MUFMech
MIDWESTERN UNIVERSITIES FLUID MECHANICS RETREAT
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FROG TAVERN LAKE WAWASEE

Session F (April 13, 2024)
Saturday

A transient theory for solute transport through redox flow battery electrodes in the creeping flow regime

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Introduction

What are batteries ???

Introduction

What are flow batteries ???

Turlock, CA

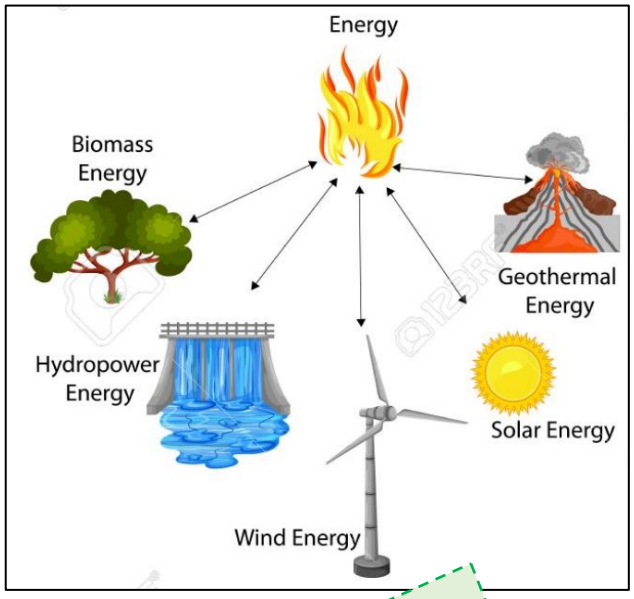
EnerVault deploys grid-scale redox flow battery for energy storage.

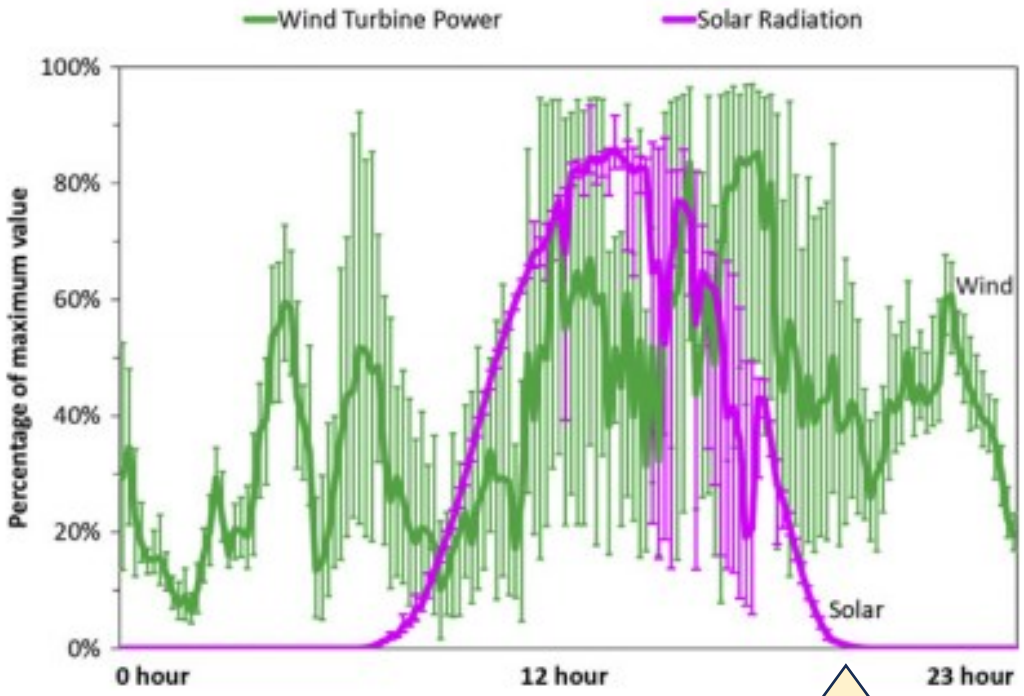
Central Valley, California. June-2014

https://worldindustrialreporter.com/redox-flow-battery-connects-solar-grid/

Introduction

What do we want to do with flow batteries ???



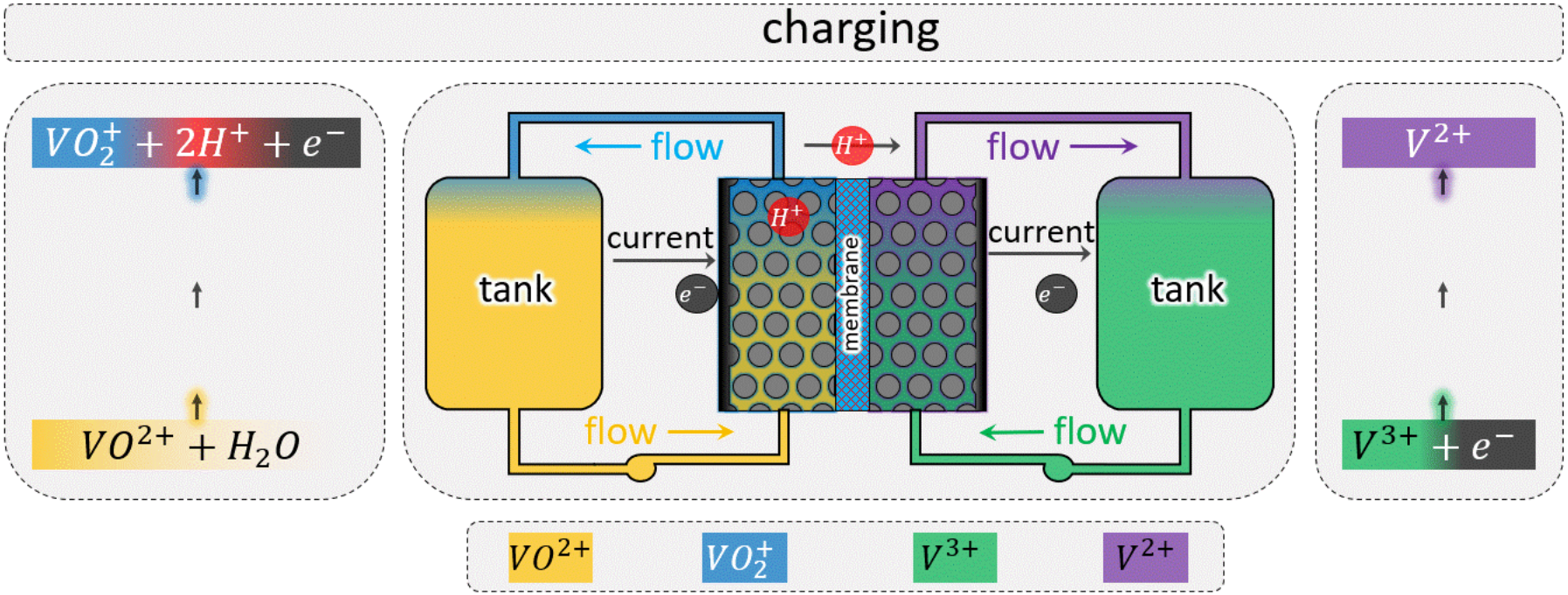


Power from **renewable** sources.

