Insight Into Li/S Batteries: Elementary Kinetic Modeling and Impedance Simulation

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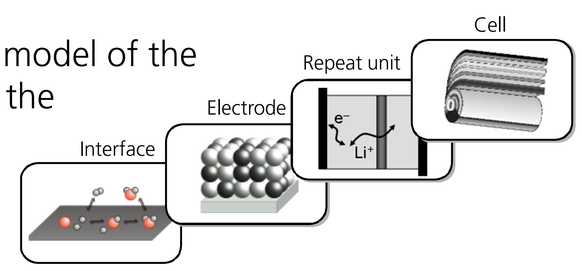
Motivation & Approach

Major challenges for lithium-sulfur (Li/S) batteries today[1]:

- Complex multi-species, multi-reaction chemistry, precise charge/discharge mechanism unknown
- Dissolution/precipitation of phases
- Unstable electrolyte interface (continuously re-formed during cycling)

A sound physically-based model of the Li/S cell can address all of the above and provide new and deeper insight into the Li/S cell.



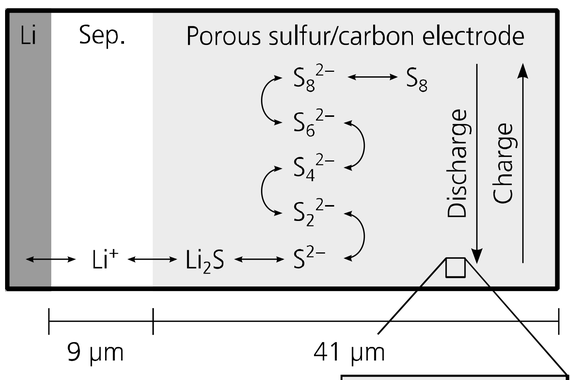
Model development and simulations are carried out using the DLR's in-house software DENIS[2]. Experimental activities at DLR and LBNL provide data for model validation and calibration, see poster by Cañas et al.: In-Situ X-Ray Diffraction (XRD) Studies of Lithium-Sulfur Batteries

Summary & Conclusions

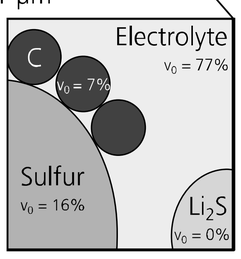
- Discharge behavior is governed by presence of solid reactant and product phases; amount and distribution of sulfur and Li_2S change dramatically during cycling
- Two plateau stages characterized by the presence of solid S_8 and Li_2S, respectively
- All sulfur is dissolved in the form of polysulfides of various length during the intermediate "dip" stage
- The impedance of the cell is simulated based on the physico-chemical model (no equivalent circuit required)
- Predicted energy density for this type of cell (per cathode weight and volume): 1300 Wh/l and 850 Wh/kg assuming quantitative conversion of S_8 to Li_2S.

Model design

Cell layout and reactions



Geometry and reaction mechanism according to Kumaresan et al.[3] No side reactions are considered.



Governing equations

- Species production rates are modeled by Arrhenius law and thermodynamics:

$$\dot{s}_i = \nu_i \left(k_f \prod_{j \in R_f} a_j^{\nu_j'} - k_r \prod_{j \in R_r} a_j^{\nu_j''} \right), \qquad \frac{k_f}{k_r} = \exp\left(-\frac{\Delta G}{RT}\right)$$

$$k_f = k_0^f T^\beta \exp\left(-\frac{E_f^{act}}{RT}\right) \exp\left(-\frac{\alpha z F}{RT} \Delta\phi\right)$$

- Faradaic current density follows from electron production rate:

$$i_F = \sum_m F \dot{s}_{electron,m} A_m^V + \sum_n F \dot{s}_{electron,n} l_n^V$$

- Volume fractions of each phase:

$$\frac{\partial(\rho_i \varepsilon_i)}{\partial t} = R_i M_i \quad , \quad \text{where} \quad R_i = \sum_m \dot{s}_{i,m} A_m^V$$

- Total volume continuously adjusted to ensure constant pressure
- Phase formation/dissolution and phase transition are handled as chemical reactions
- Microstructural surface area of each phase:
- $A_{m,n}^V = A_0^V \cdot f_{m,n}(\varepsilon_m, \varepsilon_n)$ where typically $f_m(\varepsilon_m, \varepsilon_n) = \varepsilon_m$
- Mass and charge transport:

$$\frac{\partial(\varepsilon c_i)}{\partial t} = \frac{\partial}{\partial y}\left(D_i^{eff} \frac{\partial c_i}{\partial y}\right) + \frac{z_i F}{RT} \frac{\partial}{\partial y}\left(D_i^{eff} c_i \frac{\partial \phi}{\partial y}\right) + M_i \dot{s}_i^V$$

