

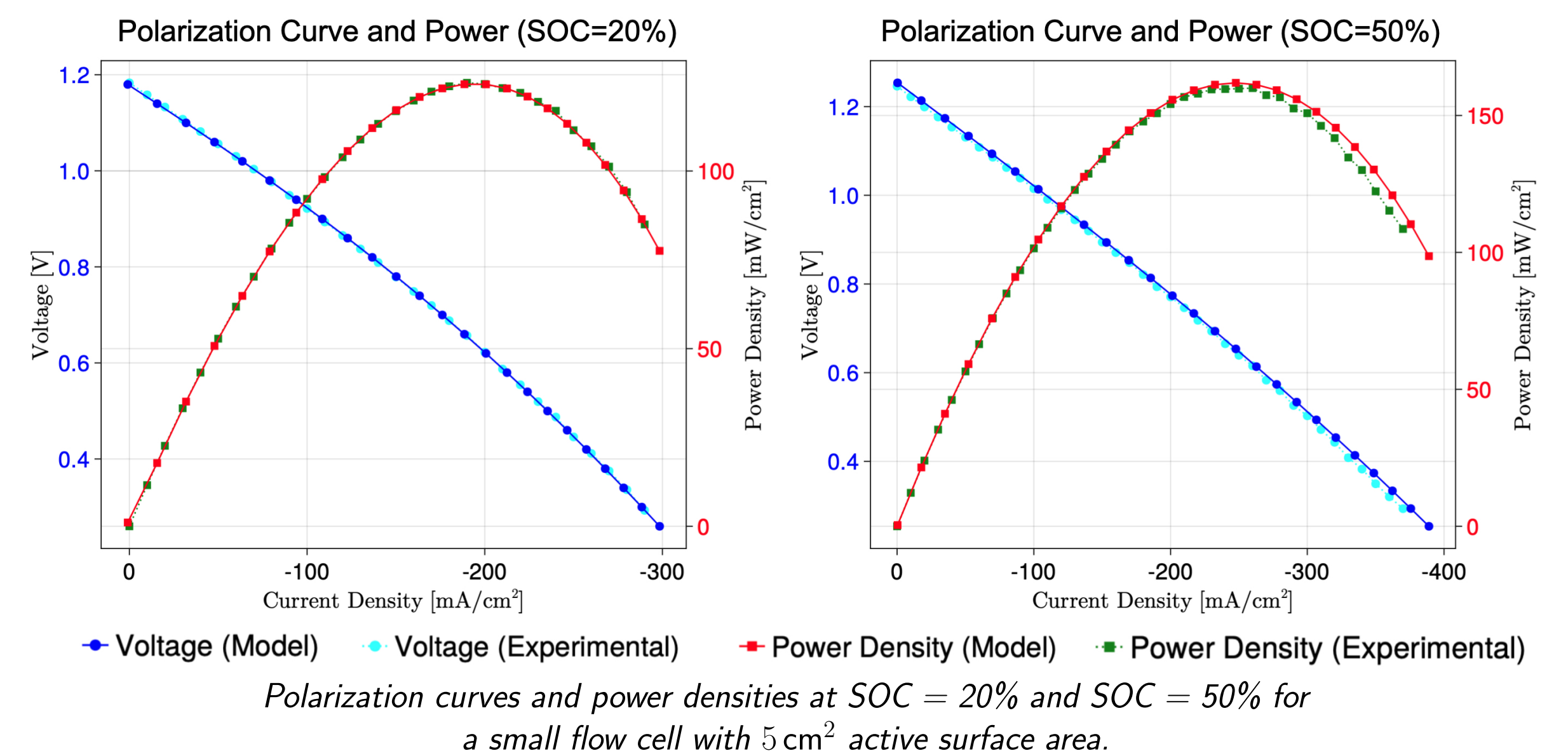
Introduction

Organic redox flow batteries (ORFBs) are a promising approach for large-scale stationary energy storage. The large chemical space available for organic electro-active redox couples allows for great chemical flexibility and has led to the development of a variety of promising chemical systems.

