Microstructure Simulations of Flow Batteries

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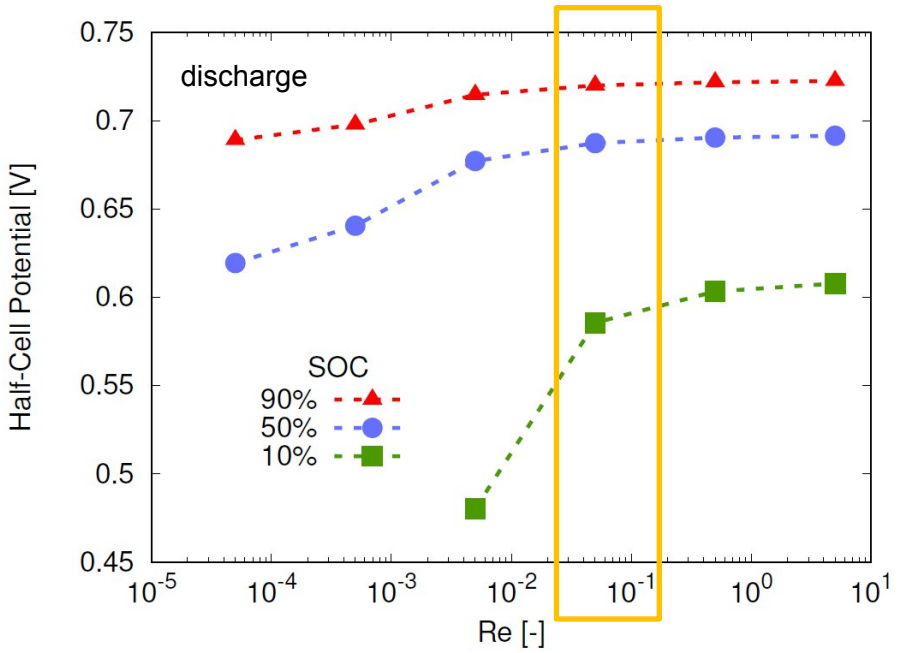
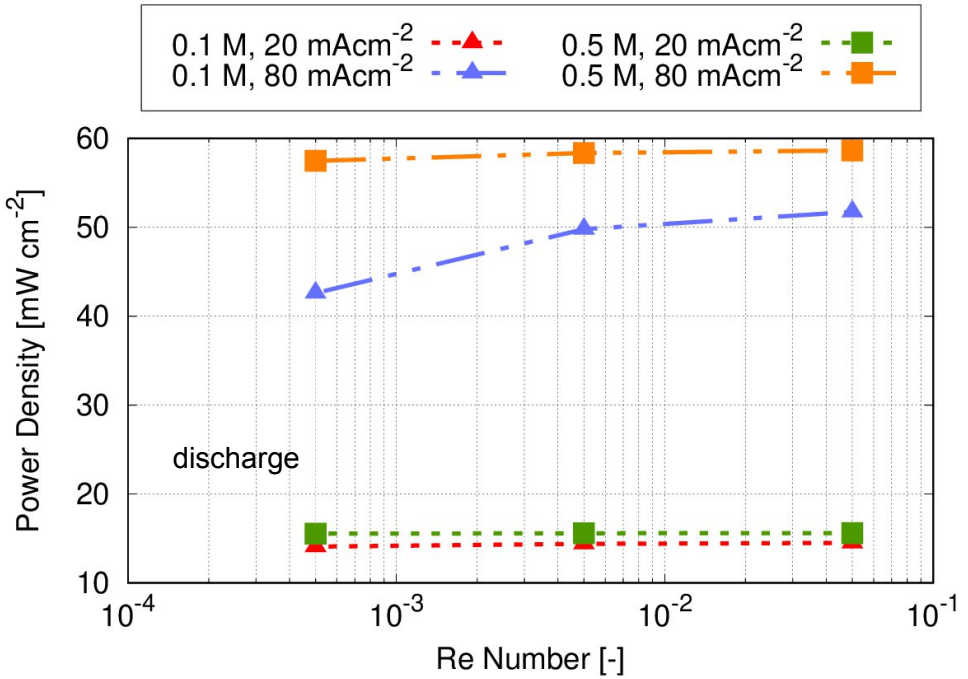
Potential and Power Density





- Discharge 40 mA cm^{-2} and 0.1M TEMPO in 1M NaCl
- For all SOC optimal Re-Number in range of $10^{-2} < Re < 10^{-1}$

- Low current density → effect of concentration marginal
- High current density and low concentration → mass transfer limitations at low Re-Numbers

Multi-Scale Flow Battery Modeling Approach Using Mass Transfer Coefficients [2]