intermittent supply and demand → Flow Battery

Introduction

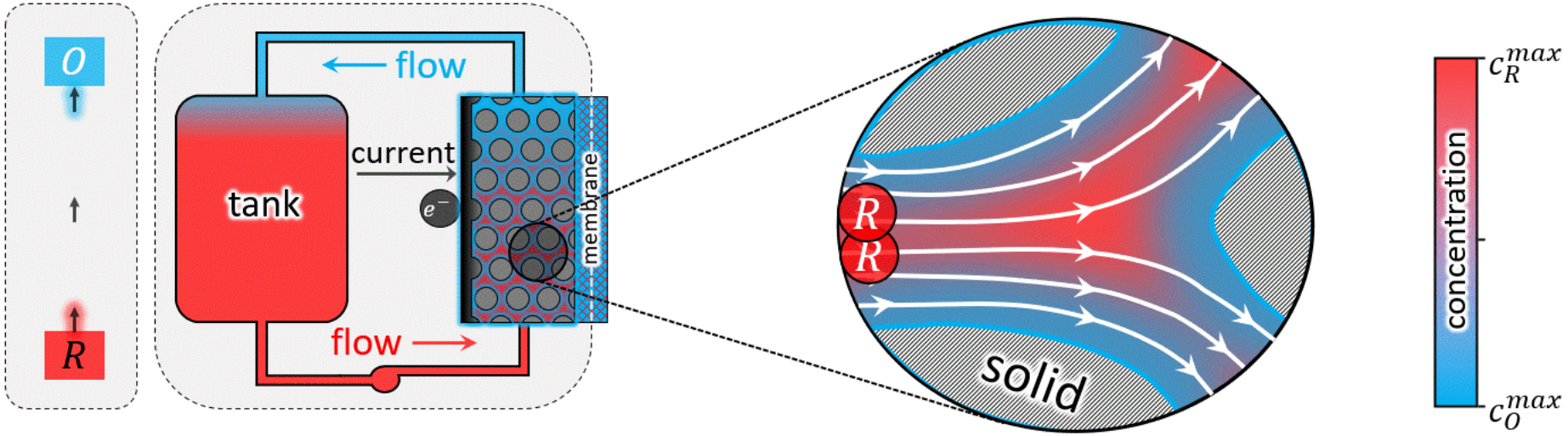
How does a flow battery work ???



Two symmetric-separated halves

Introduction

More detailed look inside porous electrode



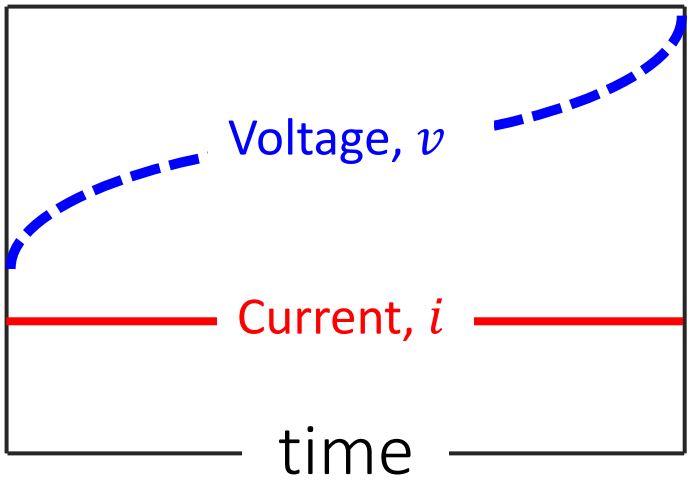
Half-cell with oxidation reaction

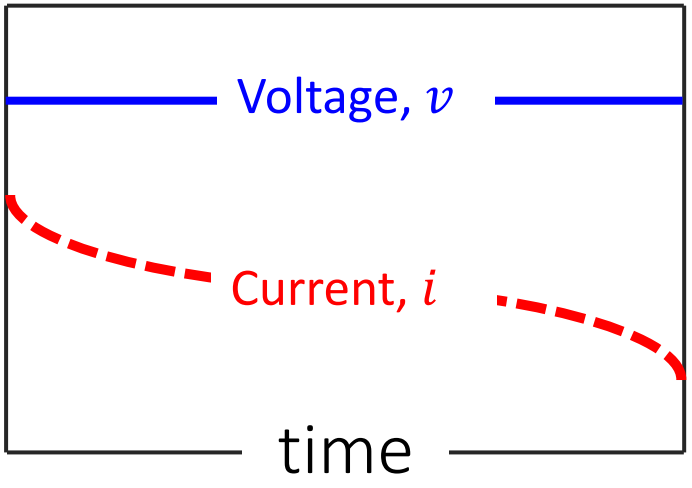
Reaction, advection and diffusion

Simplest experiment with battery

What would you do if:

