Addressing Internal “Shuttle” Effect: Electrolyte Design and Cathode Morphology Evolution in Li-S Batteries

Perla B. Balbuena
Texas A&M University
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Overview

Timeline
• Start date: October 1, 2014
• End date: September 30, 2017
• Percent complete: 50%

Barriers
• Barriers/targets addressed
  – Loss of available capacity
  – Materials evolution during cycling
  – Lifetime of the cell

Budget
• Total funding: $990,000
  – DOE share: $990,000
  – Contractor share: Personnel
• Funding received
  – FY15: $285,345
  – FY 16: $325,189

Partners
• Interactions/ collaborations
  – Partha Mukherjee (TAMU Co-PI)
  – Vilas Pol (Purdue Univ., Co-PI)
• Project lead: TAMU
Relevance/Objectives

- **Objective:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide shuttle with advanced cathode structure design.

- **FY 2016 goals:** Understand Li$_2$S deposition reactions; influence of cathode mesostructure on strain accommodation; and SEI nucleation in presence of polysulfides with atomistic and mesoscopic modeling and coin cell testing.

- **Addressing targets and barriers:**
  - Controlled cathode mesoporous structures synthesized with a novel sonochemical method and new electrolyte formulations based on mesoscale and atomistic modeling efforts.

- **Impact:**
  - Alternative electrolyte chemistries and improved cathode architectures to deliver Li/S cells operating for 500 cycles at efficiency greater than 80%.
Relevance/Milestones

• a) Synthesis of C/S hybrid cathode materials and advanced characterization. (Dec. 14) **Completed**
• b) Determine structure and reactivity of PS/Li interface. (Mar. 15). **Completed.**
• c) Identification of reactions at the C/S cathode. (June 15). **Completed.**
• d) Analysis of cathode microstructure with mesoscopic model and experimental characterization. (Sept.15) **Completed (Go/No-Go)**
• e) Coin cell testing of C/S electrodes. (Dec.15) **Completed**
• f) Electrochemical and transport analysis of deposition and diffusion rates in composite cathodes- (Mar.16) **Completed**
• g) Influence of mesostructure on strain accommodation (June 16) (Ongoing)
• h) Reaction mechanisms and SEI formation at the Li anode in presence of PS species (Sep. 16) (Ongoing) (Go/No-Go)
Overall Technical Approach/Strategy:

- A mesoscale model of electrode mesoporous structures based on stochastic reconstruction allows virtual screening of cathode microstructural features and effects on electronic/ionic conductivity and morphological evolution.
- Interfacial reactions at the anode due to the presence of polysulfide species will be characterized with ab initio methods.
- Data and detailed structural and energetic information from atomistic-level studies used in mesoscopic-level analysis of cathode interfacial reactions.
- Novel sonochemical fabrication method for controlled cathode mesoporous structures and new electrolyte formulations based on mesoscale and atomistic modeling efforts.

Progress towards FY15 and FY16 milestones and Go/No Go decisions: New understanding of interfacial anode chemistry and deposition reactions at the cathode. Analysis and test of materials for PS retention at the cathode.
Technical Accomplishments: Barriers Addressed

• Complexity of Li metal reactivity
  – *Characterized PS decomposition* at the Li metal anode and formation of a Li$_2$S film

• Control of cathode microstructure
  – *Novel sonochemical process* allows for low-cost and simple process for fabrication of effective C-S cathodes. Mesoscopic modeling reveals effects of microstructure on macroscopic properties

• PS retention at cathode
  – *Identified and tested specific materials* to retain soluble PS species at the cathode
Technical Accomplishments
Carbon compartments/S composites

- Pyrolysis of starch produces a porous carbon substrate.
- Sonochemistry allows high T (5000 K), high P (1000 atm), rapid thermal rates (100K/s), and stream speeds (400 km/h) via acoustic cavitation.
- Sonochemical reduction of $\text{Na}_2\text{S}_2\text{O}_3$ to S in presence of dil $\text{HCl}_{(aq)}$

**Milestone Q1/Y1:** Lab scale C/S composite synthesized and characterized
Technical Accomplishments
CC/S composites: characterization

- Orthorhombic $\alpha$-sulfur formed in the composite via sonochemical synthesis (from XRD analysis)

- 47.64 %-wt. sulfur loaded into the CC/S composite (from TGA analysis)

Milestone Q1/Y1: Lab scale C/S composite synthesized and characterized
Technical Accomplishments

