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

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Project ID
ES320

Overview

Timeline

- Project start date – Oct. 2016
- Project end date – Sept. 2019
- Percent complete – 22%

Budget

- Total project funding
  - DOE share: $1.25 M
  - Contractor share: $138,888
- Funding received in FY 2016

  $0
- Funding for FY 2017

  $1.25M

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

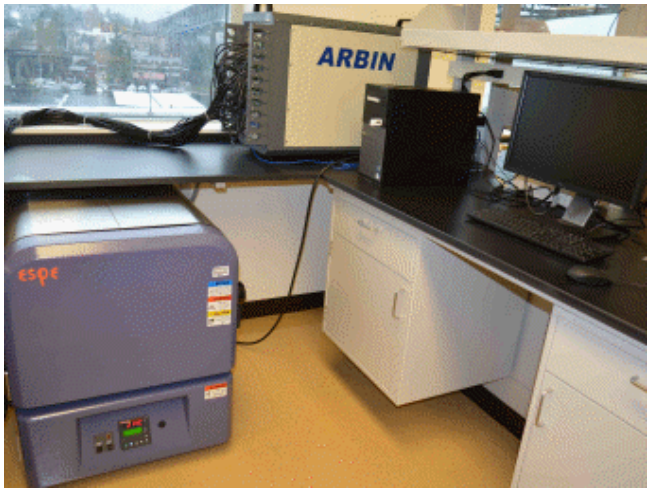
Partners

- University of Washington

Relevance

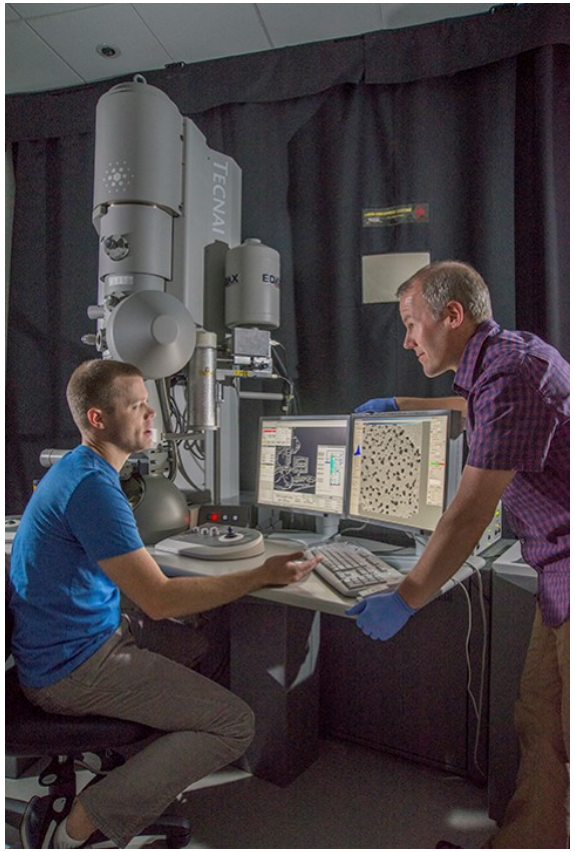
- **Overall Objective:** develop high-performance Li-S cells, based on self-healing and polysulfide-trapping polyelectrolyte gels containing room temperature ionic liquid (RTIL). The Li-S battery design will be capable of achieving gravimetric and volumetric energy densities of ≥800 Wh/kg and ≥1000 Wh/L, respectively.
- **Relevance:** Our cell design will enable a Li-S battery with long cycle life, using low cost sulfur and organic materials, to achieve high performance, such as delivering 675 mAh/g total cathode capacity with ≥ 99% Coulombic efficiency over 200+ deep cycles at C/10.
- **FY 2017 Objectives:**
  - Develop gel electrolytes with polysulfide-trapping functionality
  - Develop self-healing materials based on reversible noncovalent interactions
  - Investigate chemistry of interaction between sulfur and targeted organic groups for trapping of polysulfide species
  - Fabricate concept Li-S cells demonstrating merits of design strategy

Resources



- State-of-the-art synthetic chemistry facility
- Diverse device fabrication/testing laboratories

