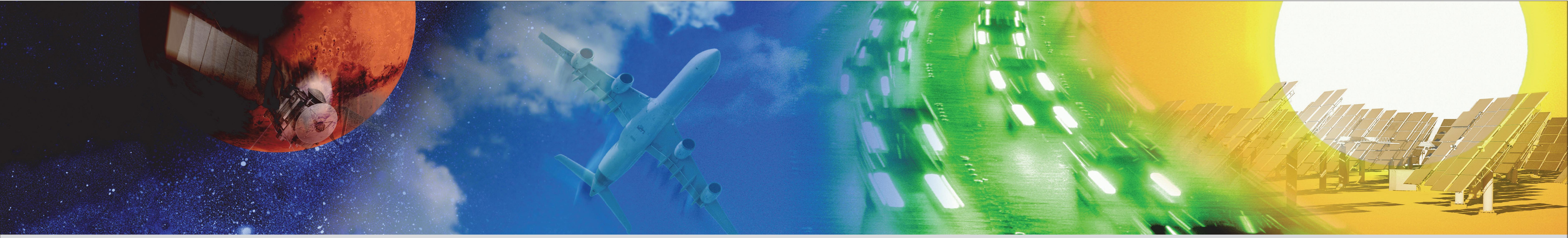

Simulating the polysulfide shuttle effect: a thermodynamically consistent, fully reversible, numerical Li/S-battery model

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Motivation: Li/S cells, promises and shortcomings

Lithium-Sulfur (Li/S) cells are promising next generation batteries[1]:

- 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 remain[1]:

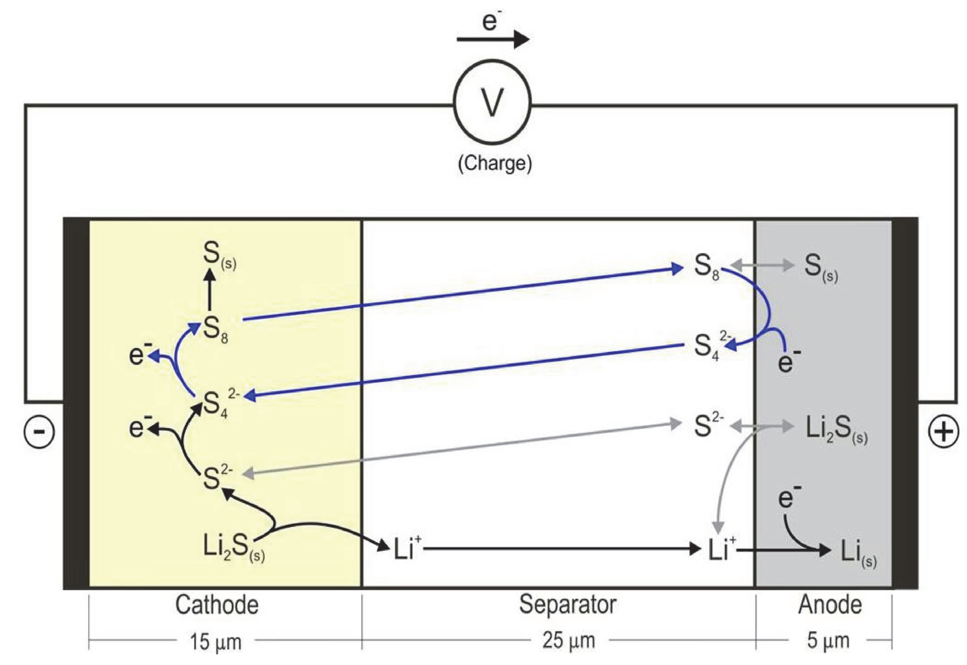
- Poor cycleability
- Low charging efficiency
- High self-discharge rate

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 electro-chemical modeling framework DENIS[4]
- Multi-phase management as described in Neidhardt et al.[5].
- Deliberately simple (electro)chemistry to investigate key mechanism:



Cathode reactions:

- $S_{8(d)} \rightleftarrows 8\,S_{(s)}$
- $S_{8(d)} + 4\,e^- \rightleftarrows 2\,S_4^{2-}$
- $S_4^{2-} + 6\,e^- \rightleftarrows 4\,S^{2-}$
- $S^{2-} + 2\,Li^+ \rightleftarrows Li_2S_{(s)}$

