Multifunctional, Self-Healing Polyelectrolyte Gels for Long-Cycle-Life, High-Capacity Sulfur Cathodes in Li-S Batteries

Alex K.-Y. Jen and Jihui Yang
Department of Materials Science and Engineering
University of Washington

2019 DOE Vehicle Technologies Office Review Meeting
June 12th, 2019

Project ID
bat320

Overview

Timeline

- Project start date – Oct. 2016
- Project end date – Dec. 2019
- Percent complete – 83%

Budget

- Total project funding
  - DOE share: $1.25 M
  - Contractor share: $138,888
- Funding received in FY 2018

  $416,667
- Funding received for FY 2019

  $416,667

Barriers

- **Cost**: Reduce $/kWh of EV batteries using high-energy-density, low-cost Li-S chemistry
- **Performance**: Double the energy density of state-of-the-art Li-ion batteries using Li metal anode
- **Life**: Mitigate capacity loss mechanisms in Li-S cells for improved cycle life

Partners

- Project Lead: University of Washington
- Interactions/collaborations: Pacific Northwest National Lab

Relevance

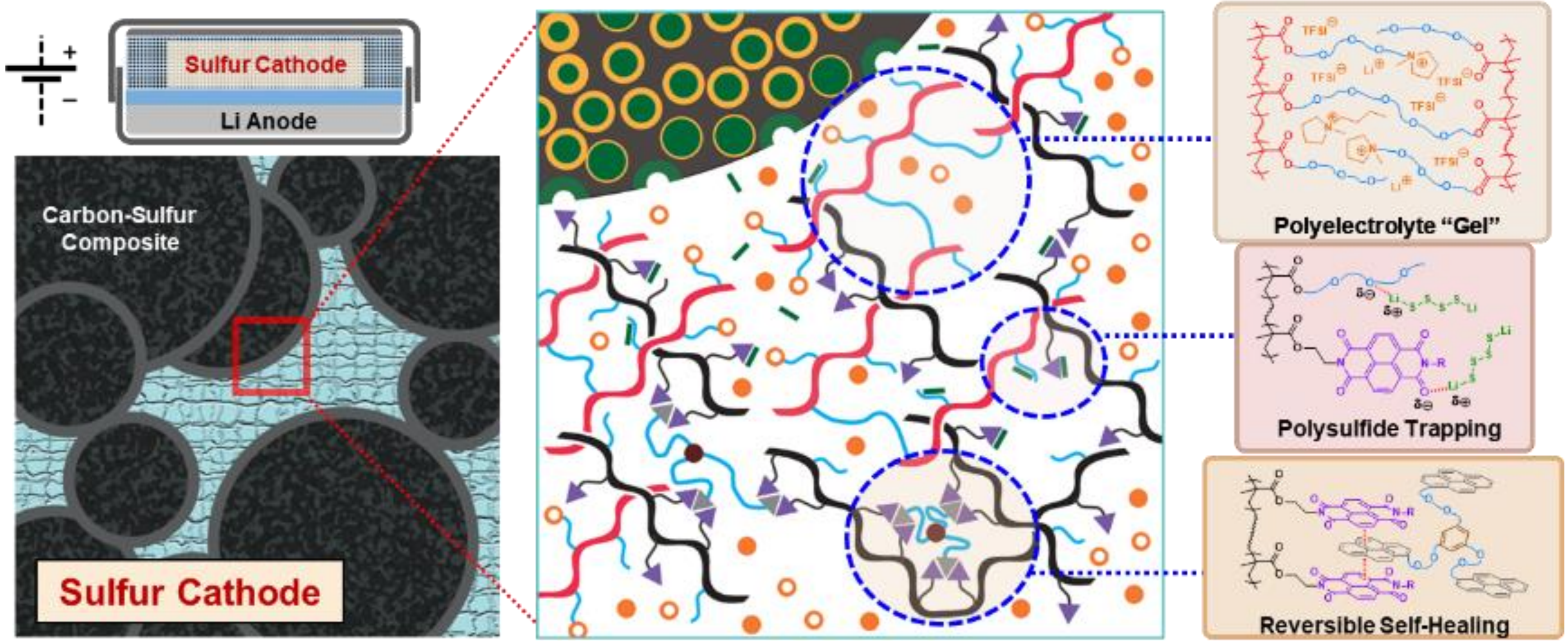
- **Overall Objective:** Develop high-performance Li-S cells, based on self-healing and polysulfide-trapping polyelectrolyte gels containing solvate ionic liquid (SIL). The Li-S cell design will be capable of achieving gravimetric energy densities in excess of commercial Li-ion cells (>250 Wh/kg).
- **Objectives This Period**
  - Develop *in-situ* fabrication methods for sulfur/carbon/ionogel cathodes and composite ionogel separators
  - Demonstrate quasi-solid-state (“all-gel” or QSS) Li-S cells and evaluate their behavior
  - Investigate the influence of self-healing, polysulfide-trapping materials on S cathode performance
- **Impact**
  - Li-S batteries have the potential to achieve the DOE goal of $100/kWh for battery pack usable energy