Resources

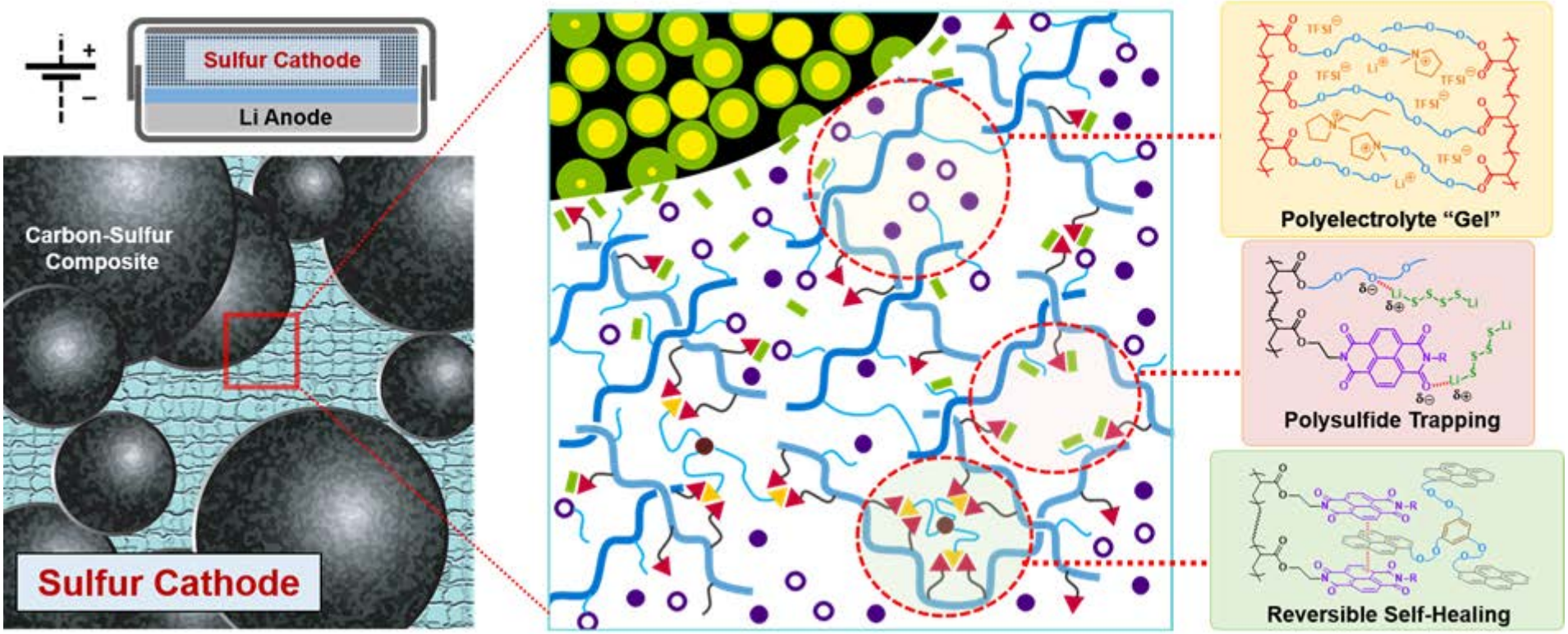


- Access to UW Molecular Analysis Facility
- Newly-opened WA Clean Energy Testbed on campus

Milestones

Date	Milestone or Go/No-Go Decision	Status
June 2017	Milestone Organic Materials Characterization	On track.
Dec 2017	Milestone Selection of Ionomer Gel Structures	On track.
Dec 2017	Milestone Cell-Based Performance Verification	On track.
Mar 2018	Go/No-Go Decision Selection of Gel Structure for Device Optimization	On track.

Approach/Strategy



Approach/Strategy

- **Carbon/Sulfur Composite**
  - Mesoporous carbon provides conductivity, physical entrapment of polysulfide intermediates
  - Platform to introduce targeted chemical functionality for performance enhancement e.g. improved retention and distribution of sulfur species and faster charge/discharge kinetics
- **Room-Temperature Ionic Liquid + Polyelectrolyte Gel**
  - RTIL electrolyte suppresses polysulfide dissolution and inhibits Li metal dendrite growth while providing ionic conductivity similar to organic electrolytes
  - Polyelectrolyte gel creates mechanical toughness and prevents crystallization at low temperature while allowing for ionic conductivity well above other solid electrolyte options

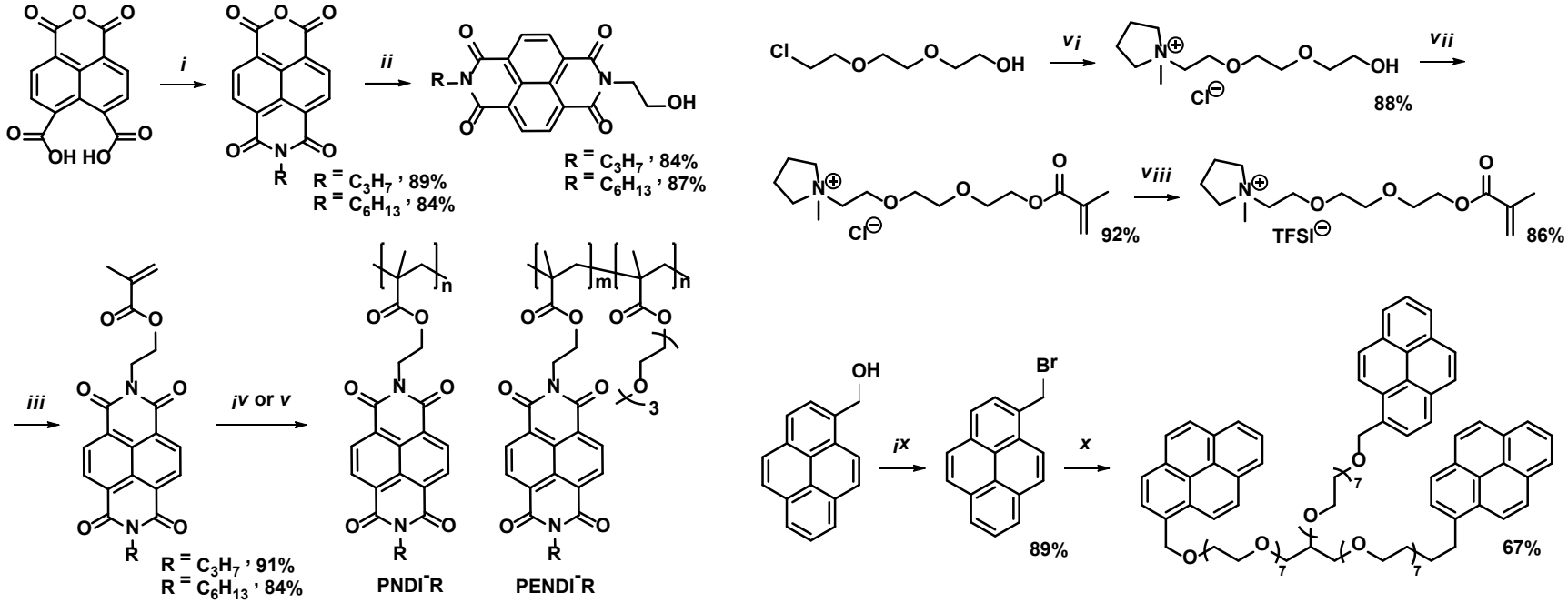
Approach/Strategy

- **Trapping of Polysulfide Species**
  - Trapping of Li_2S_x species via physical or chemical interactions eliminates redox shuttle effect and improves capacity retention
  - Redox-active polymer with tailored energy levels encourages utilization of dissolved Li_2S_x species

