Simulating the polysulfide shuttle effect: a thermodynamically consistent, fully reversible, numerical Li/S-battery model

Andreas F. Hofmann1,2, David N. Fronczek1,2, Arnulf Latz1,2, Wolfgang G. Bessler3

1German Aerospace Agency (DLR), 2Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, 3Hochschule Offenburg University of Applied Science

Motivation: Li/S cells, promises and shortcomings
Lithium-Sulfur (Li/S) cells are promising next generation batteries1:
• High theoretical specific capacity of 1675 Ah per kg sulfur
• High energy density of 2600 Wh per kg sulfur (3-5 times higher than state of the art Li-ion batteries)
• Low production costs: abundance and low cost of elemental sulfur

Even after decades of research, major problems and challenges remain1:
• Poor cycleability
• Low charging efficiency
• High self-discharge rate

The problems listed here are all related to a Li/S specific, and not yet fully understood phenomenon: the “shuttle effect” or “polysulfide shuttle mechanism”2 (i.e., the transport of soluble polysulfides between both electrodes and the associated charge “shuttle”).

Here we present a thermodynamically consistent, fully reversible, simplified, 1-D continuum model of a Li/S cell, as a step towards shedding light on the basic functioning of the polysulfide shuttle effect.

Model: computational domain, reaction mechanism
• Same basic layout, 1-D transport, and general model equations as Fronczek and Bessler 3
• Implemented in electrochemical modeling framework DENIS4
• Multi-phase management as described in Neidhardt et al.5
• Deliberately simple (electro)chemistry to investigate key mechanism:

Cathode reactions:
• \( \text{Li}_2\text{S} \rightleftharpoons \text{Li}^+ + \text{e}^- \)
• \( \text{S}_8(d) + 4 \text{e}^- \rightleftharpoons 2 \text{S}_4^{2-} \)
• \( \text{S}_4^{2-} + 6 \text{e}^- \rightleftharpoons 4 \text{S}_2^- \)
• \( \text{S}_2^- + 2 \text{Li}^+ \rightleftharpoons \text{Li}_2\text{S} \)

Anode reactions:
• \( \text{Li}_2\text{S} \rightleftharpoons \text{Li}^+ + \text{e}^- \)
• \( \text{S}_8(d) + 4 \text{e}^- \rightleftharpoons 2 \text{S}_4^{2-} \)
• \( \text{S}_4^{2-} + 6 \text{e}^- \rightleftharpoons 4 \text{S}_2^- \)
• \( \text{S}_2^- + 2 \text{Li}^+ \rightleftharpoons \text{Li}_2\text{S} \)

Note: although charging is shown, following convention, the naming of “Cathode” and “Anode” refers to the discharge process.

Discharge curves: fit to experimental literature data
• Transport and most thermodynamic parameters taken from literature
• Kinetic and unavailable thermodynamic parameters calibrated to fit experimental discharge curves from literature6

Shuttle effect
• High charging currents: lower charging efficiency can be reproduced
• Low charging currents: “infinite charging”2 can be reproduced:

Cycling and degradation
• Precipitation of solids on the anode leads to a higher anode overpotential and thus lower voltage during discharge.
• Precipitation of solids on the anode leads to a loss of active material on the cathode which leads to capacity fading.
• Charging inefficiency due to parasitic energy losses via shuttle effect leads to charge capacities significantly higher than discharge capacities.

References
1 S. S. Zhang, J. Power Sources 231, 153-162 (2013)
3 D. N. Fronczek and W. G. Bessler, J. of Power Sources, in press (2013)