Modeling the next battery generation:
Lithium-sulfur and lithium-air cells

D. N. Fronczek, T. Danner, B. Horstmann, Wolfgang G. Bessler
German Aerospace Center (DLR)
University Stuttgart (ITW)
Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU)

wolfgang.bessler@dlr.de
www.bessler.info
Research profile: Computational battery technology

- Lithium-ion technology
  - LiFePO$_4$ batteries: Electrochemistry and impedance
    - Understanding and optimization of physicochemical behavior
  - Thermal management and runaway risk
    - Understanding and optimization of thermal and safety behavior
- Post-lithium-ion cells
  - Lithium-sulfur cells: Redox chemistry and transport
    - Analysis of cycling properties and chemical reversibility
  - Lithium-air cells: Multi-phase chemistry and reversibility
    - Improvement of porous air electrode
- Multi-scale and multi-physics modeling and numerical simulation
Motivation and approach
Lithium-sulfur
Lithium-air (organic)
Lithium-air (aqueous)
Conclusions
Motivation and approach
Lithium-sulfur
Lithium-air (organic)
Lithium-air (aqueous)
Conclusions
Li-S and Li-O: Challenges

- Complex multi-phase management
  - Li-S: Solid reactant $S_8$ and product $Li_2S$, solid precipitates
  - Li-O: Solid, liquid and gas phase involved
- Complex chemistry
  - Li-S: Polysulfide ion intermediates
  - Li-O: Oxygen reduction as traditional problem of electrochemistry
- Low cycleability, low efficiency
- Computational modeling for understanding and optimization
1D/2D generic modeling framework

- Electrochemical cell of up to seven layers
- Each layer consists of arbitrary number of solid, liquid and/or gaseous bulk phases
- Each layer can contain an arbitrary number of interfaces (phase boundaries)
- Each bulk phase consists of arbitrary number of chemical species
- Chemistry takes place at interfaces
- Transport mechanisms (liquid, solid, gas)
- Continuum (homogenization) approach

Chemical reactions at interfaces

- Mass-action kinetics describes chemical source terms $\dot{s}_i$

$$\dot{s}_i = \nu_i \left( k_f \prod_{j \in R_f} c_j^{v_j} - k_r \prod_{j \in R_r} c_j^{v_j} \right)$$

- Rate constants described by modified Arrhenius expression. Reverse rate follows from thermodynamic consistency.

$$k_f = A^f T^\beta \exp\left(-\frac{E^{\text{act}}}{RT}\right) \exp\left(-\frac{\alpha z F}{RT} \Delta \phi\right)$$

$$\frac{k_f}{k_r} = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

Preexponential factor

Temperature dependence

Activation energy $E^{\text{act}}$

Potential dependence

Half-cell potential $\Delta \phi$
Multi-phase management

- The volume fraction $\varepsilon_i$ of each phase $i$ depends on time:

$$\frac{\partial (\varepsilon_i \rho_i)}{\partial t} = R_i M_i$$

- Volume fractions sum up to one. Definition of compressible phase necessary:

$$\sum \varepsilon_i = 1$$

- Microstructural effects enter via interfacial area and transport coefficients:

$$A_{m,n}^V = A_0^V \cdot f(\varepsilon_m, \varepsilon_n)$$

$$D_i^{\text{eff}} = \frac{\varepsilon_i}{\tau_i^2} D_i, \quad \sigma_i^{\text{eff}} = \frac{\varepsilon_i}{\tau_i^2} \sigma_i$$

- Symbols:
  - $\varepsilon$ volume fraction
  - $\rho$ density
  - $R$ chemical formation rate
  - $M$ molar mass
  - $A^V$ volume-specific surface area / m$^2$/m$^3$
  - $D$ diffusion coefficient
  - $\sigma$ Conductivity
Mass and charge transport in liquid electrolyte

- Species conservation (Nernst-Planck equation)
  \[
  \frac{\partial (\varepsilon c_i)}{\partial t} = -\frac{\partial J_i}{\partial y} + \sum_m A_m^V \dot{s}_{i,m}
  \]
  \[
  J_i = -D_i^{\text{eff}} \frac{\partial c_i}{\partial y} - D_i^{\text{migr, eff}} \frac{\partial \phi_{\text{elyt}}}{\partial y}
  \]

