Helmholtz Institute Ulm
Electrochemical Energy Storage

A Fresh Look On Liquid-Electrolyte-Li/S-Batteries: Non-Equilibrium Thermodynamics Based, Detailed Modeling of Transport and Reactions

Andreas F. Hofmann[1,2,*], Arnulf Latz[1,2]

[1] German Aerospace Center (DLR), Institute of Technical Thermodynamics, Pfaffenwaldring 38-40, 70579 Stuttgart, Germany

[2] Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, 89081 Ulm, Germany

[*] andreas.hofmann@dlr.de

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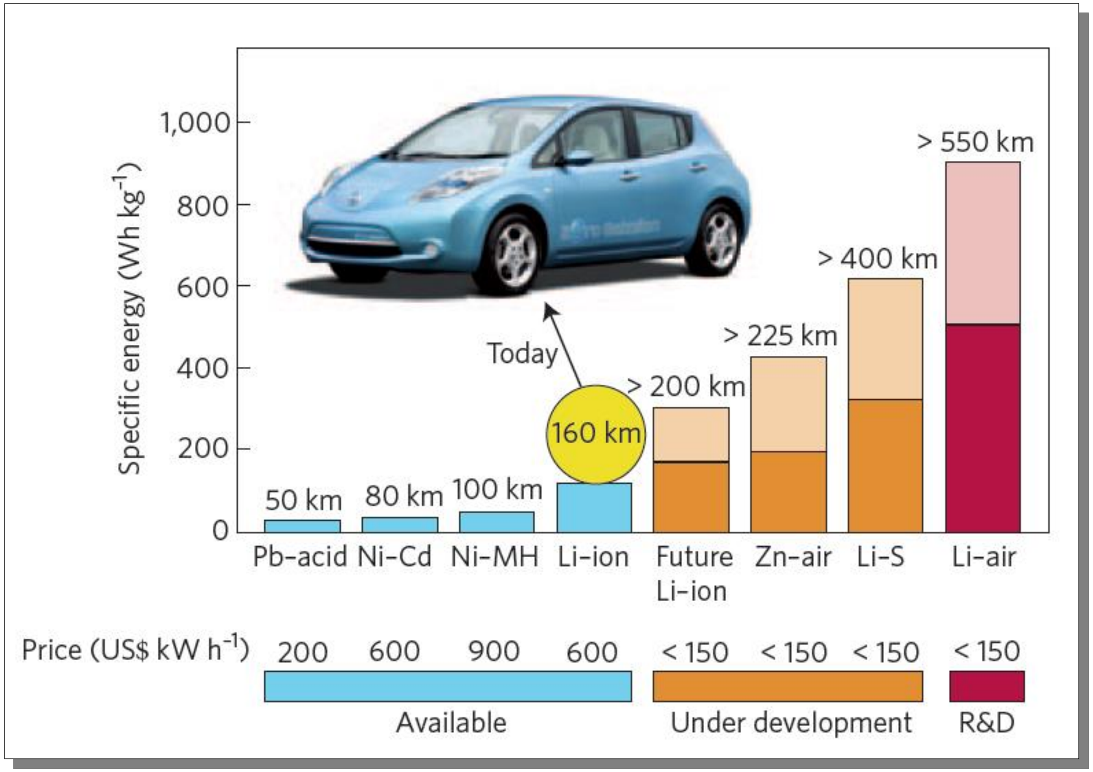
Introduction: Li/S batteries

PRO:
- High energy density
- Cost-effective

CON:
- Poor cycleability
  (capacity fading)
- Low cycling efficiency
  (voltage plateau: “infinite” charging)
- High self-discharge

“shuttle effect”: transport and interface phenomena are involved

ONE WAY FORWARD:
More understanding and fundamental inside obtained via *modeling.*



(Figure from: Bruce et al., Nature Materials, 11, p. 19-29, 2012)

Motivation: "standard" 1D Li/S modeling

- Transport description: dilute solution theory expressing diffusion and migration with the Nernst-Planck equation:

$$\left.\frac{\partial \mathrm{C_i}}{\partial \mathrm{t}}\right|_{\mathrm{tr}} = \frac{\partial}{\partial \mathrm{y}}\left(\mathrm{D_i^{eff}}\left(\frac{\partial \mathrm{C_i}}{\partial \mathrm{y}} + \frac{\mathrm{zFC_i}}{\mathrm{RT}}\frac{\partial \Phi}{\partial \mathrm{y}}\right)\right)$$

(transport of chemical species only depends on the concentration of this species and the potential; transport of unshielded ions is considered)

- The potential step between electrode and electrolyte is often treated as one single step, different potentials along the reaction coordinate are only crudely taken into account (via the symmetry factor alpha)

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

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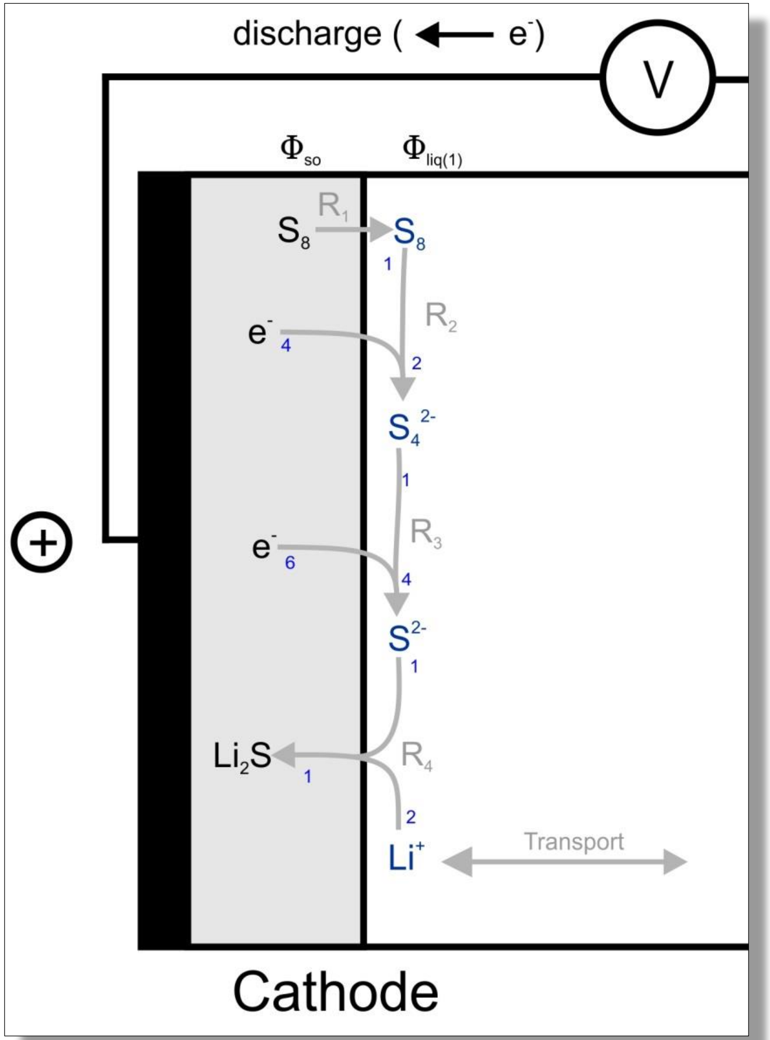
Motivation: "standard" Li/S modeling



- Desolvation, adsorption, and electron transfer reaction are usually lumped together into one single reaction expressed by one single kinetic description:
- Here, e.g. the dissolved Li^+, which is transported through the electrolyte, directly takes part in the precipitation reaction of Li_2S.
- Also, reactants and products "see" either the potential of the electrode, or the potential of the electrolyte.

