Cornell University

Highly Loaded Sulfur Cathode, Coated Separator, and Gel Electrolyte for High-Rate Lithium-Sulfur Battery

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Project ID: bat444

Overview

Project Timeline
Start: October, 2017
End: April, 2021
Percent Complete: ~70%

Budget
Total: $1.11M/3.5 years
Phase I: $360k/1.5 years
Phase II: $750k/2 years

Partners
- **Jin Suntivich, Materials Science and Engineering, Cornell University**
- **Tring Nguyen, EIC Labs**

Barriers
- Energy density for current battery electric vehicles (BEVs) is low (< 250 Wh/kg).
- Current Li-S batteries exhibit low sulfur utilization, poor cycling life and rate capability.
  - Higher sulfur loading w/o sacrificing cycle life and rate capability is needed.
  - Mitigation of polysulfides shuttling to increase capacity and improve cycle life of Li-S batteries
- Safety of BEVs are yet to be improved.

Relevance

Impact and Project's Relevance:

Lithium sulfur cells promise to increase the energy density and decrease the cost of batteries compared to the state of art Li-ion batteries (LIB). If the performance and cycling challenges can be alleviated, these systems hold the promise for meeting DOE EV targets.

The key features of the project's approach are the development of i) layered cathode with high sulfur loading ii) a polymer/ceramic separator coated with graphene, and iii) gel electrolyte for Lithium-Sulfur (Li-S) battery systems.

The developed highly loaded sulfur cathodes, conductive carbon coated separators, and gel electrolyte will mitigate the low rate capability, shuttling effect and limited cycle life in high performance Li-S batteries with improved safety. Rigorous abuse tests of Li-S batteries provide insight into the safety of Li-S batteries.

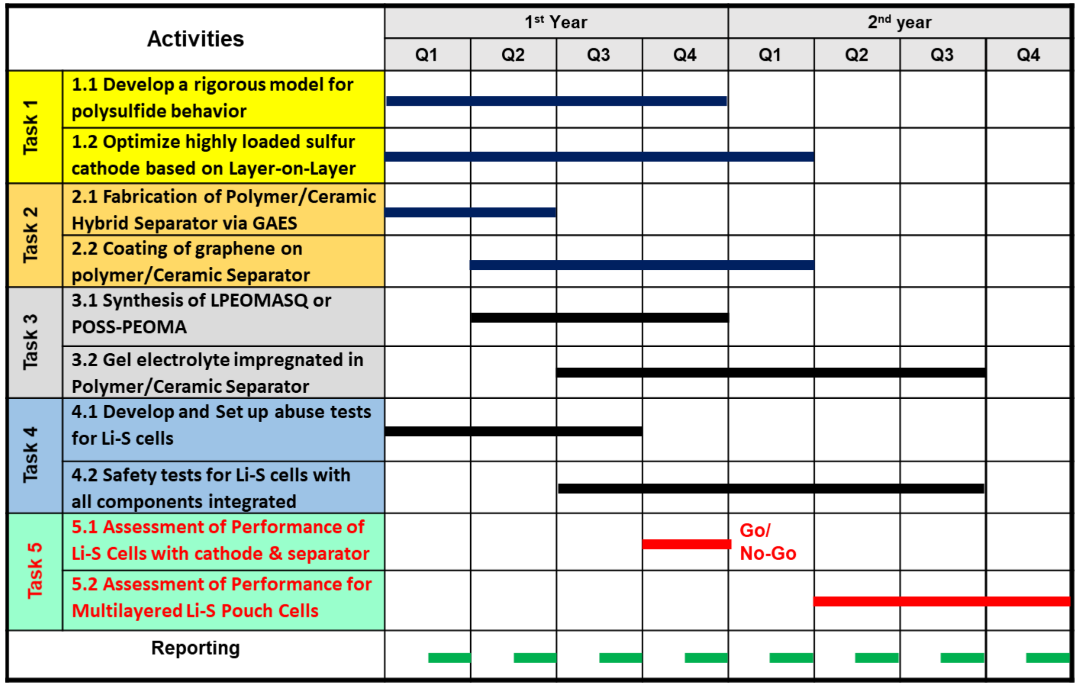
Objectives:

to research, develop, and demonstrate a 1 Ah Li-S battery prototype capable of achieving

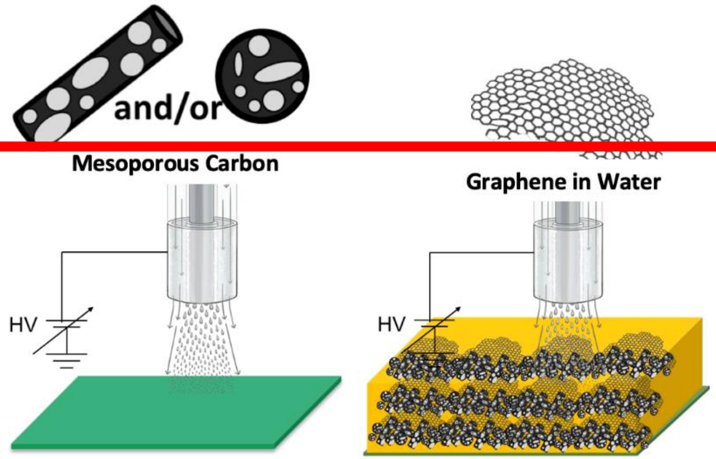
- energy density ≥500 Wh/Kg
- cycle life of ≥ 300 cycles
- at 0.5C discharge rate

Milestones

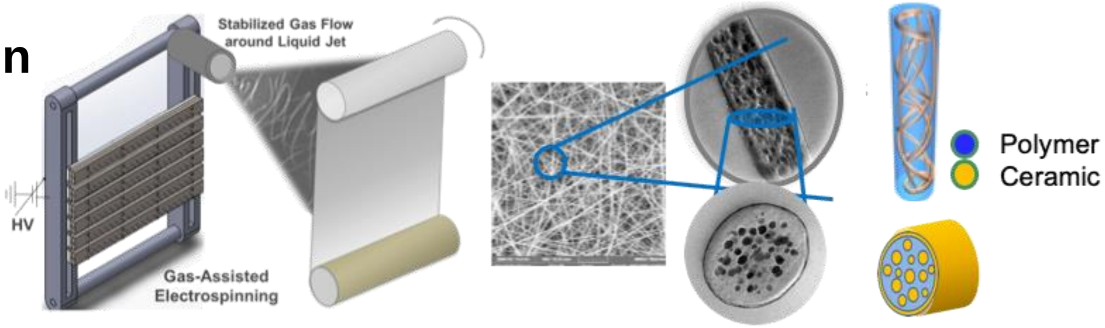
- Develop a rigorous model for polysulfide behavior (Q1 Y1 – Q4 Y1) (completed)
- Optimize highly loaded sulfur cathode based on Layer-on-Layer (Q1 Y1 – Q2 Y2) (in progress)
- Fabrication of Polymer/Ceramic Hybrid Separator via GAES (Q1 Y1 – Q2 Y1) (in progress)
- Develop Polymer/Ceramic Hybrid Separator with Graphene Coating (Q2 Y1 – Q1 Y2) (in progress)
- Synthesis of LPEOMASQ or POSS-PEOMA (Q2 Y1 – Q4 Y1) (initiated)
- Gel electrolyte impregnated in Polymer/Ceramic Separator (Q3 Y1 – Q3 Y2) (initiated)
- Set up abuse tests for Li-S cells (Q1 Y1 – Q3 Y1) (initiated)
- Safety tests for Li-S cells with all components integrated (Q3 Y1 – Q3 Y2) (initiated)
- Assessment of Performance of Li-S Cells with cathode/separator (Q4 Y1)
- Assessment of Performance for Multilayered Li-S Pouch Cells (Q2 Y2 – Q4 Y2)

