Unraveling Molecular Level Reactivity of Lithium Polysulfides: A Modeling Perspective

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Lithium Sulfur Batteries: Mechanisms, Modelling and Materials
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Outline

- Modeling approaches for understanding charge and discharge chemistries in Li-S batteries at the molecular level
  - Molecular speciation
  - Electrolyte stability

- Results for Li-S molecular reactivity
  - Thermochemical predictions for lithium polysulfide and polysulfide species
  - Electrolyte stability

- Future directions for Li-S computational studies
  - Bulk and interfacial processes
  - Related modeling studies Li-O\textsubscript{2} batteries

- Summary
Molecular aspects of discharge and charge chemistries

- **Contained architecture**
  - a porous conductive host physically retains the sulfur species within the positive electrode volume

- **Catholyte system**
  - functions as both the electrolyte and positive electrode

- Lithium polysulfides and polysulfides in electrolytes are important for both systems

Nazar et al, MRS Bull. 2014
Typical problems/concerns related to Li-S energy storage systems

- Capacity fade
  - High solubility of poly sulfides and materials loss
  - Sulfur -shuttle mechanisms
  - Electrolyte stability concerns

- Complex chemistry makes understanding charge and discharge chemistries difficult (many valence states of S compared to O)
  - Reaction thermochemistry
  - Reaction barriers – kinetics
  - Nucleation and growth

- Anode failure
  - A universal problem for lithium metal anodes
  - Li-O$_2$, Li-S, and high energy Li-ion batteries
Solution Phase Thermochemistry – computational methods

- **G4 theory**
  - Gaussian-$n$ (Gn) theories (developed by Curtiss, Raghavachari, Pople)
  - Composite method using CCSD(T) and large basis set effects
  - Accurate molecular energies (IPs, EAs, Enthalpies) to 1 kcal/mol (0.05 eV)

- **DFT methods** (e.g. B3LYP)
  - Much faster
  - Use G4 theory to assess accuracy

- **Solution phase effects**
  - Continuum methods (PCM, SMD)
  - Explicit solvent molecules

- **Enthalpies and free energies**
- **Approximations** (solution effects, neglect surfaces)

**Examples of molecular reactions:**

- **Fragmentation:** $S_8 \rightarrow S_6 + S_2$
- **Reduction:** $S_8 + 2e \rightarrow S_8^{2-}$
- **Disproportionation:** $S_8^{2-} \rightarrow 2S_3^{1-} + (1/4)S_8$
- **Reduction:** $S_3^{1-} + e \rightarrow S_3^{2-}$
- **Association:** $S_3^{2-} + 2Li^{1+} \rightarrow 3Li_2S_3$
Electrolyte stability – computational methods

- DFT for finding transition states and reaction barrier
  - B3LYP
  - G4 theory to assess accuracy in some cases
  - Solution effects included
- Equations
  - Eyring eqn
    \[ k(T) = \frac{k_B T}{h c_0} \exp\left(-\frac{\Delta G_{TS}}{RT}\right) \]
- Lifetimes
  - If \( \Delta G^{TS} > 1.1 \text{ eV} \), the reaction is kinetically slow (half life is \( \sim \text{days} \))
  - If \( \Delta G_{\text{rxn}} < 0 \), the reaction is thermodynamically feasible

Reaction example (proton/hydrogen abstraction; Assary et al JPCC 2014)
Electrolyte studies – explicit incorporation of solvent and salt molecules

- Ab initio Molecular Dynamics (AIMD)
  - Explicit solvent and salt molecules
  - Density functional based
  - Properties
    - Solvation structure
    - Solubilities
    - Decomposition pathways; barriers

- ReaxFF MD
  - Force fields can incorporate bond breaking
  - Handle larger systems

- Classical MD

Potential energy surface for decomposition of LIBOB salt from an AIMD Simulation (Energy Technology 2014)

Solubility computation
Outline

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  - Molecular speciation
  - Electrolyte stability
- Results for Li-S molecular reactivity
  - Thermochemical predictions for lithium polysulfide and polysulfide species
  - Electrolyte stability
- Future directions for Li-S computational studies
  - Bulk and interfacial processes
  - Related modeling studies Li-O₂ batteries
- Summary
Possible reaction types in Li-S systems