You are given a battery & you are told to collect some data





Measure voltage

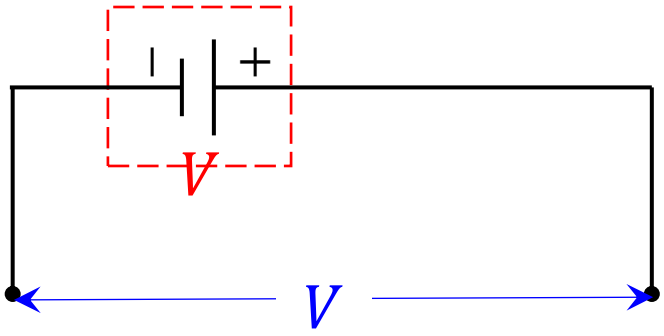
Control current

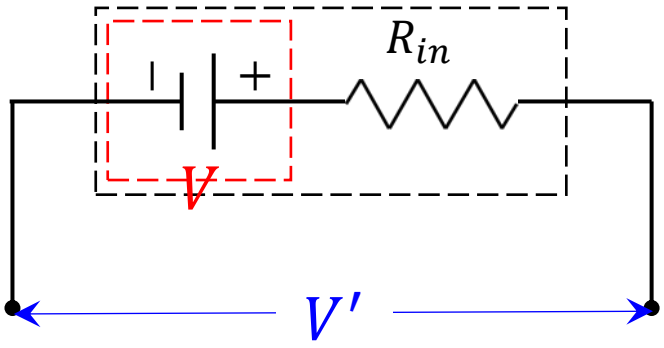
$Z_{eq}(t)$

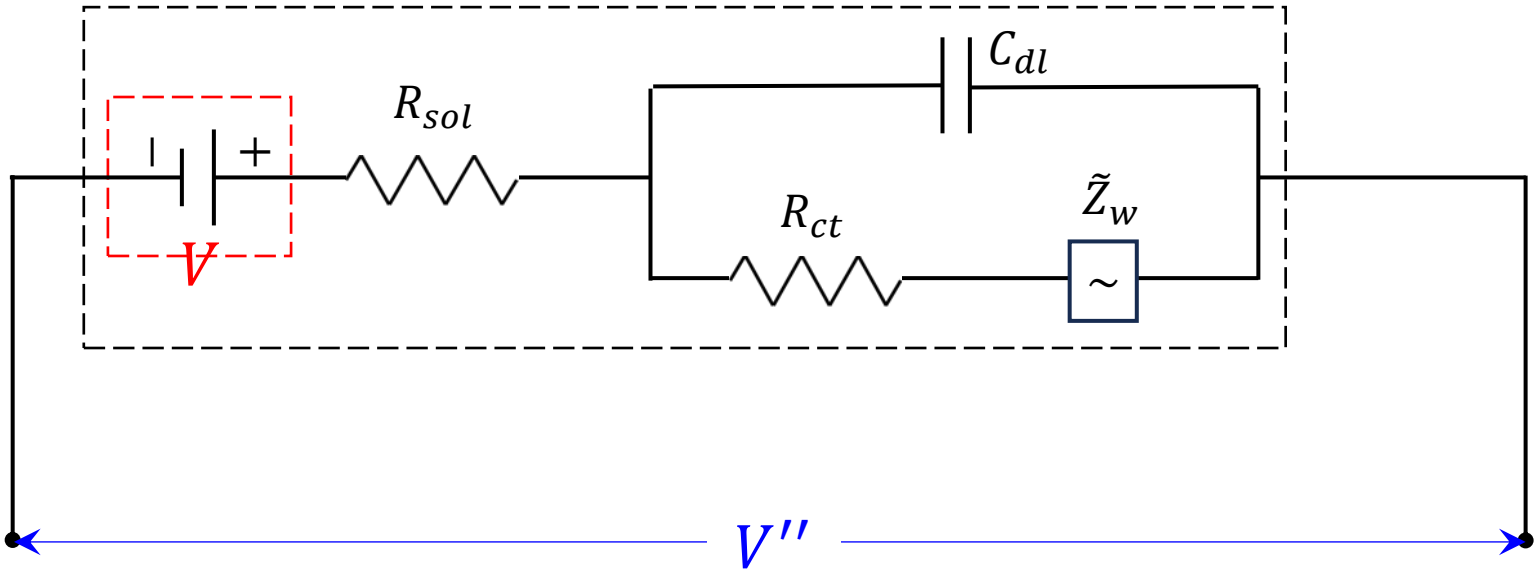
Control Voltage

Measure current

