Spatial Distributions of Electrical Potential and Current in a Lithium-Sulfur Battery

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Introduction

The lithium-sulfur (Li-S) battery is promising for applications requiring high energy density because of the extremely high gravimetric capacity of sulfur and the lithium metal anode.[1] While research efforts have provided exciting results of cells with extremely high gravimetric capacities and impressive cycling stability, commercialization of large format Li-S batteries with practical active mass loading has lagged behind.[2] One issue with scaling up Li-S batteries is due to the low density of sulfur and the essential electroconductive carbon additive, which necessitates the use of relatively thick cathodes (over 100 µm compared to ~50 µm for conventional Li-ion cathodes).[3] In this report, a mathematical model of a lithium sulfur battery is described, which has been implemented in Python with the finite volume method.

Model Formulation

Kumaresan and coworkers proposed a mathematical model[4] for a Li-S battery consisting of 1-dimensional transient species diffusion/migration in porous media. Figure 1 shows a schematic representation of the Li-S battery, consisting of a Lithium metal anode at x = 0, a porous polymer separator extending from x = 0 to x = L$_s$, and a porous carbon-supported sulfur layer extending from x = L$_s$ to x = L.
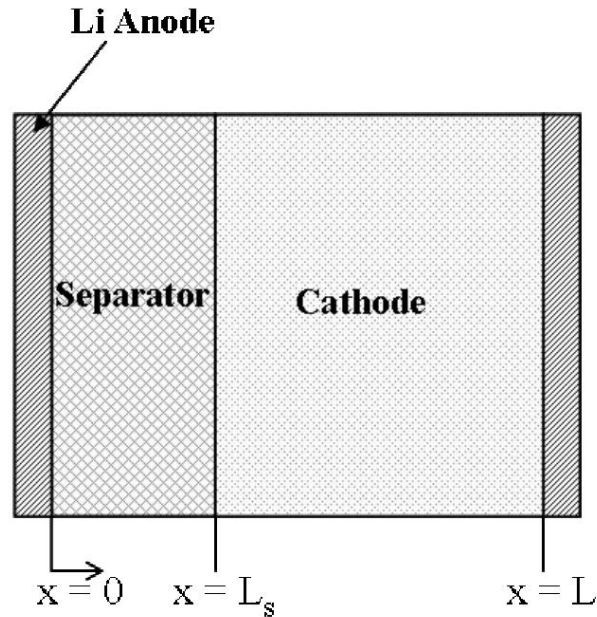

Figure 1. Schematic of the Li-S model cell.

The initial concentrations of the ionic species and electrolyte porosity for separator and cathode are known. From these, the distribution of the electric potential and currents can be calculated for time = 0. From these initial conditions, a solution for transient discharge can be obtained by integrating the species continuity equation, and the rate of dissolution/ precipitation

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of cathode reactants/products. In this report, I describe the calculation of the potential and current distributions within the cell at t = 0.

The potential is determined by combining equations 1-4 (Table 1) into two second order differential equations for the potential of solid and liquid phases respectively. (Equations 5-6, Table 1) Equations 5 and 6 are solved by discretizing the cell length into discrete node and performing finite volume calculations with the application of proper boundary conditions. The calculations are repeated until the solver converges on a solution. The solid and liquid phase current distribution can then be calculated from the solution for potential

Table 1. Governing equations

1	$$\frac{\partial i_e}{\partial x} = a \sum_j i_j$$
2	$$\frac{\partial i_s}{\partial x} = -\frac{\partial i_e}{\partial x}$$
3	$$i_e = F \sum_i z_i N_i$$
4	$$i_s = \sigma_{elec} \frac{\partial \phi_s}{\partial x}$$
5	$$\frac{d^2 \phi_e}{dx^2} = \frac{a \sum_j i_j}{-\sum_i \frac{\epsilon z_i^2 F^2 D_{i,eff} C_i}{RT}}$$
6	$$\frac{d^2 \phi_s}{dx^2} = \frac{a}{\sigma_{elec,eff}} \sum_j i_j$$