Motivation

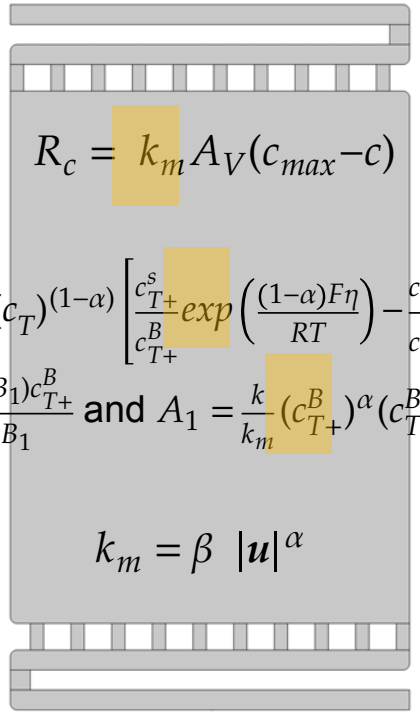
Vague description of the mass transfer coefficient k_m in homogenized cell scale models. Mostly as empirical relation to velocity.

Research Objective

Development of a method to extract k_m from MSM and subsequent usage in the HCSM. Comparison to empirical relations from literature.

Approach

Obtainment by using reaction rate at distinct concentration level and discharge rate of the MSM, as well as resolved of bulk and surface concentration. Implementation of k_m in the HSCM as function of SOC and velocity.



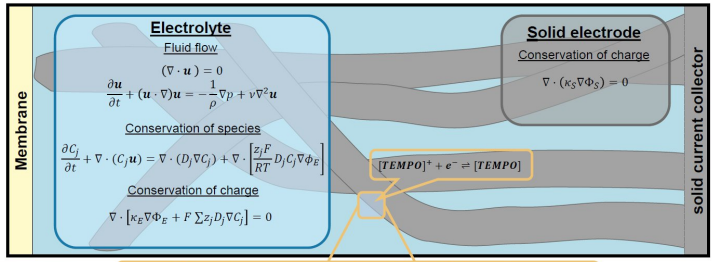
$$R_c = k_m A_V (c_{max} - c)$$

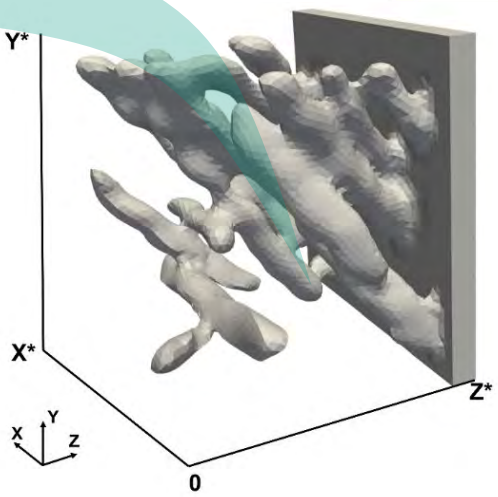
$$r^s_{T+} = k (c_{T+})^{\alpha} (c_T)^{(1-\alpha)} \left[\frac{c^s_{T+}}{c^B_{T+}} exp\left(\frac{(1-\alpha) F \eta}{RT} \right) - \frac{c^s_T}{c^B_T} exp\left(-\frac{\alpha F \eta}{RT} \right) \right]$$

$$c^s_{T+} = \frac{B_1 c_T + (1+B_1) c^B_{T+}}{1 + A_1 + B_1} \text{ and } A_1 = \frac{k}{k_m} (c^B_{T+})^{\alpha} (c^B_T)^{(1-\alpha)} exp\left(\frac{\alpha F \eta}{RT} \right)$$

$$k_m = \beta \ |\boldsymbol{u}|^{\alpha}$$

$$k_m = \frac{r}{c_{bulk} - c_{surf}}$$





Kinetic boundary condition: Butler-Volmer-Type

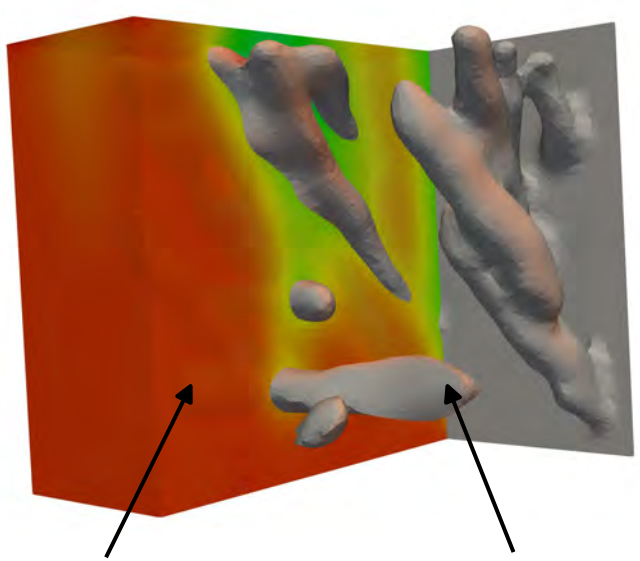
$$-r_{T^+} = +r_T = k \cdot (C^s_T)^{\alpha} \cdot (C^s_{T^+})^{(1-\alpha)} \left[exp\left(\frac{(1-\alpha) F \eta}{RT} \right) - exp\left(-\frac{\alpha F \eta}{RT} \right) \right]$$

