Design and Validation of a Computational Model of the Lithium/Sulfur Cell

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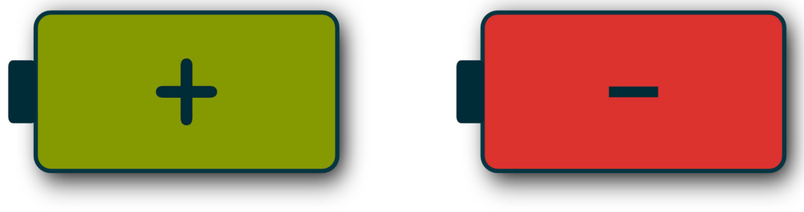
Lithium-sulfur batteries – chances and challenges[1]

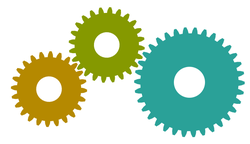


- High specific capacity, power, and energy
- Abundant, non-toxic materials
- Potentially very affordable

- Low energy efficiency
- High self discharge
- Capacity decay & degradation
- Complex electrochemistry

For lithium-sulfur (Li/S) batteries, there is a gap between the recent technological advancements and our understanding of the electrochemistry. Thus, it becomes increasingly harder to improve cells by mere engineering.
A sound physically-based model of the Li/S cell can address these issues and provide new and deeper insight into the functioning and degradation of the Li/S cell by exposing the internal state of the battery.

Summary & Conclusions



Modeling

- established a multi-phase, multi-species physically based model of the lithium-sulfur cell[2]
- model validation using experimental data mostly complete
- very good qualitative and reasonable quantitative agreement with a variety of cells and experiments

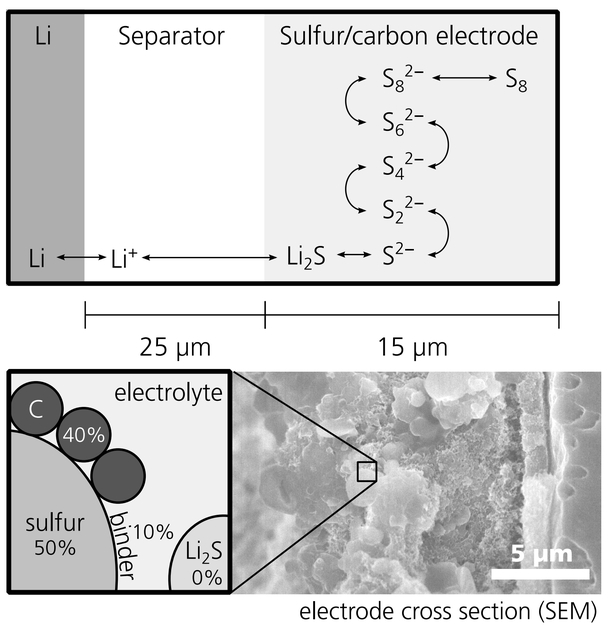
⇒ A valid description of the Li/S cell requires multi-phase and multi-species kinetics. However, the precise reaction mechanism cannot be determined by this methodology *per se*

Li/S cell behavior

- virtually all sulfur is dissolved during discharge and re-precipitated as Li_2S
- impedance is lowest at medium SOC → favorable for shallow cycling
- follow-up work will focus on degradation mechanisms

Model design and validation

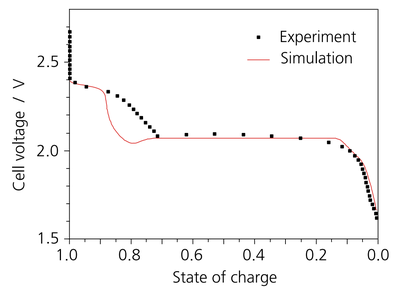
Cell layout and reaction mechanism



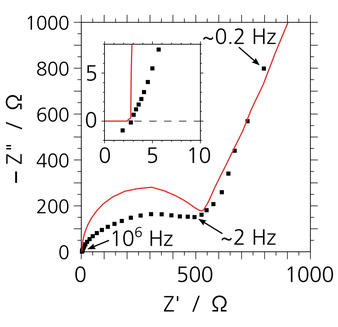
Model equations and implementation[2,3]