Milestones

Date	Milestone or Go/No-Go Decision	Status
Sep. 2019	Milestone Optimized Cell Performance Update	On track
Dec. 2019	Milestone/Deliverable Optimized Cell Performance Update / Deliver 10mAh Cells for DOE Testing	On track

Approach/Strategy

Multifunctional Polyelectrolyte Gels for Long-Cycle-Life, High-Capacity Li-S Batteries



Approach/Strategy

- **Solvate Ionic Liquid + Polyelectrolyte Gel**
  - Ionic liquid electrolyte suppresses Li_2S_x dissolution and inhibits Li dendrite growth while providing conductivity similar to organic electrolytes
  - Solvate ionogel (SIG) made of cross-linked polyelectrolytes with solvate ionic liquid creates mechanical toughness without sacrificing ionic conductivity
- **Trapping of Polysulfide (Li_2S_x) Species**
  - Containment of Li_2S_x species *via* physical and chemical interaction on cathode surfaces eliminates redox shuttle effect, improving capacity retention/efficiency
  - Incorporation of redox-active naphthalene diimide (NDI) group anchors Li_2S_x species and improves sulfur utilization by redox mediator effect
- **Self-Healing through Reversible Noncovalent Interactions**
  - Interaction of electron-rich pyrene (Py) group and electron-poor NDI group provides tunable/reversible self-healing, suppressing capacity loss due to mechanical degradation of cathode
- **Carbon/Sulfur Composite**
  - Mesoporous carbon provides conductivity and physical containment of Li_2S_x
  - Platform adds targeted chemical functionality for performance enhancement

Technical Accomplishments and Progress

Highly-Conductive Solvate Ionogels (SIGs)

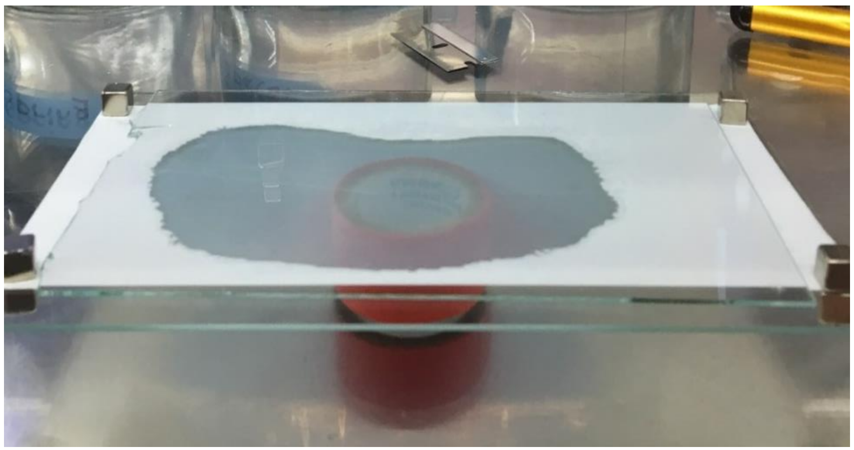
Formula	κ @ 23°C (mS/cm)	t_{Li+} (EVB Method)
Li(G4)TFSI	1.08	0.13
"SIG 1"	0.73	0.21
"SIG 2"	1.05	0.28
"SIG 3"	0.92	0.24
"SIG 4"	1.07	0.16
"DSIG 5"	**2.15**	**0.57**

