8 -2.6 V 3. Resting time: 8 h 4. Formation process: 2 cycles at C/20 rate 5. Subsequent cycling: - Discharge at C/3 rate and charge at C/5 rate for 50 cycles. Discontinue testing when cell specific capacity falls below 70% - Discharge at C/1 rate and charge at C/3 rate for 100 cycles. Discontinue testing when cell specific capacity falls below 70%

Hybrid Active Materials Performance



Hybrid active material of a novel carbon-sulfur polymer

- ✓ S (wt.%) in cathode : 49.0 %
- ✓ Cathode Area: 1.2667 cm²
- ✓ Thickness: 108 μm (No calendaring)
- ✓ **S loading : 3.88 mg/ cm²**
- ✓ Anode: Li metal (250 μm)
- ✓ Total S : 4.9 mg

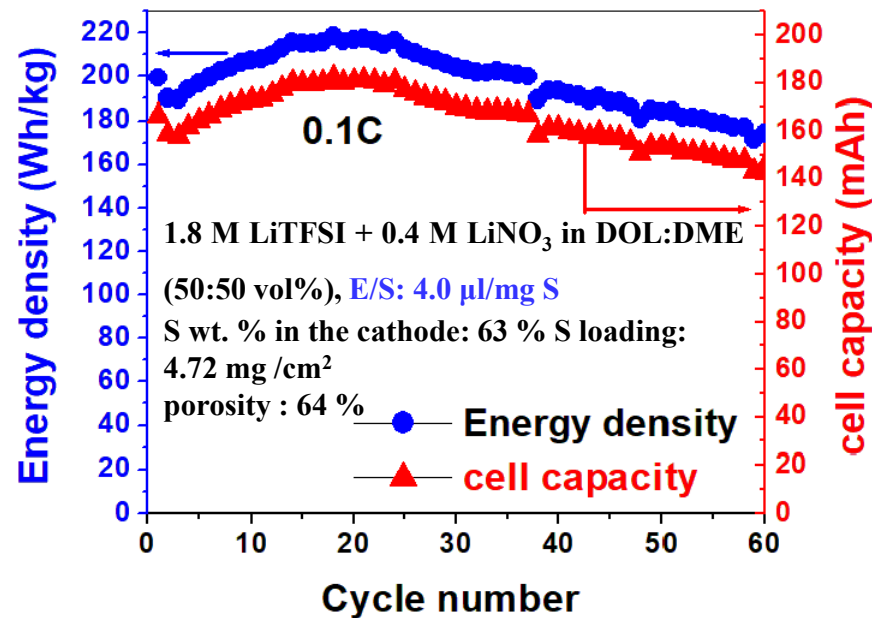
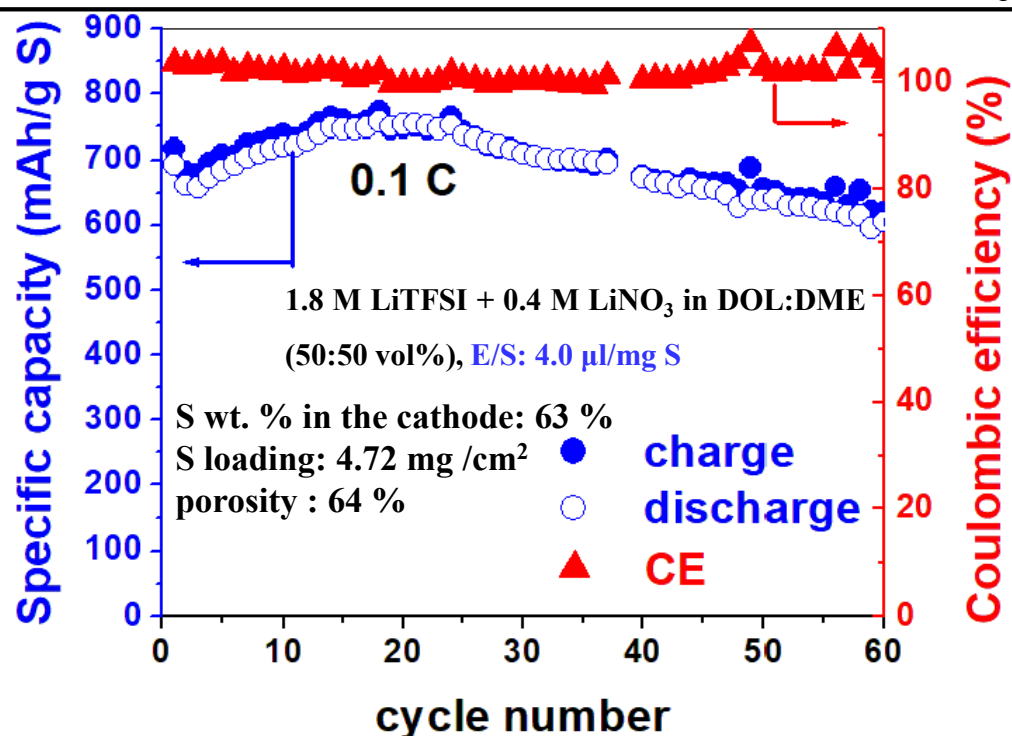