CC/S composites: SEM & mapping

- Pyrolysis of commercial starch produces a bimodal-porous carbon with large micro-compartments and small pores
- Sonochemical procedure creates a thin layer of sulfur coating surface and inhabiting pores

Milestone Q1/Y1: Lab scale C/S composite synthesized and characterized
Technical Accomplishments: Effects of Carbon at the C/S Cathode

Fast reduction of $S_8$: Main products $S_2^-$ and $S_3^-$
$S_2^-$ is reduced and trapped at the C edge

Milestone Q3/Y1: Dissolution, reduction, and lithiation of S at the C-S cathode
Technical Accomplishments: Soluble PS Retention at the Cathode Surface

PS can form strong covalent bonds but no dissociation was found on the MnO₂ (001) plane in contrast to Fe₂O₃ surfaces.

PS retention mechanisms have been identified.

Milestone Q3/Y1: Dissolution, reduction, and lithiation of S at C-S cathode
Technical Accomplishments: Microstructure variation due to deposition

**Milestone Q4/Y1:** Elucidate cathode morphology evolution and microstructure transport interaction
Technical Accomplishments:
Multiscale Modeling of Li-S Battery

Milestone Q2/Y2: Gain an understanding of the mesoscopic reactions using electrochemical and transport modeling
Technical Accomplishments

CC/S composites: rate performance

- 750mAh/g capacity at 28 mA/g specific current.
- Electrolyte: DOL (50 %-vol.), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (50 %-vol.), Li TFSI salt (1.0 M conc.)

Milestone Q1/Y2: Coin cell testing of C/S electrodes
Technical Accomplishments:
Reactivity of Soluble PS at the Li Metal Anode

Long-chain Li$_2$S$_8$ polysulfide extremely reactive with lithium

<table>
<thead>
<tr>
<th>Possible reactions</th>
<th>Gas-Phase</th>
<th>EC Solvent</th>
<th>DOL Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E$ (0K)</td>
<td>$\Delta G (298K)$</td>
<td>$\Delta E$ (0K)</td>
</tr>
<tr>
<td>$\text{Li}_2\text{S}_8 + 2\text{Li} \rightarrow \text{Li}_2\text{S} + \text{Li}_2\text{S}_7$</td>
<td>-3.56</td>
<td>-3.43</td>
<td>-5.53</td>
</tr>
<tr>
<td>$\text{Li}_2\text{S}_8 + 2\text{Li} \rightarrow \text{Li}_2\text{S}_2 + \text{Li}_2\text{S}_6$</td>
<td>-5.63</td>
<td>-5.38</td>
<td>-6.02</td>
</tr>
<tr>
<td>$\text{Li}_2\text{S}_8 + 2\text{Li} \rightarrow \text{Li}_2\text{S}_3 + \text{Li}_2\text{S}_5$</td>
<td>-5.32</td>
<td>-5.17</td>
<td>-6.19</td>
</tr>
<tr>
<td>$\text{Li}_2\text{S}_8 + 2\text{Li} \rightarrow 2\text{Li}_2\text{S}_4$</td>
<td>-6.95</td>
<td>-6.69</td>
<td>-6.28</td>
</tr>
</tbody>
</table>

All reactions exothermic and $\Delta G < 0$ (spontaneous). Energies in eV

Milestone Q2/Y1: Nucleation and growth of PS deposits at Li metal surface
Technical Accomplishments: Nucleation and Growth of Li$_2$S at Li Surfaces

Milestone Q2/Y1: Thermodynamics and kinetics of nucleation and growth of PS deposits at the Li metal surface

PS (yellow) extremely reactive; decomposes before salt or solvent
Technical Accomplishments:

Li$_2$S Film growth: Mesoscale modeling

Milestone Q2/Y1: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface

Fan et al., Adv. Mater. 27(2015)5203
Technical Accomplishments:
How to defer the surface passivation

Milestone Q2/Y1: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface
Responses to Previous Years Reviewers’ Comments

This project started FY15; it was not evaluated last year
Collaboration and Coordination with Other Institutions

• **Purdue University:** This project is a collaboration between Texas A&M University (Balbuena, Mukherjee) and Purdue University (Pol). The groups communicate via teleconference and site visits.

• **Pacific Northwest National Laboratory (PNNL):** The TAMU team interacts with the group of Dr. Jason Zhang regarding analysis of strategies to mitigate extreme Li metal reactivity. We are currently investigating the reasons for the apparent mitigation effects caused by high salt concentrations as a function of the nature of the salt.