- Physically based governing equations for species production/consumption rates, transport in the liquid electrolyte, Faradaic and double layer currents, and evolution of volume fraction and microstructural surface area of each phase
- Implemented as 1D continuum model
- Parameters chosen to match experiments as far as possible (composition, mirco-structure, operating conditions, …)
- Missing polysulfide species data from DFT calculations
- Kinetics fitted to experimental results

Parameterization & validation



Discharge profiles:
- OCV ↔ enthalpy of solvation & ionization
- relative kinetics
- sulfur utilization



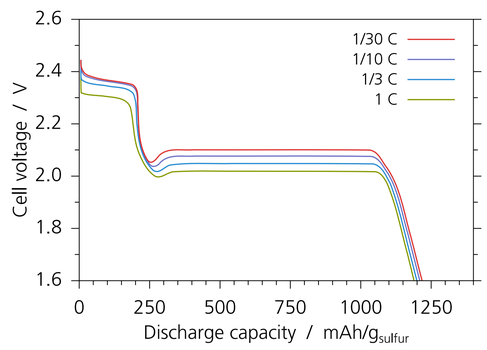
Impedance spectra:
- surface area, capacity
- average speed of kinetics
- diffusion coefficients

and more…

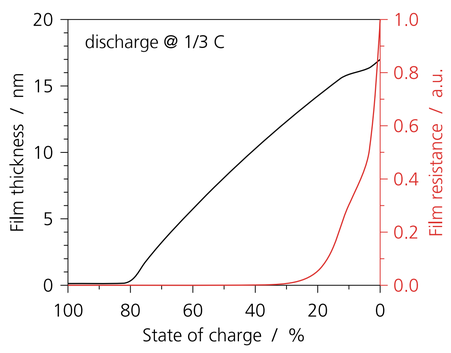
Simulation results

Discharge & charge behavior

Constant current discharge at various rates:

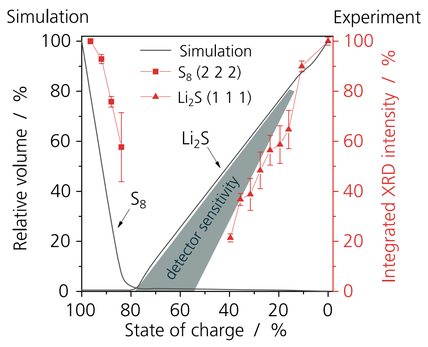


While the overpotential rises with increasing rates, the capacity is not severely affected since for this type of cell, the limiting factor is the formation of a passivating layer of Li_2S on the positive electrode's surface:

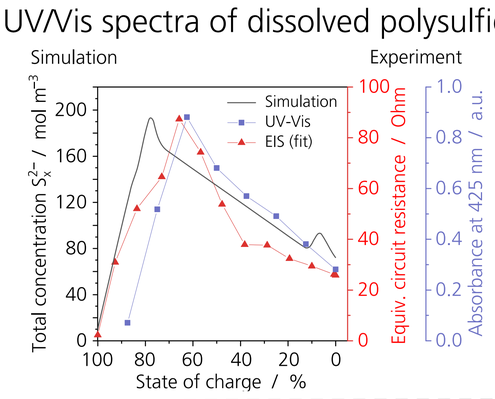


Evolution of phases and species

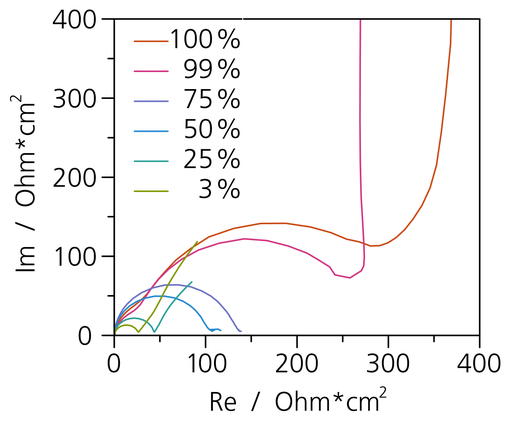
Compared to in-situ XRD of the sulfur cathode[4]:



…and UV/Vis spectra of dissolved polysulfides[4]:



Impedance



Simulated EIS at various SOC using a potential step excitation algorithm[5].

References

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