Equivalent circuit models





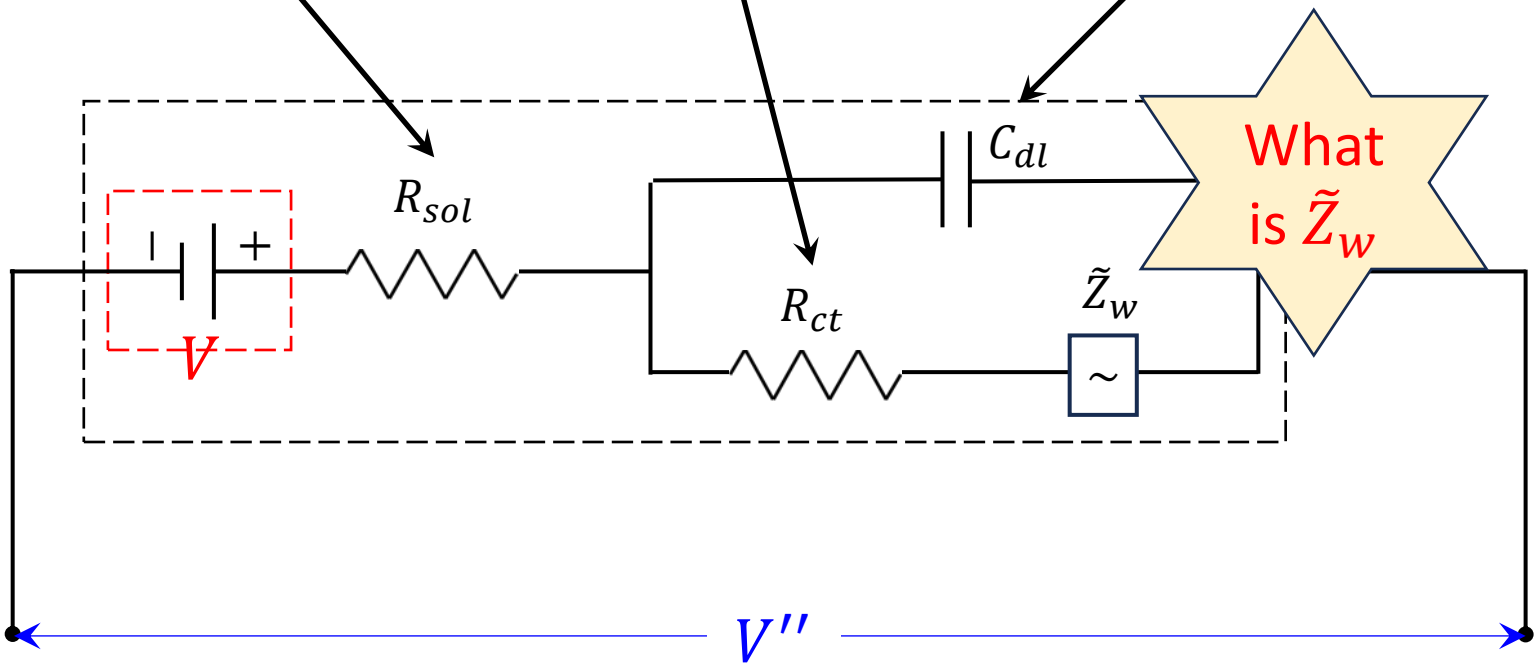


Warburg impedance

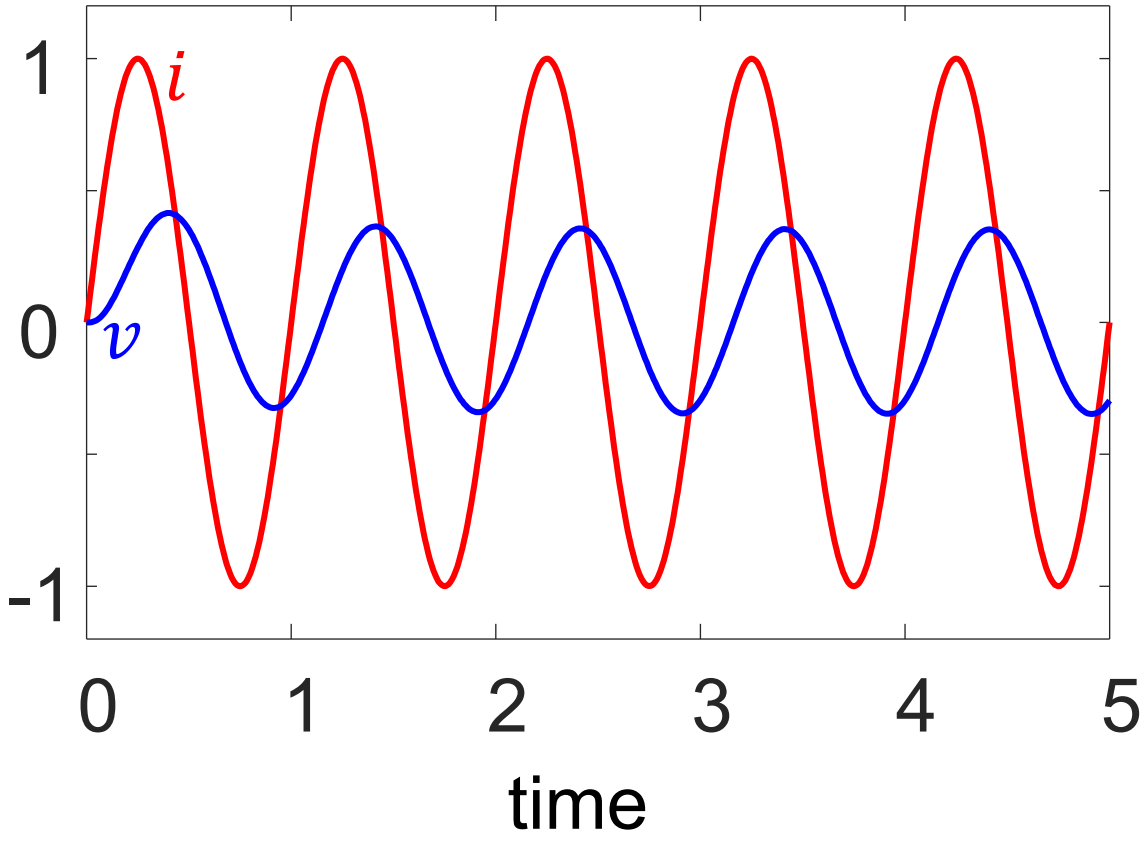
Sufficient supporting salt, negligible R_{sol}

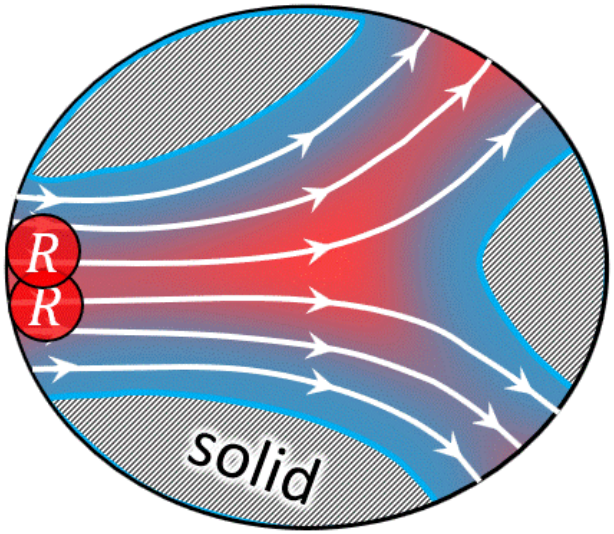
Fast reaction kinetics, Negligible R_{ct}