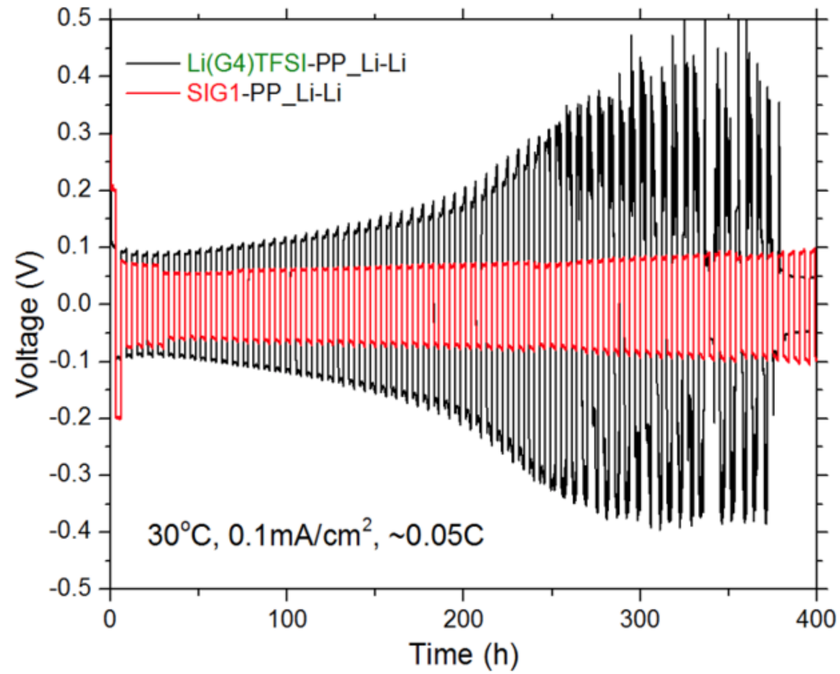
Note: This data has been previously presented and is included for context

- One-pot thermal cure of precursors can produce thin ionogel (SIG) films with remarkably high Li^+ ion conductivity and transference number
- Simple design/fabrication allows SIG incorporation into separator and cathode with minimal processing

Technical Accomplishments and Progress (cont.)

SIG/Celgard Composite Separator

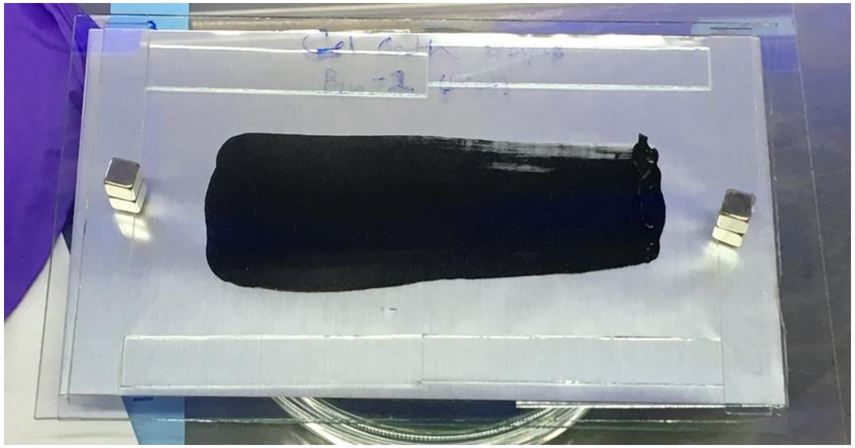




- Wetting/curing SIG resin into porous polypropylene (Celgard 2500) creates *composite ionogel separator*
- Gel composite outperforms solvate ionic liquid in Li|Li symmetric cells

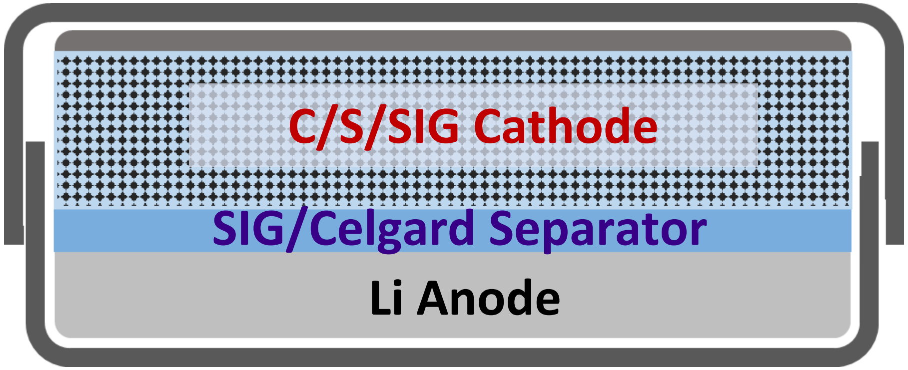
Technical Accomplishments and Progress (cont.)