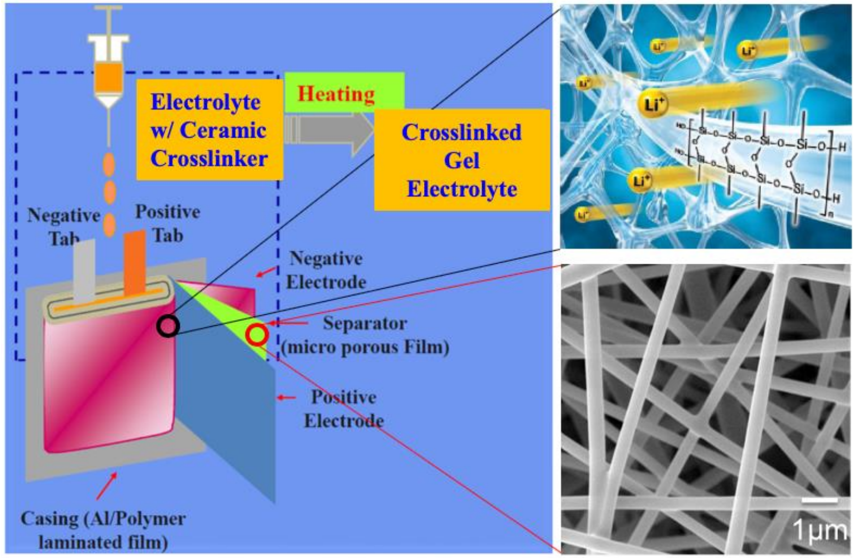


Approach



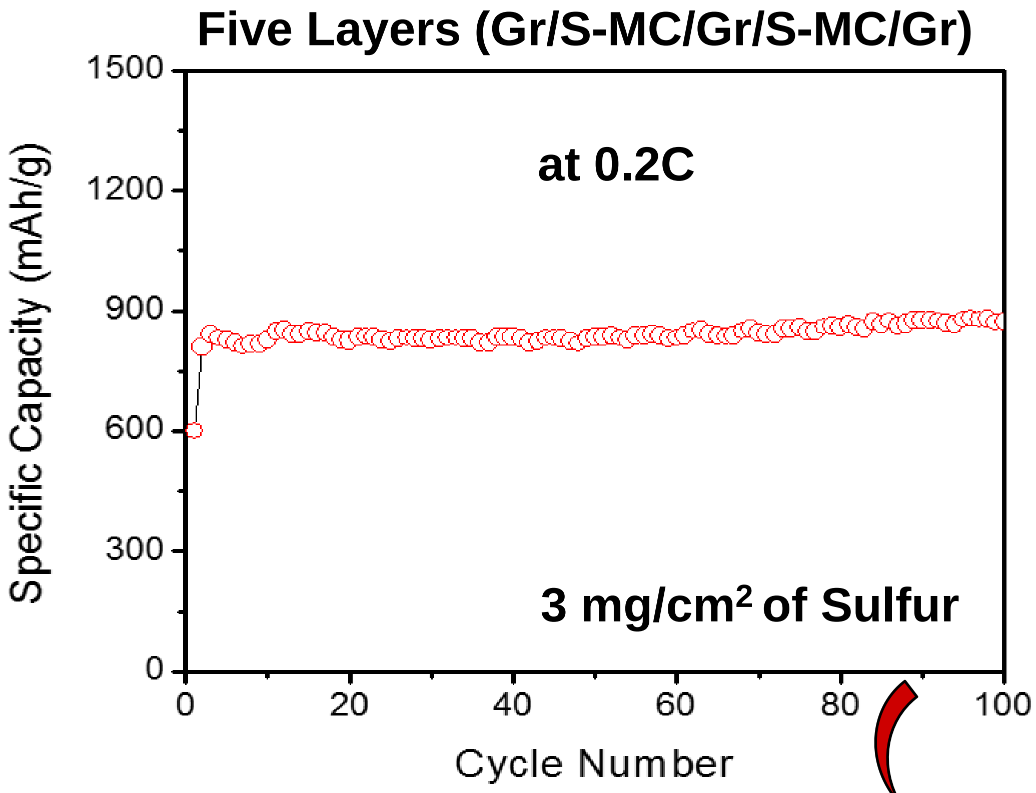
1. **Highly Loaded Sulfur Cathode for High Rate Li-S Batteries**
   - **Utilization of Layer-on-Layer Approach based on Air-Controlled Electrospray**
   - **Optimization of Layering Structures via Experiments and Simulation**
2. **Graphene Coated Polymer/Ceramic Separator for Mitigation of Polysulfide Shuttling**
   - **Development of High Rate, Thermally Stable, Non-flammable Polymer/Ceramic Separator via Gas-Assisted Electrospinning**
   - **Graphene Coating on Polymer/Ceramic Hybrid Separators**
3. **Gel Electrolyte for Enhanced Safety**
   - **Development of Gel Electrolyte based on Ceramic Crosslinker**
   - **Incorporation of Gel Electrolyte into Polymer/Ceramic Hybrid Separator**
4. **Fabricate and evaluate 1 to 3 Ah Li-S battery Pouch Cell Prototypes**
5. **Assessment of interfaces and stability of Li-S cells**