Fresh look on 1D Li/S modelling: transport

- Transport theory based on non-equilibrium thermodynamics, following Latz & Zausch (2011):

$$
\begin{aligned}
\left.\frac{\partial C_{Li+}}{\partial t}\right|^{tr} &= -\vec{\nabla}\left(-a\left(\frac{\partial \mu_{Li+}}{\partial C_{Li+}}\right)\vec{\nabla} C_{Li+} - b\left(\frac{\partial \mu_{S^{2-}}}{\partial C_{S^{2-}}}\right)\vec{\nabla} C_{S^{2-}} - c\left(\frac{\partial \mu_{S_4^{2-}}}{\partial C_{S_4^{2-}}}\right)\vec{\nabla} C_{S_4^{2-}} - d\left(\frac{\partial \mu_{S_8}}{\partial C_{S_8}}\right)\vec{\nabla} C_{S_8} - \frac{\kappa t_{Li+}}{F z_{Li+}}\vec{\nabla}\tilde{\Phi}\right) \\
\left.\frac{\partial C_{S^{2-}}}{\partial t}\right|^{tr} &= -\vec{\nabla}\left(-b\left(\frac{\partial \mu_{Li+}}{\partial C_{Li+}}\right)\vec{\nabla} C_{Li+} - e\left(\frac{\partial \mu_{S^{2-}}}{\partial C_{S^{2-}}}\right)\vec{\nabla} C_{S^{2-}} - f\left(\frac{\partial \mu_{S_4^{2-}}}{\partial C_{S_4^{2-}}}\right)\vec{\nabla} C_{S_4^{2-}} - g\left(\frac{\partial \mu_{S_8}}{\partial C_{S_8}}\right)\vec{\nabla} C_{S_8} - \frac{\kappa t_{S^{2-}}}{F z_{S^{2-}}}\vec{\nabla}\tilde{\Phi}\right) \\
\left.\frac{\partial C_{S_4^{2-}}}{\partial t}\right|^{tr} &= -\vec{\nabla}\left(-c\left(\frac{\partial \mu_{Li+}}{\partial C_{Li+}}\right)\vec{\nabla} C_{Li+} - f\left(\frac{\partial \mu_{S^{2-}}}{\partial C_{S^{2-}}}\right)\vec{\nabla} C_{S^{2-}} - h\left(\frac{\partial \mu_{S_4^{2-}}}{\partial C_{S_4^{2-}}}\right)\vec{\nabla} C_{S_4^{2-}} - i\left(\frac{\partial \mu_{S_8}}{\partial C_{S_8}}\right)\vec{\nabla} C_{S_8} - \frac{\kappa t_{S_4^{2-}}}{F z_{S_4^{2-}}}\vec{\nabla}\tilde{\Phi}\right) \\
\left.\frac{\partial C_{S_8}}{\partial t}\right|^{tr} &= -\vec{\nabla}\left(-d\left(\frac{\partial \mu_{Li+}}{\partial C_{Li+}}\right)\vec{\nabla} C_{Li+} - g\left(\frac{\partial \mu_{S^{2-}}}{\partial C_{S^{2-}}}\right)\vec{\nabla} C_{S^{2-}} - i\left(\frac{\partial \mu_{S_4^{2-}}}{\partial C_{S_4^{2-}}}\right)\vec{\nabla} C_{S_4^{2-}} - z\left(\frac{\partial \mu_{S_8}}{\partial C_{S_8}}\right)\vec{\nabla} C_{S_8}\right) \\
\left.\frac{\partial q}{\partial t}\right|^{tr} &= -\vec{\nabla}\left(-\frac{\kappa t_{Li+}}{F z_{Li+}}\left(\frac{\partial \mu_{Li+}}{\partial C_{Li+}}\right)\vec{\nabla} C_{Li+} - \frac{\kappa t_{S^{2-}}}{F z_{S^{2-}}}\left(\frac{\partial \mu_{S^{2-}}}{\partial C_{S^{2-}}}\right)\vec{\nabla} C_{S^{2-}} - \frac{\kappa t_{S_4^{2-}}}{F z_{S_4^{2-}}}\left(\frac{\partial \mu_{S_4^{2-}}}{\partial C_{S_4^{2-}}}\right)\vec{\nabla} C_{S_4^{2-}} - \kappa\vec{\nabla}\tilde{\Phi}\right)
\end{aligned}
$$

$\Rightarrow$ transport of a dissolved chemical species depends on the concentrations of all other dissolved chemical species (important for Li/S systems with potentially high polysulfide-concentrations)

$\Rightarrow$ the approach takes the shielding effects of both solvent and counter-ions into account (also especially important for Li/S systems)

Latz, A., Zausch, J.; "*Thermodynamic consistent transport theory on Li-ion batteries*", Journal of Power Sources, 196, 3296-3302, 2011

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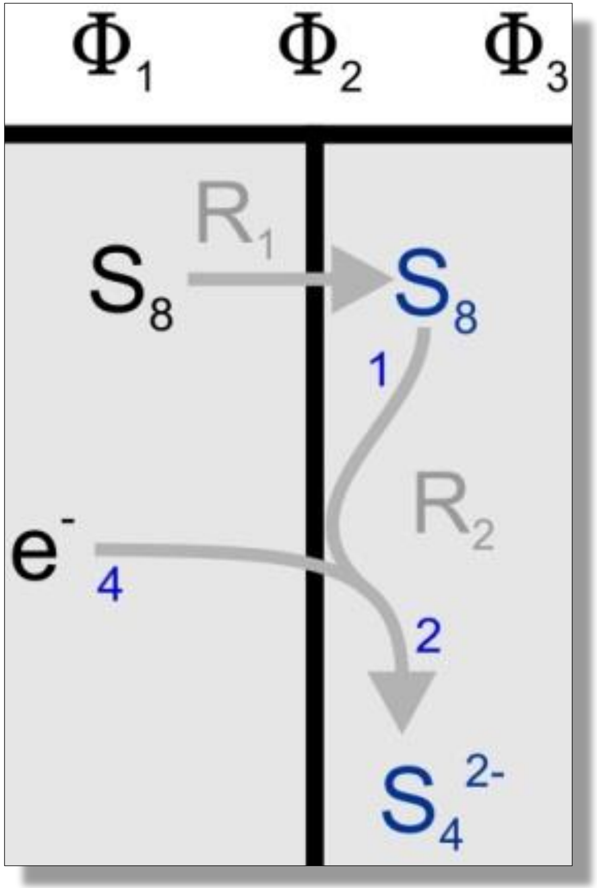
Fresh look on 1D Li/S modelling: kinetics I