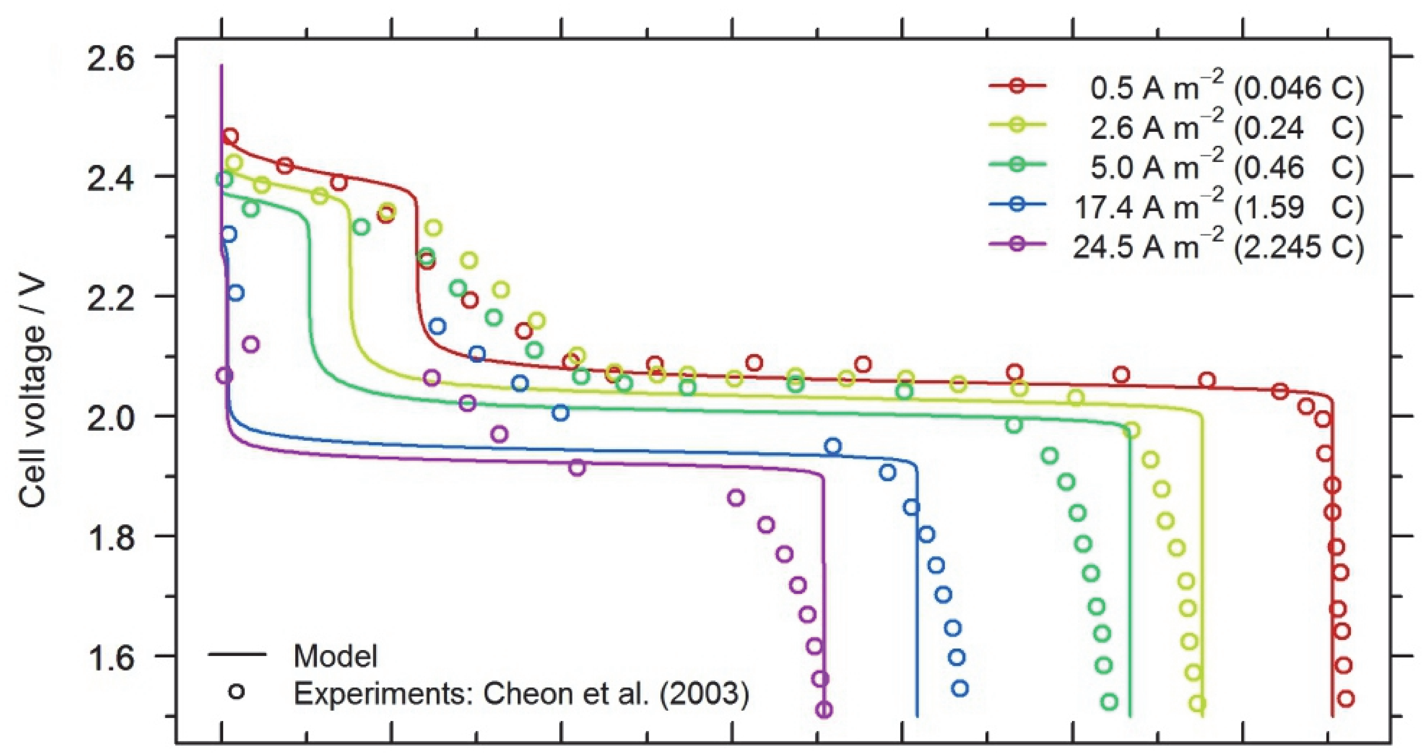
Anode reactions:

- $Li_{(s)} \rightleftarrows Li^+ + e^-$
- $S_{8(d)} + 4\,e^- \rightleftarrows 2\,S_4^{2-}$
- $S_{8(d)} \rightleftarrows 8\,S_{(s)}$
- $S^{2-} + 2\,Li^+ \rightleftarrows Li_2S_{(s)}$

Note: although charging is shown, following con-vention, the naming of *"Cathode"* and *"Anode"* refers to the discharge process.