- **Self-Healing through Reversible Noncovalent Interactions**
  - Interaction of electron-rich (pyrene or “Py”) and electron-poor (naphthalene diimide or “NDI”) aromatic groups allows tunable, reversible binding
  - Introduction of reversible noncovalent binding induces self-healing, suppressing capacity loss due to mechanical degradation of cathode

Technical Accomplishments and Progress

Chemical Synthesis of Novel Components

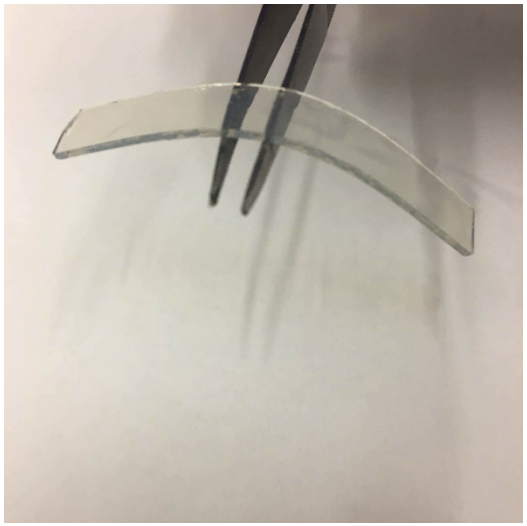


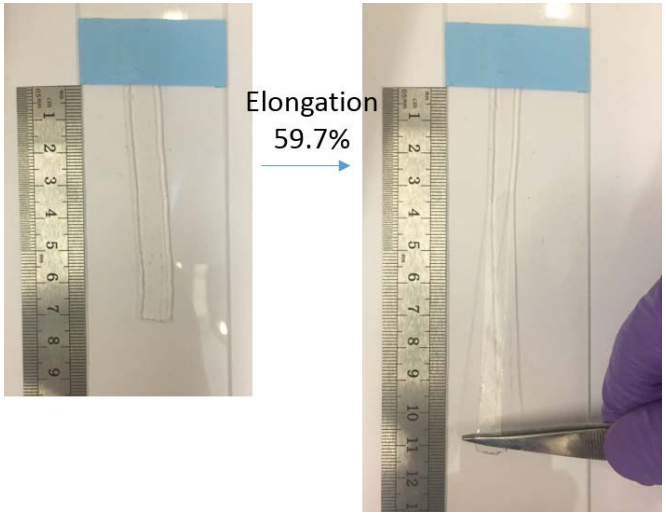
i) a) R-NH_2, water, 60 °C; b) 10 % $HCl_{(aq)}$; c) $HCl_{(conc.)}$, THF, 60 °C. *ii)* 2-aminoethanol, DMF, 100 °C. *iii)* methacryloyl chloride, Et_3N, THF, 40 °C. *iv)* 2,2'-azobis(2-methylpropionitrile) (AIBN), THF, 70 °C. *v)* triethylene glycol methyl ether methacrylate (TEGMA), AIBN, THF, 70 °C.
vi) *N*-methylpyrrole, toluene, 110 °C. *vii)* methacryloyl chloride, CH_3CN, 50 °C. *viii)* $LiTFSI_{(aq)}$, r.t.
ix) PBr_3, THF, 0 °C. *x)* NaH, glycerol ethoxylate (Mn ~ 1000), THF, 40 °C.

- All originally-proposed novel chemical precursors have been successfully synthesized

Technical Accomplishments and Progress (cont.)

In-situ Gel Formation

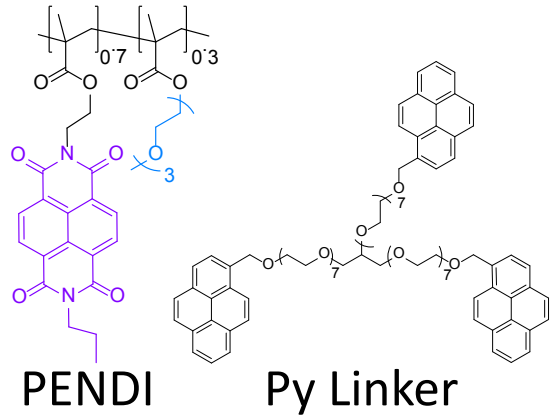




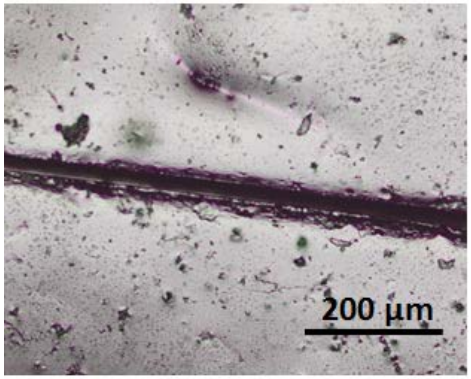
- Suitable reaction conditions found for crosslinked PEG-based gels containing either organic solvent or RTIL
- Mechanical properties tunable by adjusting length of PEG
- Materials testing and structural optimization underway

Technical Accomplishments and Progress (cont.)

