Development of High Energy Density Li-Sulfur Cells

Donghai Wang

The Pennsylvania State University

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Project ID: ES125

OVERVIEW

Timeline

76% completed

Start: Sep. 30, 2011

End: Jan. 15, 2015

Barriers Addressed

- Power and energy density
- Cycle and calendar life
- Abuse tolerance

Budget

- Total project funding: $5,291K
  - DOE share: $4,045K
  - Contractor share: $1,246K
- FY 2013: $1,724K
- FY 2014: $1,510K

Partners

- EC Power (sub)
- Argonne National Lab (sub)

RELEVANCE – OBJECTIVES (1)

Develop a **full lithium-sulfur battery system** for high energy density, efficiency, and good cycle life, and safe operation.

Project scope	Performance targets
Design of full lithium-sulfur cell:	**1Ah cells**
Nanocomposite Sulfur Cathode – high energy/power, stable	**600 Wh/L (cell level)**
Advanced Lithium- or Silicon-Based Anode – high energy/power, stable	**Cycle life 500+ cycles**
Electrolyte – nonflammable, stable, low self-discharge	**Excellent safety characteristics**
Optimized cell design	

RELEVANCE – OBJECTIVES (2)

Objectives targeted this fiscal year:

- **Scale up material production** for cathode, anode, and electrolyte to meet pouch cell demands
- **Optimize** cathode, anode, and electrolyte for improved performance (power and energy density, cycle and calendar life), especially in regards to pouch cell use
- **1 Ah pouch cell** design, development, and optimization, to begin work on more realistic Li-S systems and address issues stemming from the properties of such systems (e.g., different optimized conditions for electrode porosity, anode N/P ratio and selection, etc)

MILESTONES (1)

1. **Advanced material development and characterization** (10/2011-09/2012)
   - Evaluate baseline cells
   - Develop and test 1st-generation cathode, anode, electrolyte
   - Thermal and failure mechanism studies
2. **Material scale up and 1Ah pouch cell development** (10/2012-09/2013)
   - Cathode and anode scale-up, continued improvement, and 1 Ah pouch cell design and testing
   - Continued investigation of electrolytes and failure mechanisms
3. **Improved large format prismatic cell design** (10/2013-09/2014)
   - Continued scale-up, failure mechanism analysis, and improved 1 Ah prismatic cell design and testing
   - Cell modeling and optimization

MILESTONES (2)

Phase II Milestones:

- Active material scale-up to 1 kg level (*Completed*)
- Demonstrate 1 Ah prismatic cell with > 400 Wh/L energy density, 80% capacity retention in 200 cycles at C/2 (*In Progress*)
- Nail Penetration Test: USABC EUCAR Level 3 (*In Progress*)
- Delivery of interim cells (*In Progress*)

APPROACH - OVERVIEW

Anode	Investigating/optimizing Li and Si composite anodes Exploring polymer electrolytes
Cathode	Investigating sulfur-carbon nanocomposites Pursuing methods for increased sulfur loading
Electrolyte	Determining new electrolytes and additives Assessing and developing novel solvents Optimizing electrolytes for high capacity and low self-discharge
Cell design	Optimizing cells design for chemistry requirements Conducting modeling and experimental testing

Approach - Cathode

- Generate new, well-structured carbon frameworks to improve volumetric energy density
- Optimize framework pore geometry and investigate new framework materials and structures to maximize sulfur loading and conductivity, and thus energy and power density
- Make intelligent use of dopants to prevent polysulfide dissolution by chemical adsorption and improve cycling and overall performance
- Optimize electrode coating methods to maximize sulfur loading

Approach - Anode

- Design composite lithium powder-based and silicon-based anodes to suppress dendrite growth, promote stable SEI formation, improve anode stability
- Develop an effective anode protection layer to prevent dendrite growth and lithium polysulfide deposition, and thus mitigate capacity fading and self-discharge and improve efficiency

Approach - Electrolyte

- Develop new electrolyte systems to improve safety, energy density, rate capability, and anode SEI formation, and to limit polysulfide dissolution, irreversible lithium sulfide deposition, and battery self-discharge
- Investigate the mechanisms of polysulfide dissolution and self-discharge to provide complementary insight

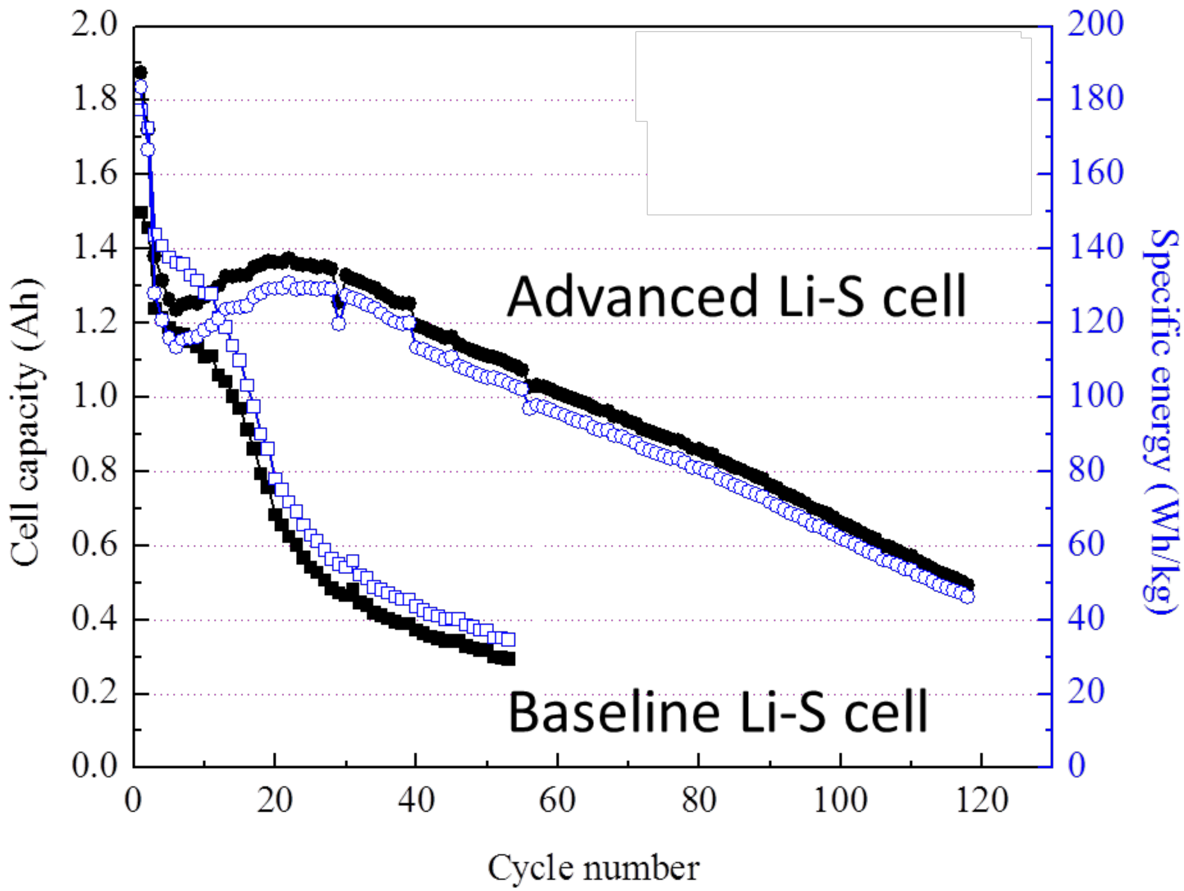
APPROACH – CELL DESIGN

- Optimize prismatic full cell parameters – electrode size, electrode matching, number of electrodes in stack, etc.
- Synergistically leverage cell modeling and experimental testing to iteratively improve design

Technical Accomplishments and Progress: Summary

- Scaled up cathode material production to 1 kg level
- Developed electrolytes capable of stable cycling ~1000 mAh/g suitable for pouch cell use
- Characterized and addressed Li-S cell self-discharge over short and long time-scales
- Developed optimized Li powder-based anodes
- Extensively tested and optimized 1 Ah Li-S prismatic cells with regards to various battery parameters