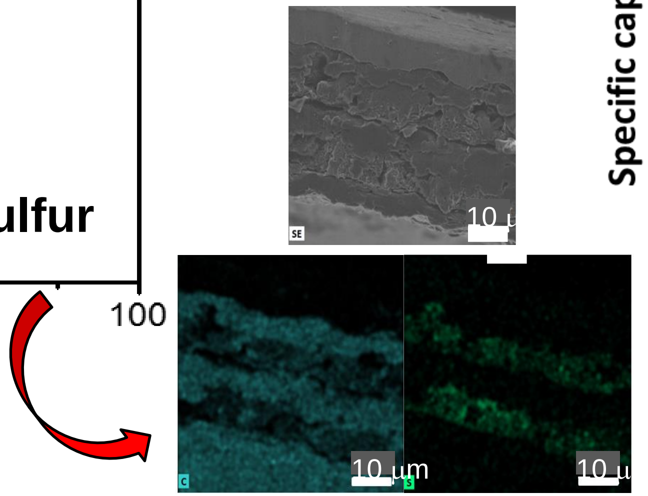


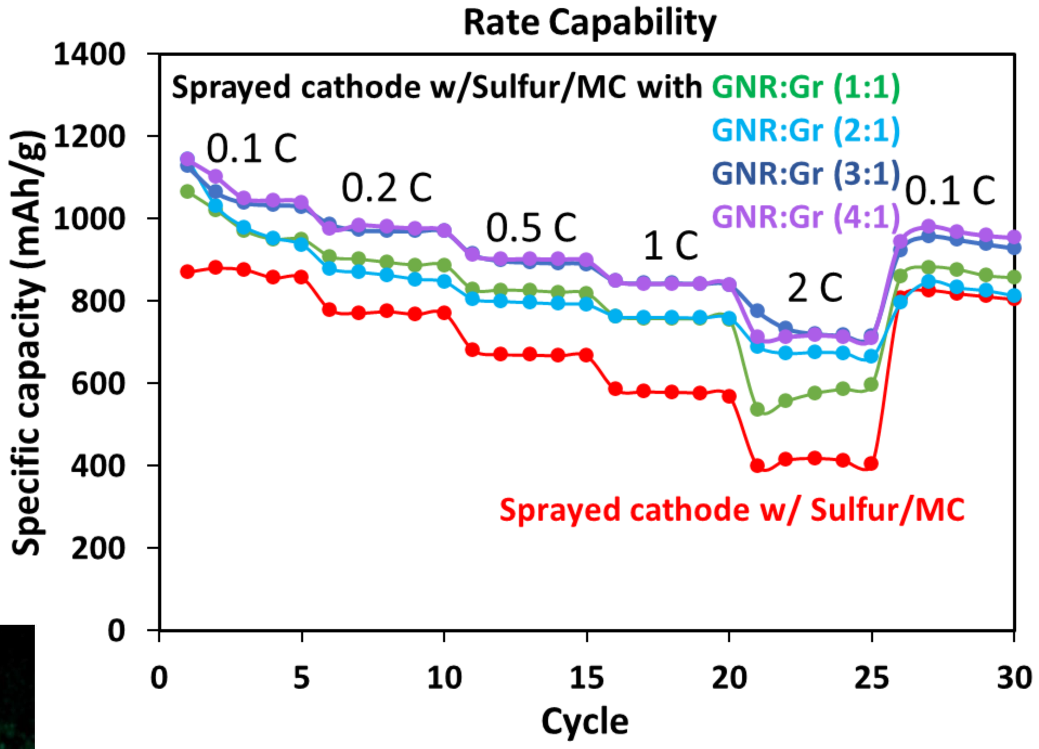


Accomplishments: Highly Loaded Cathodes via Layering Approach

Based on the newly developed model with a cascade of polysulfide reactions and mass transport, we designed out layered cathodes where the thickness of sulfur-filled mesoporous carbon (S-MC) and graphene (GR) layered are optimized. **This layer-on-layer approach (up to 5 layers) improves the capacity retention significantly (over 95% after 100 cycles) without compromising the capacity. Incorporation of Graphene Nanoribbon (GNR) further increases the capacity and rate capability.**

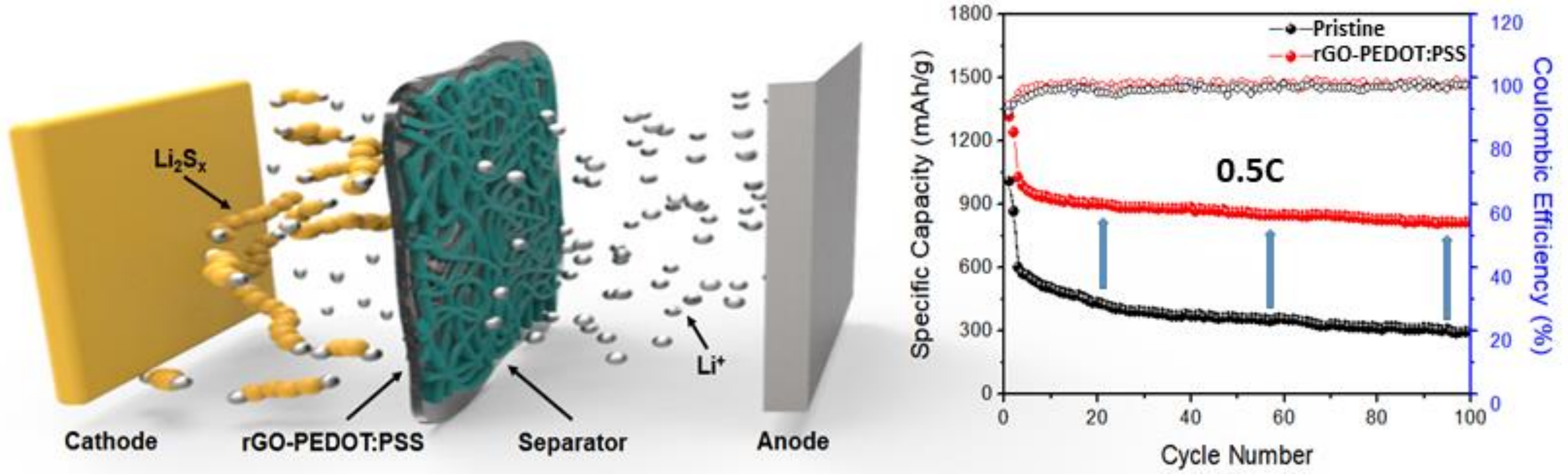




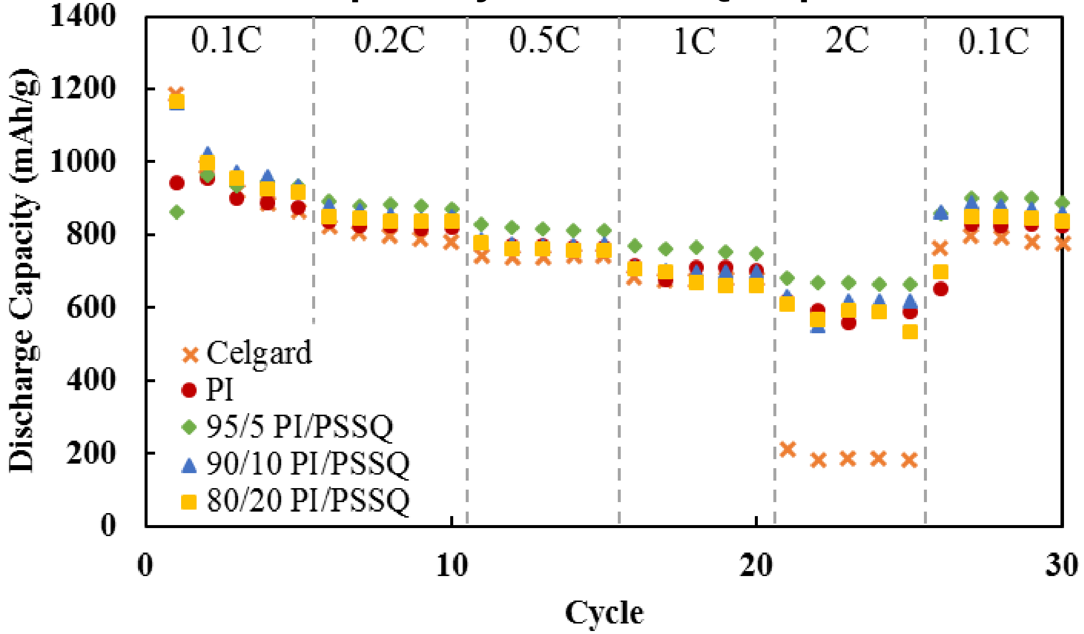


Accomplishments: Ceramic/Polymer Separator and Graphene Coating

The capacity and rate capacity are drastically improved via **coating the commercial separator with reduced graphene oxide (rGO)/conducting polymer (PEDOT:PSS),** leading to more than twice the capacity of over 800 mAh/g after 100 cycles at 0.5 C rate, when it is compared to those with the pristine separator.