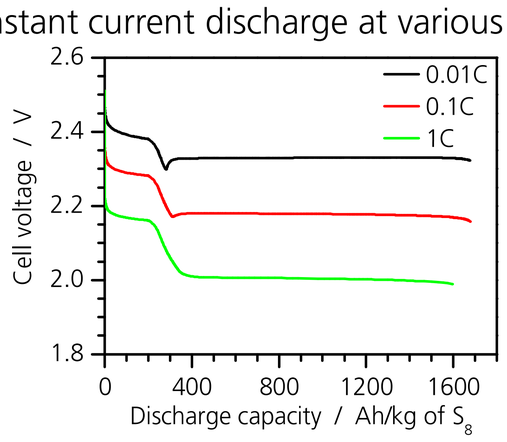
where $D_i^{eff} = \frac{\varepsilon_i}{\tau_i^2} D_i$ and $\sigma_i^{eff} = \frac{\varepsilon_i}{\tau_i^2} \sigma_i$.

For a detailed list of parameters, see ref. 4.

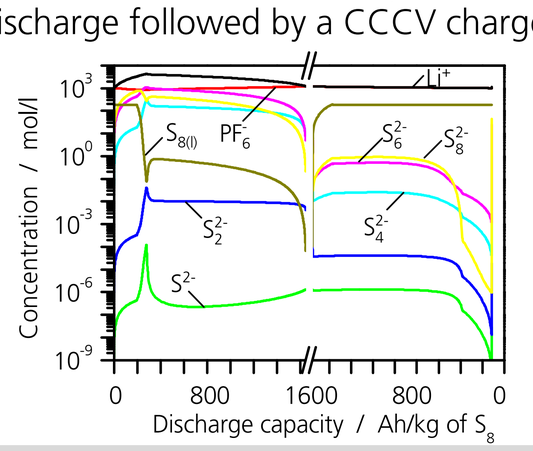
Results

Discharge behavior

Constant current discharge at various rates:

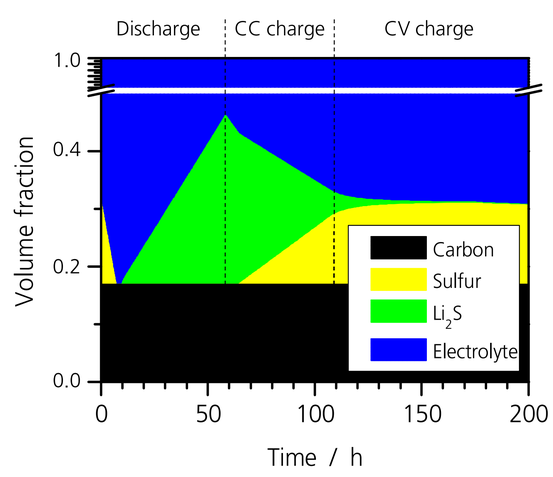


Concentrations of dissolved species during a discharge followed by a CCCV charge:



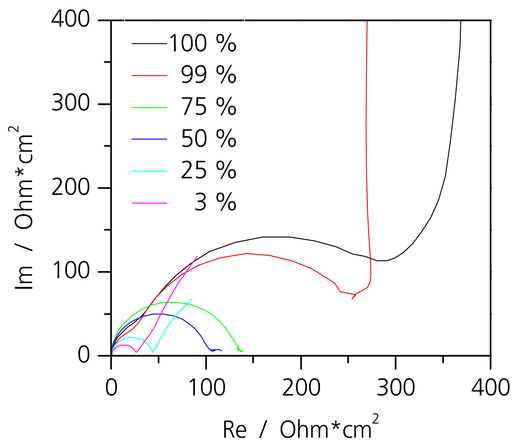
Transport & phase management

Volume fractions of the main cathode components during CCCV cycling:



Impedance

Simulated EIS at various SOC using potential step algorithm[5]:



References

[1]Goodenough & Kim, J. Power Sources, **196** (2011), 6688–6694
[2]Bessler et al., Electrochim. Acta, **53** (2007), 1782–1800
[3]Kumaresan et al., J. Electrochem. Soc., **155** (2008), A576–A582
[4]Neidhardt et al., J. Electrochem. Soc., in press (2012)
[5]Bessler, J. Electrochem. Soc., **154** (2007), B1186–B1191

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