PREVIEW SLIDE – POUCH CELL PERFORMANCE

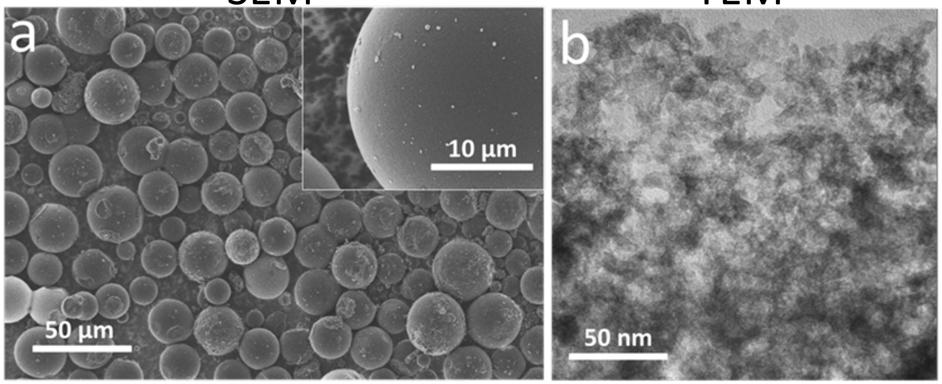


- Performance of 1 Ah pouch cells with novel cathode, anode, and electrolyte developed in this project is significantly better than that of pouch cells with baseline components

Technical Accomplishments and Progress: Cathode Development and Testing

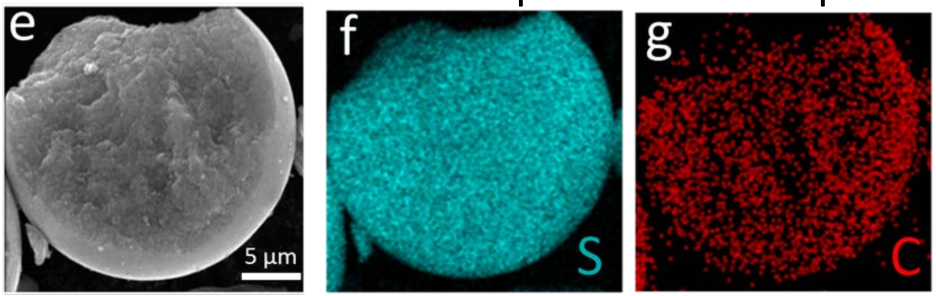
PSU-3 carbon framework:

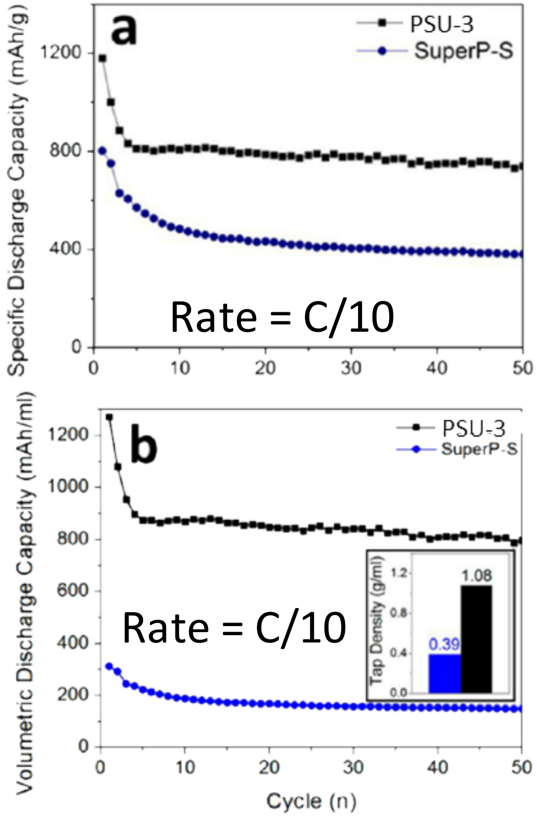
SEM TEM



PSU-3 cathode material:

SEM EDS map: S EDS map: C





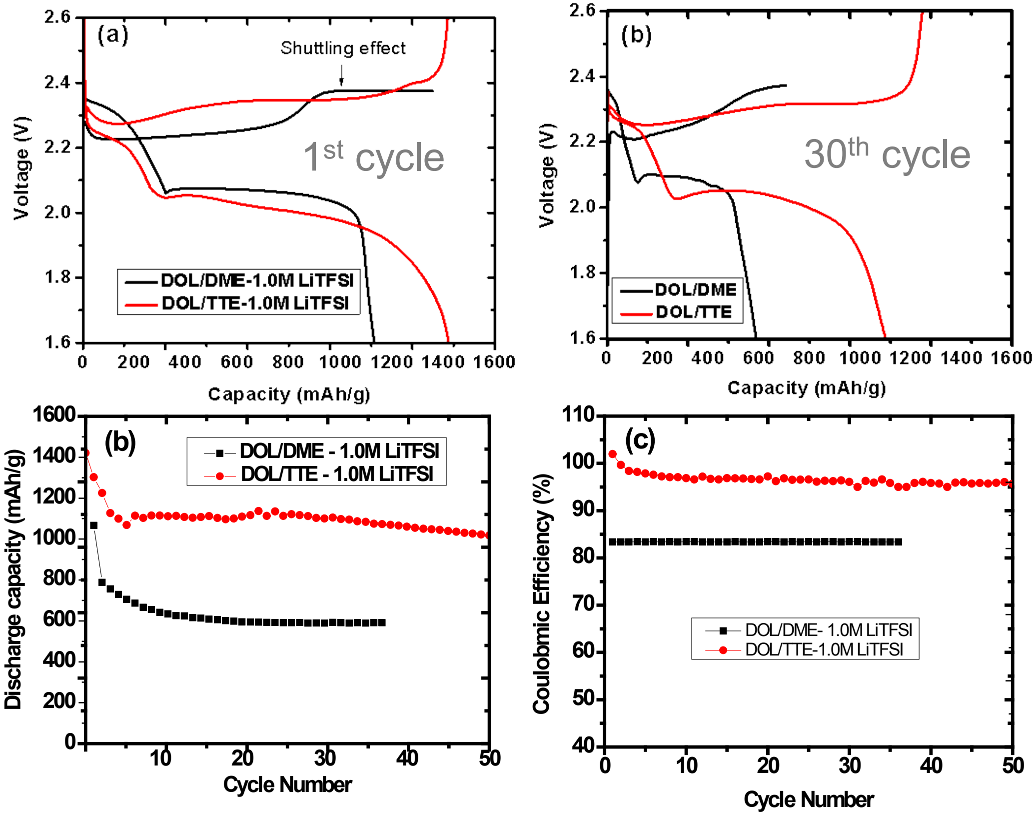
- In Phase I, developed PSU-3 spherical mesoporous carbon/sulfur composite cathode with 70 wt% sulfur loading
- Micron-sized spherical shape allows high volumetric energy density, high sulfur loading cathodes

Technical Accomplishments and Progress:

Cathode Production Scale-Up

- PSU-3 cathode production scaled to 1 kg level; photo shows 100 g cathode material for scale.
- Testing shows performance consistent with material made by small-batch synthesis

ELECTROLYTE FOR IMPROVED CAPACITY, STABILITY, SELF-DISCHARGE (1)



- ANL-E-4 electrolyte can dramatically improve capacity and stability of Li-S cells
- Cells to left tested with PSU-3 cathodes, Li foil anodes, C/10 rate

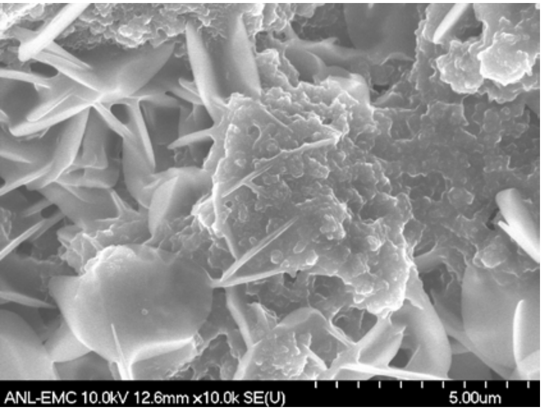
ANL-E-4 electrolyte: 1M LiTFSI in DOL/TTE