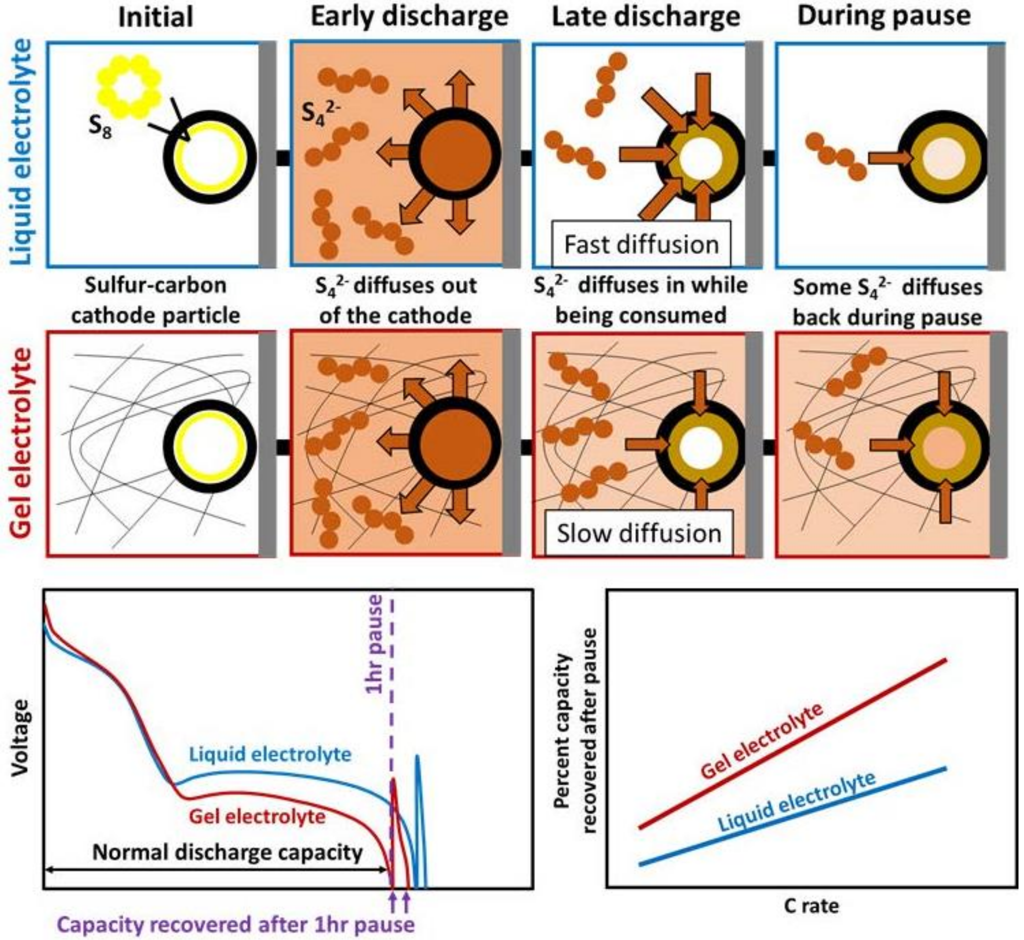
Hybrid separators obtained by gas-assisted electrospinning of polymer (polyimide, PI)/ceramic (polysilsesquioxane, PSSQ) blends significantly enhances the rate capability, exhibiting the capacity of 800 mAh/g at 2C charge/discharge rate. Polybenzimidazole (PBI)/alumina separator is being developed to improve the electrochemical and mechanical properties.



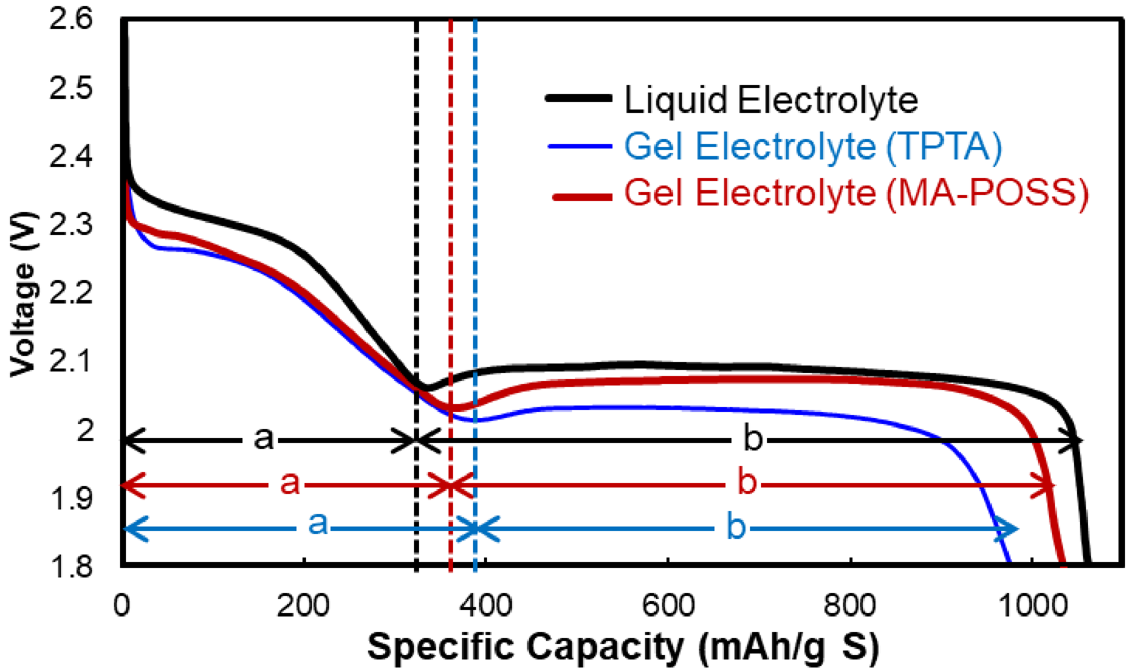
Accomplishments: Polysulfide Mitigation via Safe Gel Electrolyte

Our **gel electrolyte (GE)** demonstrates that gel network created by the ceramic cross-linker can **effectively trap soluble polysulfides**, leading to a better capacity retention and improved rate capability than liquid electrolyte (LE).

Designed tests: discharge with pause, LE *vs.* GE



First Discharge Curve Profiles, LE *vs.* GE



Responses to Previous Year Reviewers’ Comments

This Battery 500 Seedling Project was not participated in AMR last year.

Collaboration/Partnership

Cornell University

- **PI: Yong Joo** (Chemical & Biomolecular Engineering)
  - Fabrication of Highly Loaded Sulfur Cathodes
  - Development of Polymer-ceramic Hybrid Separator and Graphene coated Separators
  - Incorporation of Gel Electrolyte
- **Co-PI: Jin Suntivichi** (Materials Science & Engineering)
  - Quantification of Surface-Polysulfide Interactions
  - Measuring Transport through Separators

EIC Laboratories

- **Collaborator: Trung Nguyen** (EIC Labs)
  - Fabrication and Evaluation of Li-S Pouch Cells
  - Rigorous Safety Tests.

Proposed Future Research

- **Optimize and Create Synergy among Highly Loaded Cathode, Coated Separator and Gel Electrolyte**
  - **Perform Integrated Assessment of Performance of Li-S Cells with Cathode/Separator**
  - **Incorporate Gel Electrolyte into Polymer/Ceramic Separator w/ and w/o Graphene Coating**
- **Perform Rigorous Safety Tests.**
  - Develop rigorous abuse test system for Li-S batteries.
  - Perform Safety tests of Li-S cells with all components integrated.
- **Fabricate and evaluate 1 - 3 Ah Li-S Battery Pouch Cell Prototype.**

Milestones of Phase II – 2nd Year

Milestone	Type	Description
Optimize highly loaded sulfur cathode based on Layer-on-Layer	Technical	Optimize Layer Structure to Achieve Areal capacity > 5 mAh/cm^2 for 300 cycles
Develop Polymer/Ceramic Hybrid Separator w/ Gr Coating	Technical	Achieve Coating thickness < 10 µm and Gr loading < 0.5 mg/cm^2
Gel electrolyte impregnated in Polymer/Ceramic Separator	Technical	Achieve 80% of capacity with liquid electrolyte at 2C
Assessment of Performance for Multilayered Li-S Pouch Cells	Technical	Validate that multi-layered Li-S pouch cells (two layered 2” x 6” or four layered 2” x 3”) exhibit ≥ 1 Ah, ≥ 500Wh/kg and cycle life of ≥ 500 cycles at approximately 0.5C

Summary of Phase II – 1st Year

We laid a firm foundation on proposed approaches to develop highly loaded sulfur cathode, coated separator and gel electrolyte for high rate capable Li-S batteries. Methodology for quantifying surface-polysulfide interactions as well as polysulfide transport has been set up.