To accelerate the design and optimization of ORFB cells we develop a spatially resolved model that solves for the transient solution of the coupled mass, momentum, and energy transport equations within the porous electrodes, current collectors, and the ion-exchange membrane.

To account for the effective macroscopic transport properties in the porous electrodes, such as the dispersion of electro-active species, we integrate a porous electrode model based on the volume averaging method. Additionally, we use an effective membrane model that accounts for pressure-driven and electro-osmotic flow.

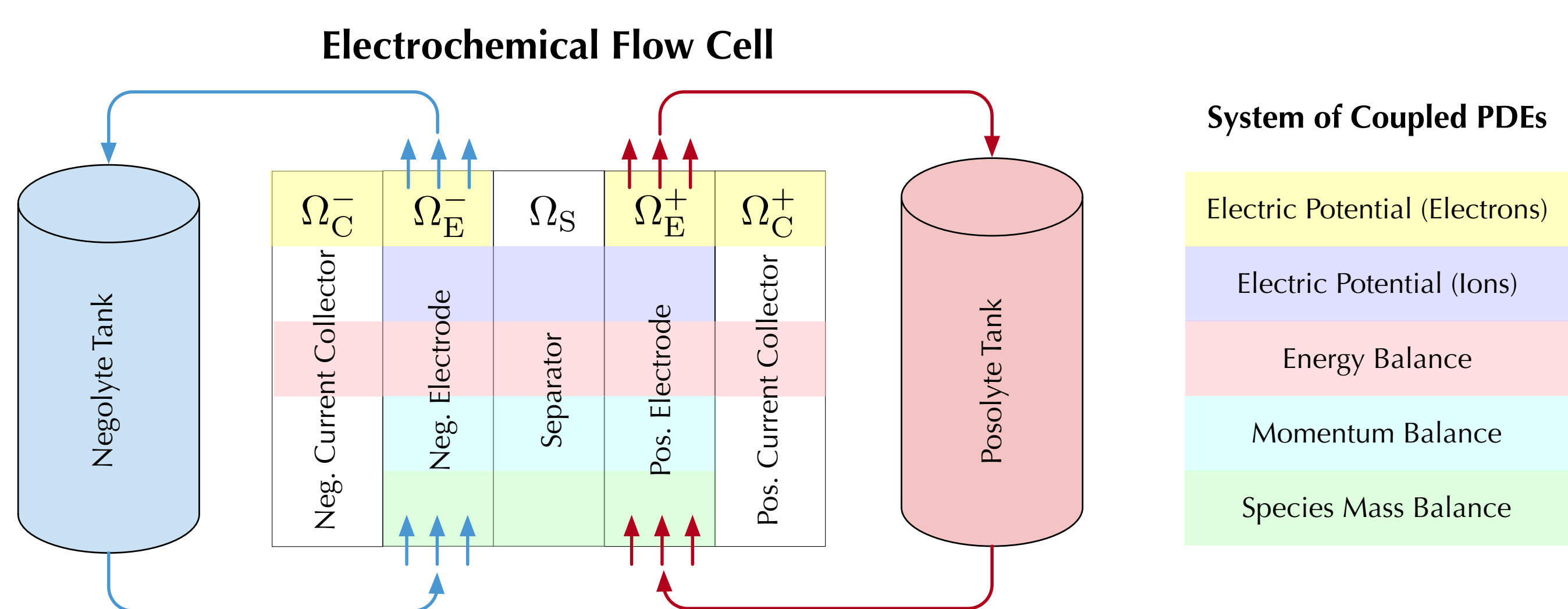
Validation with the MV/TEMPTMA System



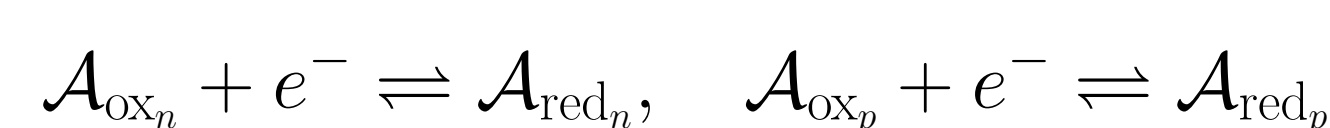
Modelling Assumptions and Simplifications