Self-Healing Materials

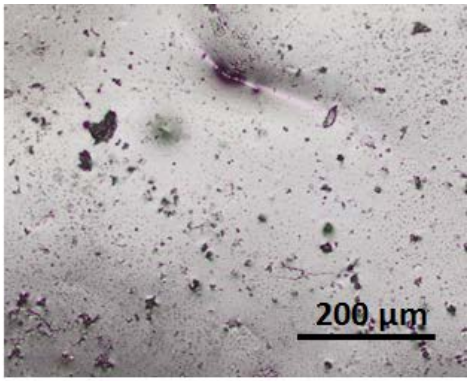


PENDI Py Linker

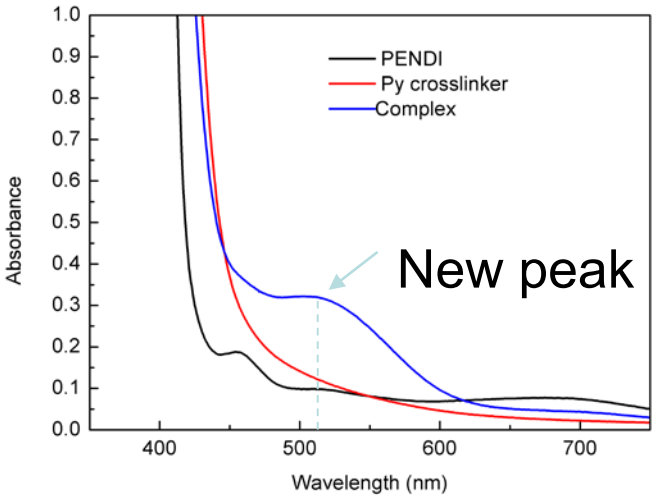


Damaged

6 h, 50 °C



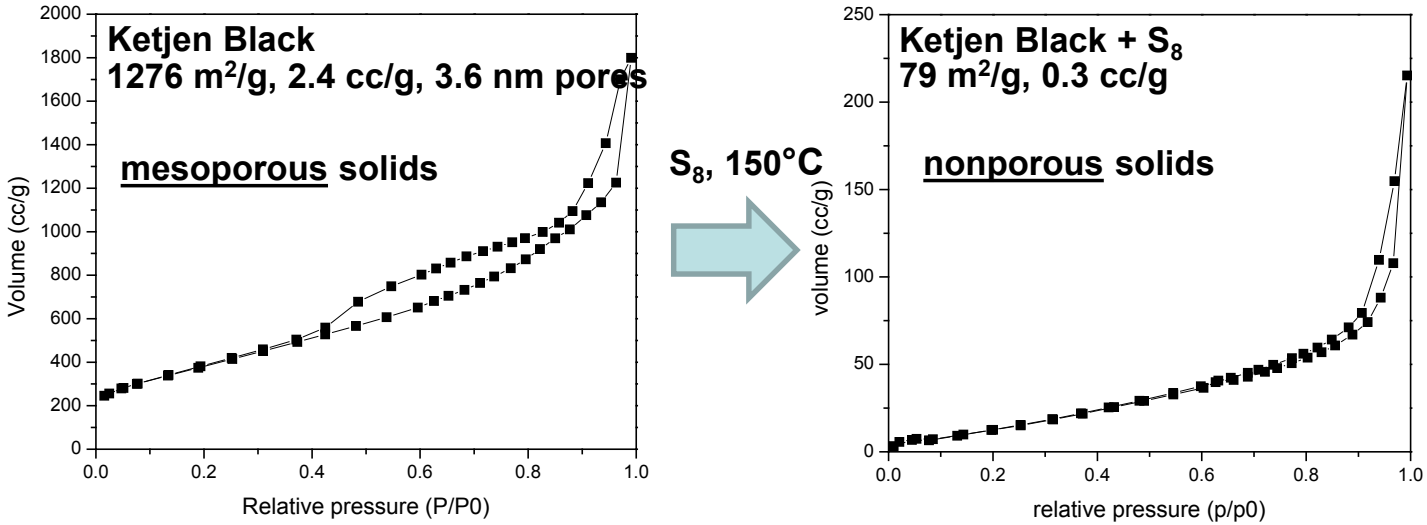
Healed



- Interaction of PENDI w/ tris-Pyrene molecule ("Py linker") confirmed *via* UV-Vis
- Spontaneous self-healing observed in film of PENDI/Py crosslinker mixture

Technical Accomplishments and Progress (cont.)

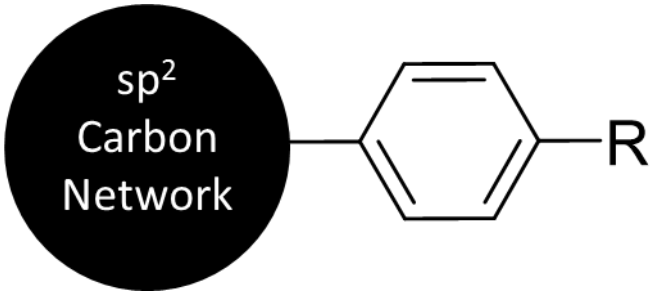
Synthesis/Characterization of S/C Composites

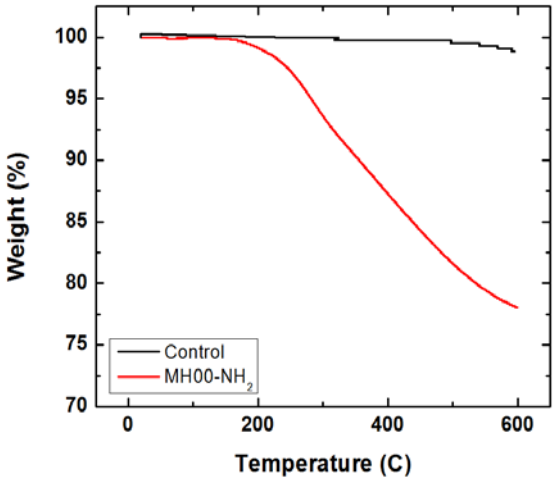


- S/C composites fabricated through melt-diffusion of S_8 w/ mesoporous carbons at 150°C
- Successful infiltration confirmed *via* BET surface-area analysis and XRD (disappearance of S_8 peak)

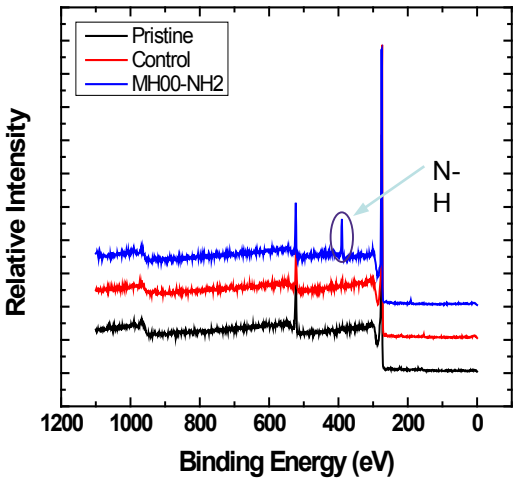
Technical Accomplishments and Progress (cont.)