1. Highly Loaded Cathodes: Two failure mechanisms of the sulfur/carbon cathode (surface passivation and diffusion limit) have been analyzed via a newly developed model with a cascade of polysulfide reactions, mass transport, nucleation, and adsorption, and are verified in various sulfur/carbon cathodes. The layer-on-layer approach (up to 5 layers) improves the capacity retention significantly (over 95% after 100 cycles) without compromising the capacity.

2. Polymer/Ceramic Hybrid Separators: Hybrid separators obtained by gas-assisted electrospinning of polymer/ceramic blends significantly enhances the rate capability, exhibiting the capacity of 800 mAh/g at 2C charge/discharge rate.

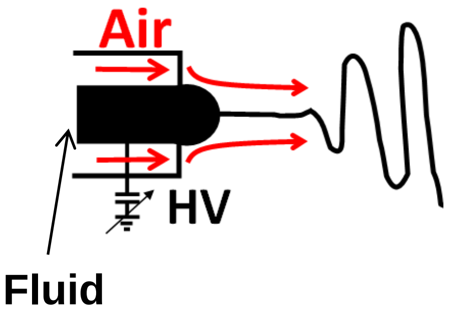
3. Gel Electrolyte: Our recent work on gel electrolyte demonstrates that gel network created by the ceramic cross-linker can effectively trap soluble polysulfides, leading to a better capacity retention and improved rate capability than liquid electrolyte.

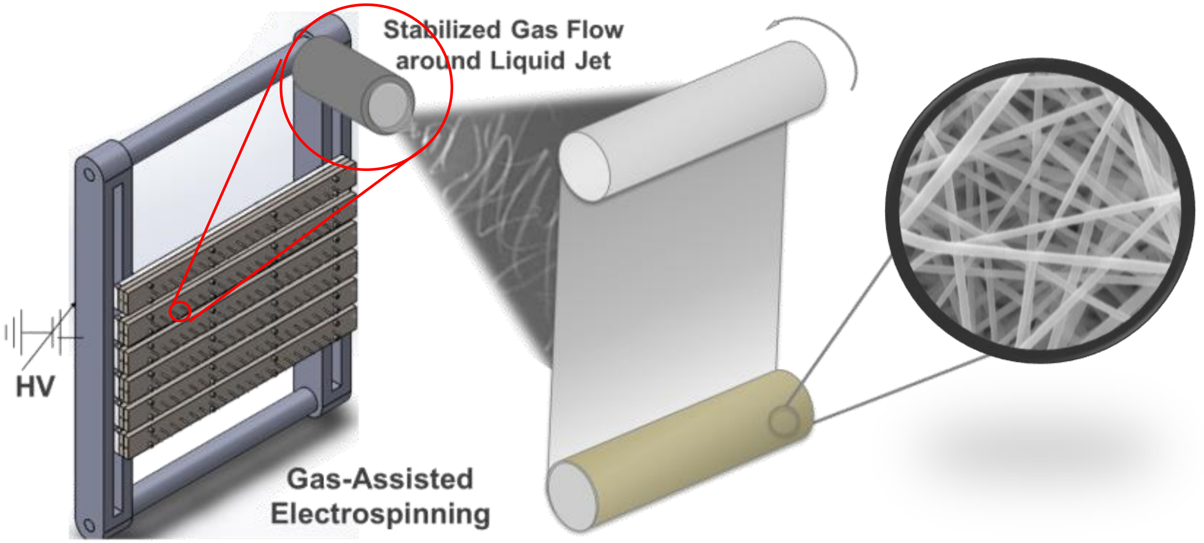
4. Creating the Synergy among Components: To create the synergy among the components, coin cells with layered cathode and graphene coated polymer/ceramic hybrid separator with and without gel electrolyte will be fabricated and the cell performance for the cells with all the developed components integrated will be evaluated.

Technical Back-up Slides

Scalable Nanofiber Manufacturing Processes:

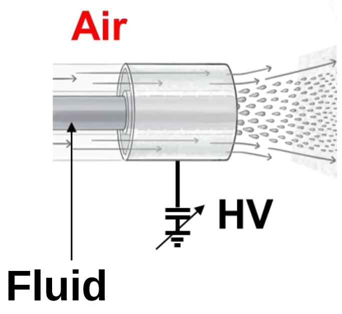
Gas-Assisted Electrospinning

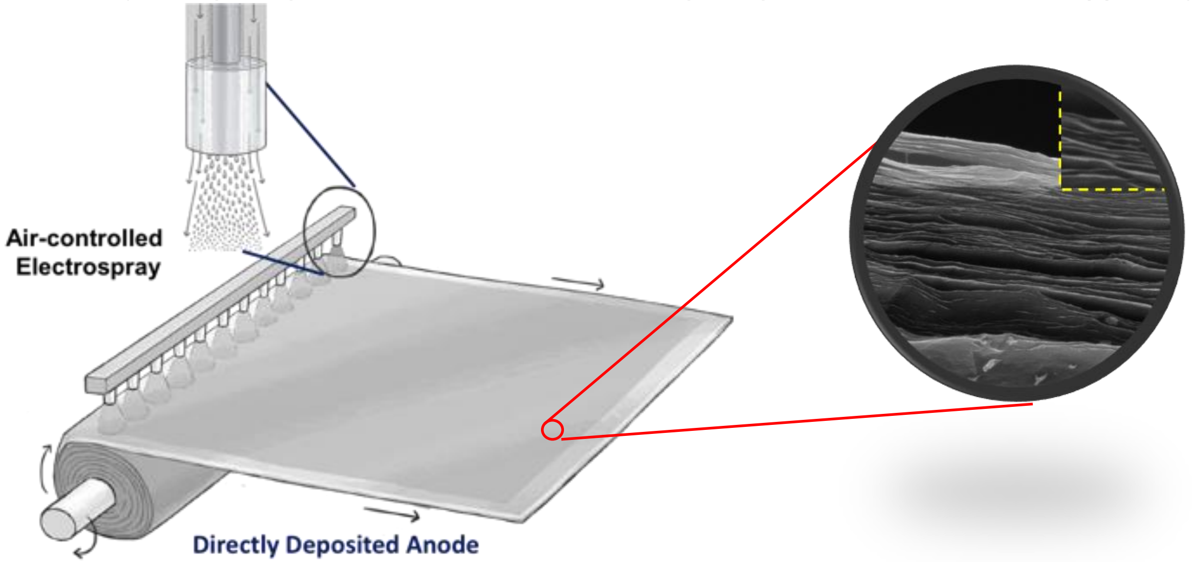




Zhmayev, Cho, Joo, *Polymer* (2010), Hansen, Cho, Joo, *Small* (2012), Divvela and Joo, *J. Appl. Phys.* (2017)