- Laminar, creeping electrolyte flow
- Negligible crossover of electro-active species
- Negligible side reactions
- Dilute-solution approximation
- Isotropic and homogeneous material properties per compartment
- Local thermal equilibrium

Cell Geometry and Transport Equations



Half cell redox reactions:



Scaling parameters:

$$\epsilon_L^0 = \frac{l^0}{L^0}, \quad \text{Pe}_L^0 = \frac{L^0 v^0}{D^0}, \quad \text{Sc}^0 = \frac{\nu^0}{D^0}, \quad \text{Le}^0 = \frac{\lambda^0 / (\rho^0 c_p^0)}{D^0}, \quad \text{Ki}_l = \frac{k_l^0 l^0}{D^0}, \quad \text{Sh}_l = \frac{k_m^0 l^0}{D^0}$$

Dimensionless transport equations:

Description	Variable	Balance Law
Electrostatic potential (solid)	ϕ_s	$\nabla \cdot \mathbf{J}_s = \epsilon_L^{-2} S_s$
Electrostatic potential (liquid)	ϕ_l	$\nabla \cdot \mathbf{J}_l = \epsilon_L^{-2} S_l$
Molar species concentration	c_α	$\epsilon \text{Pe}_L^0 \partial_t c_\alpha + \nabla \cdot (\text{Pe}_L^0 c_\alpha \mathbf{v} + \mathbf{N}_\alpha) = \epsilon_L^{-2} S_\alpha$
Electrolyte flow	\mathbf{v}	$\nabla \cdot \mathbf{v} = 0$
Energy balance	T	$\text{Pe}_L^0 \partial_t (\rho c_p T) + \nabla \cdot (\text{Pe}_L^0 \rho c_p \mathbf{v} T + \text{Le}^0 \mathbf{q}) = S_T$

Fluxes:

$$\mathbf{J}_s = -\sigma_s^{\text{eff}} \nabla \phi_s, \quad \mathbf{J}_l = -\left(\sigma_l^{\text{eff}} \nabla \phi_l + \sum_\alpha z_\alpha \mathbf{D}_\alpha^* \nabla c_\alpha \right), \quad \mathbf{q} = -\lambda \nabla T$$

$$\mathbf{N}_\alpha = -\left(\mathbf{D}_\alpha^* \nabla c_\alpha + z_\alpha \mathbf{D}_\alpha^{\text{eff}} c_\alpha \nabla \phi_l \right), \quad \mathbf{v} = -\left(\frac{k_h}{\mu} \nabla p + \frac{n_d \sigma_l}{z_c \text{Pe}_L^0} \nabla \phi_l \right)$$

Source terms (in the porous electrodes):

$$\text{Electrochemical reactions: } |S_s| = |S_l| = |S_\alpha| = |i_v|$$

$$\text{Joule and reaction heat: } S_T = \sigma_l^{\text{eff}} |\nabla \phi_l|^2 + \sigma_s^{\text{eff}} |\nabla \phi_s|^2 + \epsilon_L^{-2} i_v \eta$$