➤ **Areal Capacity: 3.57 mAh/cm² at C/20**

❖ **Strategies to improve the specific capacity**

- Explore use of functional electro-catalysts (ECs) for PS conversion, higher S utilization and PS trapping agents
- Microstructure control
- In-situ generation of ECs and LIC within and at S grain boundary

LIC-CFM-S: Li-S; Two layer Pouch Cell (~180 mAh)



- First five cycles at C/20 after first two formation cycles
- **Areal Capacity : ~4 mAh/cm² at 0.1C**
- **Successful generation of multilayer pouch cells matching single layer performance**

Strategies for further improvement

- reduce inactive mass
- **Improve reaction kinetics and sulfur utilization by microstructure engineering**
- Use of FCs and microstructure control
- Effective PS trapping for higher S loading for improved cycle life

Al mass (mg)	90
Cu mass (mg)	45
Electrolyte (mg)	970
Li metal (mg)	180
Separator (mg)	70
Cathode (mg)	384
Total mass (mg)	1738

Summary of computational study

➤ This study showed the following trends for Li-to-catalyst and S-to-catalyst binding:

✓ **Strength of binding Li to the materials**

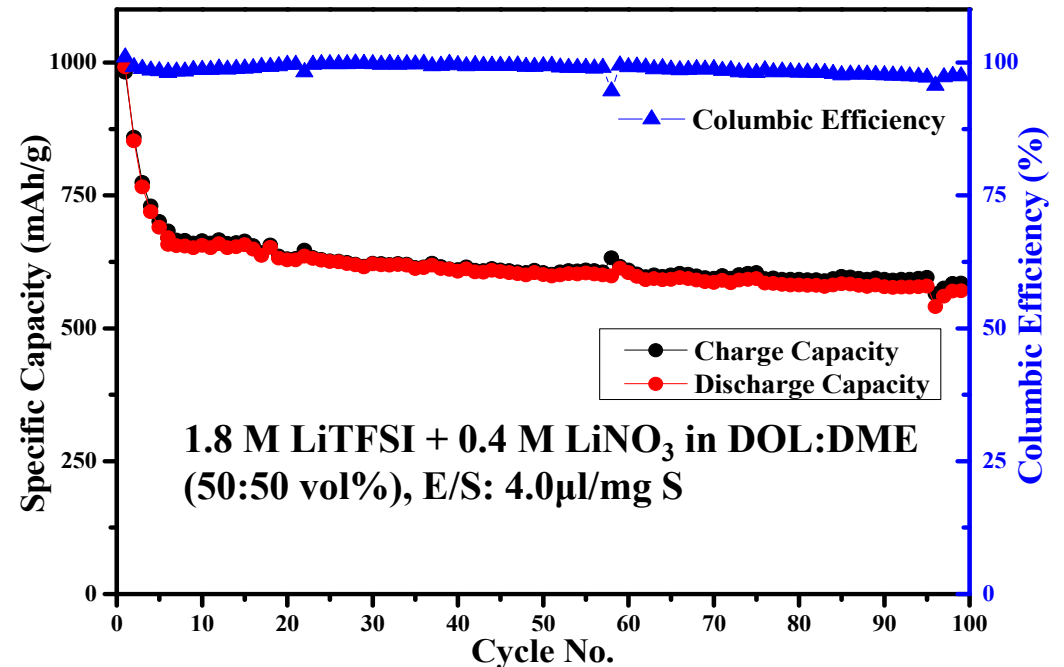
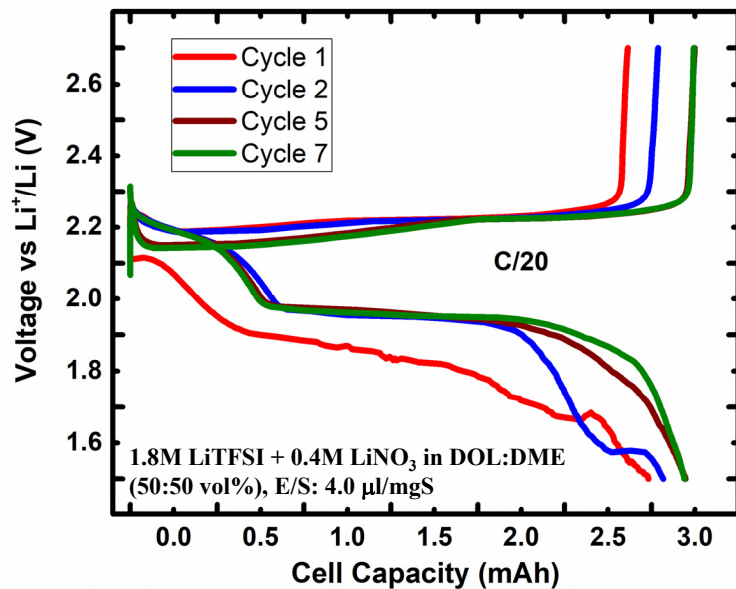
Borides > Oxides > Arsenides > Sulfides $\geq$ Nitrides $\approx$ Phosphides > Selenides > Tellurides