• **Argonne National Laboratory (ANL):** Dr. Vilas Pol (Purdue) collaborates with the group of Dr. Jeffrey Elam and Dr. Anil Mane at ANL in the applications of ALD coatings for polysulfide capture at the cathode.
Remaining Challenges and Barriers

• Characterize **SEI reactions at the Li metal anode** and effects of higher salt concentration on such reactions.
• Evaluate influence of **mesostructure on strain accommodation** in the cathode.
• Identify **reasons for failures and successes of specific electrolyte compositions** and impact on Li anode behavior.
• Estimate the influence of cathode microstructure and electrolyte properties on **cathode performance**.
• **Scale up** of cathode composites.
Proposed Future Work

• **Rest of FY16:**
  - effects of deposition induced stress in cathode structure
  - mechanisms of SEI reactions at anode as functions of electrolyte composition
  - reasons for electrolyte failure and success

• **FY17:**
  - influence of cathode structure and electrolyte properties on cell performance
  - develop stable electrolytes
  - produce 3-5gr of C/S composite and achieve capacity > 800 mAh/g during at least 400 cycles
• **Relevance:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide shuttle with advanced cathode structure design.

• **Approach:** Synthesis, characterization, and testing of a C/S composite cathode guided by multiscale modeling (atomistic and mesoscopic) focusing on electrolyte composition and cathode morphology effects on cell performance.

• **Technical Accomplishments:** Development of low-cost synthesis and characterization of a C/S composite cathode with promising performance; identification of effects of carbon on sulfur reductions; effects of microstructure variation due to deposition; elucidation of reactions of the polysulfides on the Li metal anode.

• **Collaborations:** Purdue University (Co-PI); evaluation of additives and salts (with PNNL); cathode coatings (with ANL).

• **Future Work:** Development of stable electrolytes; scale up cells and achieve target capacity; model effects of cathode microstructure on cell performance.
Technical Back-Up Slides
Methodology

DFT optimization: Anode Model and Electrolyte Species

- **Optimizations performed using the Vienna ab initio simulation package (VASP)**
- Perdew-Burke-Ernzerhof functional (GGA-PBE)
- Cutoff energy: 400 eV
- LiTFSI (G09: B3PW91/6-311++G(p,d))

*Most stable facet*
Methodology

Ab-initio MD simulations at 330 K (~20 ps)

**Methodology**

- Ab-initio MD performed using VASP
- GGA-PBE functional
- Cutoff energy: 400 eV
- 2x2x1 k-points Monkhorst–Pack mesh sampling
- Timestep: 1 fs
- NVT ensemble

\( \rho = 1.32 \text{ g/cm}^3 \)  \hspace{1cm} \rho = 1.06 \text{ g/cm}^3 \hspace{1cm} \rho = 0.87 \text{ g/cm}^3 

(Pure Solvents)
Li$_2$S Growth Model: Deposition + Diffusion

**Coarse-Grained Kinetic Monte Carlo Method**

- Only consider the insoluble Li$_2$S molecule deposition on crystal Li$_2$S (111) surface
- A coarse-grained model is developed to describe the structure of Li$_2$S (111) film.

$k_0$: reaction rate constant
$N_A$: Avogadro constant
$V$: Volume of electrolyte
$S$: solid-electrolyte interfacial area
$S_a$: area per Li$_2$S unit
$C$: reactant concentration
$\Theta$: Li$_2$S solubility
$\nu$: jump frequency
$E_b$: diffusion barrier
$\kappa$: Boltzmann constant
$T$: temperature

- The diffusion process is governed by
  \[ K_{diff} = \nu \cdot \exp\left(-\frac{E_b}{\kappa T}\right). \]
- The deposition process is governed by
  \[ K_{dep} = k_0 N_A V \frac{S_a}{S} \left( C_{Li}^2 + C_{S^2-}^2 - \Theta \right). \]
Li$_2$S Growth Model: Desorption

Li$_2$S desorption should be considered due to the relatively weak chemical interaction.

\[ R_{des} = \frac{2\pi T}{h} \exp\left(\frac{E_{ads}}{\kappa T}\right) \]

\[ E_{ads} = \frac{1}{x}(E(G, xLi_2S) - E(G) - xE(Li_2S)) \]
Impedance Response of Cathode of Li-S Battery

\[ R_{film} = \rho \cdot \delta \]
\[ C_{film} = \frac{\varepsilon \cdot \delta}{\delta} \]

- \( R_{contact} \): Contact Resistance between carbon substrate and thin layer.
- \( R_{Film} \): Resistance from thin layer.
- \( R_{ct} \): Charge transfer resistance from electrochemical reaction.
- \( C_{Film} \): Capacitance from thin layer.
- \( C_{di} \): Capacitance from double layer.