TTE: 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether

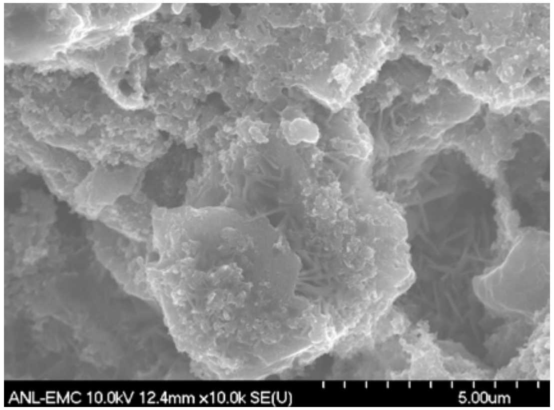
ELECTROLYTE FOR IMPROVED CAPACITY, STABILITY, SELF-DISCHARGE (2)

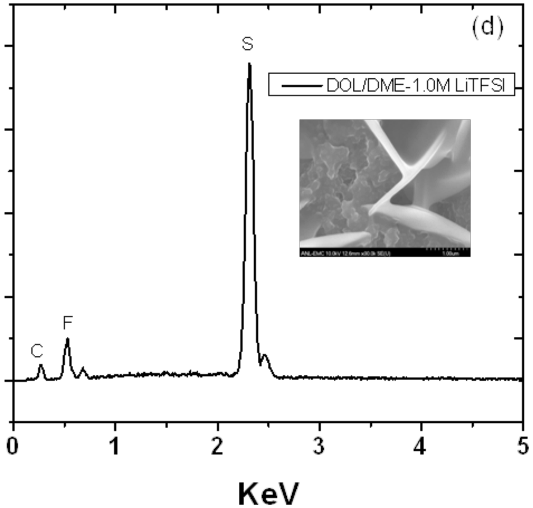
SEM and EDS of PSU-3 cathode after cycling with:

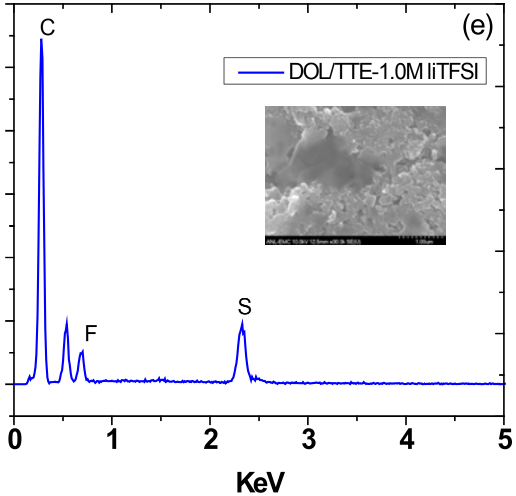
1M LiTFSI in DOL/DME



ANL-E-4 electrolyte

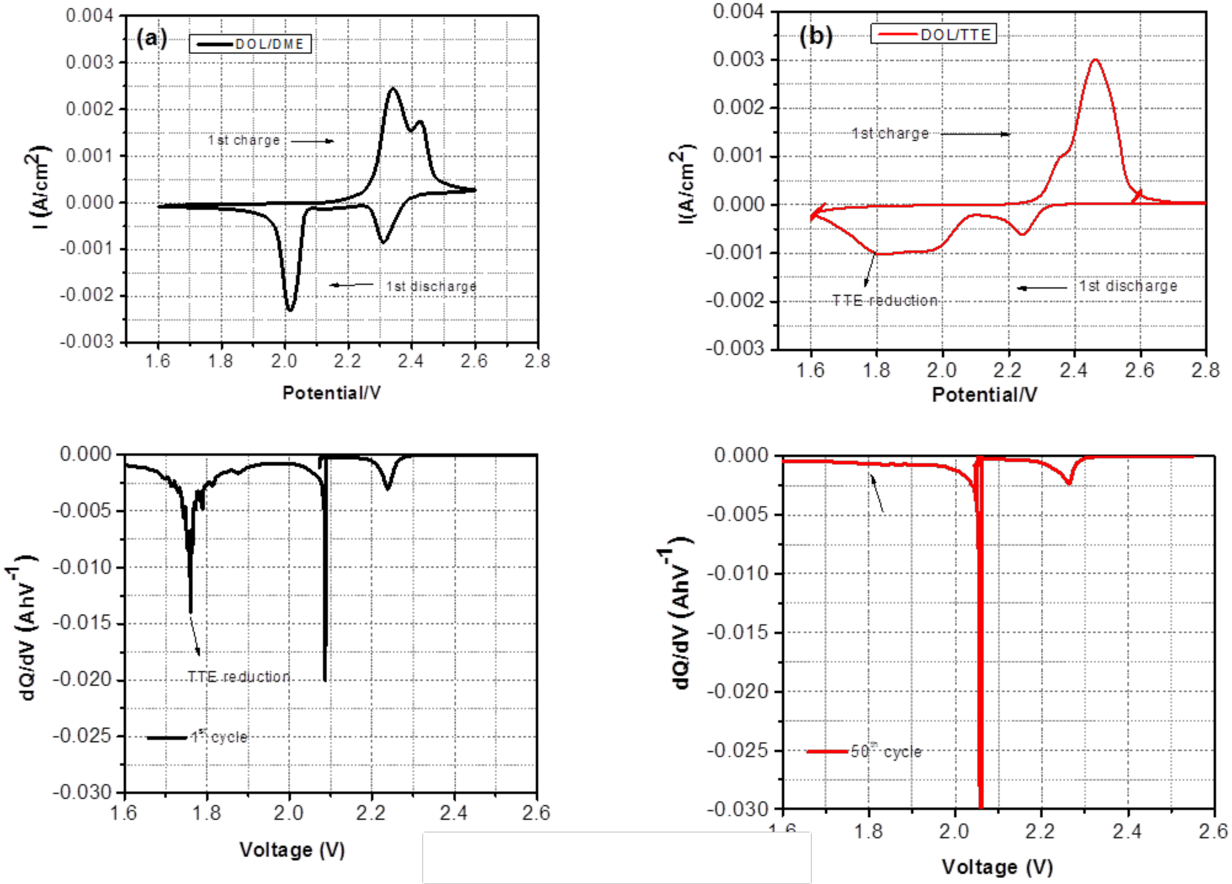






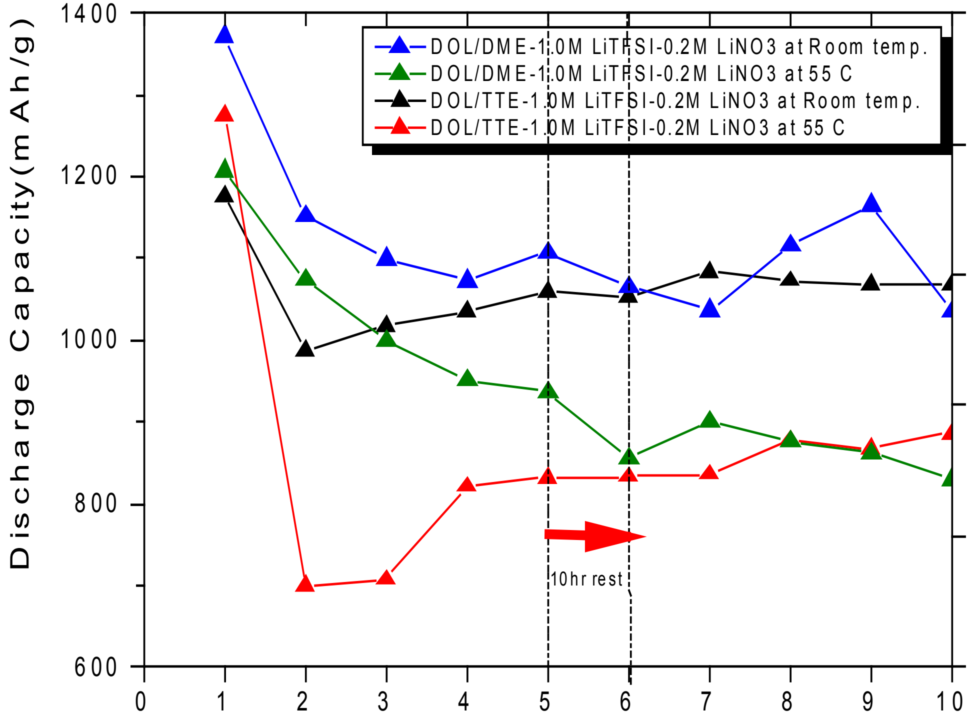
- Less Li_2S deposition on the cathode
- Better performance and decreased Li_2S deposition Likely enabled by formation of protective films on the cathode
- Cells to left tested with PSU-3 cathodes, Li foil anodes, C/10 rate

ELECTROLYTE FOR IMPROVED CAPACITY, STABILITY, SELF-DISCHARGE (3)



- CV and dQ/dV curves of cells with PSU-3 cathodes and ANL-E-4 electrolyte indicate reduction of TTE on the cathode to form a protective film; nothing similar seen with baseline electrolyte.