Chemical Functionalization of Carbons



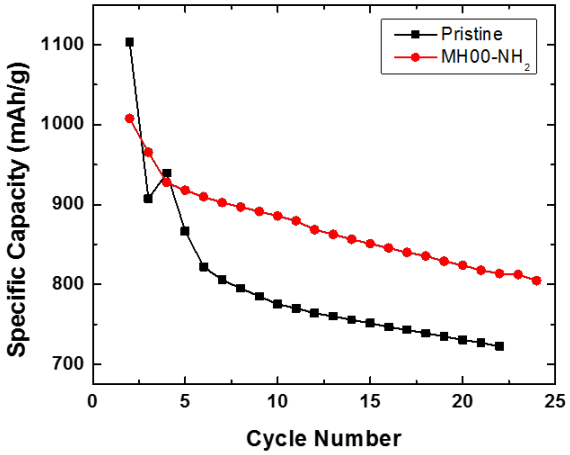


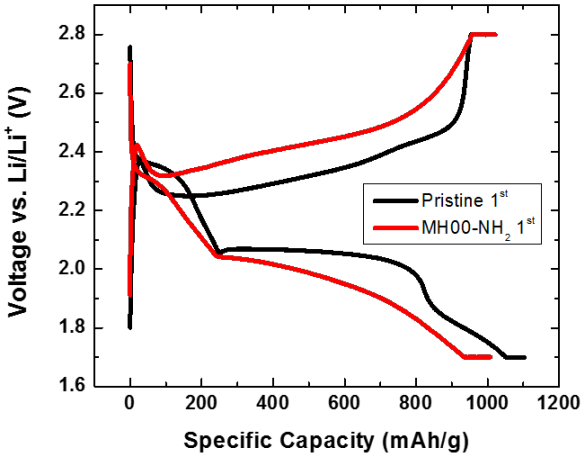
- Chemical procedure developed, based on diazonium chemistry, to functionalize mesoporous carbon surface w/ nearly any “R” group
- Successful functionalization with 1,4-phenylenediamine confirmed *via* BET, XPS, TGA
- Testing w/ other functional groups in-progress

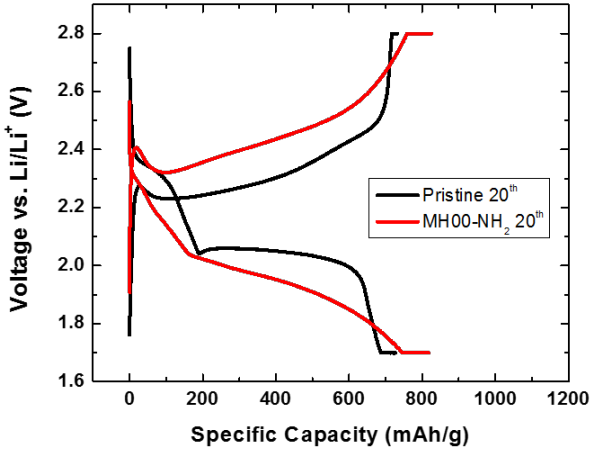


Technical Accomplishments and Progress (cont.)

Li-S Concept Cell Data







- S/C cathode fabrication process developed and optimized
- RTIL electrolyte confirmed to eliminate redox-shuttle effect of Li_2S_8
- Amine functionalization of carbon before melt-diffusion, with no other changes, increases capacity retention
- Testing in combination with RTIL-based gel electrolytes upcoming

Responses to Previous Year Reviewers' Comments

- Our project started in Oct, 2016, therefore it was not reviewed at last year's AMR

Collaboration and Coordination with Other Institutions

- The project is carried out by Jen's group and Yang's group at University of Washington
  - Jen: design and characterization of RTIL, design and characterization of fictionalized polyelectrolytes, surface modification of mesoporous carbon
  - Yang: mesoporous carbon characterization, surface modification of mesoporous carbon, design and electrochemical characterization of battery cells

- In the past year, we did not have any other collaborator.

Remaining Challenges and Barriers

- Gel electrolyte designs which incorporate novel chemical groups into the crosslinked PEG framework must continue to be optimized, and their subsequent effect on the gel's properties determined unambiguously.
- The relevant electrochemical (redox potential and reversibility, charge transport and transfer kinetics) and mechanical (tensile strength, toughness, self-healing ability) properties of NDI-based materials must be characterized and tuned.
- Interaction of Li_2S_x species with chemical "trapping" groups of varying design must be carefully studied to ascertain the relevant mechanisms of interaction, and their resulting effect on battery performance.
- Procedures for incorporation of S/C active materials into host gel matrices must be developed, and the resulting cathodes tested to determine the effect of gel composition on battery performance.