> Antimonides > Bismuthides >> Silicides

✓ **Strength of binding S to the materials**

Silicides $\approx$ Oxides > Borides > Nitrides $\approx$ Phosphides $\approx$ Sulfides $\approx$ Selenides $\geq$ Arsenides > Antimonides > Bismuthides $\approx$ Tellurides

- Thus, metal phosphides, nitrides and arsenides are identified as good functional electrocatalyst candidates pending complete experimental validation currently ongoing
- Opportunity for exploring multicomponent systems as FECs for reducing kinetic barriers and accelerating reversible conversion of PSs to Li_2S and back to Li and S

Bifunctional Catalyst Cathode Material (BCCM-S)



Bifunctional electrocatalyst cathode containing FEC and S-CFM

- ✓ Coin cell: 2032
- ✓ Slurry- 70:20:10 (wt.%)
- ✓ S (wt.%) in cathode : 63.0 %
- ✓ Cathode Area: 1.266 cm²
- ✓ Thickness: 107 μm (No calendaring)
- ✓ **S loading : 3.6 mg/ cm²**
- ✓ Anode: Li metal (250 μm)
- ✓ Total S : 4.53 mg

■ Good stability indicative of possible effective PS trapping

➤ **Areal Capacity: 2.38 mAh/cm² at C/20**

➤ **Lack of high capacity attainment**

➤ **Inefficient catalyst utilization**

➤ **Optimization (*in situ* process) to achieve microstructure control of FEC within S grain or at the S grain boundary**²⁴