*Note: Diffusion resistance is not included and discussed in this model.*
Cell Performance Prediction: Electrochemical Reactions

**Anodic Reaction**

\[ Li \rightleftharpoons Li^+ + e^- \]

**Cathodic Reactions**

\[ S_{8(l)} \rightleftharpoons S_{8(s)} \]

\[ \frac{1}{2} S_{8}^{2-} \rightleftharpoons \frac{1}{2} S_{8(l)} + e^- \]

\[ 2S_{6}^{2-} \rightleftharpoons S_{8}^{2-} + e^- \]

\[ \frac{3}{2} S_{4}^{2-} \rightleftharpoons S_{6}^{2-} + e^- \]

\[ S_{2}^{2-} \rightleftharpoons \frac{1}{2} S_{4}^{2-} + e^- \]

\[ S^{2-} \rightleftharpoons \frac{1}{2} S_{2}^{2-} + e^- \]

\[ 2Li^+ + S^{2-} \rightleftharpoons Li_2S \downarrow \]

Other reactions are electrochemical in nature
Cell Performance Prediction: Governing Equations

Balance for species $i$

$$\frac{\partial}{\partial t} (\varepsilon C_i) = \nabla \cdot \left( D_i \nabla C_i + z_i \frac{D_i}{RT} F C_i \nabla \phi_e \right) + R_i$$

Charge conservation

$$\nabla \cdot \left( \sum_i z_i F \left( D_i \nabla C_i + z_i \frac{D_i}{RT} F C_i \nabla \phi_e \right) \right) = -a \sum_j i_j$$

Butler-Volmer Equation for reaction $j$

$$M \rightleftharpoons M^+ + e^-$$

$$i_j = i^0_j \left\{ \exp \left( \frac{F}{2RT} \eta_j \right) - \left( \frac{C_{M^+}}{C_{M^{ref}}} \right) \exp \left( - \frac{F}{2RT} \eta_j \right) \right\}$$

$$\eta_j = \phi_s - \phi_e - U_j$$

- $C_i$: Concentration
- $D_i$: Diffusivity
- $\phi_e$: Electric potential in electrolyte
- $R_i$: Species generation rate
- $i_j$: Current generation rate due to electrochemical reaction $j$
Details of Poromechanics: Lattice Spring Method

\[ u_{\text{total}} = u_{\text{elastic}} + u_{\text{swelling}} + u_{\text{creep}} \]

Current configuration: (n+1)-th step

Initial configuration

Previous equilibrium configuration: (n)-th step

\[ \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{\partial u_k}{\partial x_i} \frac{\partial u_k}{\partial x_j} \right) \]

Governing differential equation:

\[
\int_{t'}^{t+\Delta t} S_{ij} \delta^{t+\Delta t} \varepsilon_{ij} \, dV - \int_{t'}^{t+\Delta t} F_i \delta^{t+\Delta t} u_i \, dV \approx 0
\]

Internal energy

External energy

Random Lattice Spring Method

Axial spring

Shear spring

Fracture in Lithium Ion Battery Particles

Delithiation → 4C

High capacity anode materials
Details of Poromechanics: Volume Expansion

\[
\frac{d\varepsilon}{dt} = V_{S_8(s)} \cdot r_{S_8(s)} - V_{Li_2S} \cdot r_{Li_2S} + \Delta \varepsilon_{\text{mech}}
\]

Effective volume change due to precipitation induced volume expansion.

- External load is the pressure induced by precipitation:
  \[\Delta p_{\text{precip}} = B_{\text{elec}} \Delta \varepsilon_{\text{precip}}\]
  Bulk modulus of the electrolyte \(\rightarrow\) Electrolyte property
  Precipitation induced strain \(\rightarrow\) Pore confinement effect

- Precipitation induced strain is given as:
  \[\Delta \varepsilon_{\text{precip}} = V_{Li_2S} \cdot \Delta m_{Li_2S} - V_{S_8(s)} \cdot \Delta m_{S_8(s)}\]
  where, \(\Delta m_{Li_2S} = 8 \Delta m_{S_8(s)}\)