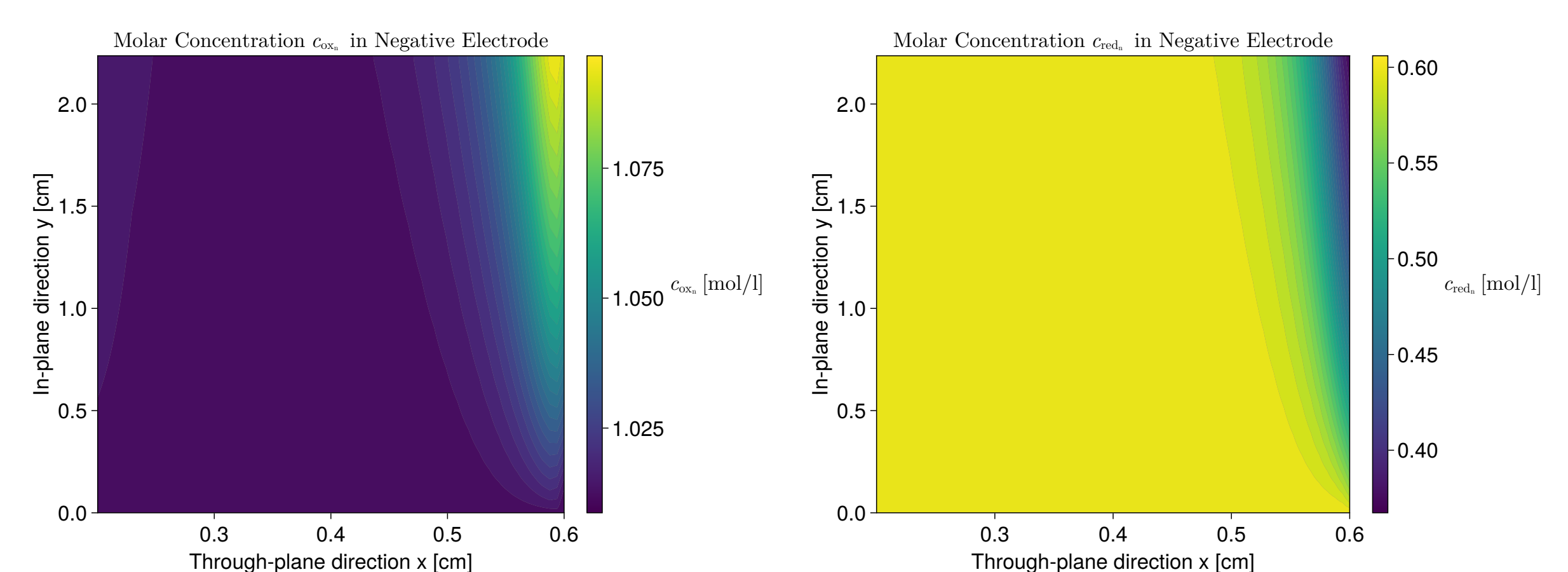
Volumetric reaction rate:

$$i_v = a_v \text{Ki}_l c_{\text{ox}} \frac{e^\eta - 1}{\left(1 + \frac{c_{\text{ox}}}{c_{\text{red}}} e^\eta \right) \frac{\text{Ki}_l}{\text{Sh}_l} + \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \right)^\alpha e^{\alpha \eta}}, \quad \eta = (\phi_s - \phi_l) - \Delta \phi_{\text{eq}}$$