Air-Controlled Electrospray



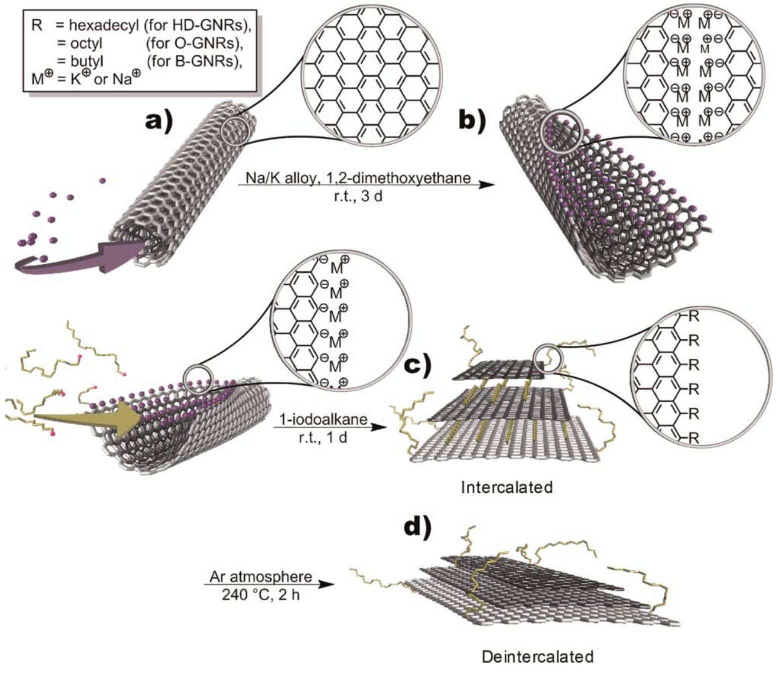


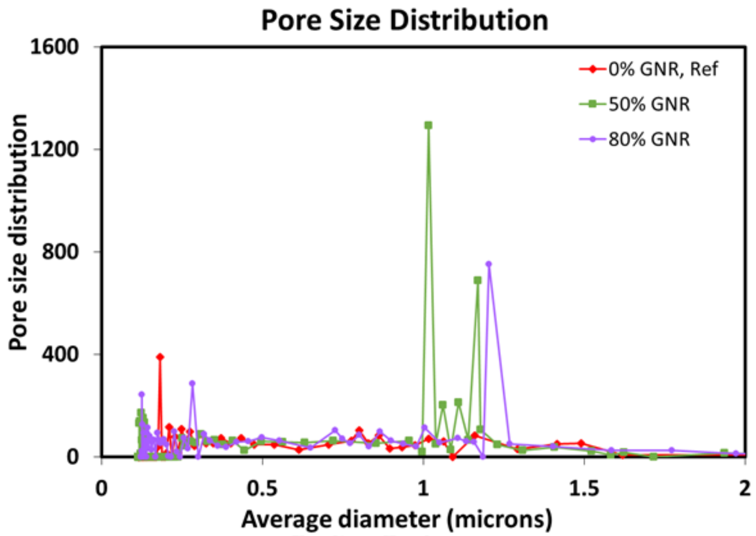
L. Fei, Joo *et. al, ACS Appl. Mater. & Interfaces* (20017), J. Lee and Joo *et. al, Materials Today Energy* (2017)

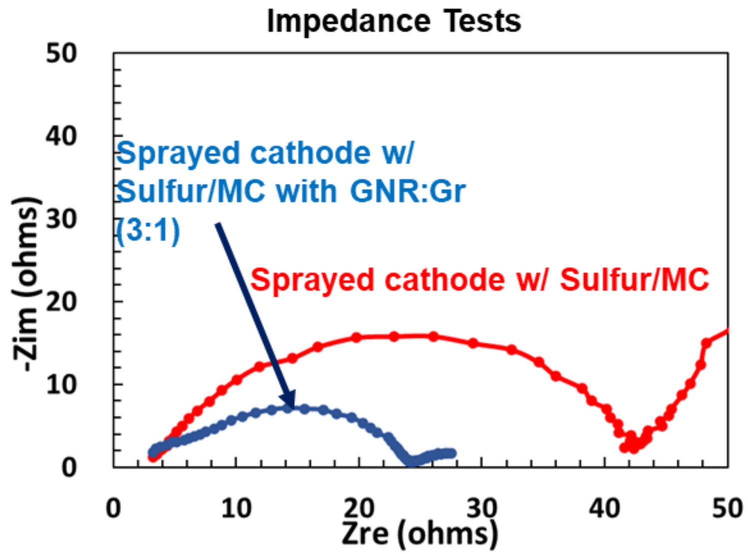
Inclusion of Graphene Nanoribbon (GNR) in Cathode Materials

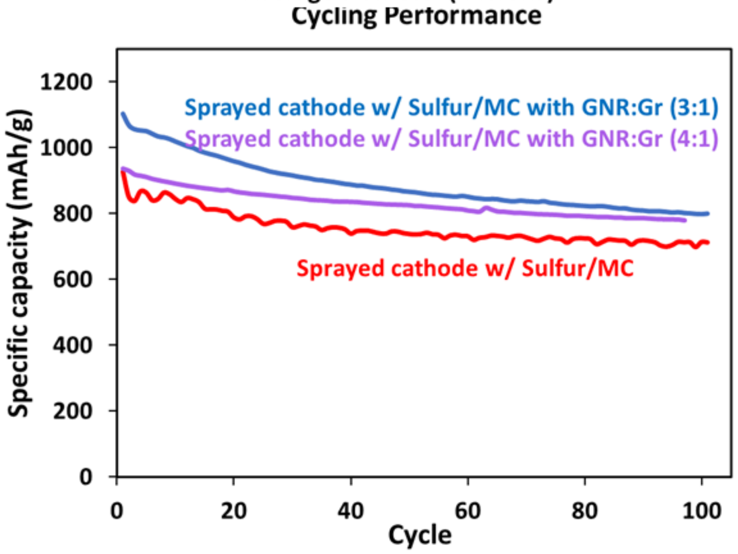
- **Replacement of graphene (Gr) with Graphene Nanoribbon (GNR) leads to higher capacity at high rates due to better conductivity and bimodal pore size distribution.**

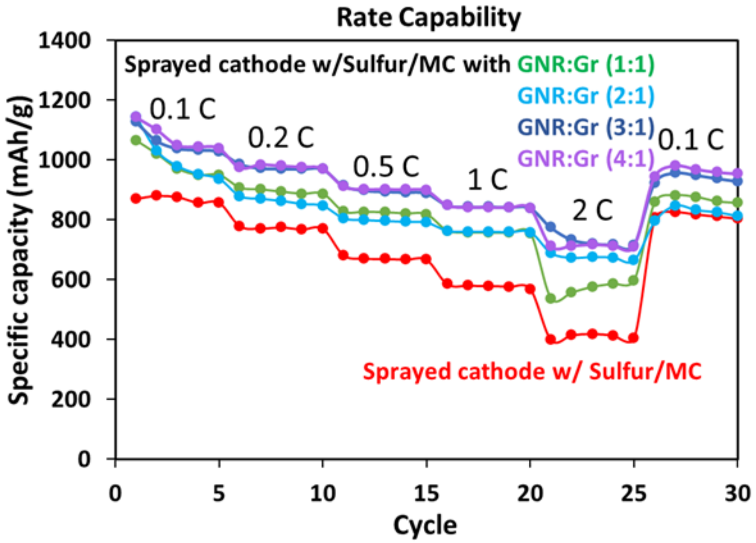
Creation of Graphene Nanoribbon (GNR) via unzipping carbon nanotube (CNT)