Proposed Future Research

- **Immediate Future**
  - Study conductivity, Li stripping/plating, and tensile strength of gel electrolytes
  - Study redox properties, tensile strength, and tunable self-healing ability of NDI-Py materials
  - Incorporate S/C particles into gel materials to form functional cathode
  - Characterize Li_2S_x solubility and diffusion in both liquid and gel electrolytes
  - Functionalize mesoporous carbons with unique chemical groups and study their interaction with Li_2S_x species via in-situ spectroscopy and concentration measurements
- **Before March 2018**
  - Synthesize and characterize new chemical starting materials
  - Demonstrate a gel electrolyte with self-healing properties
  - Develop structure-property relationships amongst gel electrolytes of varying composition
  - Combine best-performing materials to demonstrate gel-based S/C cathodes with high capacity and vastly improved retention

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

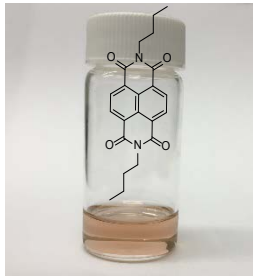
Summary

- **Relevance**
  - Rational molecular design 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**
  - Mesoporous carbon with attached chemical functionality for improved kinetics and distribution/retention of sulfur
  - RTIL-based polyelectrolyte gels for Li metal compatibility, reduced polysulfide solubility
  - Polysulfide “trapping” through interaction with designed molecular components to retain and utilize sulfur in cathode
  - Self-healing materials based on NDI/Py to heal mechanical damage from cell operation
- **Technical Progress**
  - Initial novel chemical materials successfully synthesized
  - Gel fabrication conditions developed and first gels produced
  - Self-healing demonstrated in polymeric NDI material with Py-based linker
  - S/C composites synthesized and characterized
  - Versatile carbon functionalization procedure developed
  - Initial cell results indicate proof-of-concept for functionalized S/C and RTIL-based electrolyte
- **Future Work**
  - Improved polyelectrolyte gel and self-healing materials design and testing underway
  - Novel molecular groups being developed for carbon and electrolyte improvement
  - In-situ methods for study of polysulfide interaction w/ molecules being developed

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

Technical Back-Up Slides

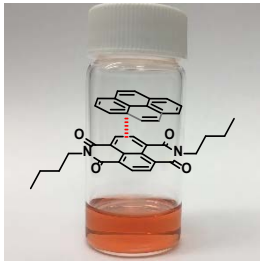
NDI-Py Interaction

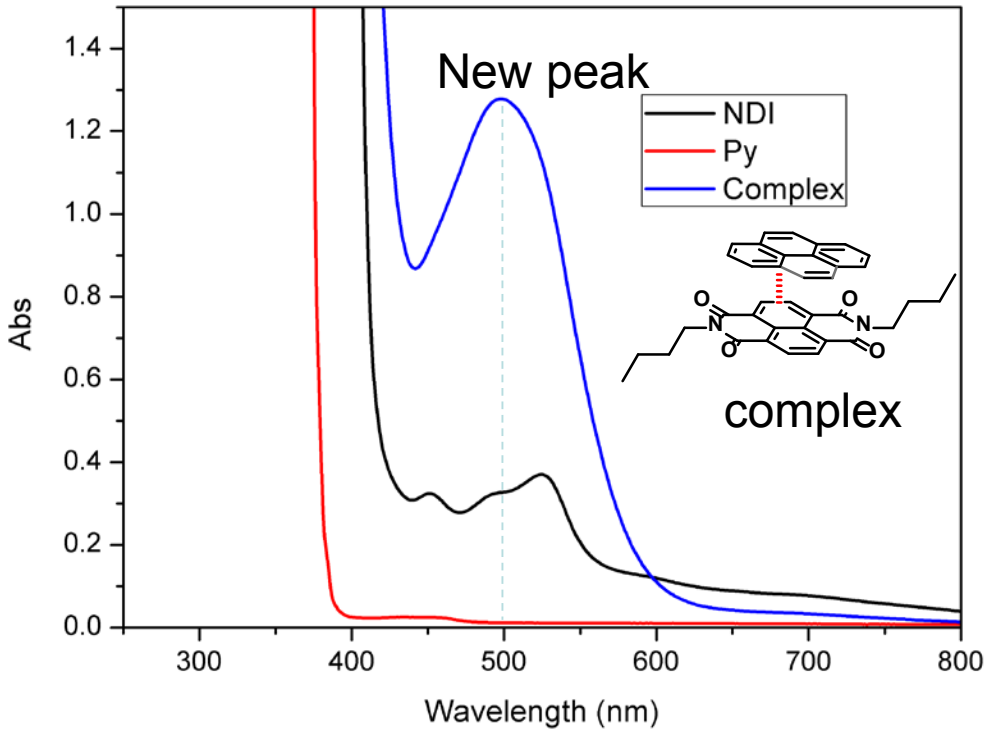


N,N'-dibutyl-1,4,5,8-naphthalenediimide (NDI)

+

Pyrene (Py)





- Interaction between NDI and Py demonstrated in model compounds. The location of the new peak is almost identical to that displayed by PENDI + Py Linker. Interaction strength determined by UV-Vis dilution method.