$$\eta = \Phi_S - \Phi_E - E^0 - \frac{RT}{F} \ln\left(\frac{C^s_{T^+}}{C^s_T} \right)$$

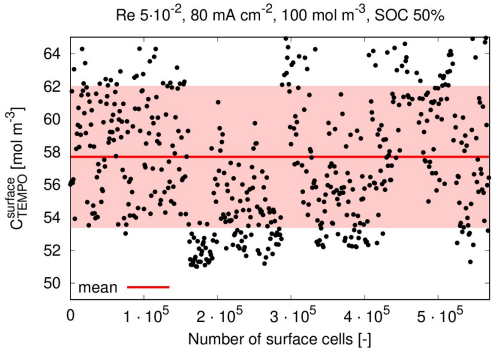
$$r = \frac{i}{F}$$

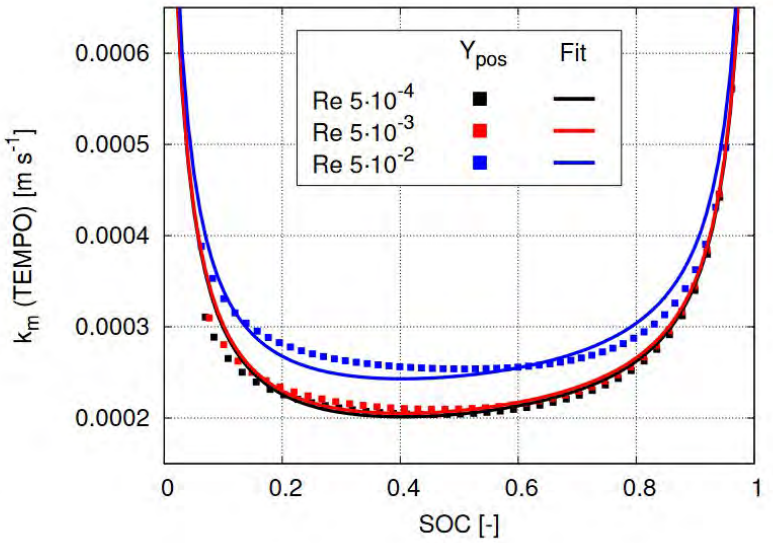
[2] Wolf, A., Baudrin, E., Nirschl, H., (2023) „A Multiscale Flow Battery Modeling Approach Using Mass Transfer Coefficients." Energy Technology. https://doi.org/10.1002/ente.202300175

Multi-Scale Flow Battery Modeling Approach Using Mass Transfer Coefficients [2]



$c^B_{T+} = \bar{c}_{T+}$ $c^S_{T+} = \bar{c}^S_{T+}$





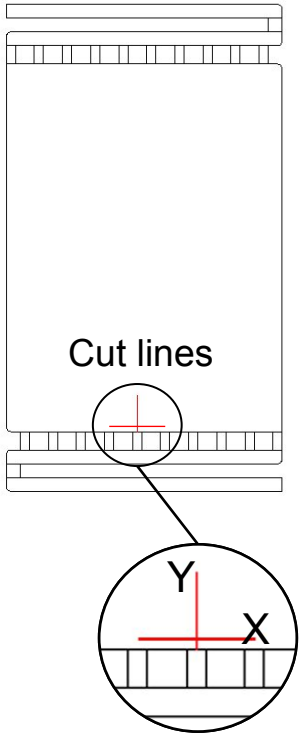
$$k_m = c + d \cdot U + \frac{b}{sin\left(\pi \cdot a \cdot \left(SOC + 0.5 \cdot \left(\frac{1}{a} - 1\right)\right)\right)} + e \cdot SOC$$

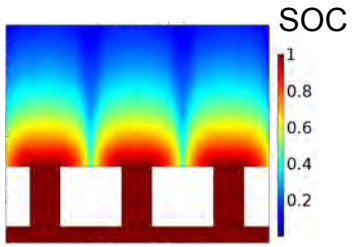
- Reaction rate: $r = \frac{i_{BV}}{F} = k_m(c^B_{T+} - c^S_{T+})$
- $\rightarrow k_m = \frac{i_{BV}}{F} \frac{1}{(c^B_{T+} - c^S_{T+})}$ for 0.1M TEMPO in 1M NaCl and 80 mA cm^{-2}