Results

The Python program was run for a specified cathode composition (70 wt% S, ~90% porosity carbon support, neglecting binders, 1 S/cm electrical conductivity) and the mass loading of sulfur was changed to vary cathode thickness. The current density was held constant at 1 mA cm^{-2}. Unfortunately, I couldn't seem to get the solution right. Figure 1 shows the result for a cell with 1 mg S cm^{-2} mass loading at a cathode thickness of ~ 350 µm. The potentials don't vary much within the cathode due to the high porosity of the carbon support. Qualitatively the potentials match the expected cell voltage of ~ 2.3 V. The currents however did not match the expected outcome despite trying several different approaches.
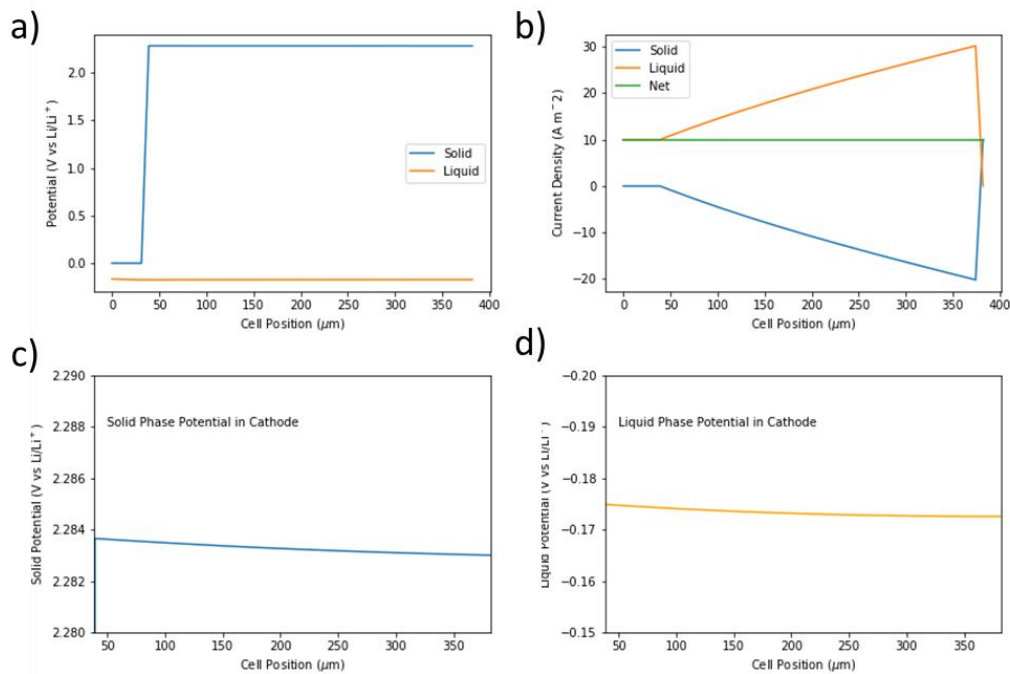
Figure 2. 10 mg/cm^2, 1 mA/cm^2, 90% cathode porosity, 10 S/cm electrical conductivity. Full-cell potential distribution a), current distribution b) and zoom of solid c) and and liquid d) potentials in the cathode layer.

Figure 2 shows the same results for a cell of 15 mg S cm^{-2} with a thickness of over 500 µm. The results are similar with a larger solid-phase voltage drop across the cathode due to the greater thickness.
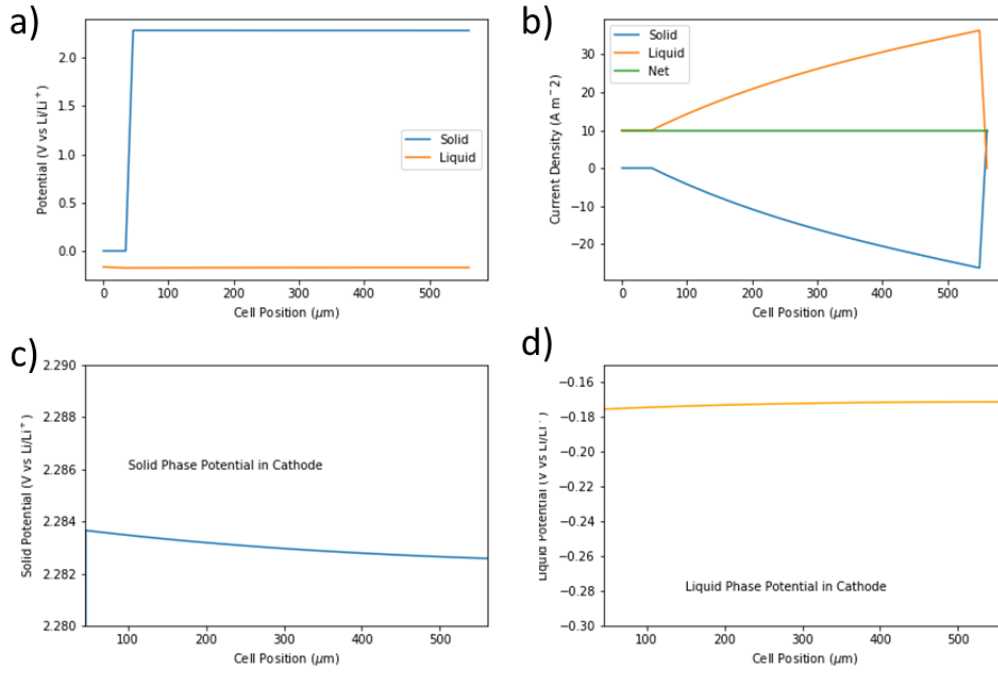
Figure 3. 15 mg/cm^2, 1 mA/cm^2, 90% cathode porosity, 10 S/cm electrical conductivity. Full-cell potential distribution a), current distribution b) and zoom of solid c) and and liquid d) potentials in the cathode layer.