(I) Fragmentation reactions of S₈
   - Formation of S₁, S₂, S₃, S₄, S₅, S₆, S₇

(II) Electrochemical reduction reactions of polysulfides and lithium polysulfides
   - S₈¹⁻, S₈²⁻, S₇¹⁻, S₇²⁻, S₆¹⁻, S₆²⁻, S₅¹⁻, S₅²⁻, S₄²⁻, S₄¹⁻, S₃¹⁻, S₃²⁻, S₂¹⁻, S₂²⁻, S¹⁻, S²⁻
   - Li₂S₈, Li₂S₇, Li₂S₆, Li₂S₄, Li₂S₃, Li₂S₂, Li₂S

(III) Association, dissociation, disproportionation reactions of polysulfides (Sₙ⁻ₓ⁻) and lithium poly sulfides (LiPS)

IV) Electrolyte decomposition by polysulfides
Over 100 reaction energies (in solution – DOL, DME) calculated for the Li-S system using the accurate G4MP2 method (Assary, Moore, and Curtiss, JPCC 2014) – provides accurate thermochemical data for interpretation of experiments

(I) 8 fragmentation reactions of S₈

(S₈ + 2e → S₈²⁻)

S₈ → S₆ + S₂

S₈²⁻ → 2S₃¹⁻ + (1/4)S₈

S₃¹⁻ + e → S₃²⁻

S₃²⁻ + 2Li¹⁺ → 3Li₂S₃

(II) 30 reduction potentials

(III) 75 association, dissociation, disproportionation reactions
Summary of likely reaction mechanisms based on the computed free energies and reduction potentials (~100 reactions)

- **R = reactions (Green cell)**
- **Green cell with 2Li+: Addition of 2Li+ and subsequent fragmentation**
- **Blue cell: Addition of 2Li+ ions**
- **Red cell: undergoes further reductive decomposition**

### Lithium polysulfides

<table>
<thead>
<tr>
<th>Polysulfide anions</th>
<th>S\textsubscript{8}</th>
<th>S\textsubscript{8}\textsuperscript{1-}</th>
<th>S\textsubscript{8}\textsuperscript{2-}</th>
<th>2Li\textsuperscript{+}</th>
<th>Li\textsubscript{2}S\textsubscript{8}</th>
<th>Li\textsubscript{2}S\textsubscript{8}\textsuperscript{2-}</th>
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**Assary et al., Journal of Physical Chemistry C, 2014, 118, 11545**
Some key conclusions of the study

- Fragmentation energies of $S_8$ and $Li_2S_8$ to small sulfur clusters ($S_n$, $n=1$ to 7) and lithium sulfides in solution
  - relative stability of fragments is $S_8 > S_6 + S_2 > S_5 + S_3 > 2S_4$.
  - fragmentation reaction of $Li_2S_8$ to $Li_2S_6$ and $Li_2S_4$ are exergonic.
  - further fragmentation reactions of $Li_2S_6$ and $Li_2S_4$ are endergonic.

- Reduction potentials
  - polysulfides and lithium sulfides except $Li_2S_3$ and $Li_2S_2$ can occur under discharge conditions of 2.5-2.0 V.
  - reduction potentials of $Li_2S_3$ and $Li_2S_2$ are 0.5 and 0.06 V, respectively, indicating that deep discharge is required to reduce these species.

- Dissociation/association reactions of polysulfide anions and lithium polysulfides in solution
  - Explored a detailed reaction network - explains likely reaction mechanisms during the discharge process.
  - major intermediates are $S_2^{2-}$, $S_3^{2-}$, $S_4^{2-}$, $S_3^{1-}$; a likely intermediate upon complete utilization of $S_8^{2-}$ is $S_3^{2-}$.
  - suggests that transformation of $Li_2S_8$ to $Li_2S$ and $Li_2S_2$ upon the discharge is likely.
Assessment of C-H bond stability of TEGDME in the presence of reactive intermediates

- Hydrogen/proton abstraction from TEGDME is thermodynamically not feasible
Assessment of C-O bond Stability of TEGDME against polysulfides in Li-S systems

- Most reactive species for TEGDME are Li$_2$S$_2$, Li$_2$S$_3$, and S$_2^{2-}$
- Explains PC instability
Computed reaction profile of C-O bond breaking of ether via chemical reaction with \( S_{2}^{2-} \) and \( \text{Li}_2\text{S}_2 \)

- Reaction of ether with \( \text{Li}_2\text{S}_2 \) is irreversible and results in the decomposition of the electrolyte initiated by the C-O bond cleavage.

