Next Generation Battery Electrochemistry Analyzed
Towards a Validated Computational Model of the Lithium/Sulfur Cell

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Approach

2011/2012

model design and implementation

2012/2013

experimental characterization and optimization

2013/2014

model validation and simulations

DLR

BERKELEY LAB

Hochschule Offenburg

University of Applied Sciences

Helmholtz Institute Ulm
Electrochemical Energy Storage
Experimental procedure for Li$_2$S cell preparation

Li$_2$S particles with added carbon

SEM, 5000 ×

Ø particle size:
~1 µm
Li$_2$S electrodes (pristine)

SEM, 5000 ×

Inset: EDX, with estimated electrode composition
Components of a CR2032 cell (left to right): Stainless steel bottom casing, positive (Li2S) electrode, separator (cellgard 2400 membrane), negative electrode (150 µm Li foil), stainless steel spacer, bell washer, rubber seal, stainless steel top casing.
Cycling performance

- CCCV charge CC discharge cycles
- slow cycle (0.02C) every 25 cycles to estimate rate capability
Impedance spectroscopy during cycling

• significant changes during discharge

• sensitive to electrolyte composition and cathode surface area
Modeling the lithium/sulfur battery model layout and reaction mechanism

D.N. Fronczek, W.G. Bessler, *J. Power Sources* 2013, 244, 183–188
List of governing equations

<table>
<thead>
<tr>
<th>Physicochemical process</th>
<th>Model equation</th>
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| Charge transport in liquid electrolyte                     | \[
\frac{\partial (\varepsilon_i c_i)}{\partial t} = - \frac{\partial J_i}{\partial y} + \sum_m A_m \dot{s}_{i,m} \]
| Species conservation in liquid electrolyte                | \[
J_i = -D_{i,eff} \frac{\partial c_i}{\partial y} - \frac{z_i F}{RT} \cdot c_i D_{i,eff} \frac{\partial \phi_{elyt}}{\partial y} \]
| Species fluxes                                             | \[
0 = \sum_{i,m} z_i F A_m \dot{s}_{i,m} - \sum_i z_i F \frac{\partial J_i}{\partial y} \]
| Electroneutrality and charge conservation                  |                                                                                   |

| **Cell current and voltage**                               |                                                                                   |
| Cell voltage                                               | \[
E = \phi_{ele,ca} - \phi_{ele,an} \]
| Total current density (anode and cathode)                 | \[
i = \int_{y=0}^{l_{electrode}} (i_F + i_{dl}) dy \]
| Current density due to electrical double layer (anode and cathode) | \[
i_{dt}(t) = A_{dt} C_{dl} \frac{\partial (\Delta \phi)}{\partial t} \]
| Faradaic current density                                   | \[
i_F = \sum_m F A_m \dot{s}_{electron,m} \]
| Potential step (anode and cathode)                        | \[
\Delta \phi = \phi_{ele} - \phi_{elyt} \]

| **Electrochemistry**                                       |                                                                                   |
| Rate equations                                             | \[
\dot{s}_i = \nu_i \left( k_{fwd} \prod_j a^\nu_j - k_{rev} \prod_j a^{\nu_j} \right) \]
| Arrhenius rate law (forward and reverse reactions)         | \[
k = k_0 \exp \left( -\frac{E_{act}}{RT} \right) \exp \left( -\frac{\alpha z F}{RT} \Delta \phi \right) \]

| **Multi-phase management (cathode)**                       |                                                                                   |
| Continuity equation for bulk phases                        | \[
\frac{\partial (\rho_i \varepsilon_i)}{\partial t} = M_i \cdot \sum_m A_m \dot{s}_{i,m} \] with \[
\sum_i \varepsilon_i = 1 \]
| Dependence of diffusion coefficients on bulk phases        | \[
D_{i,eff} = D_i \cdot \varepsilon_i / \tau_i^2 \]

1D, continuum scale, physicochemical model, implemented in DENIS
Model validation using EIS

Impedance spectrum of a discharged Li/S cell.

- ohmic (high frequency) resistance → electrolyte resistance, composition
- charge transfer resistance (semicircle) → interface kinetics
- low frequency resistance (tail position & slope) → diffusive transport
Preliminary model results – phase changes

Volume fractions of various phases in the porous cathode:

- composition changes tremendously
- asymmetric discharge and charge, causing hysteresis

for experimental evidence (XRD) see e.g.: N.A. Cañas et al., *J. Power Sources* 2013, 226, 313–319
Summary

- Cells based on lithium sulfide/carbon electrodes analyzed and optimized
- Experimental data for model optimization/validation recorded, including cycling, EIS, CV, and ex-situ micrographs
- Li/S model implemented, accounting for transport, electrochemical kinetics, and evolution of phases and surfaces
Appendix

Knowledge for Tomorrow
Electrode layout – SEM images

top down, 5000 ×

cross section, 2500 ×
Charge/discharge of a Li/S cell

Stages:
I  formation of polysulfides
II  reduction of polysulfides
III  formation of solid Li$_2$S
IV  const. current charge
V  const. voltage charge

Global reaction: $S_8 + 16 \text{Li} \rightleftharpoons 8 \text{Li}_2\text{S} + 3400 \text{kJ/mol}$
Preliminary model results – electrolyte composition

- electrolyte composition highly SOC-dependent
- concentrations of $S_8$ and $S^{2-}$ buffered by presence of solid phases
- polysulfide mixture equilibration faster than SOC changes
Cell performance – activation and first cycles

- loading: 0.985 mg/cm²
- composition: 80% Li₂S, 10% carbon, 10% SBR
- act.: 0.02C to 3.4V, disc.: 0.1C to 1.5V, ch. 0.1C to 2.8V
Parameters of the model

Technical properties: Thickness, surface area and distances of cathode, separator, and anode; resistance in the current collectors

Material/composite properties: Composition (volume fractions and densities of all components), porosity, and tortuosity of cathode, separator, and anode; internal (specific) surface area and specific capacity of cathode and anode; composition of the electrolyte (weight fractions of liquids, concentrations of salts), total density and viscosity

Chemical: diffusion coefficients (or functions) of the dissolved species; enthalpies of formation for all reacting species, reaction mechanism and rates