- Kinetic theory based on the law of mass action (e.g. Baird, 1999) including effects of the electric potential via the electrochemical potential, following Rubi & Kjelstrup (2003) and Latz & Zausch (2012)



Baird, J. K.; *"A Generalized Statement of the Law of Mass Action"*, Journal of Chemical Education, 76 (8), 1146-1150, 1999

Rubi, J. M., Kjelstrup, S.; "*Mesoscopic Nonequilibrium Thermodynamics Gives the Same Thermodynamic Basis to Butler-Volmer and Nernst Equations*", Journal of Physical Chemistry B, 107, 13471-13477, 2003

Latz, A., Zausch, J.; *"Thermodynamically derived model and simulation of intercalation for a microscopic transport model of Li-ion batteries"*, submitted to Electrochimica Acta, 2012

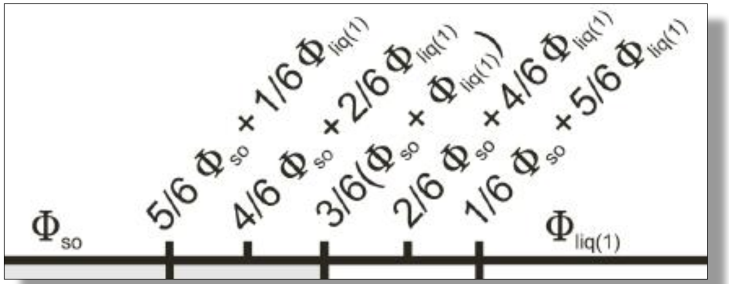
$\Rightarrow$ Reactants, products and intermediates "see" different potentials along the potential gradient from the electrode to the electrolyte.

Fresh look on 1D Li/S modelling: kinetics II

- Using thermodynamic consistency:

  from $K = e^{-\frac{\Delta G^0}{RT}}$ and $K = \frac{k_f}{k_b}$ follows $k_b = \frac{k_f}{K} = \frac{k_f}{e^{-\frac{\Delta G^0}{RT}}} = k_f e^{\frac{\Delta G^0}{RT}}$

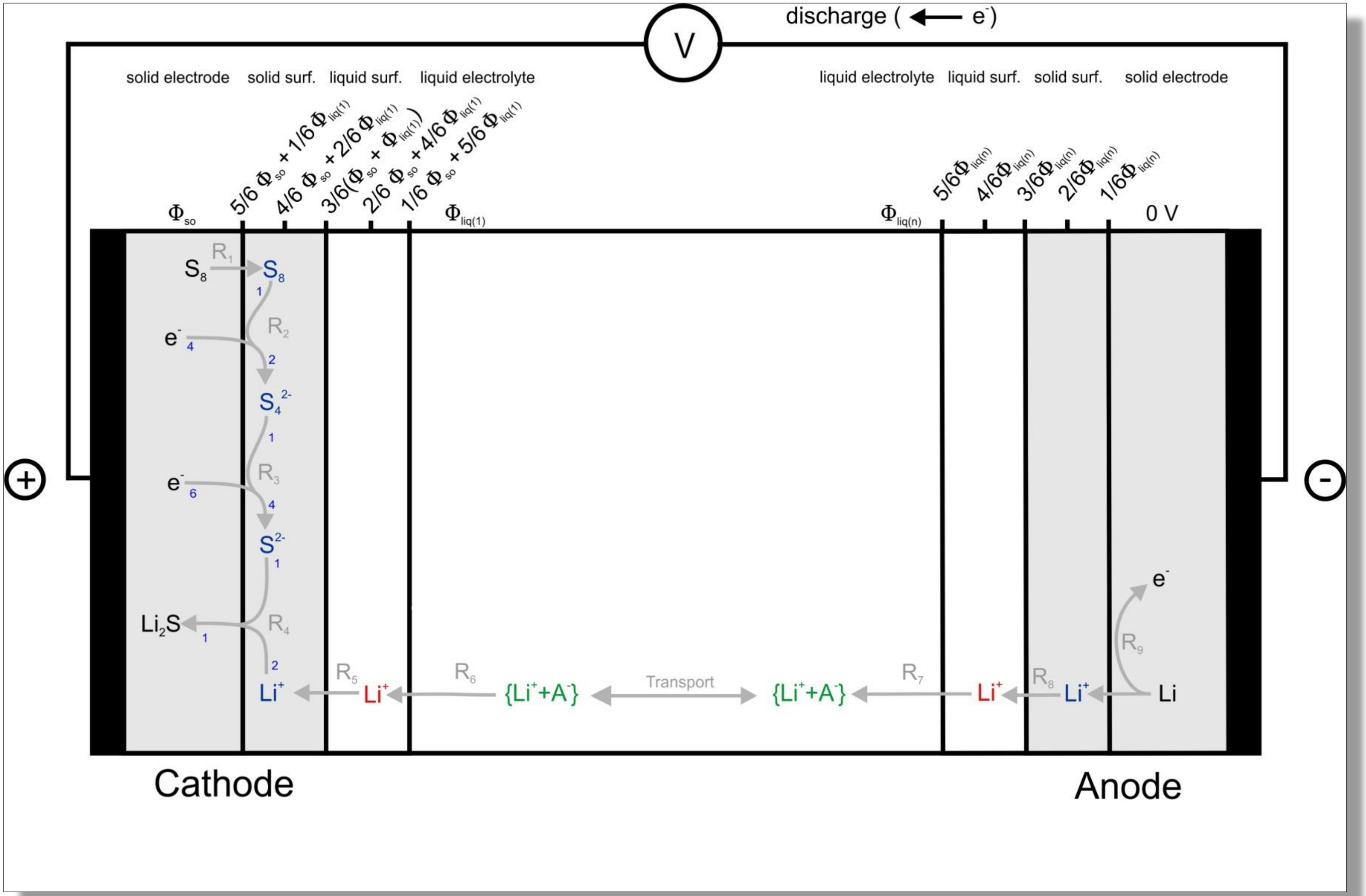
- An expression for the electrochemical potential of $\bar{\mu} = \mu^0 + \mathrm{RT}\ln\left(\gamma \mathrm{e}^{\frac{\mathrm{zF\Phi}}{\mathrm{RT}}} \frac{\mathrm{c}}{\mathrm{c}^0}\right)$
- And a six-point linear interpolation of the potential step between the electrode and the bulk electrolyte