<u>Quasi-Solid-State ("All-Gel") Device Design</u>



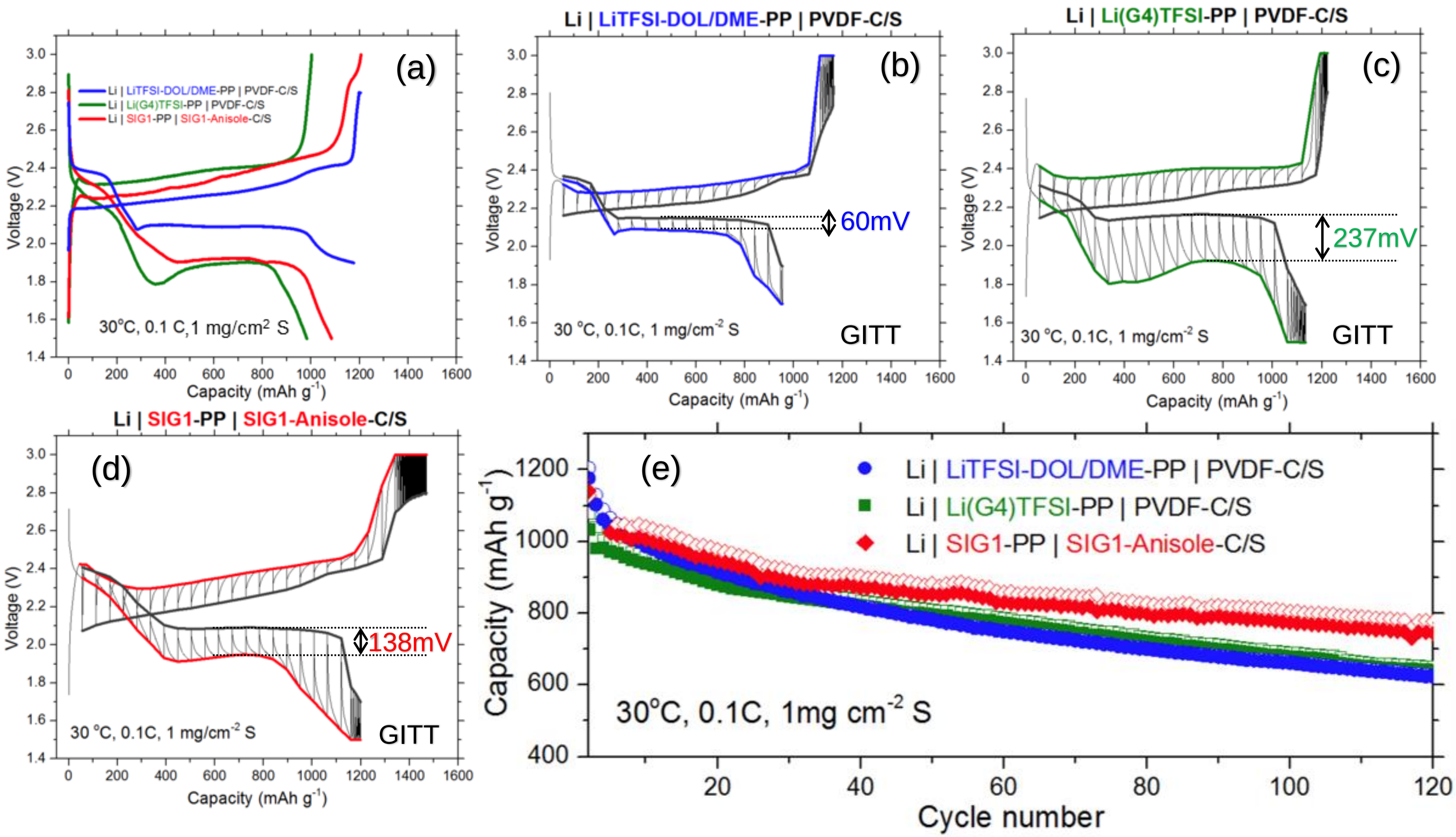
- C/S slurry made with SIG resin instead of PVDF binder and NMP solvent
- Slurry is cast and cured in place to produce an *in-situ* x-linked *C/S/SIG cathode*

- Gel cathode and separator laminated together with Li metal to produce a *<u>quasi-solid-state Li-S cell</u>*



Technical Accomplishments and Progress (cont.)