Current variation frequency $\ll MHz$, Effect of C_{dl} negligible



Warburg impedance and mass transfer

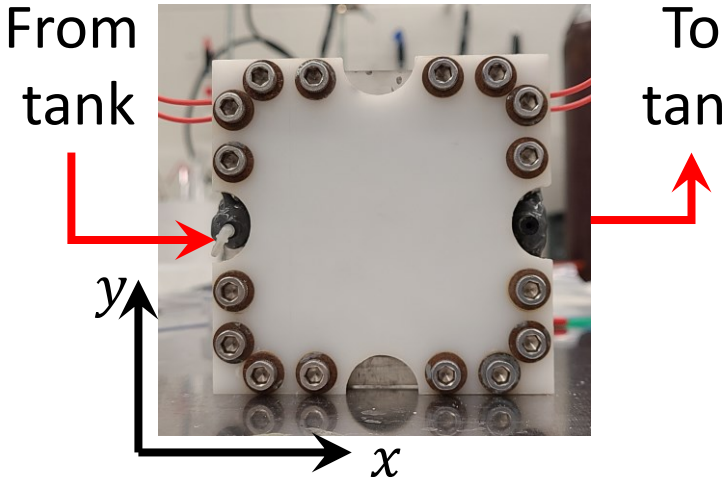


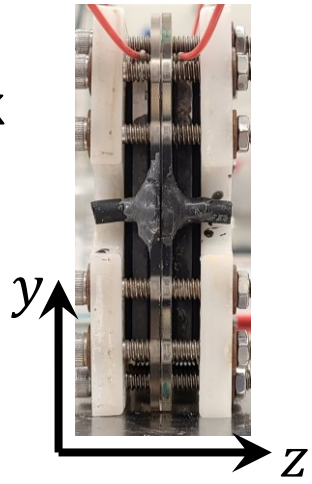


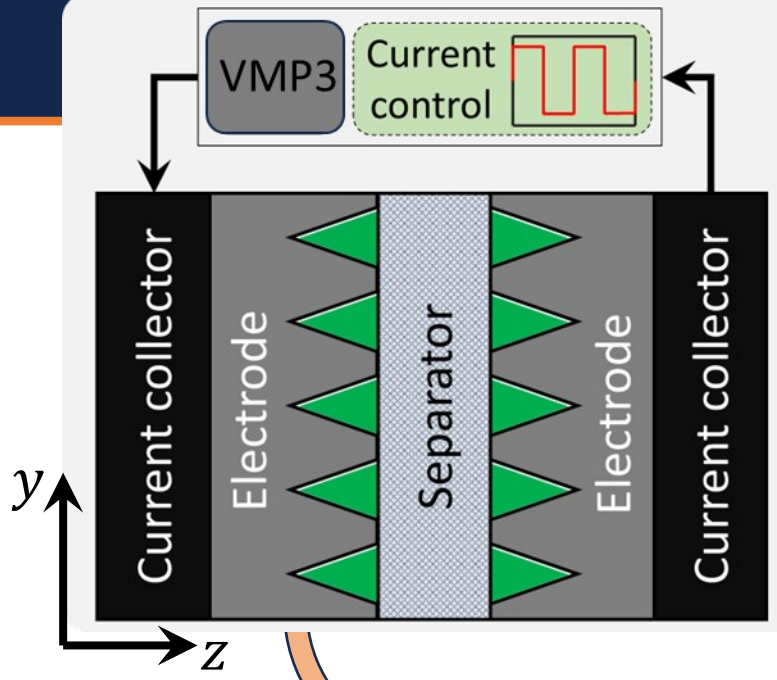
$Re \ll 1$

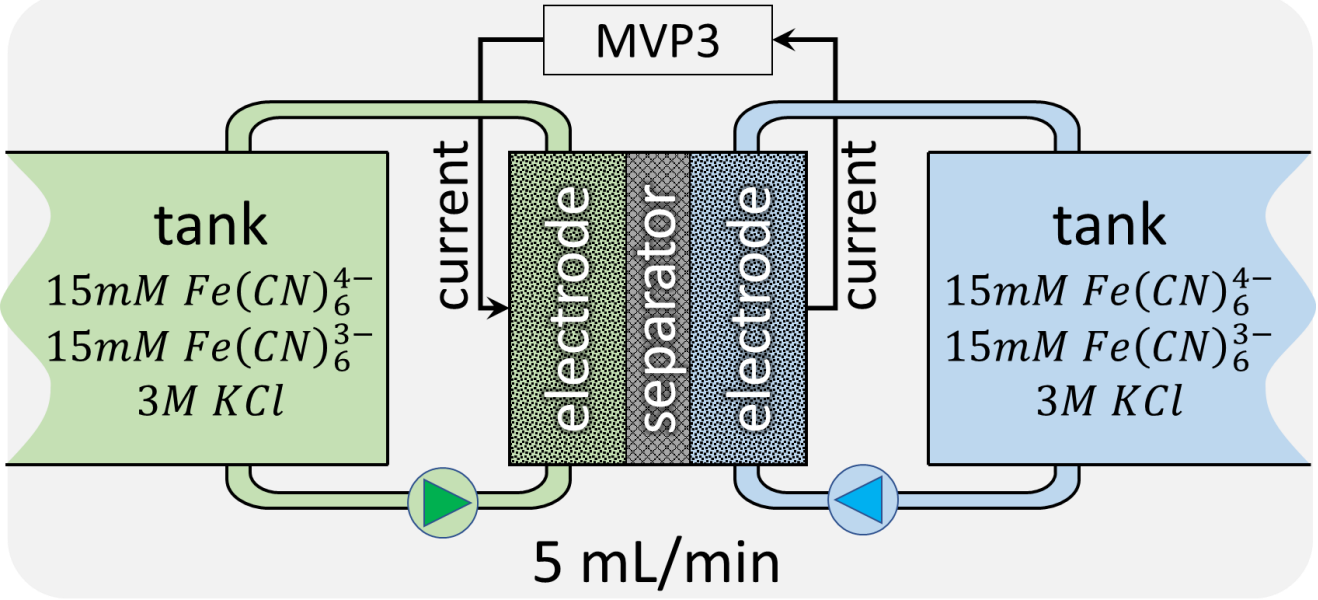
$$Pe = \frac{vl_c}{D} = \frac{advection\ rate}{diffusion\ rate} \longrightarrow Pe = Re \cdot Sc$$