- Charge neutrality
  \[
  0 = -\sum_i z_i F \frac{\partial J_i}{\partial y} + \sum_m z_i F A_m^V \dot{s}_{i,m}
  \]

- Diluted solution theory (Li-S)
  \[
  D_i^{\text{migr}} = \frac{z_i F}{RT} c_i D_i
  \]

- Concentrated solution theory (Li-O)
  \[
  D_\pm = D^0 + \frac{t_\pm \sigma D}{z_\pm F c_\pm}
  \]
  \[
  D_\pm^{\text{migr}} = \frac{t_\pm \sigma}{z_\pm F c_\pm}
  \]
DENIS: Detailed Electrochemistry and Numerical Impedance Simulation
In-house C/C++ software
Workhorse of the group

Multi-scale simulation framework

- Interfaces
- Electrode
- Cell
- Stack
- System
- MATLAB
  Coupling DNIS-SIMULINK
- ANSYS/COMSOL
  Coupling DNIS-ANSYS/COMSOL for CFD simulations
- LIMEX
  Implicit DAE solver (Deuflhard, Berlin)
- CANTERA
  Coupling with CANTERA (Goodwin, Caltech) for chemistry source terms and transport coefficients
Motivation and approach

Lithium-sulfur
Lithium-air (organic)
Lithium-air (aqueous)
Conclusions
Li-S battery modeling domain

Cathode properties:
- Thickness: 41 µm
- Phases (charged state):
  - Sulfur $\varepsilon = 0.16$
  - Carbon $\varepsilon = 0.06$
  - Electrolyte $\varepsilon = 0.78$
  - $\text{Li}_2\text{S}$ $\varepsilon = 10^{-7}$
- Interfaces:
  - Sulfur-Electrolyte
  - Carbon-Electrolyte
  - $\text{Li}_2\text{S}$-Electrolyte

Anode: Lithium metal
# Li-S battery model: Thermodynamics and transport

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar Gibbs energy / kJ·mol⁻¹</th>
<th>Density / Initial concentration</th>
<th>Diffusion coefficient / m²·s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0</td>
<td>5.34·10² kg·m⁻³</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>2.26·10³ kg·m⁻³</td>
<td></td>
</tr>
<tr>
<td>S₈(solid)</td>
<td>0</td>
<td>2.07·10³ kg·m⁻³</td>
<td></td>
</tr>
<tr>
<td>Li₂S</td>
<td>−441.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₄H₆O₃</td>
<td>0</td>
<td>9.831·10³ mol·m⁻³</td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>0</td>
<td>9.841·10² mol·m⁻³</td>
<td>1·10⁻¹⁰</td>
</tr>
<tr>
<td>PF₆⁻</td>
<td>0</td>
<td>9.830·10² mol·m⁻³</td>
<td>4·10⁻¹⁰</td>
</tr>
<tr>
<td>S²⁻</td>
<td>−405.08</td>
<td>8.127·10⁻¹⁰ mol·m⁻³</td>
<td>1·10⁻¹⁰</td>
</tr>
<tr>
<td>S₂²⁻</td>
<td>−422.29</td>
<td>5.141·10⁻⁷ mol·m⁻³</td>
<td>1·10⁻¹⁰</td>
</tr>
<tr>
<td>S₄²⁻</td>
<td>−450.91</td>
<td>1.966·10⁻² mol·m⁻³</td>
<td>1·10⁻¹⁰</td>
</tr>
<tr>
<td>S₆²⁻</td>
<td>−460.23</td>
<td>3.185·10⁻¹ mol·m⁻³</td>
<td>6·10⁻¹⁰</td>
</tr>
<tr>
<td>S₈²⁻</td>
<td>−461.20</td>
<td>1.750·10⁻¹ mol·m⁻³</td>
<td>6·10⁻¹⁰</td>
</tr>
<tr>
<td>S₈(liquid)</td>
<td>−48</td>
<td>1.868 mol·m⁻³</td>
<td>1·10⁻⁹</td>
</tr>
</tbody>
</table>