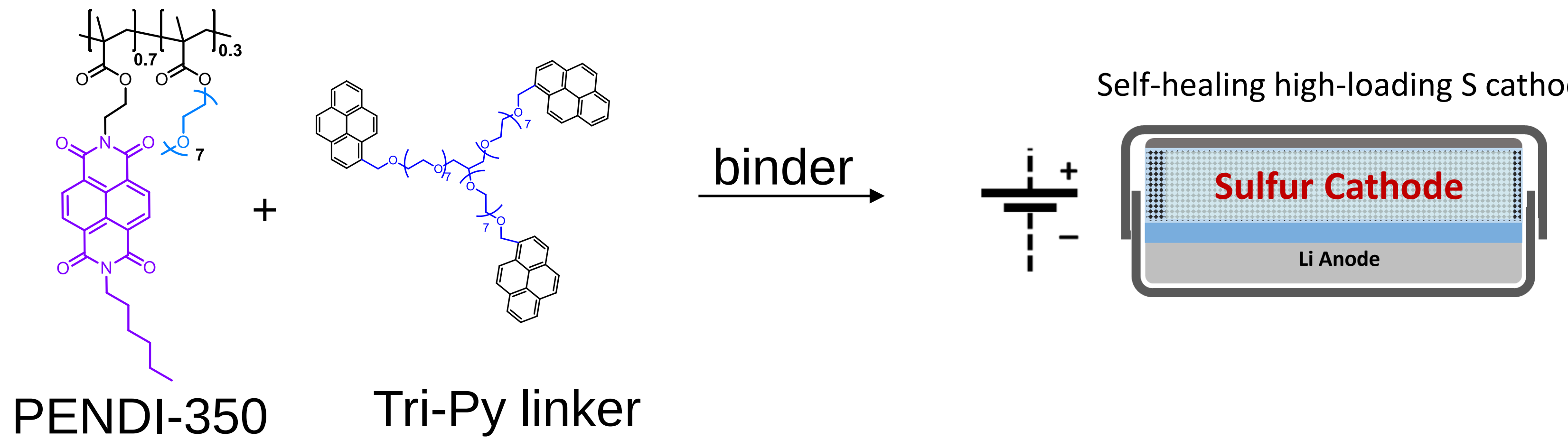
Quasi-Solid-State Device Performance

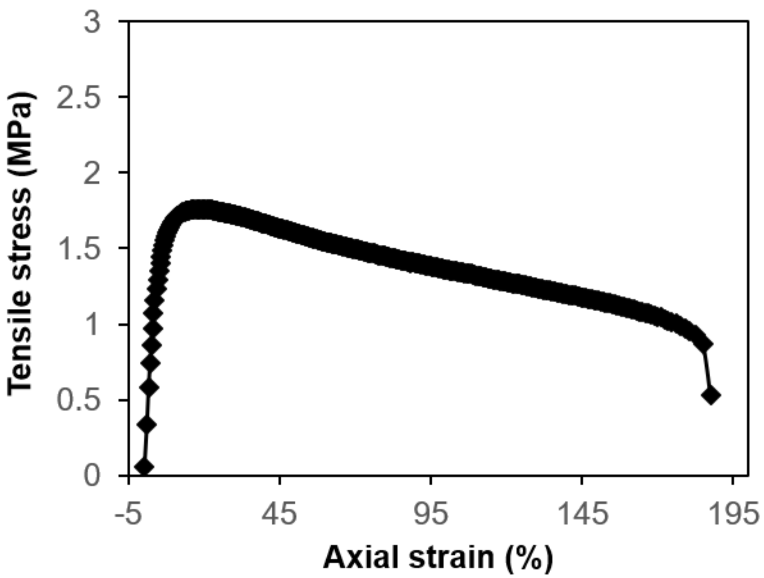


- All-gel design gives improved capacity compared to organic electrolyte (w/$LiNO_3$) or Li(G4)TFSI alone
- Overpotential reduced by using a "solvating diluent" anisole

Technical Accomplishments and Progress (cont.)

Design of New Self-Healing Polymers





- Young's modulus: 29.2 MPa
- Maximum tensile stress: 1.8 MPa
- Maximum tensile strain: 185%

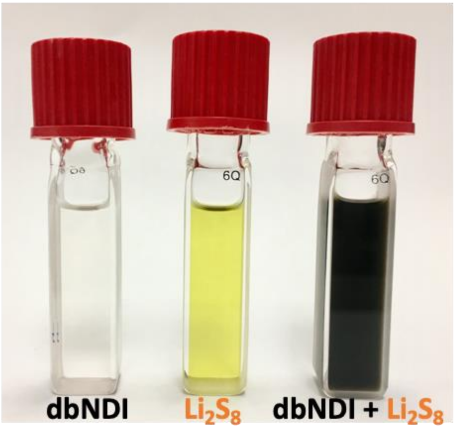
- Ionic conductivity: 2.57×10^{-7} S/cm (RT) (doped w/ LiTFSI, 1:20 Li^+:[EO])