- One can write a kinetic expression for, e.g., reaction 2 (previous slide):

$$
\begin{aligned}
\mathrm{R_2} &= \frac{\mathrm{k_f}}{\gamma^{*\prime}\ \mathrm{e}^{\frac{-4\mathrm{F}}{\mathrm{RT}}\left(\frac{5}{6}\Phi_{\mathrm{so}} + \frac{1}{6}\Phi_{\mathrm{liq}}\right)}} \left(\mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S_8}\right) \left(\mathrm{a}^{\mathrm{c}}_{\mathrm{e}}\right)^4\ \mathrm{e}^{\frac{-1\cdot 4\mathrm{F}}{\mathrm{RT}}\Phi_{\mathrm{so}}} - \mathrm{e}^{\frac{\Delta \mathrm{G}^0_2}{\mathrm{RT}}}\ \mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S}^{2-}_4\right)^2\ \mathrm{e}^{\frac{-2\cdot 2\mathrm{F}}{\mathrm{RT}}\left(\frac{4}{6}\Phi_{\mathrm{so}} + \frac{2}{6}\Phi_{\mathrm{liq}}\right)} \right) \\
&= \frac{\mathrm{k_f}}{\gamma^{*\prime}} \left(\mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S_8}\right) \left(\mathrm{a}^{\mathrm{c}}_{\mathrm{e}}\right)^4 \mathrm{e}^{\frac{4\mathrm{F}}{\mathrm{RT}}\left(\frac{1}{6}(\Phi_{\mathrm{liq}} - \Phi_{\mathrm{so}})\right)} - \mathrm{e}^{\frac{\Delta \mathrm{G}^0_2}{\mathrm{RT}}}\ \mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S}^{2-}_4\right)^2\ \mathrm{e}^{\frac{4\mathrm{F}}{\mathrm{RT}}\left(\frac{1}{6}(\Phi_{\mathrm{so}} - \Phi_{\mathrm{liq}})\right)} \right) \\
&= \frac{\mathrm{k_f}}{\gamma^{*\prime}} \left(\mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S_8}\right) \left(\mathrm{a}^{\mathrm{c}}_{\mathrm{e}}\right)^4 \mathrm{e}^{\frac{4}{6}\frac{\mathrm{F}}{\mathrm{RT}}(\Phi_{\mathrm{liq}} - \Phi_{\mathrm{so}})} - \mathrm{e}^{\frac{\Delta \mathrm{G}^0_2}{\mathrm{RT}}}\ \mathrm{a}\left({}^{\mathrm{so}}_{\mathrm{sr}}\mathrm{S}^{2-}_4\right)^2\ \mathrm{e}^{\frac{4}{6}\frac{\mathrm{F}}{\mathrm{RT}}(\Phi_{\mathrm{so}} - \Phi_{\mathrm{liq}})} \right)
\end{aligned}
$$

Fresh look on Li/S modelling: Xplicit procs.



Fresh look on Li/S modelling: eq. system I

$$
\begin{aligned}
R_1 &= \left(\frac{k_f}{\gamma^*}\right)_{R_1} \left(\left(1 - \frac{1}{1 + e^{z_1^a \cdot \left([{}^{so}_{sr}S_8] - z_1^b \right)}} \right) - \frac{[{}^{so}_{sr}S_8]}{[{}^{so}_{sr}S_8]_{eq}} \right) \\
R_2 &= \left(\frac{k_f}{\gamma^{*\prime}}\right)_{R_2} \left(a\left({}^{so}_{sr}S_8\right) \left(a_e^c\right)^4 e^{\frac{4}{6}\frac{F}{RT}(\Phi_{liq}-\Phi_{so})} - e^{\frac{\Delta G_2^0}{RT}} a\left({}^{so}_{sr}S_4^{2-}\right)^2 e^{\frac{4}{6}\frac{F}{RT}(\Phi_{so}-\Phi_{liq})} \right) \\
R_3 &= \left(\frac{k_f}{\gamma^{*\prime}}\right)_{R_3} \left(a\left({}^{so}_{sr}S_4^{2-}\right) \left(a_e^c\right)^6 e^{\frac{4}{6}\frac{F}{RT}(\Phi_{liq}-\Phi_{so})} - e^{\frac{\Delta G_3^0}{RT}} a\left({}^{so}_{sr}S^{2-}\right)^4 e^{\frac{8}{6}\frac{F}{RT}(\Phi_{so}-\Phi_{liq})} \right) \\
R_4 &= \left(\frac{k_f}{\gamma^*}\right)_{R_4} \left(a\left({}^{so}_{sr}S^{2-}\right) a\left({}^{so}_{sr}Li^+\right)^2 - e^{\frac{\Delta G_4^0}{RT}} \left(1 - \frac{1}{1 + e^{z_1^a \cdot \left([{}^{so}_{sr}Li_2S] - z_1^b \right)}} \right) \right) \\
R_5 &= \left(\frac{k_f}{\gamma^{*\prime}}\right)_{R_5} \left(a\left({}^{liq}_{sr}Li^+\right) e^{-\alpha_{R_5}\frac{2}{6}\frac{F}{RT}(\Phi_{so}-\Phi_{liq})} - e^{\frac{\Delta G_5^0}{RT}} a\left({}^{so}_{sr}Li^+\right) e^{(1-\alpha_{R_5})\frac{2}{6}\frac{F}{RT}(\Phi_{so}-\Phi_{liq})} \right) \\
R_6 &= \left(\frac{k_f}{\gamma^*}\right)_{R_6} \left(a\left({}^{liq}\{Li^+ + A^-\}\right) - e^{\frac{\Delta G_6^0}{RT}} a\left({}^{liq}_{sr}Li^+\right) \right) \\
R_7 &= \left(\frac{k_f}{\gamma^*}\right)_{R_7} \left(a\left({}^{liq}_{sr}Li^+\right) - e^{\frac{\Delta G_7^0}{RT}} a\left({}^{liq}\{Li^+ + A^-\}\right) \right) \\
R_8 &= \left(\frac{k_f}{\gamma^{*\prime}}\right)_{R_8} \left(a\left({}^{so}_{sr}Li^+\right) e^{\alpha_{R_8}\frac{F}{RT}\frac{2}{6}\Phi_{liq}} - e^{\frac{\Delta G_8^0}{RT}} a\left({}^{liq}_{sr}Li^+\right) e^{-(1-\alpha_{R_8})\frac{F}{RT}\frac{2}{6}\Phi_{liq}} \right) \\
R_9 &= \left(\frac{k_f}{\gamma^*}\right)_{R_9} \left(1 - e^{\frac{\Delta G_9^0}{RT}} \left(a_e^c\right) a\left({}^{so}_{sr}Li^+\right) \right)
\end{aligned}
$$

Fresh look on Li/S modelling: eq. system II

$$
\begin{aligned}
&\text{electrolyte:} && \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{i} = \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{i}^{tr} \\
&\text{cathode:} && \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{1} = \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{1}^{tr} - R_6\,\frac{A_1^{reac}}{V_1} \\
&\text{anode:} && \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{n} = \left.\frac{\partial[^{liq}\{Li^{+}+A^{-}\}]}{\partial t}\right|_{n}^{tr} + R_7\,\frac{A_n^{reac}}{V_n}
\end{aligned}
$$