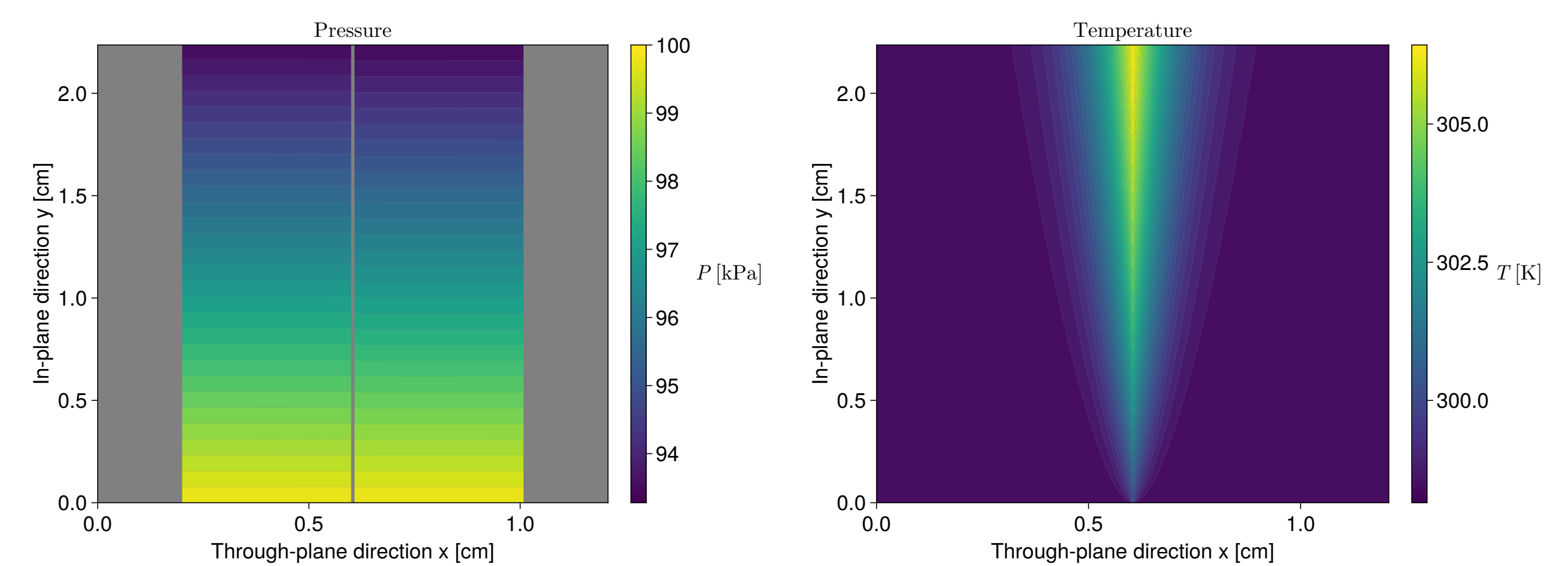
Effective diffusion tensor in isotropic porous electrodes:

$$\mathbf{D}_\alpha^* = D_\alpha (\alpha_G \mathbf{I} + \mathbf{D}^{\text{disp}}), \quad \mathbf{D}^{\text{disp}} = \alpha_L^{(1)} (\|\mathbf{v}\|) \mathbf{I} + \alpha_L^{(2)} (\|\mathbf{v}\|) \frac{\mathbf{v} \otimes \mathbf{v}}{\|\mathbf{v}\|}$$

Spatially Resolved Fields



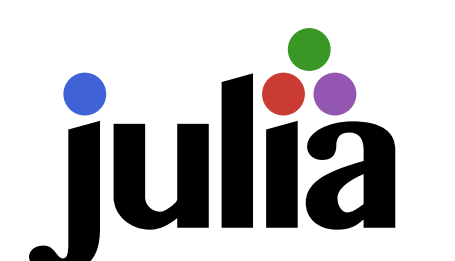
Molar species concentration fields in the half cell at discharging current density $i_{\text{cell}} \approx -103 \text{ mA cm}^{-2}$.



Pressure and temperature distribution for a non-isothermal case at $i_{\text{cell}} \approx -52 \text{ mA cm}^{-2}$.

Software Package: RfbScFVM.jl

- Open source model implementation in Julia (MIT licence)
- FV discretization using the *VoronoiFVM.jl* package
- Parameter specification with JSON configuration files



Summary and References

- Separator model accounting for pressure-driven and electro-osmotic flow
- Effective pore-scale model is used for parameterization of the total dispersion
- Implementation published as open source software package *RfbScFVM.jl*
- Model validation showing accurate prediction of cell polarization curves

References

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