- Self-healing temperature: 30 °C

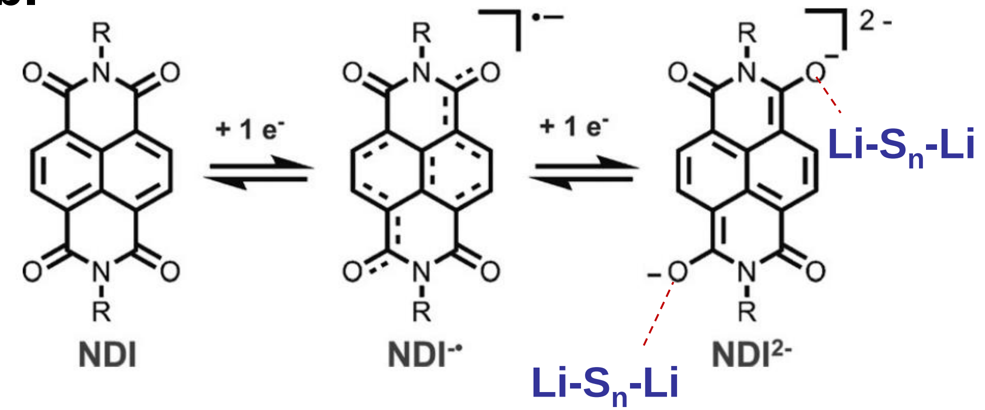
Technical Accomplishments and Progress (cont.)

Interaction with Li_2S_x and Redox-Mediator Effect of NDI

a.

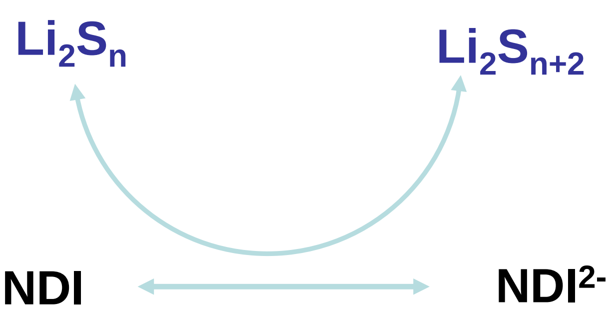


b.



- Two-step reduction of NDI & ion-dipole interaction with Li_2S_x

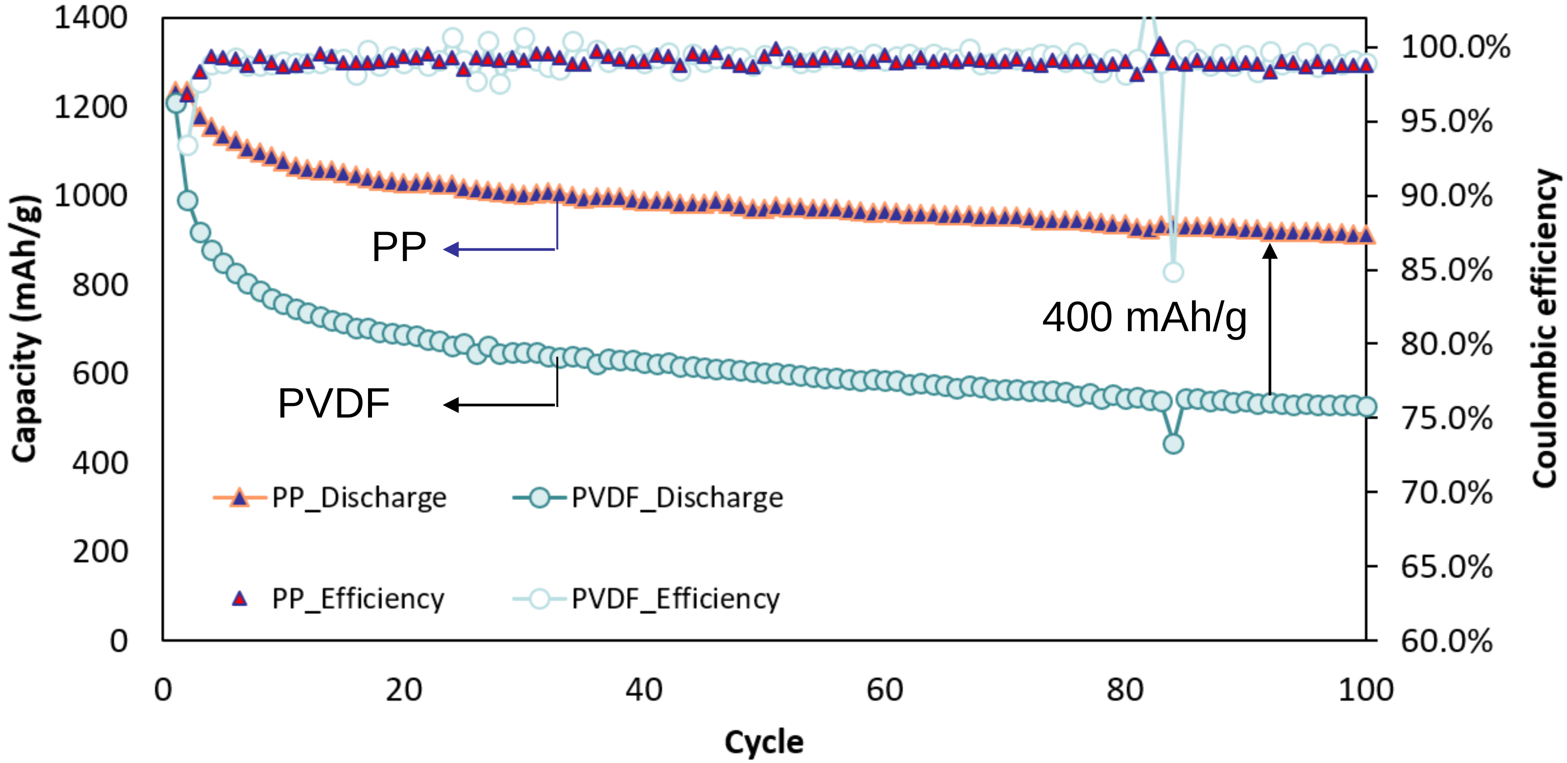
c.