ELECTROLYTE FOR IMPROVED CAPACITY, STABILITY, SELF-DISCHARGE (4)

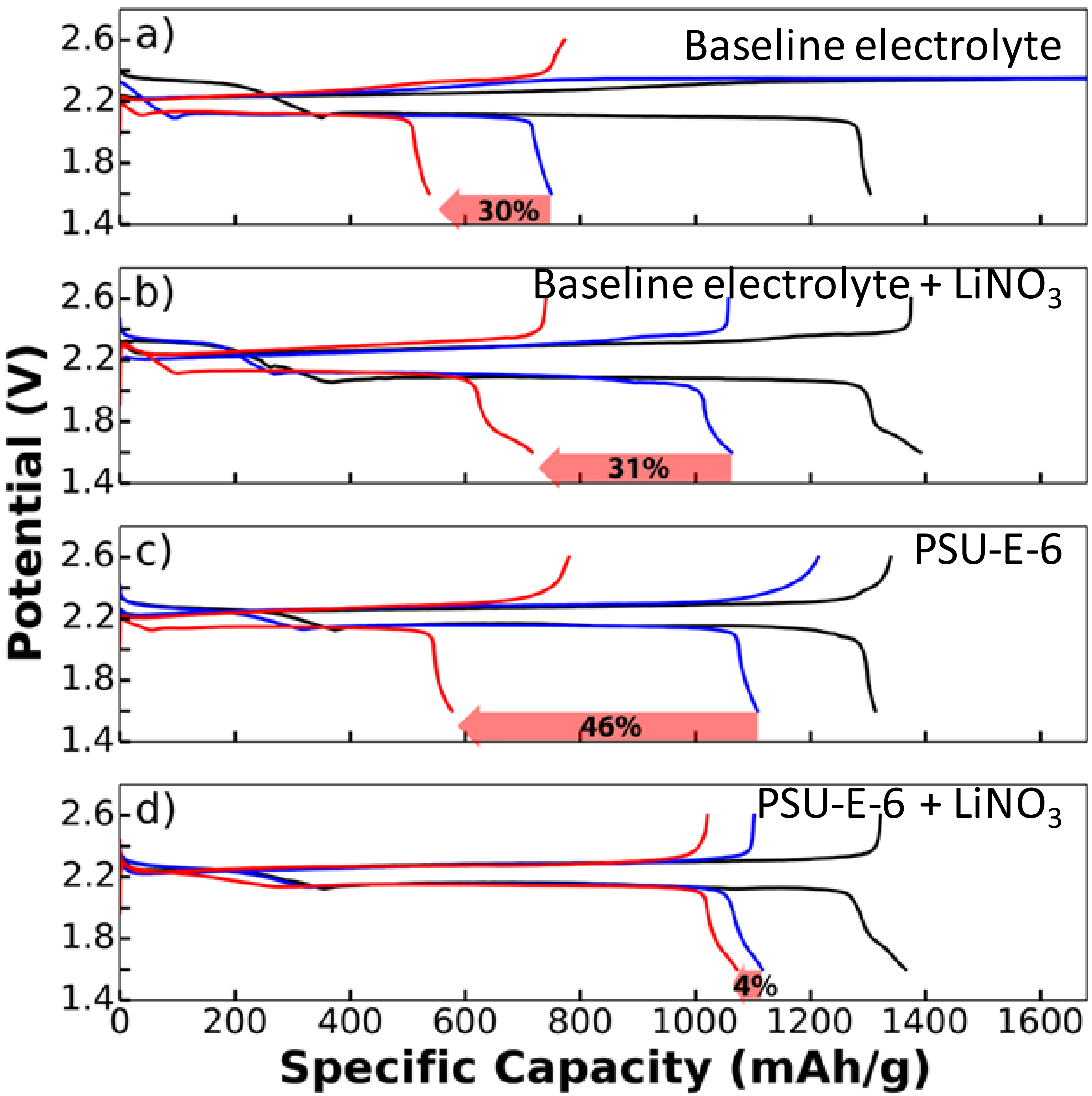


- Cells with ANL-E-4 electrolyte plus 0.2M $LiNO_3$ additive show negligible self-discharge after 10 h rest

	Capacity change after 10h rest	
Temperature	**Baseline**	**ANL-E-4**
Room temp.	3.8% decrease	0.7% decrease
55°C	8.6% decrease	0% decrease

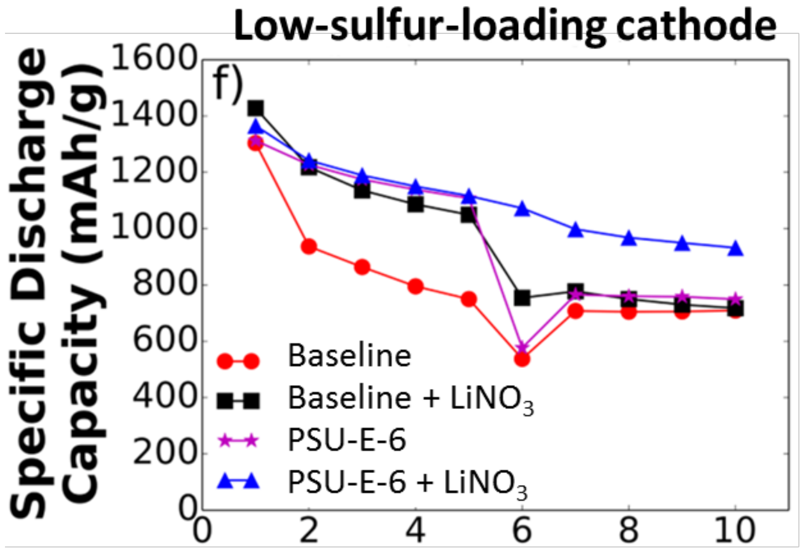
Technical Accomplishments and Progress:

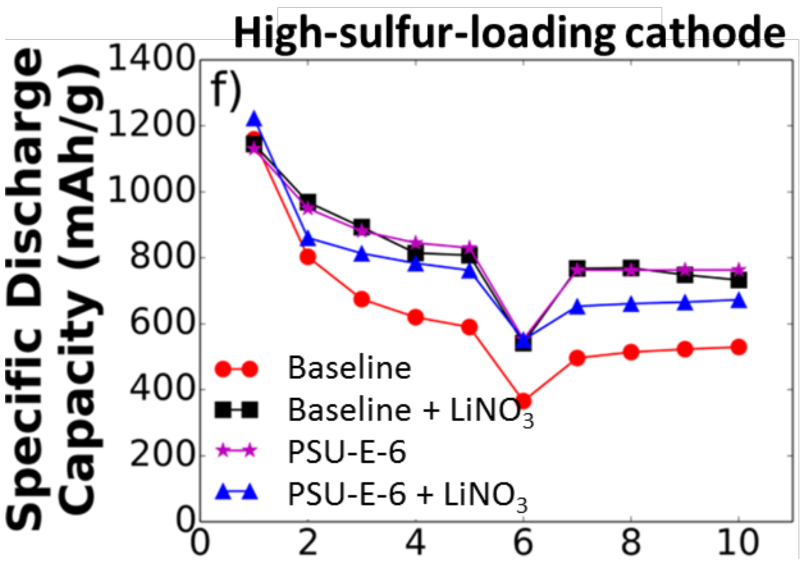
Electrolyte for Improved Capacity, Stability, Self-Discharge (5)



- Cells with PSU-E-6 electrolyte with $LiNO_3$ additive show decreased self-discharge after 2 week rest at 45°C
- $LiNO_3$ alone does not prevent self-discharge over this longer time scale
- Cells to left have low-loading PSU-3 cathodes, Li foil anodes

ELECTROLYTE FOR IMPROVED CAPACITY, STABILITY, SELF-DISCHARGE (6)