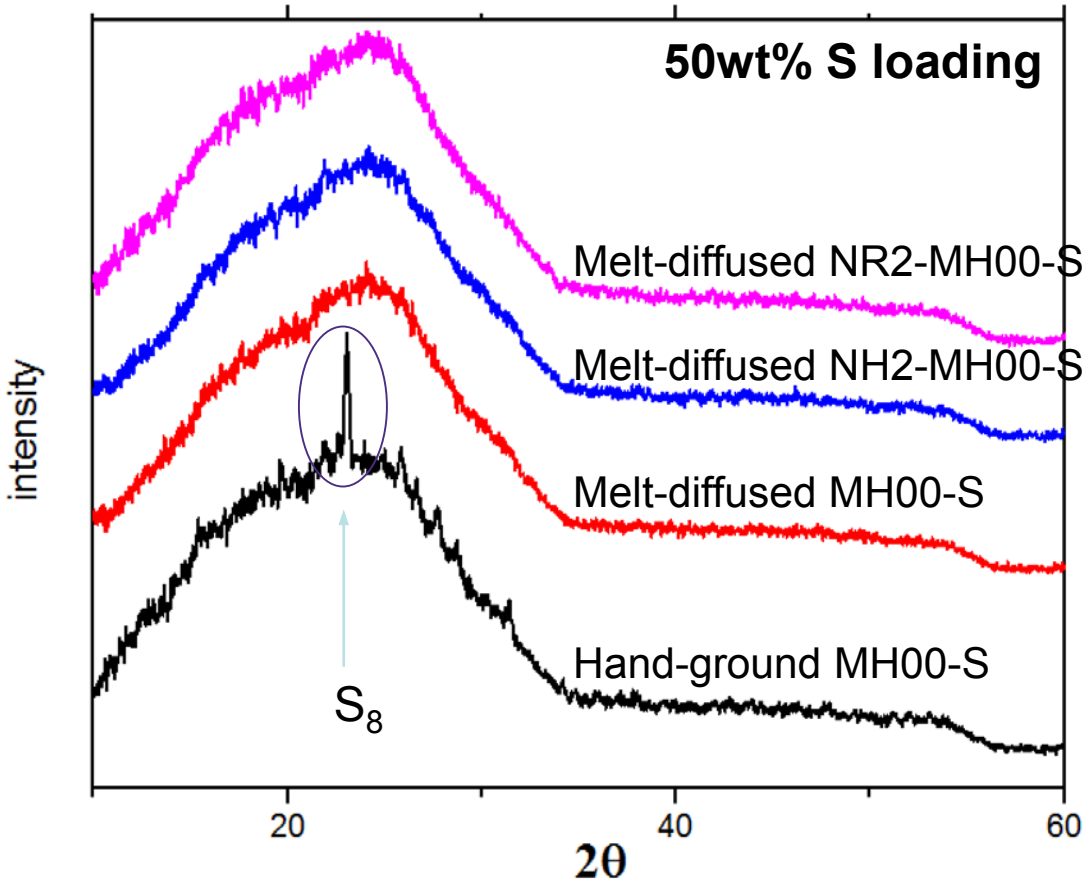
0.03 mol/L in dichloromethane (DCM), 25°C.

K_a= 65.15 M^{-1}

△G = **-8.19** KJ/mol

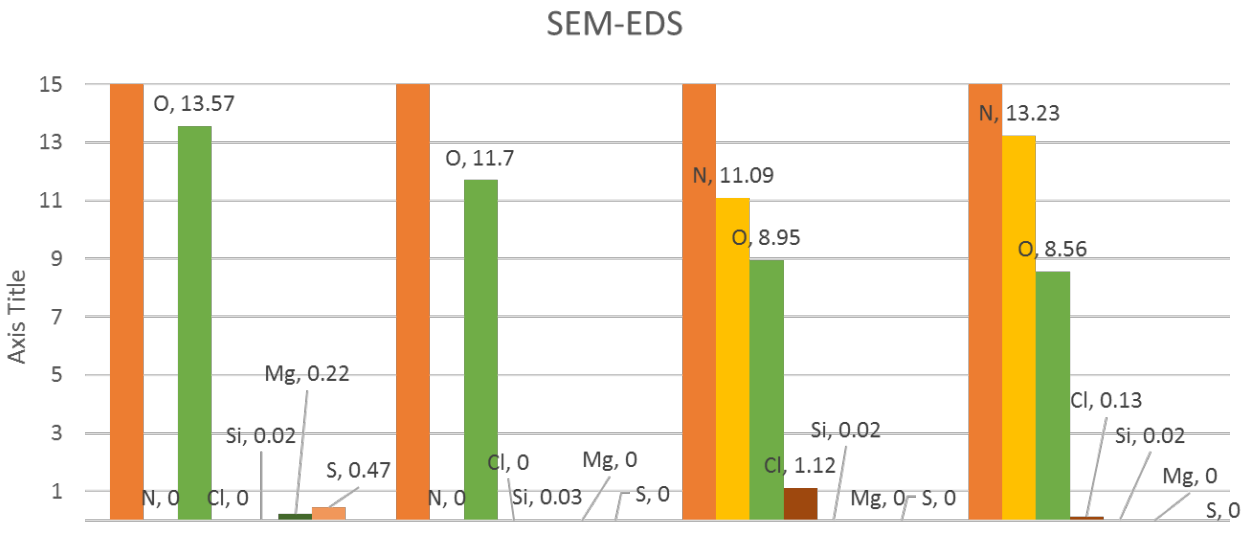
(Tested in DCM)

Mesoporous Carbon with S_8



- XRD of mesoporous carbon samples with S_8, either physically ground together or infiltrated *via* melt-diffusion.
- Disappearance of the bulk S_8 peak indicates that the melt-diffusion procedure successfully integrated all S_8 into the carbon mesopores.