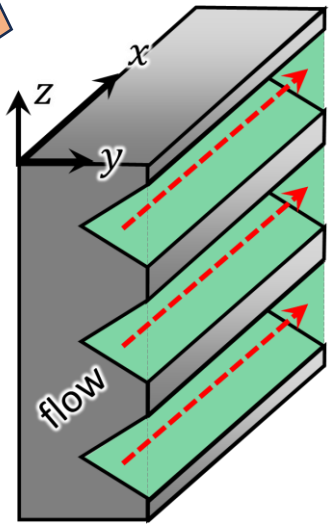
Transient experiment



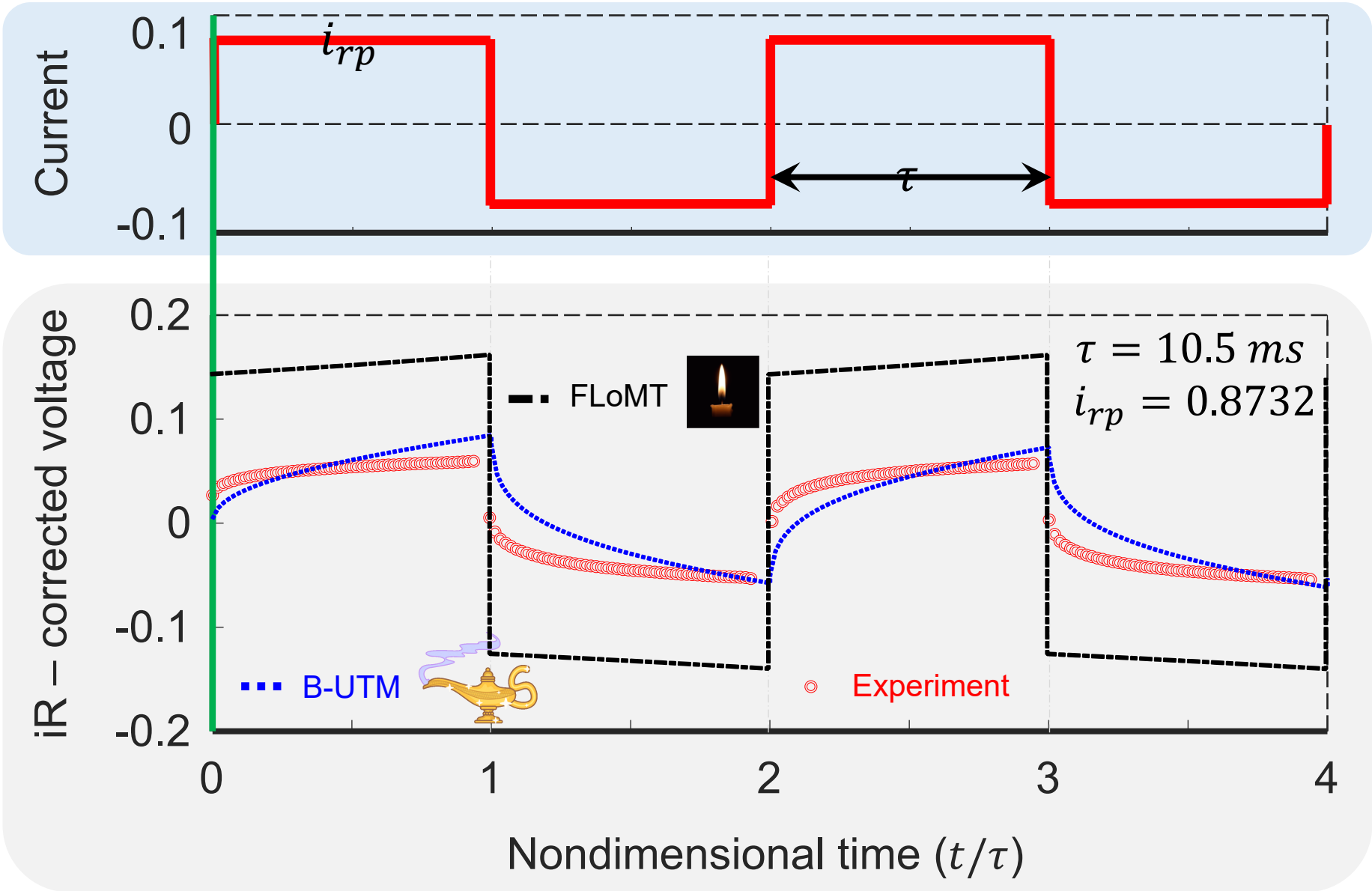








Experiment and simulations



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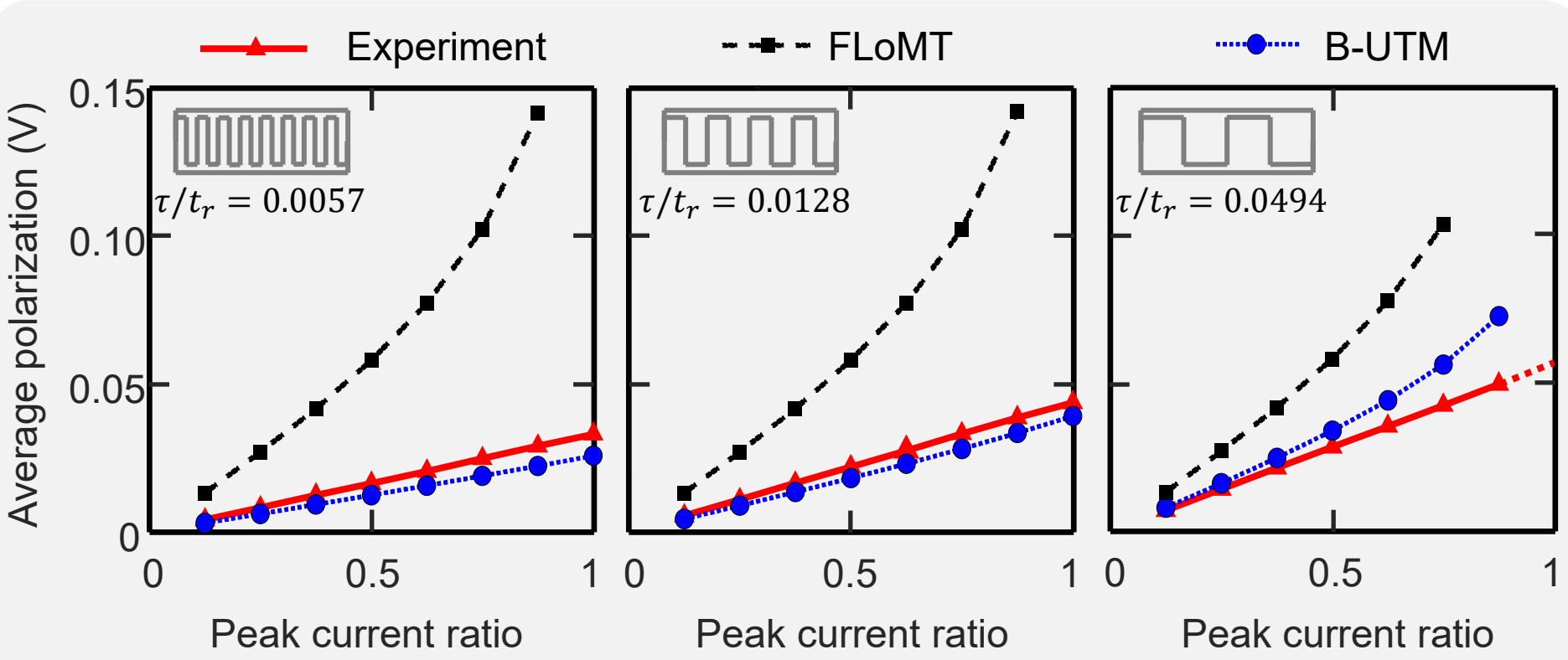
Experiment and simulations (cont..)



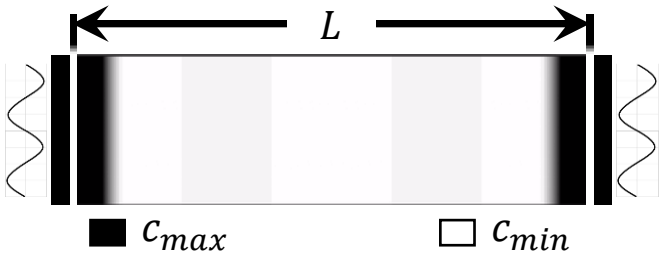
Mean residence time

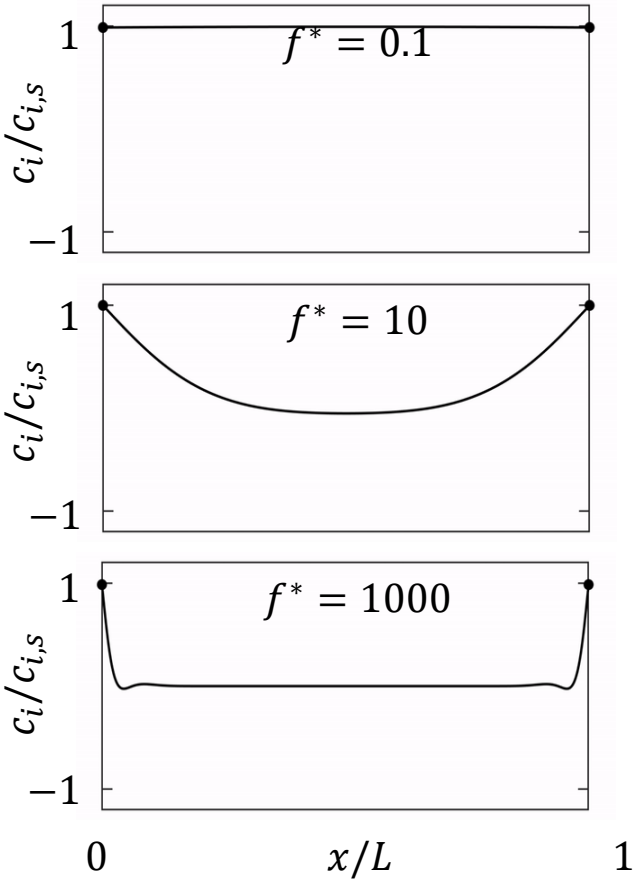
$$t_r = \frac{flow\ length}{superficial\ velocity}$$

FLoMT : Up to 400% overprediction

B-UTM : Significant improvement

Why  overpredicts $\tilde{Z}_w$





- In conventional theories  the diffusion length is taken as constant.
- Usually the pore dimension/size is taken as characteristics diffusion length.
- At high frequency actual diffusion length decreases considerably.
- Transient theory  is mandatory for such high frequency operation.