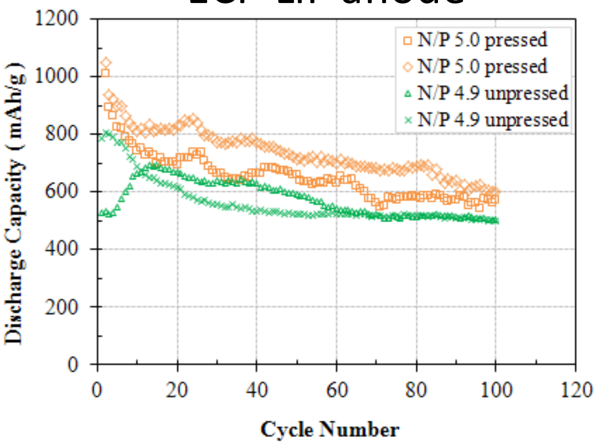


- Compared self-discharge behavior in low- and high-sulfur-loading cathodes
- Based on differences in capacity recovery, key mechanism in low-loading is believed to be active material loss, while key mechanism in high-loading is believed to be the shuttle effect

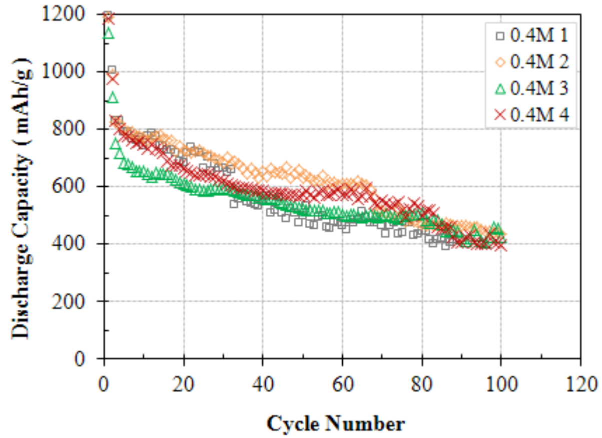
ADVANCED LI POWDER ANODE DESIGN

Cycling of full coin cells with PSU-3 cathodes, baseline electrolyte, and:

ECP-LiP anode

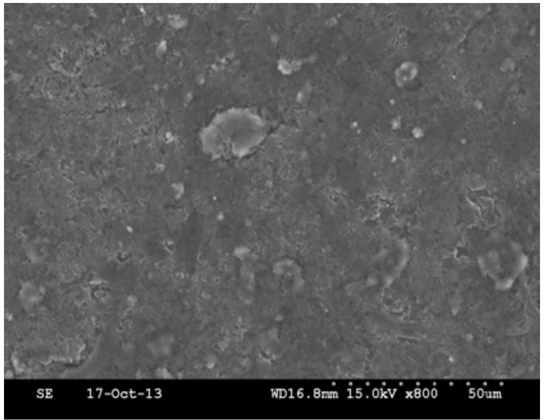


Li foil anode

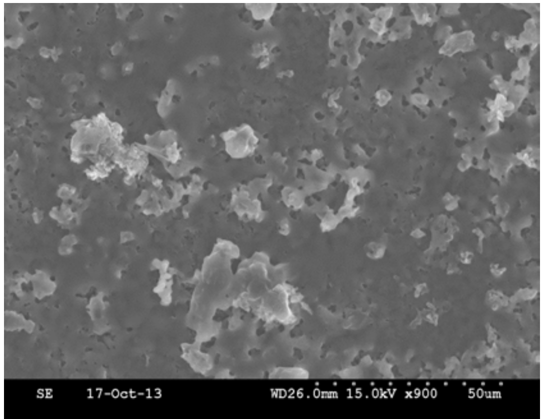


SEM of anodes post-cycling:

ECP-LiP anode

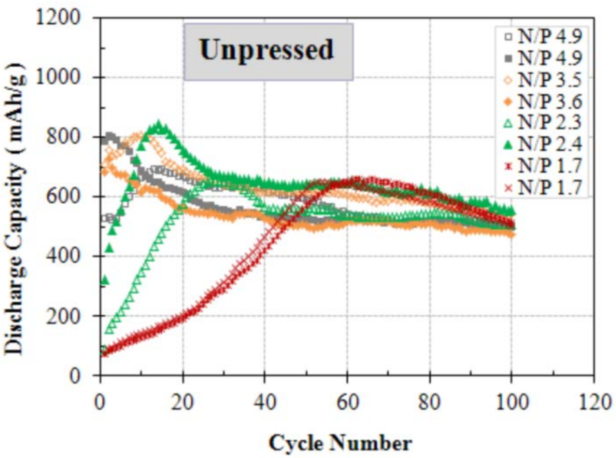


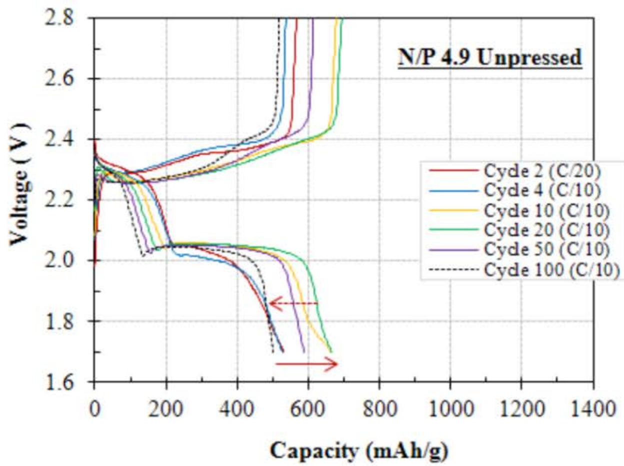
Li foil anode

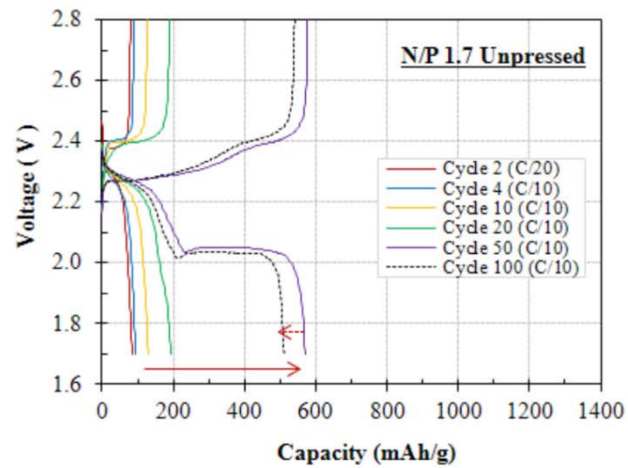


- ECP-LiP lithium powder based anodes show superior capacity retention with cycling compared to Li foil anodes
- ECP-LiP anode morphology after cycling found to be smoother, less dendritic than Li foil anode morphology