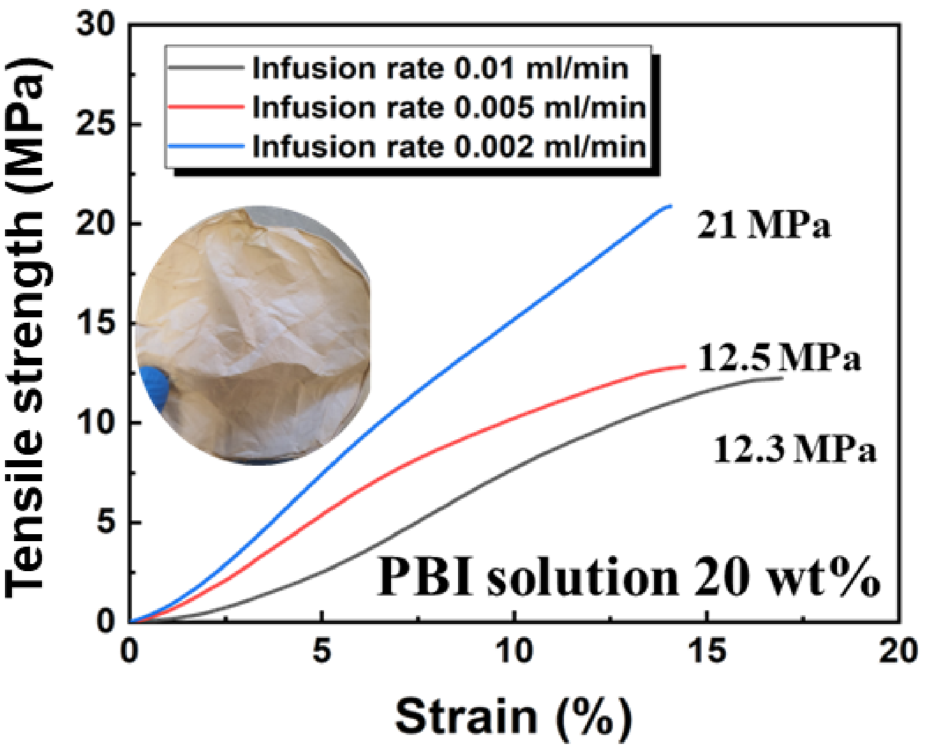




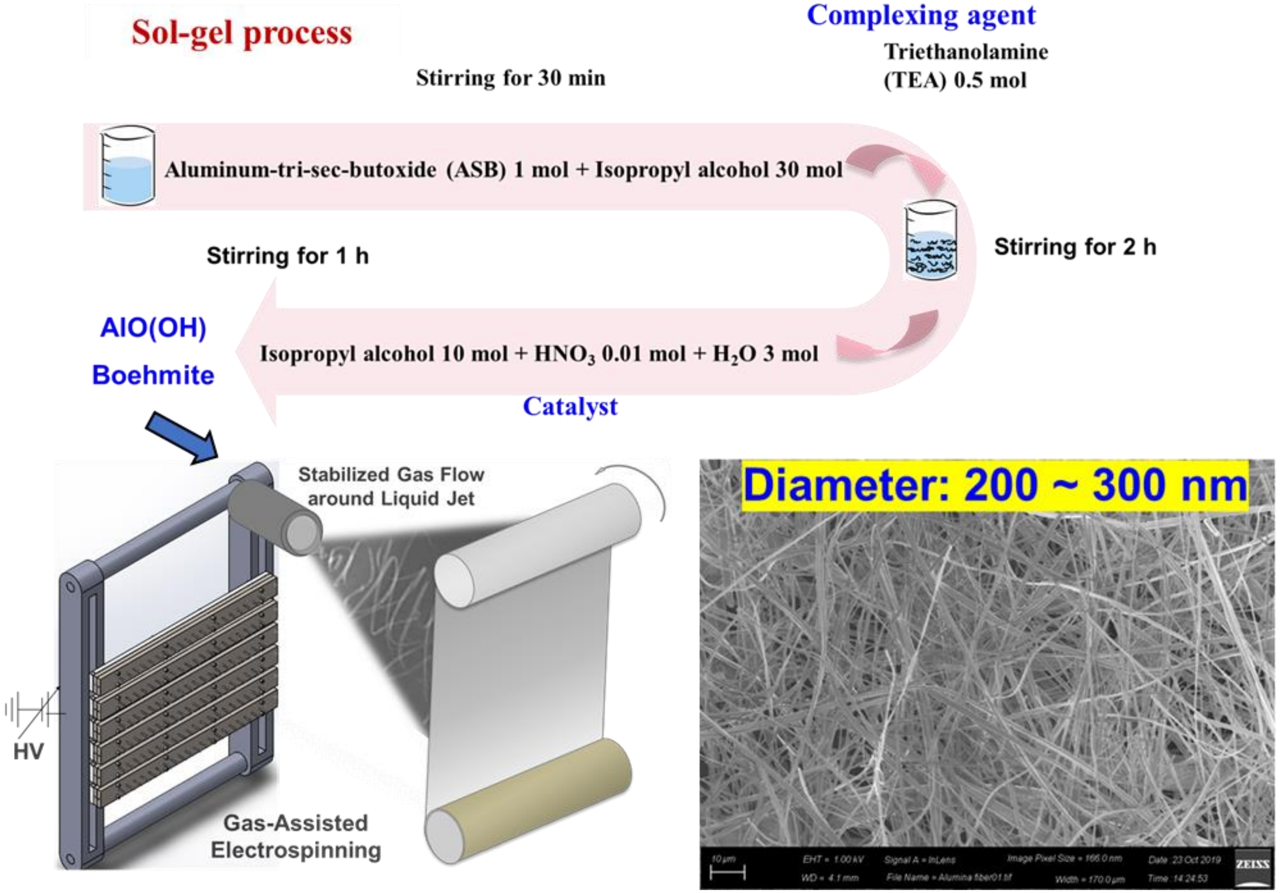
Improvement of Polymer/Ceramic Separator: PBI/alumina Separator

To further improve mechanical properties (tensile strength and ductility), PI is replaced with Polybenzimidazole (PBI).
To further improve the electrochemical stability of the ceramic component, silica based ceramic is replaced with alumina by combining sol-gel synthesis and electrospinning.