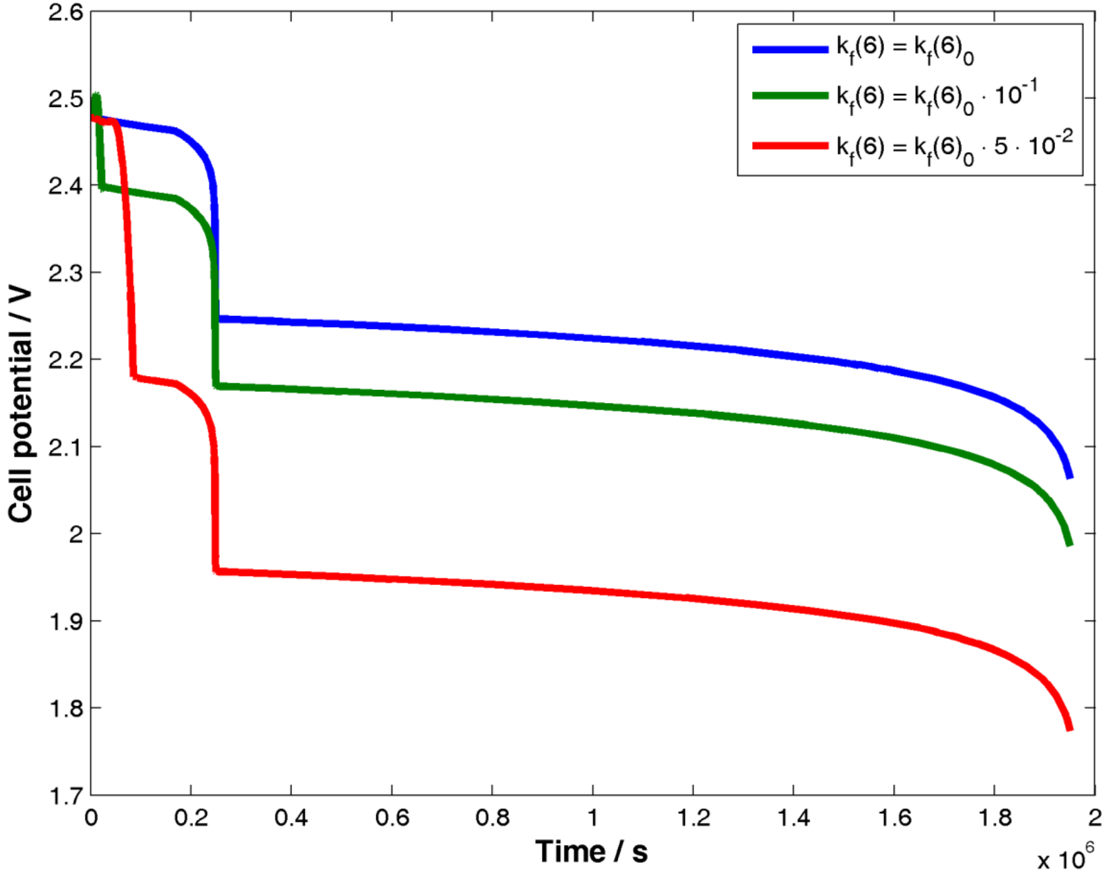
$$
\begin{aligned}
&\text{cathode:} && \left.\frac{\partial[^{liq}_{sr}Li^{+}]}{\partial t}\right|_{ca} = R_6 - R_5 \\
& && \left.\frac{\partial[^{so}_{sr}Li^{+}]}{\partial t}\right|_{ca} = R_5 - 2R_4 \\
& && \frac{\partial[^{so}_{sr}S^{2}-]}{\partial t} = -R_4 + 4R_3 \\
& && \frac{\partial[^{so}_{sr}S_4^{2}-]}{\partial t} = -R_3 + 2R_2 \\
& && \frac{\partial[^{so}_{sr}S_8]}{\partial t} = -R_2 + R_1 \\
& && \frac{\partial v(^{so}S_8)}{\partial t} = -R_1\,A_i^{reac}\,\frac{M^{S_8(S)}}{\rho^{S_8(S)}} \\
& && \frac{\partial v(^{so}Li_2S)}{\partial t} = R_4\,A_i^{reac}\,\frac{M^{Li_2S(S)}}{\rho^{Li_2S(S)}}
\end{aligned}
$$

$$
\begin{aligned}
&\text{anode:} && \left.\frac{\partial[^{liq}_{sr}Li^{+}]}{\partial t}\right|_{an} = R_8 - R_7 \\
& && \left.\frac{\partial[^{so}_{sr}Li^{+}]}{\partial t}\right|_{an} = -R_8 + R_9 \\
& && \left.\frac{\partial v(^{so}Li)}{\partial t}\right|_{an} = -R_9\,A_n^{reac}\,\frac{M^{Li(S)}}{\rho^{Li(S)}}
\end{aligned}
$$

$$
\begin{aligned}
&\text{electrolyte:} && 0 = \left.\frac{\partial q}{\partial t}\right|_{i}^{tr} \\
&\text{cathode:} && 0 = (4R_2 + 6R_3)\;F - I
\end{aligned}
$$

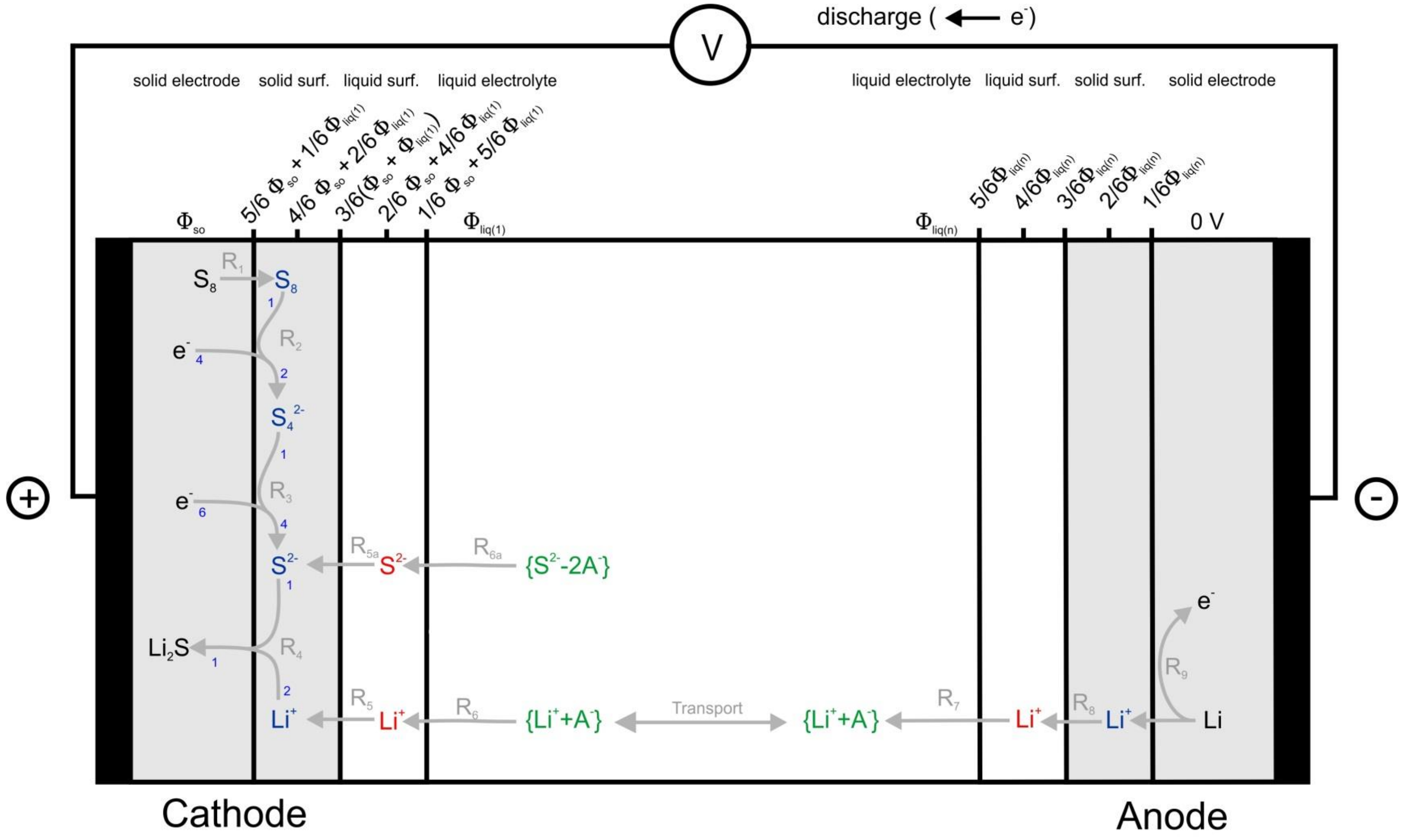
- 1D continuum type model: discretized in 1D
- Resulting DAE solved with MATLAB solver ode15i