Frequency dependent pore-scale transport

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\boldsymbol{u}^{\blacksquare} c_i - D_i \nabla c_i) = 0$$

$$c_i\Big|_s = c_{i,s}(t)$$

Valid for facile reaction

$$Da \gg min\left[1, e^{\alpha \frac{F\eta}{RT}}\right]$$

Fourier transform

$$\mathcal{F}\{A(t)\} = \bar{A}(\omega)$$

$$\nabla \cdot (\boldsymbol{u}^{\blacksquare} \bar{c}_i - D_i \nabla \bar{c}_i) + j\omega \bar{c}_i = 0$$

$$\bar{c}_i\Big|_s = \bar{c}_{i,s}(\omega)$$

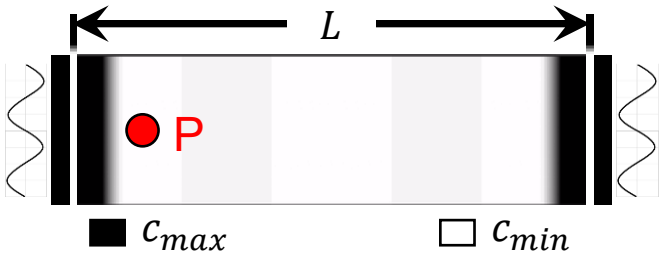
Transfer function:

$$\mathbb{C}_i(\omega, \boldsymbol{r}) \equiv \frac{\bar{c}_i(\omega, \boldsymbol{r})}{\bar{c}_{i,s}(\omega)}$$

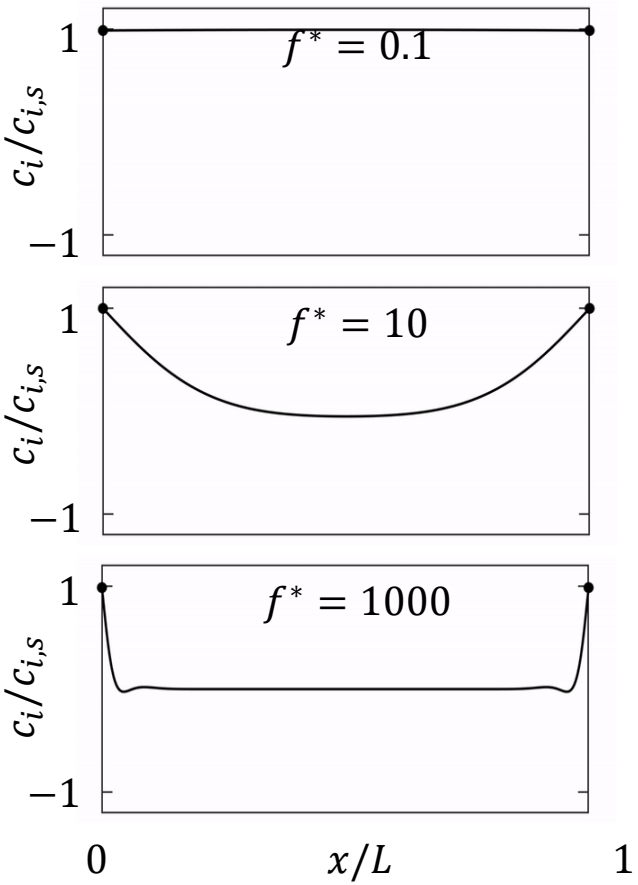
$$\nabla \cdot (\boldsymbol{u}^{\blacksquare} \mathbb{C}_i - D_i \nabla \mathbb{C}_i) + j\omega \mathbb{C}_i = 0$$

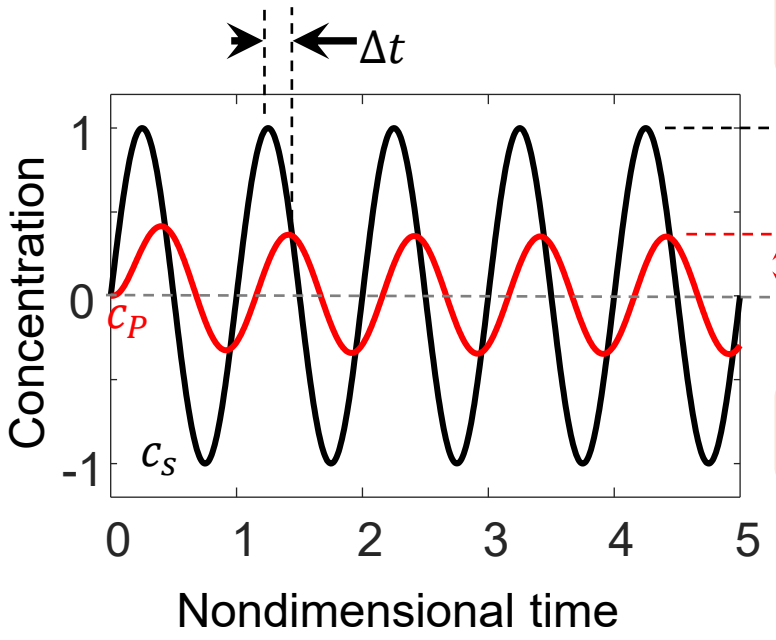
$$\mathbb{C}_i\Big|_s = 1$$

Transfer function $\mathbb{C}(\omega, r)$ in parallel plates



- $\mathbb{C}$ provides local transient response under pure-sinusoidal *disturbance.*
- At surface $|\mathbb{C}| = 1$ and $\theta_{\mathbb{C}} = 0$.