- e^- exchange with NDI accelerates conversion of Li_2S_x (redox mediation effect)

Technical Accomplishments and Progress (cont.)

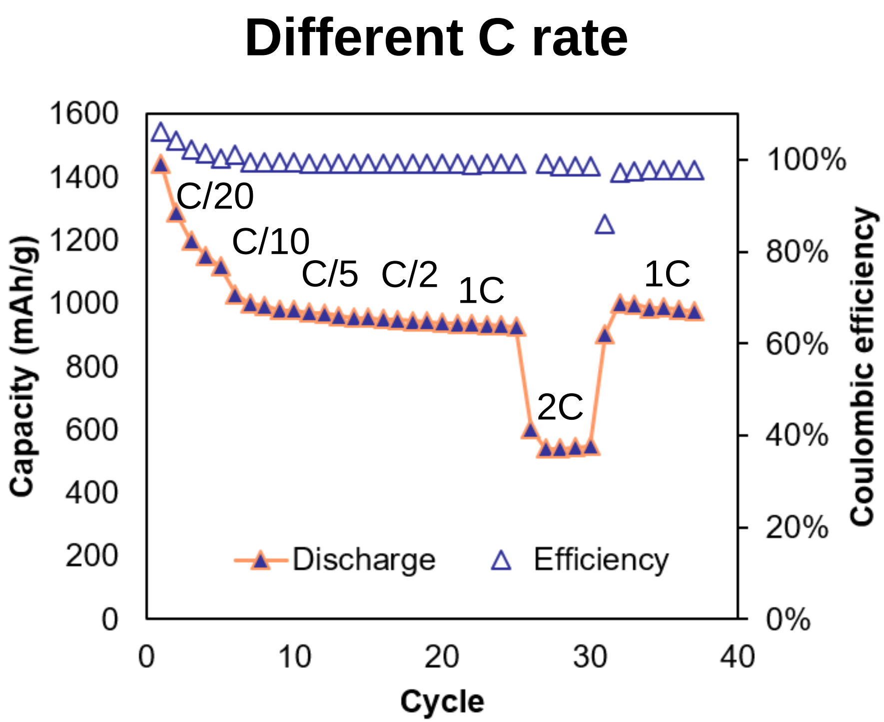
Performance of S Cathode w/Self-Healing Polymers