First qualitative results: dependency on $k_f(6)$

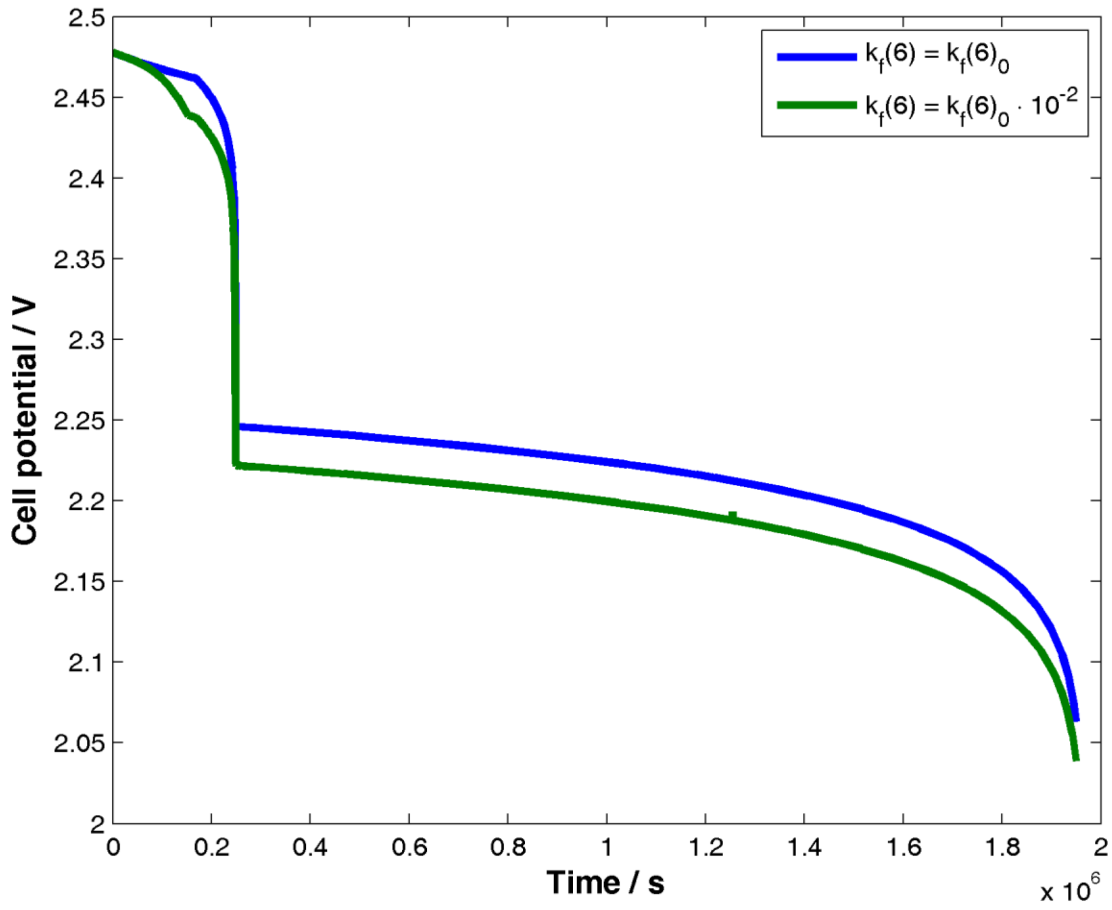


It is important to explicitly describe desolvation kinetics in the model, as desolvation kinetics are most likely more influenced by, e.g., low temperatures than charge-transfer reaction kinetics.

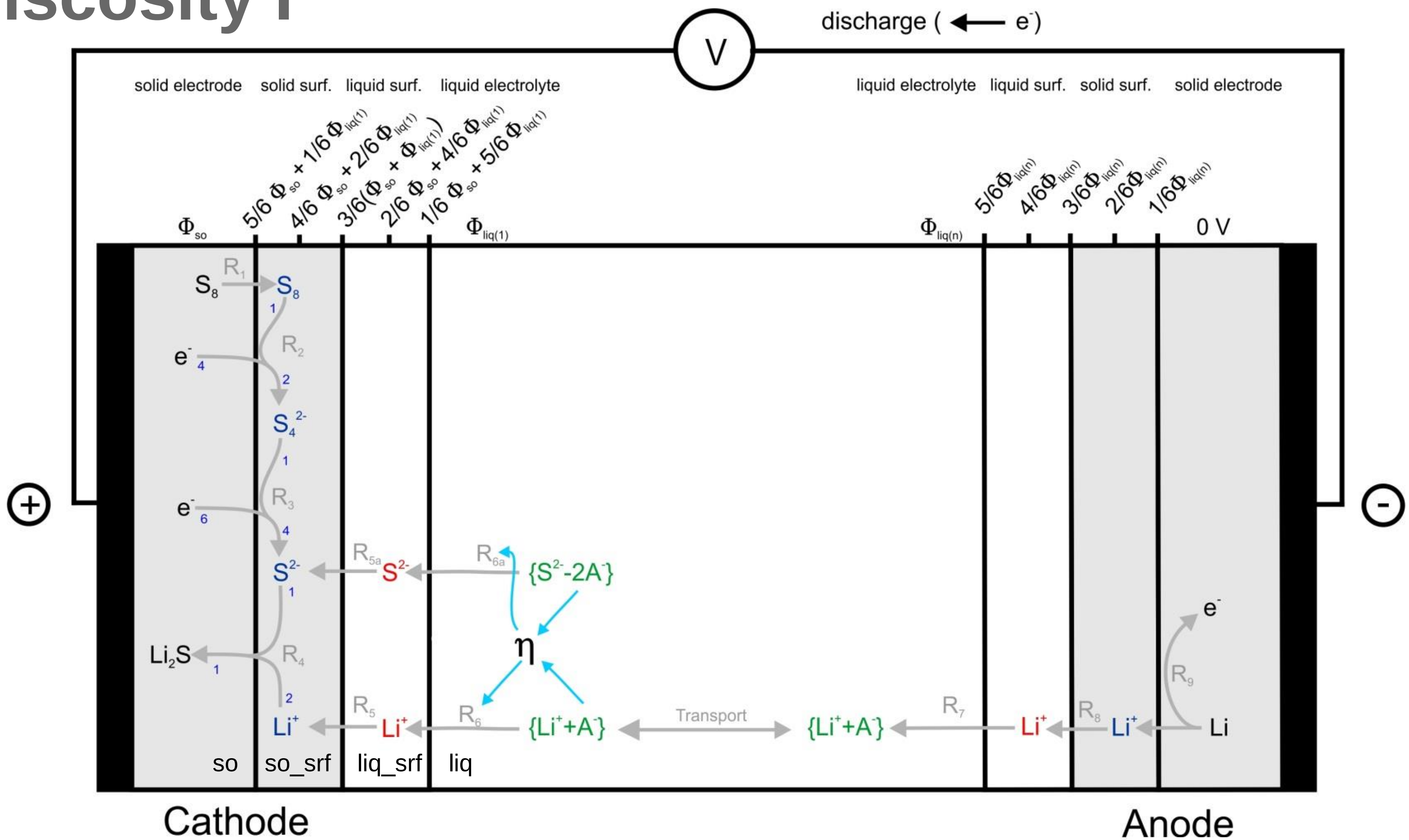
First qualitative results:
dissolution of polysulfides I