*Parameters converted from Kumaresan et al., J. Electrochem. Soc. 155, A576 (2008)*
Li-S battery model: Reactions and kinetics

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Preexponential factor, forward reaction</th>
<th>Preexponential factor, reverse reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li} \rightleftharpoons \text{Li}^+ + e^-$</td>
<td>$4.086 \cdot 10^{-9} \text{ m}^{-5} \cdot \text{mol}^2 \cdot \text{s}^{-1}$</td>
<td>$1 \text{ m}^{-2} \cdot \text{mol} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\text{S}_8^{(\text{solid})} \rightleftharpoons \text{S}_8^{(\text{liquid})}$</td>
<td>$1.900 \cdot 10^{-2} \text{ m}^{-0.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$</td>
<td>$1 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{S}_8^{(\text{solid})} + e^- \rightleftharpoons \frac{1}{2} \text{S}_8^{2-}$</td>
<td>$7.725 \cdot 10^{13} \text{ m}^{-0.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$</td>
<td>$2.940 \cdot 10^{-27} \text{ m}^{-0.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\frac{3}{2} \text{S}_8^{2-} + e^- \rightleftharpoons 2 \text{S}_6^{2-}$</td>
<td>$4.331 \cdot 10^{16} \text{ m} \cdot \text{mol}^{-0.5} \cdot \text{s}^{-1}$</td>
<td>$1.190 \cdot 10^{-23} \text{ m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\text{S}_6^{2-} + e^- \rightleftharpoons \frac{3}{2} \text{S}_4^{2-}$</td>
<td>$3.193 \cdot 10^{14} \text{ s}^{-1}$</td>
<td>$4.191 \cdot 10^{-24} \text{ m} \cdot \text{mol}^{-0.5} \cdot \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{S}_4^{2-} + e^- \rightleftharpoons \text{S}_2^{2-}$</td>
<td>$2.375 \cdot 10^{11} \text{ m}^{-0.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$</td>
<td>$7.505 \cdot 10^{-24} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{S}_2^{2-} + e^- \rightleftharpoons \text{S}^{-2}$</td>
<td>$4.655 \cdot 10^{12} \text{ m}^{-0.5} \cdot \text{mol}^{0.5} \cdot \text{s}^{-1}$</td>
<td>$4.738 \cdot 10^{-22} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$2 \text{Li}^+ + \text{S}^{2-} \rightleftharpoons \text{Li}_2\text{S}^{(\text{solid})}$</td>
<td>$2.750 \cdot 10^{-5} \text{ m}^6 \cdot \text{mol}^2 \cdot \text{s}^{-1}$</td>
<td>$8.250 \cdot 10^{-19} \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>

Li-S: Simulated discharge curve and phase change

- Discharge shows typical two-stage behavior.
- Solid $S_8$ is fully consumed before solid $Li_2S$ is formed.
Li-S: Simulated ionic species concentrations

- First stage: Sulfur polyanions are formed
- Second stage: Sulfur polyanions are reduced
- End of discharge: No more sulfur polyanions
Motivation and approach
Lithium-sulfur
Lithium-air (organic)
Lithium-air (aqueous)
Conclusions
Li-O battery modeling domain

Cathode properties:
- Thickness: 750 µm
- Phases:
  - Carbon $\varepsilon = 0.25$
  - Electrolyte $\varepsilon = 0.75$
  - Li$_2$O$_2$ $\varepsilon = 10^{-7}$
- Interfaces:
  - Carbon-Electrolyte-Li$_2$O$_2$

Electrolyte: LiPF$_6$ / Stable organic solvent
Anode: Metallic lithium
Li-O battery model: Thermodynamics and kinetics