Energy profile of TEGDME: decomposition by \( \text{Li}_2\text{S}_2 \)

C-O bond in linear ethers are more stable than in cyclic ethers against \( S_{2}^{2-} \) ions
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- Summary
Atomistically informed larger scale modeling -future

- Example: modeling of Li-S nucleation and growth during discharge
- Input from lower-scale computations (DFT, G4MP2, AIMD, etc)
  - Reaction kinetics
  - Interfacial processes
  - Bulk properties – diffusion, conductivity
- Large-length and long-time scale modeling
  - Capture the nucleation and growth processes taking place during discharge
  - Mesoscale/phase field modeling
  - Continuum level modeling

(AIMD thermal equilibrated sample of Li$_2$S, S$_8$, Li$_2$S$_6$ and Li$_2$S$_8$@CNTs system at T ~ 300 K)
Disproportionation reactions of LiO$_2$ – quantum chemical studies

- Disproportionation
  - $2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$
  - $n\text{LiO}_2 \rightarrow \left(\frac{n}{2}\right)\text{Li}_2\text{O}_2 + \left(\frac{n}{2}\right)\text{O}_2$

- Thermodynamically bulk LiO$_2$ is less stable than Li$_2$O$_2$ from DFT calculations

- DFT calculations reveal large differences in disproportionation barrier depending on cluster size – affects lifetimes

Implications: early (fast) disproportionation through dime and late (slow) disproportionation from LiO$_2$ deposits

Experimental confirmation from Raman studies


Interface processes – density functional studies

- A lithium superoxide-based battery (J. Lu et al, Nature 2016)
  - Cathode based on a reduced graphene oxide (rGO) with Ir nanoparticles and TEGDME/LiCF$_3$SO$_3$ as the electrolyte
  - Results provide evidence that LiO$_2$ is stable enough that it can be repeatedly charged and discharged with a very low charge potential (~3.2 V)
- DFT calculations provided insight into interface processes

DFT calculations reveal that templated nucleation and growth may be responsible for formation of crystalline LiO$_2$

DFT calculations show suppression of disproportionation by electrolyte at a LiO$_2$/electrolyte interface
Nucleation and growth in Li-O$_2$ batteries - atomistically informed mesoscale modeling

Mesoscale LiO$_2$ simulation
- growth will eventually takeover from nucleation
- ripening occurs (small particles disappear; large ones get larger)

Consistent with experiment from activated carbon based cathode

M. Welland et al, JCP, 2016
Summary and Future Perspective

Li-S thermochemistry and electrolyte stability

- **Reaction energies**
  - Highly accurate energies of over 100 Li-S reactions computed
  - Used these energies to explore possible reaction networks and find likely mechanisms during discharge

- **Stability**
  - Sulfides and polysulfides are reactive predominately due to the nucleophilicity
  - $\text{Li}_2\text{S}_2$ is most reactive intermediate
    - Decomposes ether solvent molecules via nucleophilic reaction with the C-O bond
  - Formation of $\text{CH}_3\text{-O-Li}$ and C-S moieties may present in the decomposition product

Future

- **Molecular level**
  - Screen electrolytes for stability, solubility, ion pairing
  - Reaction barriers for microkinetic modeling

- Atomistically informed mesoscale modeling of growth and nucleation in Li-S batteries

- Connection to experiment
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  - Argonne Leadership Computing facility
  - Center for Nanoscale Materials

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- **Thank you for listening**
  - Feel free to reach us: assary@anl.gov or curtiss@anl.gov