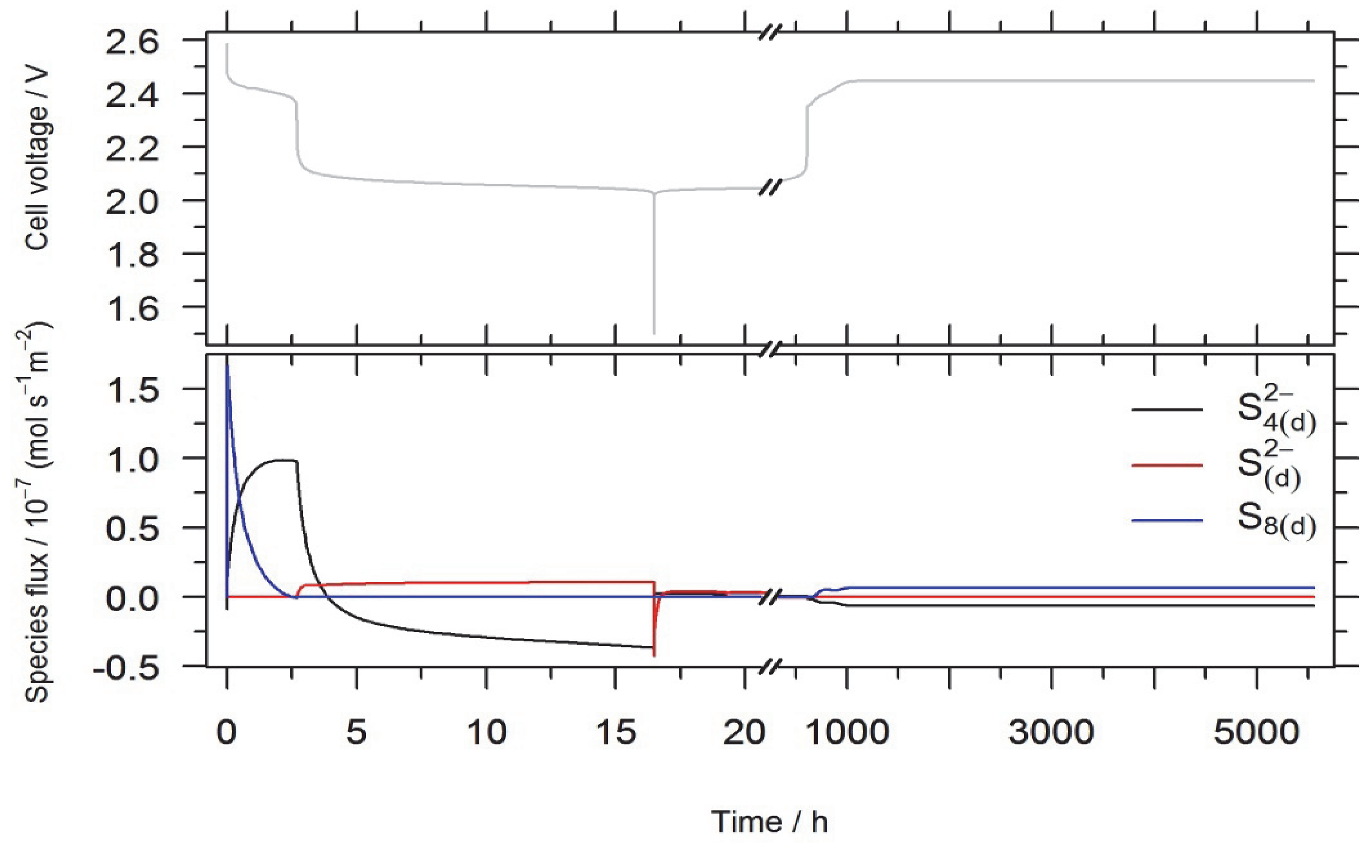
Discharge curves: fit to experimental literature data

- Transport and most thermodynamic parameters taken from literature
- Kinetic and unavailable thermodynamic parameters calibrated to fit experimental discharge curves from literature[6]