ANODE N/P RATIO STUDY

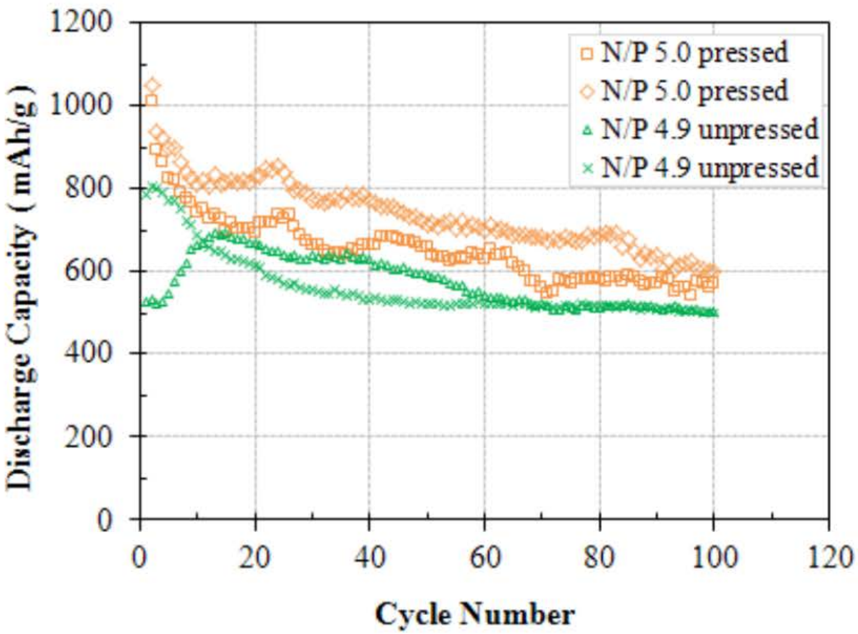


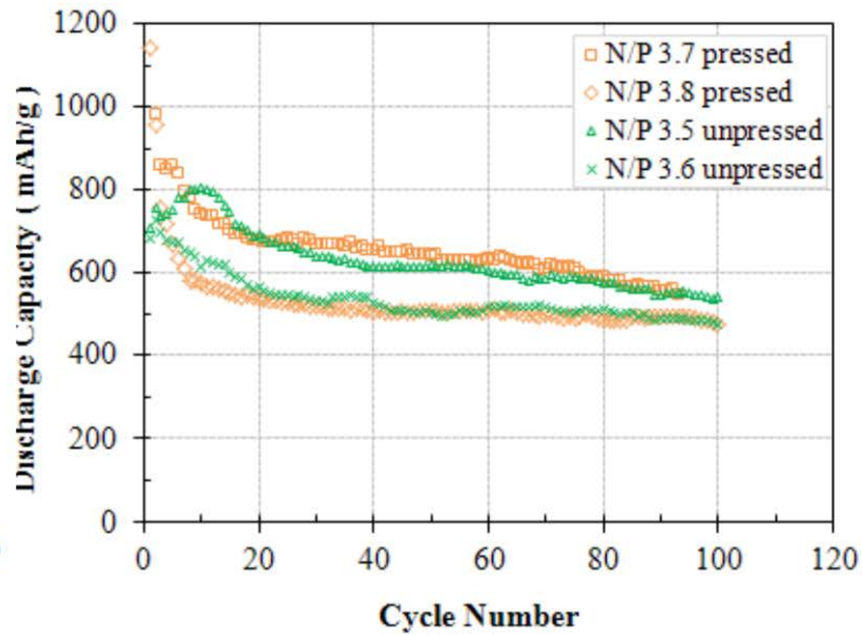




- Lower N/P ratio leads to lower initial capacity, with the capacity gradually increasing over a number of cycles
- Voltage profiles show steadily increasing 2.1 V plateau, likely due to initial trapping of soluble polysulfides in the porous unpressed ECP-LiP anodes

ANODE PRESSING STUDY





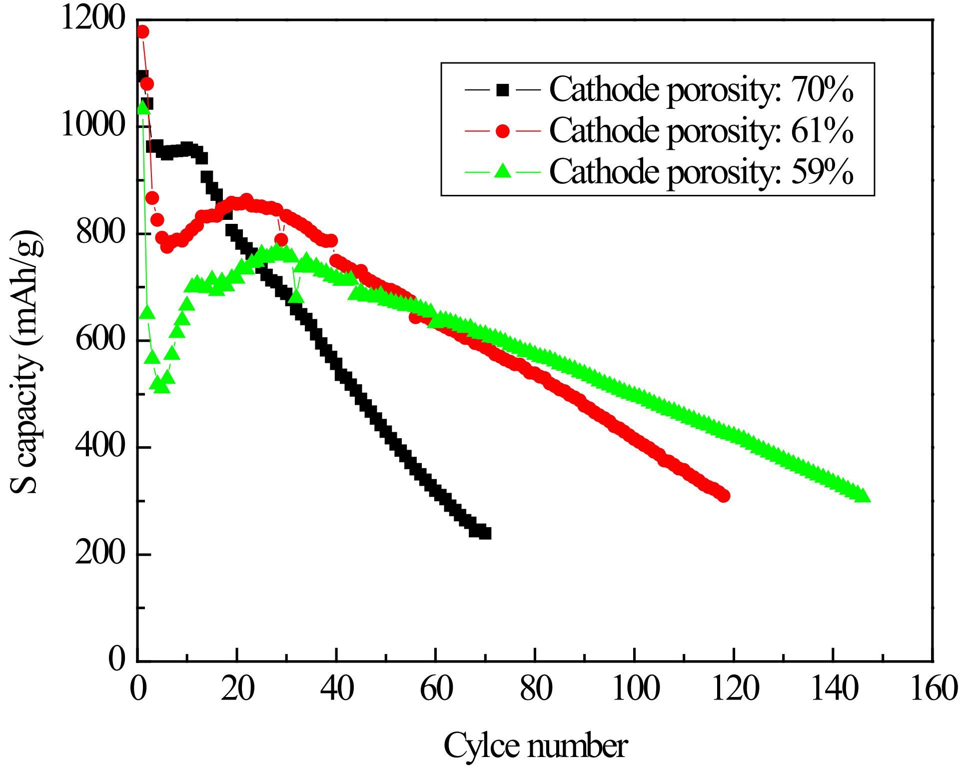
- Pressed electrodes at different N/P ratios found to have higher initial capacity than unpressed electrodes, and similar capacity after 100 cycles – overall better performance with pressed anodes.

FULL CELL DEVELOPMENT (1)

- Designed and fabricated 1 Ah pouch cells for performance testing and delivery
- Cells use PSU-3 cathodes, ECP-LiP anodes, ANL-E-4 electrolyte

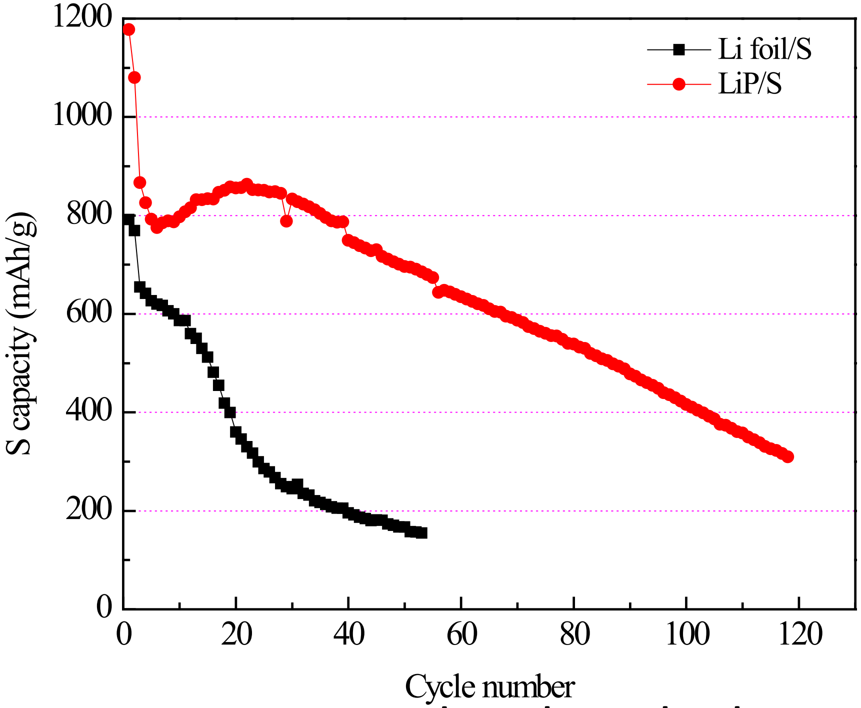
Technical Accomplishments and Progress:

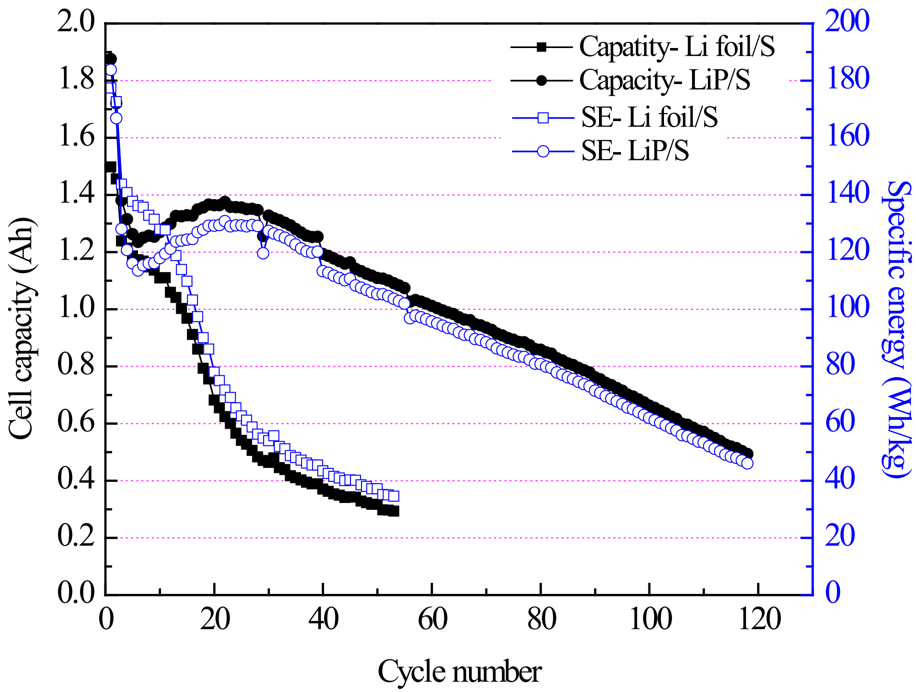
Full Cell Development (2) – Cathode Porosity Optimization