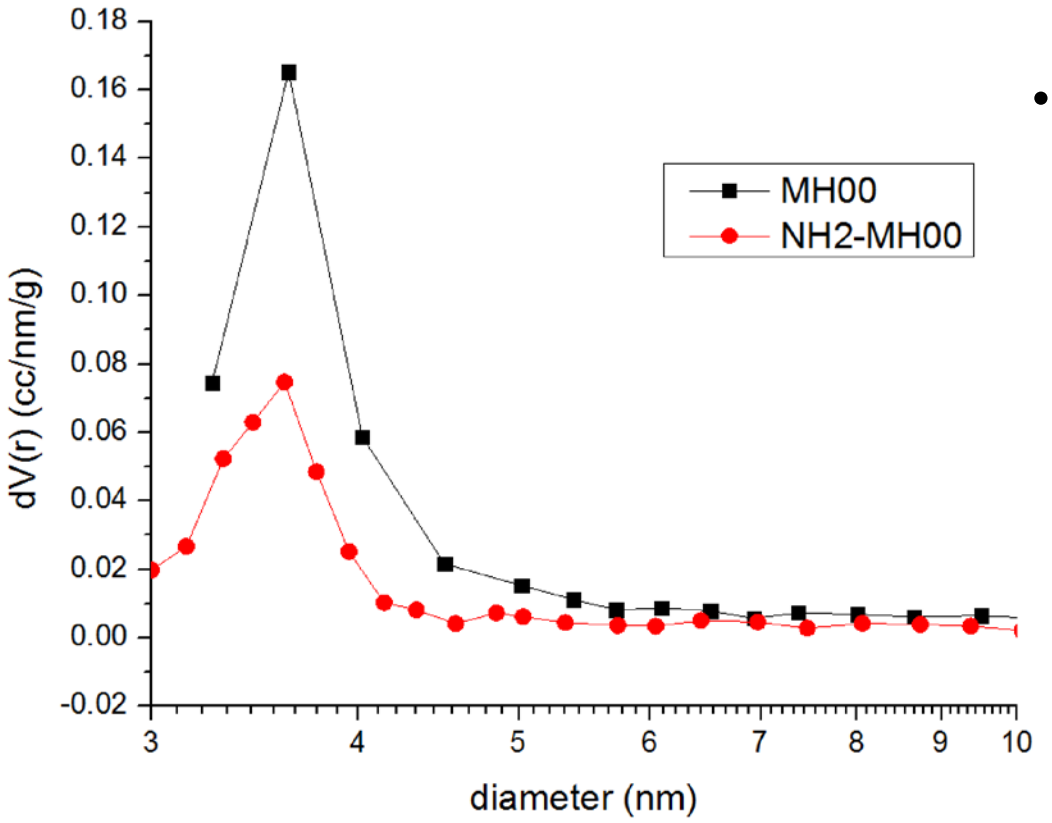
Functionalizing Mesoporous C



	Pristine MH00	washed MH00	NH2 MH00	NR2 MH00
C	85.72	88.27	78.82	78.07
N	0	0	11.09	13.23
O	13.57	11.7	8.95	8.56
Cl	0	0	1.12	0.13
Si	0.02	0.03	0.02	0.02
Mg	0.22	0	0	0
S	0.47	0	0	0

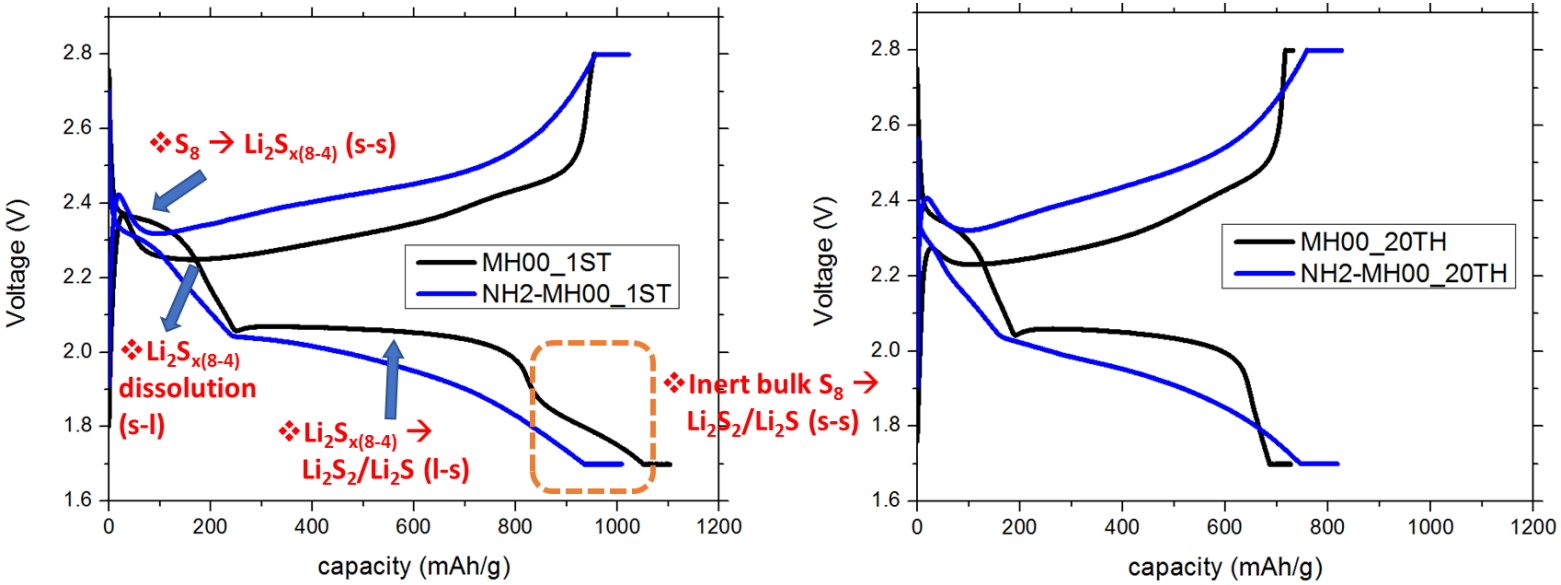
- EDS data confirms presence of nitrogen after functionalization with two different types of amine groups

Functionalizing Mesoporous C



- Pore size analysis of mesoporous carbon using the BET method, before and after chemical treatment, also confirms successful functionalization due to the reduction in pore volume and shift towards smaller pore sizes.

Electrochemical Properties



- 1st and 20th cycle voltage traces from melt-diffused S/C cathodes, fabricated with either as-received mesoporous carbon or –NH_2-funtionalized carbon. Notably, capacity of the –NH_2-containing sample is higher after 20 cycles, but cell overpotential is also higher during both charge and discharge. Perhaps an indication that entrapment of Li_2S_x in the carbon matrix, due to physical interaction with amine, forces further reaction to proceed *via* a kinetically-limited solid-state mechanism.
- We are exploring other functional groups which may provide both improved retention and improved kinetics.