Tensile Properties of PBI Nanofiber Membrane

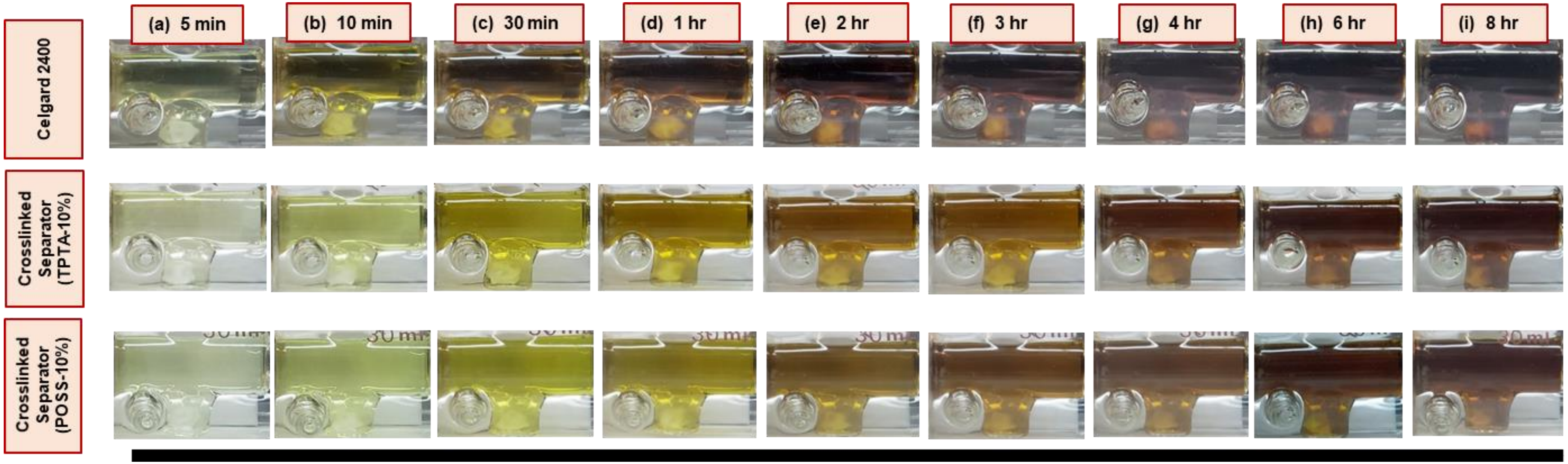


Fabrication of Alumina Nanofiber Membrane



Diffusion Experiments of Li_2S_6

Qualitative diffusion tests revealed a 4 times faster diffusion for Celgard to TPTA (Trimethylolpropane Trimethacrylate).
Therefore, polysulfides can be entrapped and retarded by gel electrolyte.

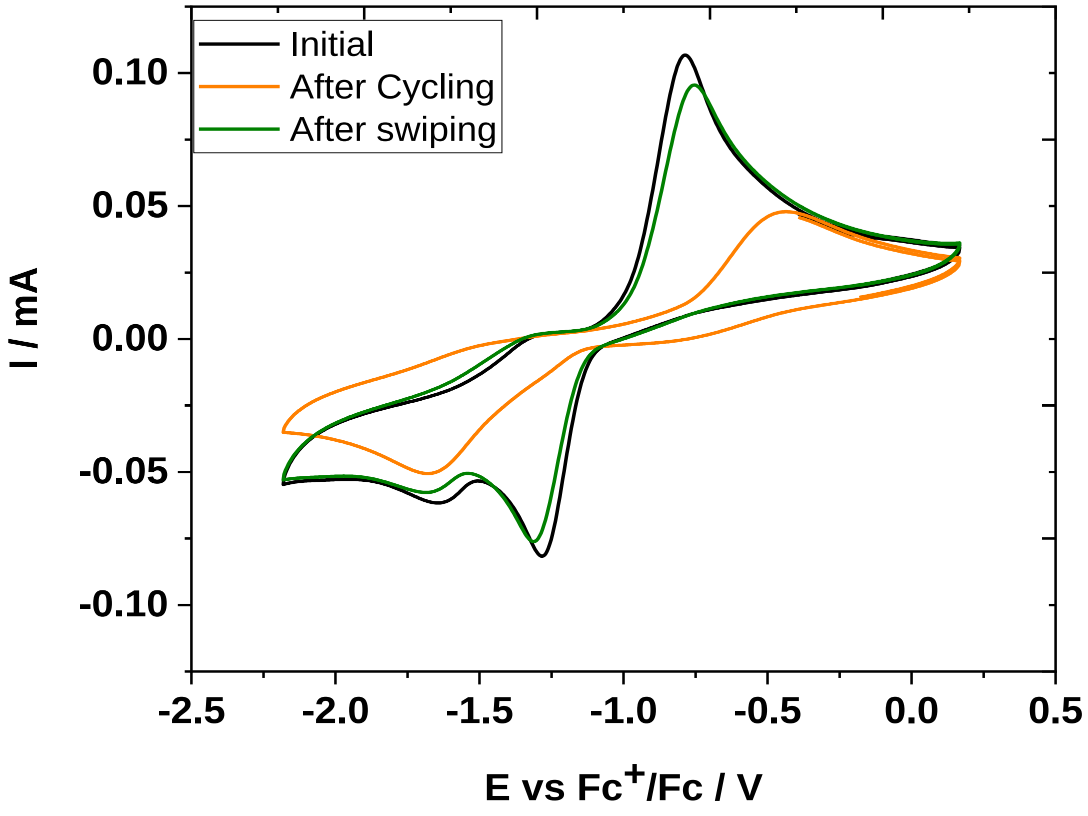


Predicted decrease in diffusion rate by gellation in *simulation*: $1x10^{-10}$ to $5x10^{-12}$ m^2/s

Membrane	Li_2S_6 Diffusion Coefficient (Experimental) [m^2/s]	Li_2S_4 Diffusion Coefficient (Simulation) [m^2/s]
Celgard 2400 (LE)	$1.7x10^{-10}$	$1.0x10^{-10}$
TPTA-10%	$3.4x10^{-12}$	$5.0x10^{-12}$

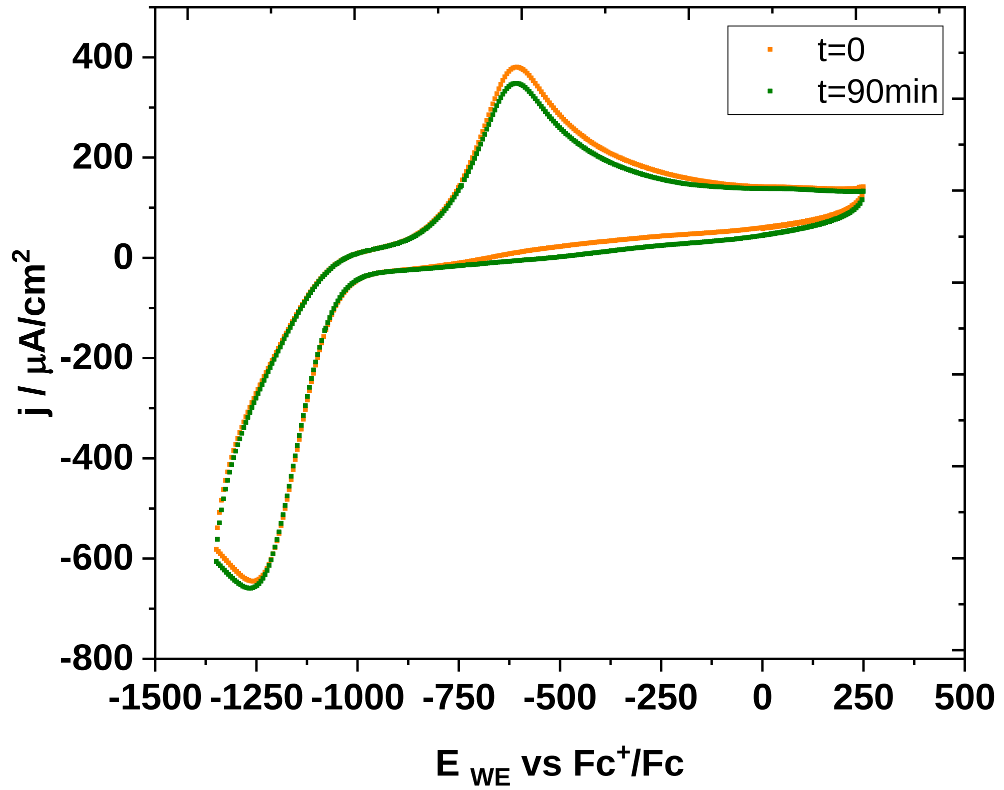
Li_2S_6 Cycling Causes Surface Deposition

Initial pristine CV can be restored with mechanical swipe



Restricting the lower potential prevents surface deposition

- The deposition likely involves Li_2S_6 reduction product (Li_2S_4?)



4 mM Li_2S_6, 1.0 M LiTFSI, DOL/DME (Scan rate: 200 mV/s)