Finally, figure 3 reports results for 15 mg S cm^{-2} again, but with a higher current density and lower electrolyte porosity and electronic conductivity to exaggerate the voltage drops.
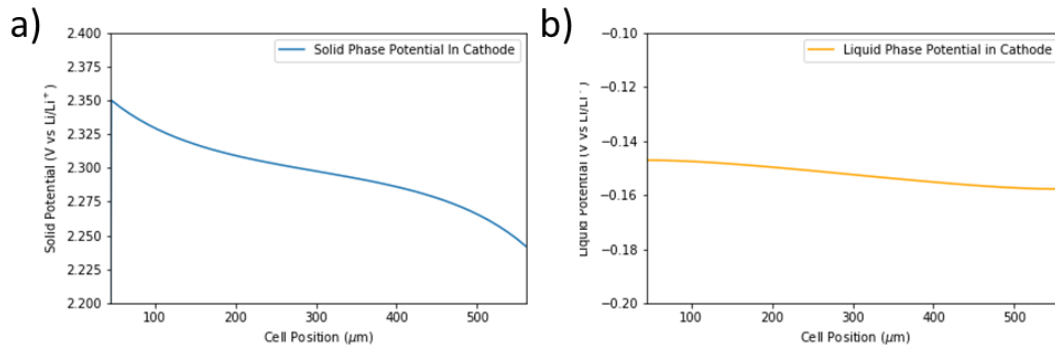

Figure 4. 15 mg/cm^2, 1 mA/cm^2, 80% cathode porosity, 0.1 S/cm electrical conductivity. Full-cell potential distribution a), current distribution b) and zoom of solid c) and and liquid d) potentials in the cathode layer.

Discussion

While the results above may not be right, they at least capture the correct trend of increasing voltage drop across the cathode with increasing thickness and current, and decreasing electrolyte porosity and electronic conductivity. The more interesting result would have come from the transient solution, especially for higher current densities. Kumaresan et al solved the transient problem using ComSol for very low current densities, which resulted in an absence of concentration gradients within the cell. At higher applied currents, concentration gradients are

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expected to play a larger role. However, the model leaves out solid-state diffusion (e.g. within sulfur particles) which is most likely also a limiting factor at high discharge rates.

Conclusions

Although the results are a little lackluster, they seem to capture the qualitative behavior, at least for the potential distribution. The results highlight the importance of electrolyte porosity and electrical conductivity in the design/fabrication of high mass-loading sulfur cathodes. Computing the transient solution would be more useful, but requires accounting for concentration gradients as well as multiple faradaic and precipitation reactions.

Symbols

ϵ = liquid volume fraction,

C_i = liquid-phase species concentration,

i = liquid-phase species,

t = time,

N_i = molar flux of liquid-phase species,

r_i = rate of generation of liquid-phase species from faradaic reactions,

R_i = rate of generation of liquid-phase species i from dissolution,

k = solid-phase species,

$\tilde{V}_k$ = partial molar volume of solid species,

R'_k = rate of generation of solid-phase species from dissolution,

$D_{i,eff}$ = effective diffusivity coefficient,

z_i = ion valence,

F = Faraday's Constant,

R = gas constant,

T = temperature,

ϕ_e = liquid-phase potential,

a = surface area,

j = faradaic reaction,

$s_{i,j}$ = stoichiometric coefficient of species i in reaction j,

i_j = current from reaction j,

n_j = electron charges transferred in reaction j,

$i_{o,j\ ref}$ = reference exchange current density of reaction j,

$C_{i,ref}$ = reference concentration for exchange current density,

$\alpha_{a,j} = \alpha_{c,j}$ = symmetry coefficient = 0.5,

η_j = overpotential of reaction j,

ϕ_s = solid-phase potential,

$U_{j,ref}$ = half-cell potential of reaction j,

U_j^θ = standard half-cell potential of reaction j,

$\gamma_{i,k}$ = number moles ionic species I in solid species k,

R'_k = rate of generation of solid species k,

k_k = rate constant of dissolution/precipitation of species k,

$K_{sp,k}$ = solubility constant of species k,

τ = tortuosity,

b = Bruggeman coefficient = 0.5

i_e = liquid-phase current

i_s = solid-phase current

$\sigma_{elec,eff}$ = effective electronic conductivity

References

1. A. Manthiram, Y. Fu, S. H. Chung, C. Zu and Y. S. Su, Rechargeable lithium-sulfur batteries, *Chemical Reviews*, 2014, **114**, 11751-11787.

2. K. Zhu, C. Wang, Z. Chi, F. Ke, Y. Yang, A. Wang, W. Wang and L. Miao, How Far Away Are Lithium-Sulfur Batteries From Commercialization?, *Frontiers in Energy Research*, 2019, **7**.

3. M. Singh, J. Kaiser and H. Hahn, Thick Electrodes for High Energy Lithium Ion Batteries, *J. Electrochem. Soc.*, 2015, **162**, A1196-A1201.

4. K. Kumaresan, Y. Mikhaylik and R. E. White, A Mathematical Model for a Lithium–Sulfur Cell, *J. Electrochem. Soc.*, 2008, **155**, A576.

The main attraction

Running a code block in a Jupyter Notebook:

Shift+Enter

"I am inevitable."

import numpy as np
import matplotlib.pyplot as plt
from math import *