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<th>Molar Gibbs energy / kJ·mol(^{-1})</th>
<th>Density / Initial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0</td>
<td>5.34·10(^2) kg·m(^{-3})</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0</td>
<td>1.0·10(^3) mol·m(^{-3})</td>
</tr>
<tr>
<td>PF(_6)^-</td>
<td>–</td>
<td>1.0·10(^3) mol·m(^{-3})</td>
</tr>
<tr>
<td>O(_2)(^{\text{gas}})</td>
<td>–61</td>
<td>21 %</td>
</tr>
<tr>
<td>O(_2)(^{\text{dissolved}})</td>
<td>–43</td>
<td>1.62 mol·m(^{-3})</td>
</tr>
<tr>
<td>Li(_2)O(_2)</td>
<td>–644</td>
<td>2.14·10(^3) kg·m(^{-3})</td>
</tr>
<tr>
<td>EC-EMC</td>
<td>–</td>
<td>1.07·10(^4) mol·m(^{-3})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Preexponential factor, forward reaction</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li ⇄ Li(^+) + e(^-)</td>
<td>1.31·10(^{-1}) m·s(^{-1})</td>
<td>0</td>
</tr>
<tr>
<td>O(_2)(^{\text{gas}}) ⇄ O(_2)(^{\text{dissolved}})</td>
<td>Assumed in equilibrium</td>
<td>–</td>
</tr>
<tr>
<td>2 Li(^+) + O(_2)(^{\text{dissolved}}) + 2 e(^-) ⇄ Li(_2)O(_2)</td>
<td>9.23·10(^{31}) m(^7)·mol(^{-2})·s(^{-1})</td>
<td>0</td>
</tr>
</tbody>
</table>

Li-O: Simulated discharge behavior

- Discharge curves simulated for different current densities
- Polarization losses increase with increasing current density
- Capacity strongly depends on current density
Li-O: Spatial distribution

- Strong gradients of dissolved O₂ in organic electrolyte
- At high currents, reactions are confined to regions close to channel
- Rate-limiting O₂ diffusion is origin of polarization losses
Li-O: Pore clogging

- Free porosity decreases upon discharge
- Pore clogging by product Li$_2$O$_2$
- Clogging stronger close to channel
- Strong gradients for high currents
- Pore clogging is origin of current-dependent capacity loss
Motivation and approach
Lithium-sulfur
Lithium-air (organic)
**Lithium-air (aqueous)**
Conclusions
Aqueous Li-O: LiOH as soluble intermediate

- Oxygen reduction:
  \[ \text{O}_2 + 4 \text{e}^- + 2 \text{H}_2\text{O} \rightleftharpoons 4 \text{OH}^- (\text{aq}) \]

- Precipitation:
  \[ \text{Li}^+ + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{LiOH} \cdot \text{H}_2\text{O}(s) \]
Aqueous Li-O modeling domain

Cathode properties:
- Thickness: 500 µm
- Phases (start composition):
  - Carbon $\varepsilon = 0.25$
  - Water $\varepsilon = 0.75$
  - LiOH·H$_2$O $\varepsilon = 10^{-7}$
- Interfaces:
  - Carbon-Electrolyte-LiOH·H$_2$O

Separator properties:
- Porous thickness: 100 µm
- Ideal separation from anode assumed (e.g., Li$^+$-conducting glass)
Results: Aqueous Li-O battery

- Two-stage discharge
  - I: Dissolved LiOH
    Small voltage variation
  - II: Precipitation of LiOH·H₂O
    Constant voltage
- End of discharge:
  Capacity limited by LiOH precipitation

![Graph showing two stages of discharge with voltage profile and reaction equations]
Concentration distribution

A Li\(^+\)/OH\(^-\) concentration gradient, peak at anode
B Increasing Li\(^+\)/OH\(^-\) concentration
C Beginning LiOH precipitation within separator close to anode
D LiOH precipitation at oxygen inlet and anode surface

\[ \rightarrow \text{End of discharge due to LiOH film on anode surface} \]
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Conclusions
Summary: Next-generation battery modeling

- Li-S and Li-O batteries: High energy density, low cycleability
- Challenges: Complex chemistry and complex multi-phase behavior
- Chemistry, phases and transport included into modeling framework
- Li-S: Two-stage behavior: Dissolution, charge transfer, precipitation mechanism
- Li-O organic: Low oxygen diffusivity and pore clogging at channel
- Li-O aqueous: Low oxygen diffusivity and pore clogging at anode

Thank you for your attention!

wolfgang.bessler@dlr.de · www.bessler.info