- Found tradeoff between cycle life and initial capacity in pouch cells based on cathode porosity
- Cells above are 1 Ah pouch cells with PSU-3 cathode, ECP-LiP anode, ANL-E-4 electrolyte

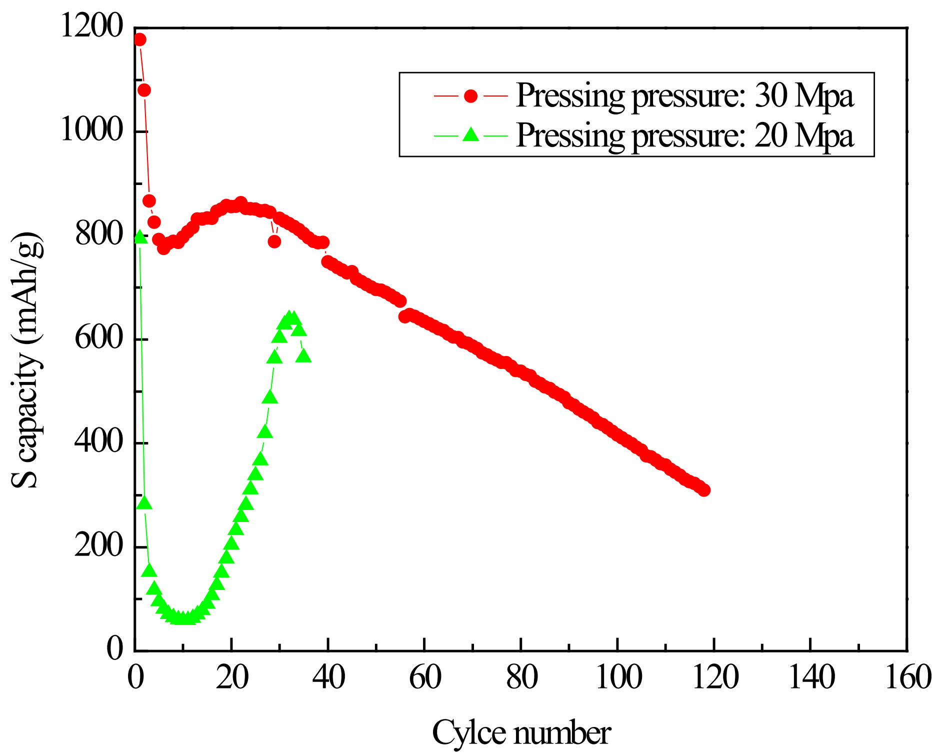
TECHNICAL ACCOMPLISHMENTS AND PROGRESS: FULL CELL DEVELOPMENT (3) – ANODE SELECTION





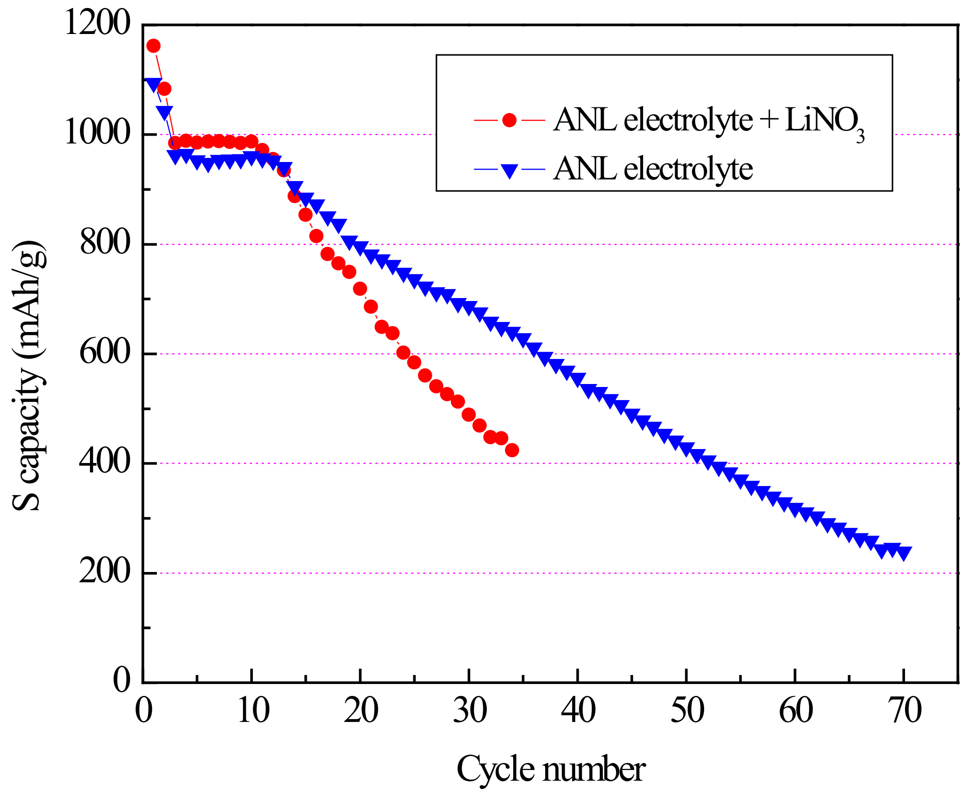
- ECP-LiP anodes show higher capacity, stability in pouch cells (cells above are 1 Ah pouch cells with PSU-3 cathode and ANL-E-4 electrolyte)
- Severe corrosion of Li foil observed post-cycling; less corrosion with ECP-LiP

FULL CELL DEVELOPMENT (4) – ANODE PRESSING OPTIMIZATION



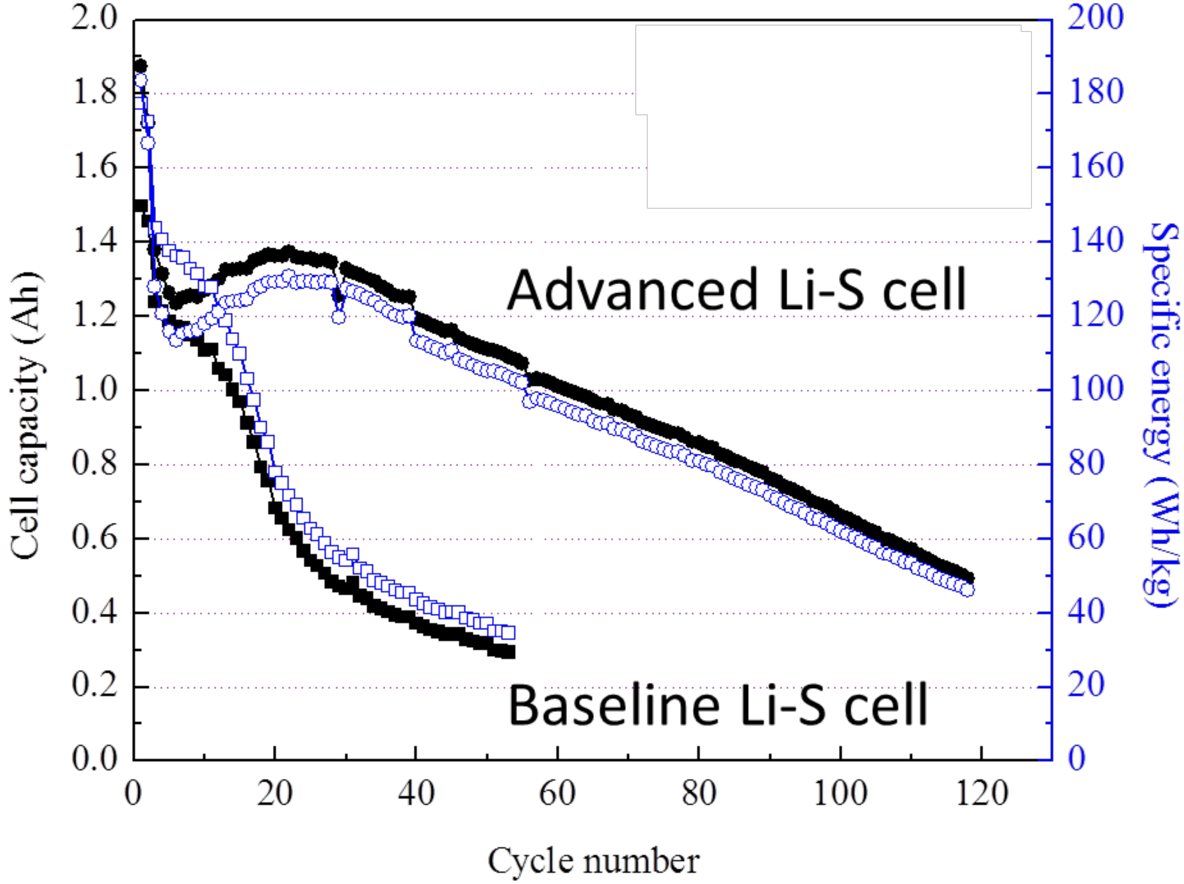
- Pouch cell performance found to improve when higher pressure was applied to the anode during electrode fabrication
- Cells above are 1 Ah pouch cells with PSU-3 cathodes and ANL-E-4 electrolyte