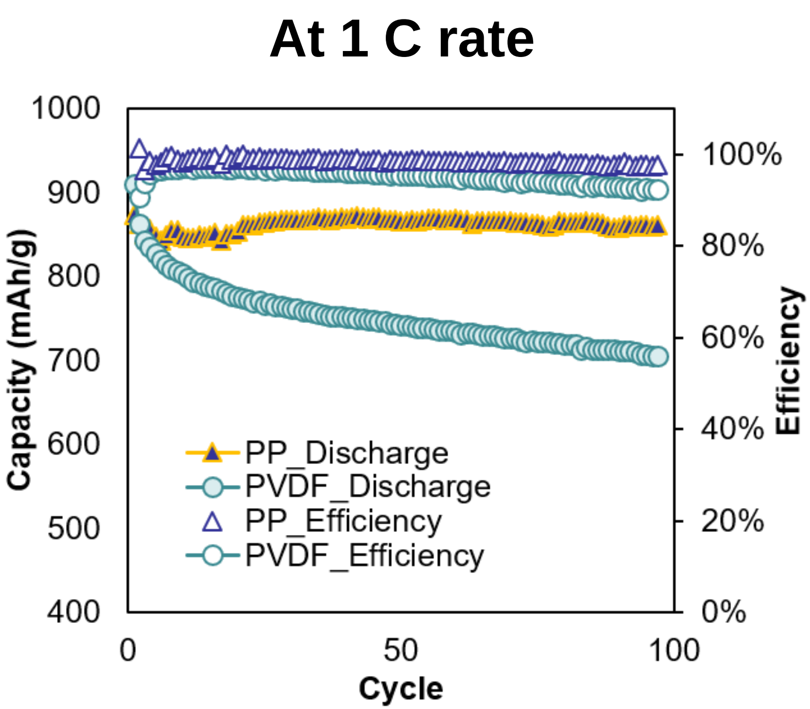


- Capacity with new self-healing PP polymer retains more than 87% (~910 mAh/g) after 100 cycles compare to control device using PVDF (75%, ~5300 mAh/g) at C/20 with S loading of ~0.9 mg_S/cm^2

Technical Accomplishments and Progress (cont.)

Performance of S Cathode w/Self-Healing Polymers





- Capacity reaches about 980 mAh/g at 1C with S loading of ~1.0 mg_S/cm^2
- Capacity retains 98% after 100 cycles with S loading of ~1.1 mg_S/cm^2
- Testing of cathodes with > 4 mg_S/cm^2 is on-going

Responses to Previous Year Reviewers' Comments

- This project was not reviewed at last year's AMR.

Collaboration and Coordination with Other Institutions

- The project is carried out by the Jen and Yang groups at the University of Washington
  - Jen: design, characterize, and optimize ionogel electrolytes and self-healing materials, perform surface modification of mesoporous carbon, electrochemically characterize materials and concept cells
  - Yang: characterize carbon/sulfur composites and surface modified mesoporous carbon, design and electrochemically characterize practical cells

- FY 19 Collaborator – Pacific Northwest National Laboratory
  - Diffusion NMR characterization of ionogels

Remaining Challenges and Barriers

- We have successfully produced high-loading (>4 mg_S/cm^2) cells, but must continue to optimize our fabrication methods and collect performance data.
- The primary degradation mechanisms in practical (high-loading) cells, as opposed to demonstration cells, must be identified and addressed.
- We must directly observe whether self-healing occurs during cathode operation with our novel binders, and identify its effect on cycle life
- We must identify, fabricate, and test the most efficient cell designs which integrate our approaches (quasi-solid-state cells, self-healing binder)

Proposed Future Research

- **Before September 2019**
  - Optimize the design and fabrication of high-loading (>4mg_S/cm^2) S cathodes containing SIGs
  - Adjust design of C/S/SIG cathodes to produce optimal conductivity and Li_2S_x solubility
  - Demonstrate self-healing behavior in a functioning S cathode
  - Efficiently integrate self-healing materials into quasi-solid-state design
  - Identify prominent performance degradation pathways in Li-S cells with novel materials using a combination of microscopy, spectroscopy, and electrochemical behavior
- **Before December 2019**
  - Fabricate optimized 10mAh coin cells based on our designs and deliver to designated DOE facility for validation testing

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

Summary

- **Relevance**
  - Rational molecular design of electrolyte materials has potential to systematically address Li-S cell performance issues, leading to a battery system with 2x energy density compared to Li-ion and high capacity retention
- **Approach**
  - Develop freestanding gels containing solvate ionic liquid for Li metal compatibility and polysulfide solubility reduction
  - Incorporate polysulfide trapping and redox mediation functions into polymeric binders using inter-molecular interactions to retain and effectively utilize sulfur in cathode
  - Develop self-healing materials based on NDI/Py to heal mechanical damage during extended cell operation
- **Technical Progress**
  - High conductivity demonstrated for a series of freestanding ionogel electrolytes
  - Long-term compatibility of ionogels with Li metal demonstrated
  - Ionogels seamlessly integrated into cathode and separator to produce quasi-solid-state Li-S cells
  - Quasi-solid-state cells shown to cycle with improved capacity over traditional designs
  - Significantly-improved cathode performance (capacity, retention, rate-performance) demonstrated using NDI/Py-based polymer binder
  - Redox mediator effect of NDI contributes to improved sulfur utilization
- **Future Work**
  - Optimize and characterize selected gel cathodes with improved cell performance
  - Identify and develop methods to mitigate degradation pathways of our cell designs
  - Deliver 10mAh optimized cells for DOE testing