First qualitative results:
dissolution of polysulfides II



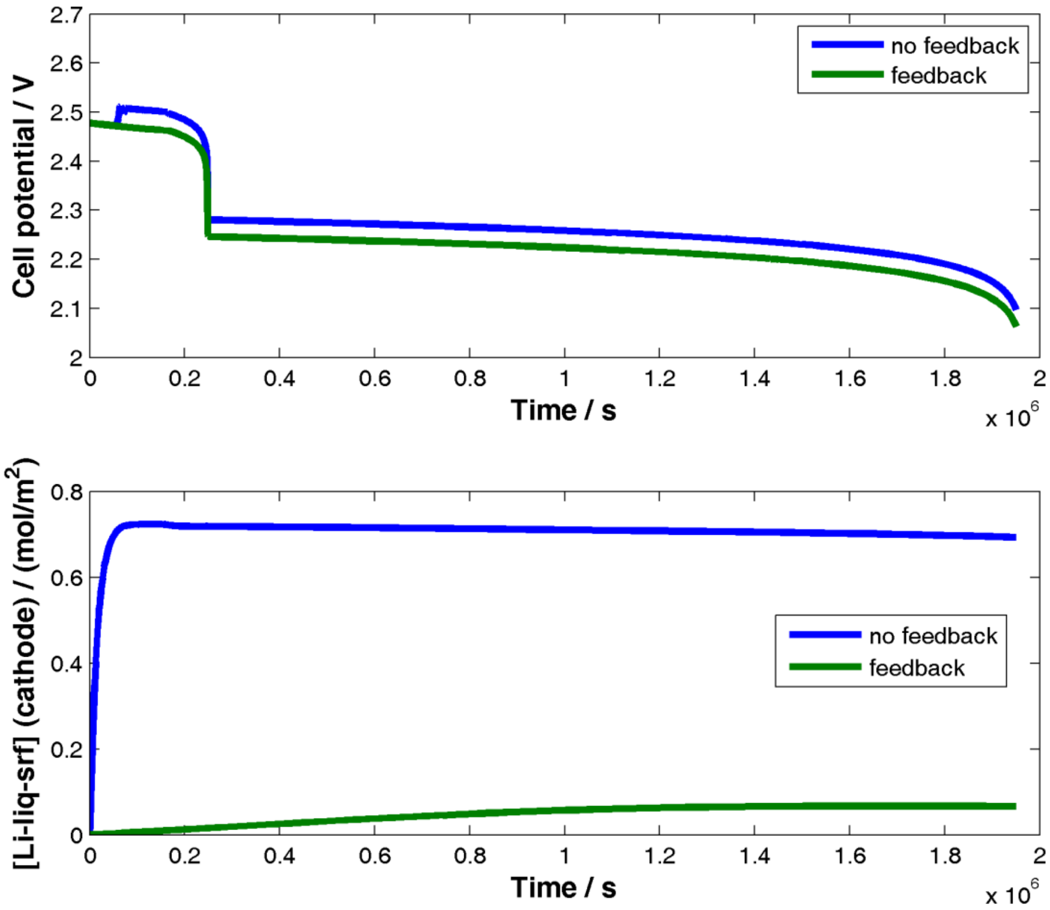
First qualitative results: feedback on $k_f(6)$ via viscosity I



Roughly following Mahiuddin & Ismail (1982): $\eta \approx A\, e^{\left(B \sum c_i + C \left(\sum c_i\right)^2\right)}$ and $k_f\big|_{R_6} \approx \dfrac{k_f^0\big|_{R_6}}{\eta}$

Mahiuddin, S., Ismail, K.; "*Temperature and concentration dependence of viscosity of Mg(N0$_3$),-H$_2$0 systems*", Canadian Journal of Chemistry 60(23), 2883-2888, 1982