FULL CELL DEVELOPMENT (5) – ELECTROLYTE ADDITIVE OPTIMIZATION



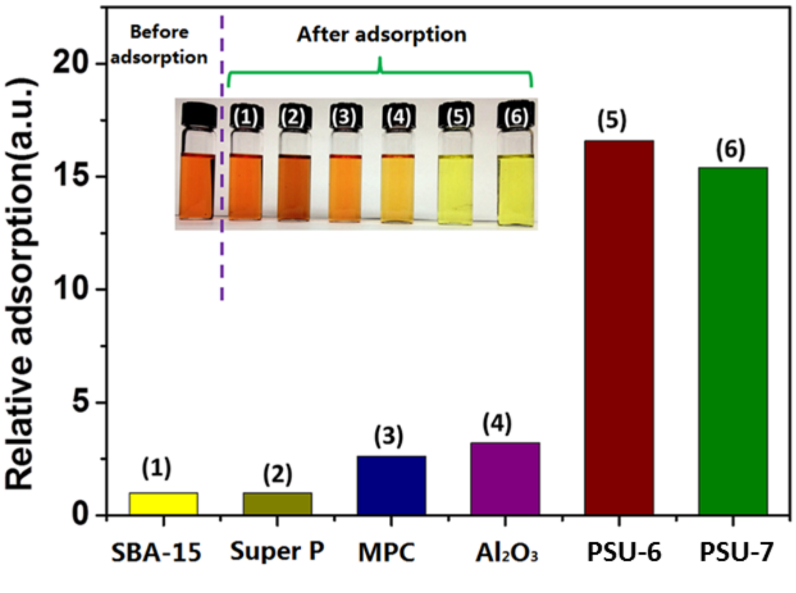
- Full cell performance found to be better without $LiNO_3$ electrolyte additive
- Cells above are 1 Ah pouch cells with PSU-3 cathodes and ANL-E-4 electrolyte

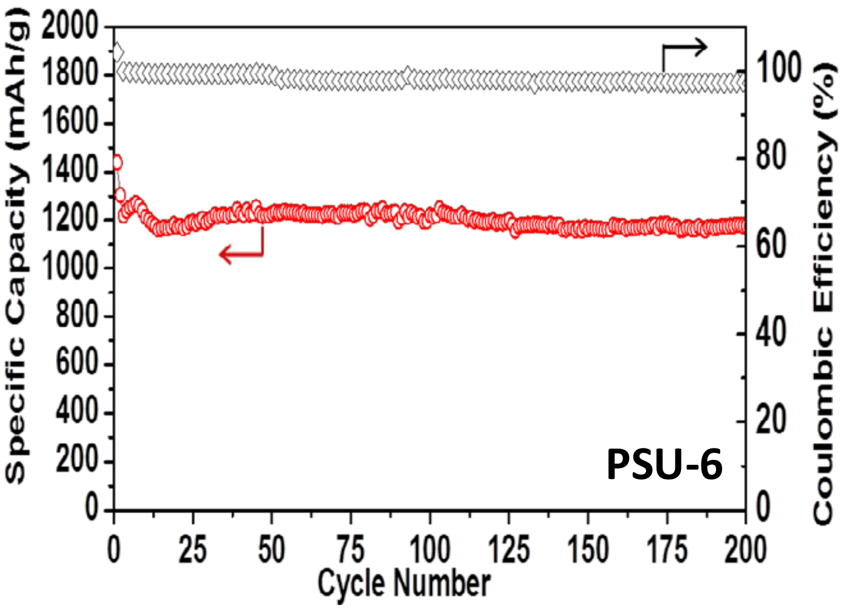
Technical Accomplishments and Progress: Full Cell Development (6) – Full Cell Performance



- Performance of 1 Ah pouch cells with PSU-3 cathodes, ECP-LiP anodes, and ANL-E-4 electrolyte significantly better than that of pouch cells with baseline components

ADVANCED CATHODE MATERIAL DEVELOPMENT





- New PSU-6 and PSU-7 cathodes have optimized structure and the ability to effectively chemisorb polysulfides, giving it excellent cyling stability and high capacity
- Cell above made with Li foil anode, baseline electrolyte plus $LiNO_3$

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

- **"The reviewer stated that although progress has been made in self-discharge reduction, greater emphasis and focus on this would be desirable as the current capability in the best case seems to be show-stopping"**

  Further progress has been made on self-discharge reduction in Li-S cells. In particular, novel electrolytes (ANL-E-4 and PSU-E-6) have been shown to decrease self-discharge over various time-scales. Further work in characterizing self-discharge performance improvement with these electrolytes, in designing new electrolytes with still-lower self-discharge, and designing and scaling up new cathode materials for improved polysulfide trapping is also ongoing.

- **"The cycling life, however, is still not where it needs to be."**

  We agree with the reviewer that cycling life continues to demand improvement; in particular, achieving stable cycling in prismatic full cells has been shown to be even more challenging that in coin cell tests. We are aiming to further address this issue with further design of novel electrolyte which help prevent polysulfide side-reaction and irreversible Li_2S deposition, designing and scaling up new cathode materials for improved polysulfide trapping, and revisiting Si-based anodes.

- **"hitting the energy density goal of 600 Wh/L will require increasing the stable capacity and cathode loading, which the team needs to work towards by optimizing the electrolyte, cathode composition, and coating techniques."**

  As noted above, we working on several methods that will, besides improving stability and self-discharge, also improve cell capacity. In addition, we are further investigating ways to optimize electrode and prismatic cell fabrication techniques for increased energy density.

Collaboration

- Working with Argonne National Lab (subcontract, in VT program) on concurrent electrolyte development, testing, and self-discharge mitigation.
- Working with EC Power (subcontract, in VT program) on lithium powder-based anode development, full cell development, and prismatic cell design, testing, optimization, and failure analysis.
- Independent testing of prismatic cells is being conducted by Idaho National Lab.

Remaining Challenges and Barriers

- Key challenges are improving prismatic cycle life and energy density to meet project goals
- Addressing these challenges will require optimizing full cell parameters, as well as electrode materials and electrolyte composition

PROPOSED FUTURE WORK

- Continue development and scale-up of improved cathode and anode materials (e.g., PSU-7 cathode material) and electrodes to enhance capacity and stability, particularly in the context of prismatic full cell performance
- Continue development of electrolyte systems to help prevent polysulfide shuttling and irreversible lithium sulfide deposition, particularly in the context of prismatic full cell performance
- Perform extensive safety tests (nail penetration, oven testing, etc)
- Optimize full cell design (e.g., N/P ratio, electrolyte choice, etc) to maximize energy density and stability
- Investigate the source of differences in prismatic vs. coin cell performance

SUMMARY

- Scaled up cathode material production (1 kg level)
- Developed electrolytes which can produce good stability and capacity, plus low self-discharge, in coin cell tests
- Developed improved Li powder-based anodes
- Developed and fabricated 1 Ah pouch cells with PSU-3 cathodes, ECP-LiP anodes, and ANL-E-4 electrolyte
- Tested the dependence of pouch cell performance on several critical parameters (cathode porosity, anode pressing, anode and electrolyte choice)