Parameter	Value	Unit
a	0.9695	-
b	6.241×10^{-5}	$m\,s^{-1}$
c	1.114×10^{-4}	$m\,s^{-1}$
d	8.425×10^{-3}	-
e	6.036×10^{-5}	$m\,s^{-1}$

RMSE = 2.45e-5

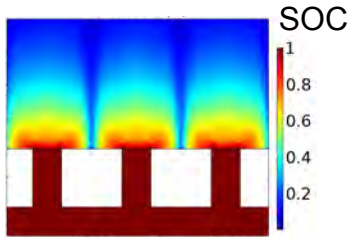
Multi-Scale Flow Battery Modeling Approach Using Mass Transfer Coefficients [2]





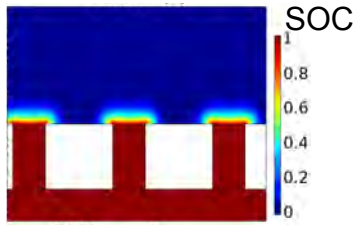
Schmal et al.

$$k_m = 1.6 \cdot 10^{-4} \ |u|^{0.4}$$

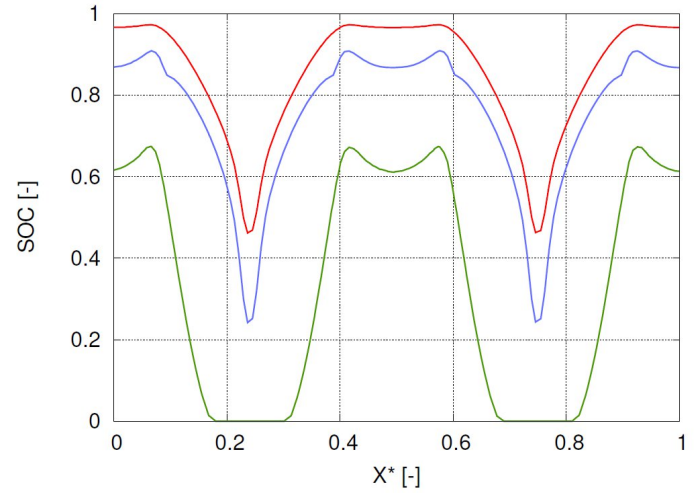


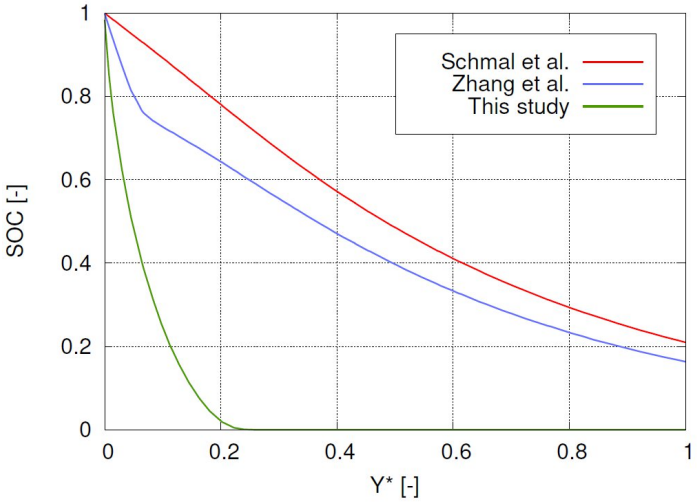
Zhang et al.

$$k_m = \left(\left(1 + exp\left(-4665 \frac{u}{1\ ms^{-1}} + 42.302\right)\right)^{-1} + 0.235\right) \cdot 8.511 \times 10^{-5} \cdot 1\ ms^{-1}$$



This study





- Kinetic parameters play **crucial role** for designing the cell
- The kinetic parameters **extracted with our method predict a much faster species conversion** in the vicinity of the channels compared to values commonly assumed in the literature.
- Electrode too large in vertical flow direction → can be **engineered smaller**

[1] Zhang et al., 2020,, Understanding the role of the porous electrode microstructure in redox flow battery performance using an experimentally validated 3D pore-scale lattice Boltzmann model,. *Journal of Power Sources,*, Volume 447,, https://doi.org/10.1016/j.jpowsour.2019.227249.

[2] Schmal, D., Van Erkel, J. & Van Duin, P.J. Mass transfer at carbon fibre electrodes. *J Appl Electrochem* **16**, 422–430 (1986). https://doi.org/10.1007/BF01008853

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