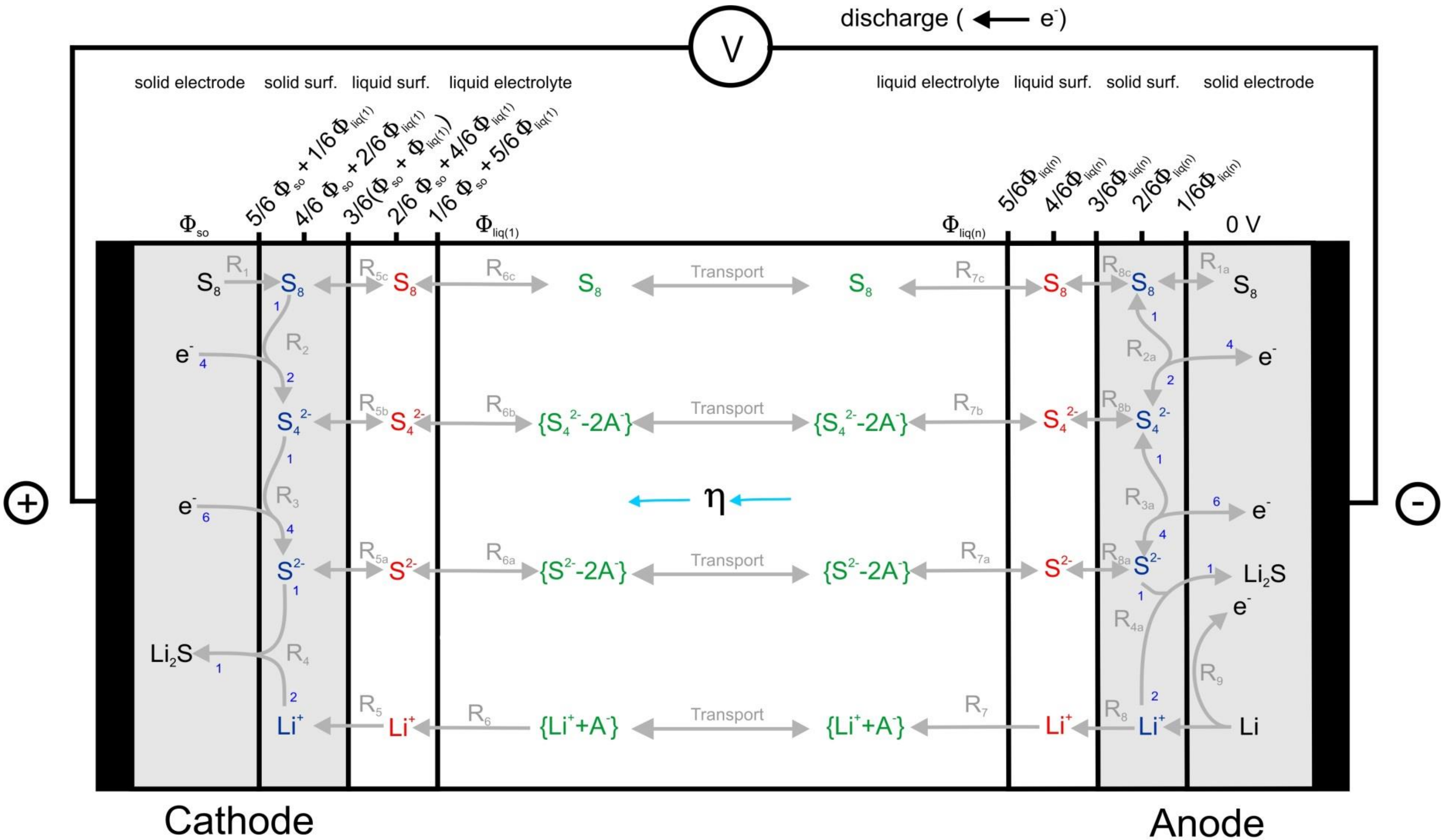
First qualitative results: feedback on $k_f(6)$ via viscosity II



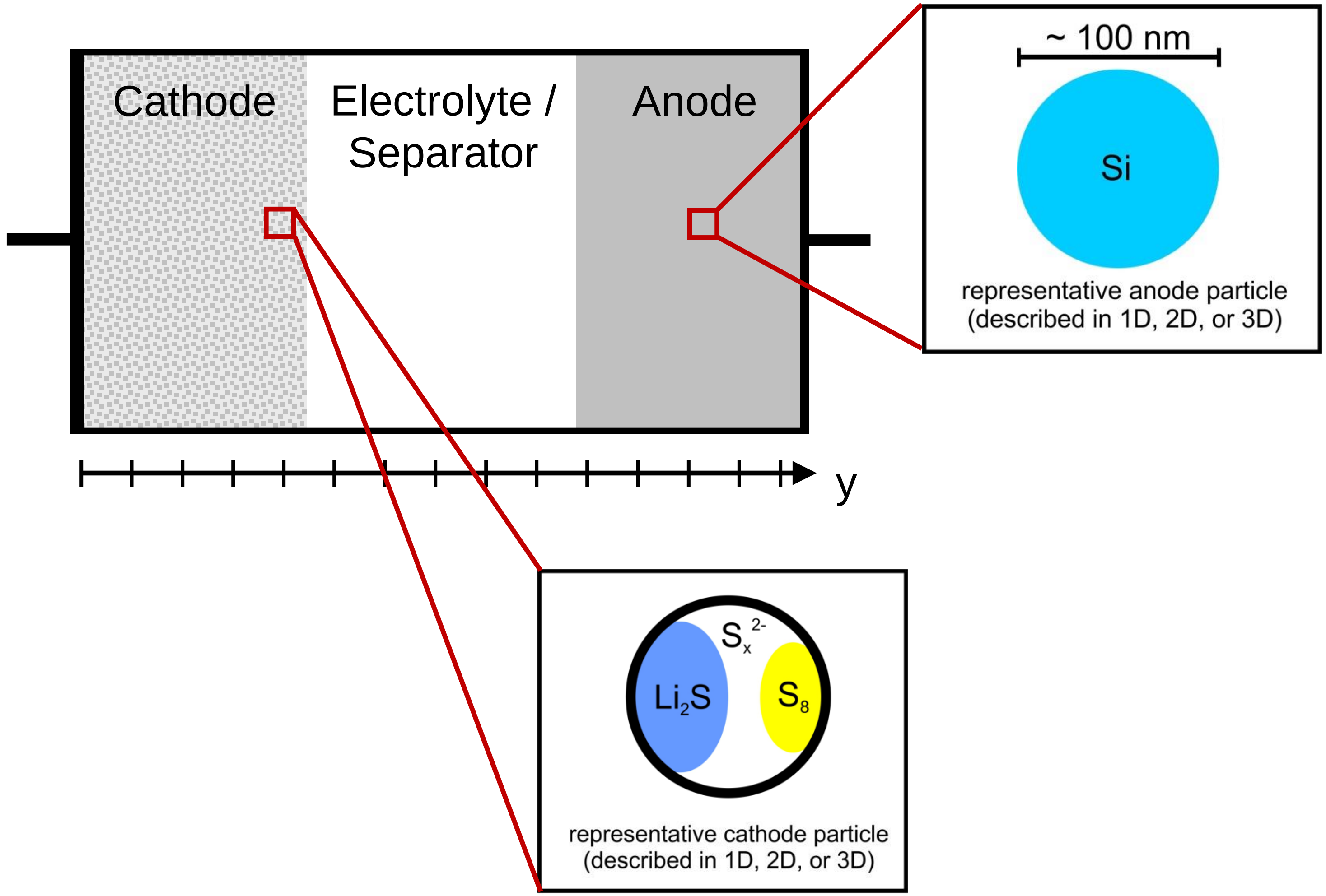
Summary:

- This is WORK IN PROGRESS!
- Three main differences to “standard” Li/S modeling:
  1. Transport (allowing for interactions between species, taking shielding effects into account explicitly)
  2. Explicit treatment of desolvation and adsorption (allowing for various explicit feedback loops)
  3. More detailed treatment of potential step between electrode and electrolyte
- As first results, we qualitatively showed the “effect” of point 2, but all of them bring the model closer to reality and allow for a more detailed analysis of important processes
- Adaptation and comparison of the model to experimental data and ab-initio calculations is planned, but we are always looking for additional cooperation with experimental groups!

Outlook I: Shuttle effect & degradation



Outlook II: Micro- & Nanostructures



Deutsches Zentrum für Luft- und Raumfahrt e.V.
German Aerospace Center

Institute of Technical Thermodynamics - Computational Electrochemistry

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LISSEN – LIthium Sulfur Superbattery Exploitating Nanotechnology

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Thank you very much for your attention