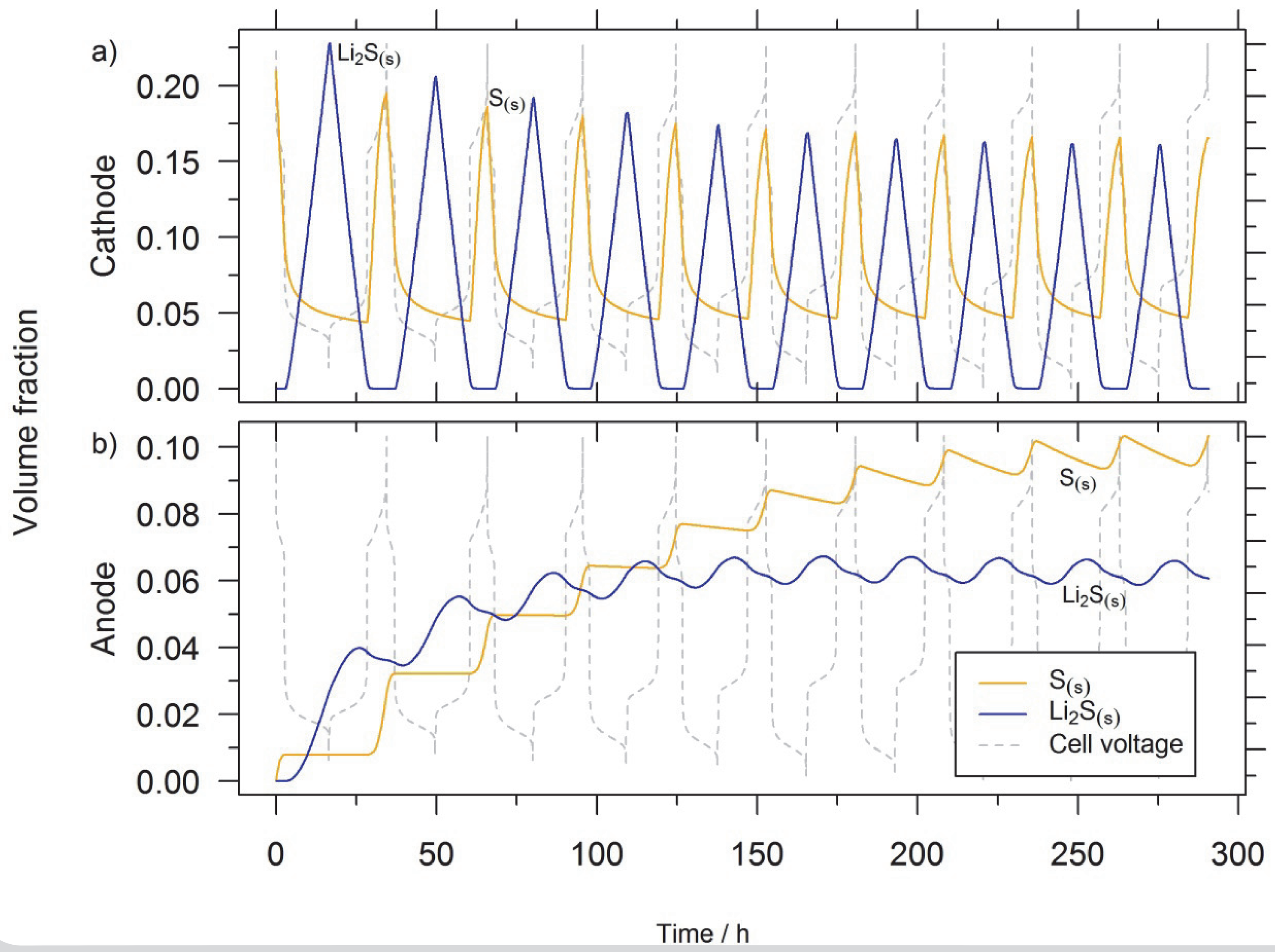


Shuttle effect

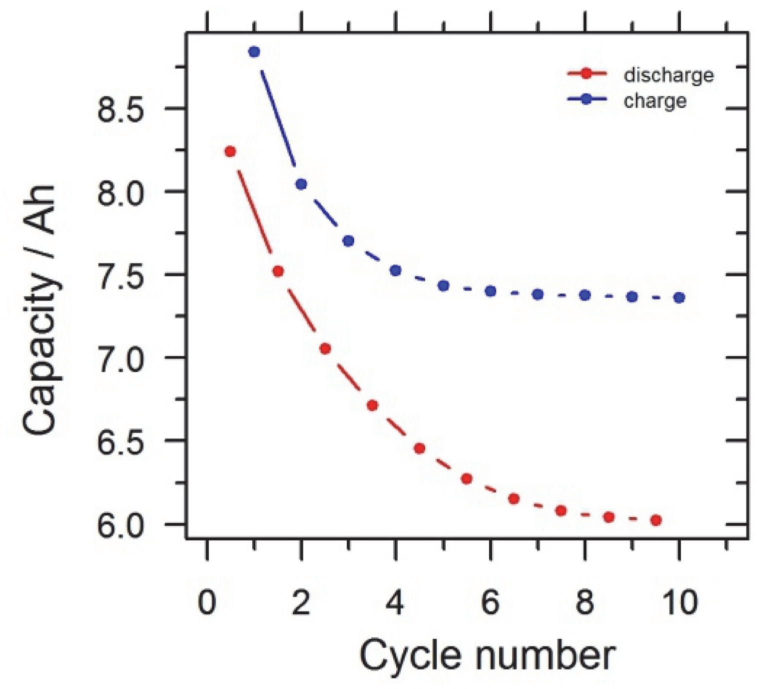
- High charging currents: lower charging efficiency can be reproduced
- Low charging currents: "infinite charging"[2] can be reproduced:



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 inefficency due to parasitic energy losses via shuttle effect leads to charge capacities significantly higher than discharge capacities.



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LIthium Sulfur Superbattery Exploitating Nanotechnology

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