$$\theta_{\mathbb{C},P} = \omega\,(\Delta t)_P$$

$$|\mathbb{C}_P| = c_P/c_s$$

Volume averaged TF - Diffusion

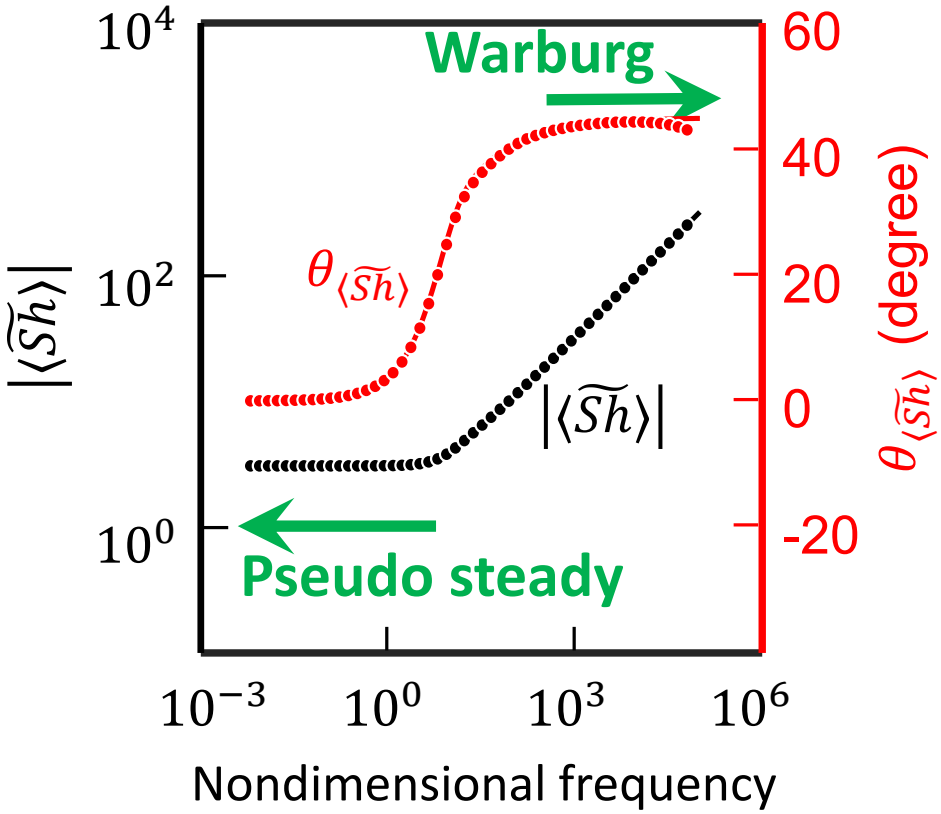
Spectral Sherwood number

$$\langle \widetilde{Sh} \rangle(\omega) \equiv \left(\frac{b}{D}\right) \frac{\langle \vec{j} \rangle_s}{\bar{c}_s - \langle \bar{c} \rangle}$$

$$= \frac{-\langle \partial \mathbb{C} / \partial n^* \rangle}{1 - \langle \mathbb{C} \rangle}$$

Gives Instantaneous reaction rate

$\langle \dots \rangle$ and $\langle \dots \rangle_s$ are respectively integral averages over solution volume and solid/solution interfaces



Volume averaged TF - advection

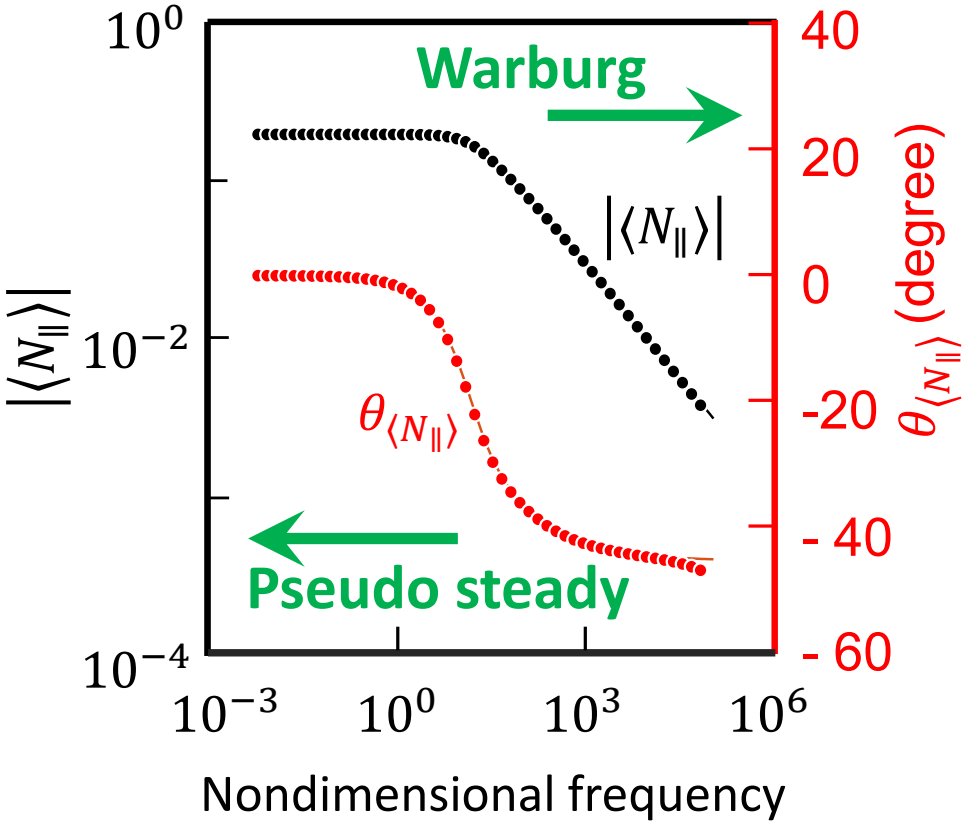
Advective-flux transfer function

$$\langle N \rangle \equiv \left(\frac{\varepsilon}{|u_s|} \right) \frac{\langle \overline{W} \rangle}{\bar{c}_s - \langle \bar{c} \rangle}$$

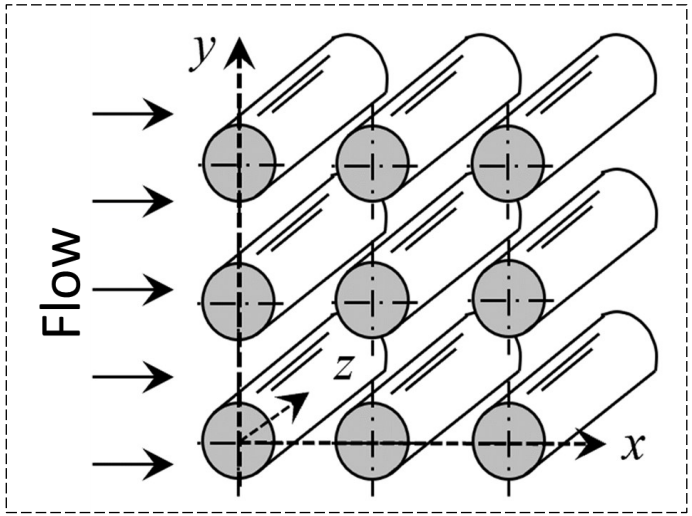
$$\langle W \rangle \equiv -\mathrm{covar}(u^{\blacksquare}, c)$$

$$= (u_s/\varepsilon)\langle c \rangle - \langle u^{\blacksquare} c \rangle$$

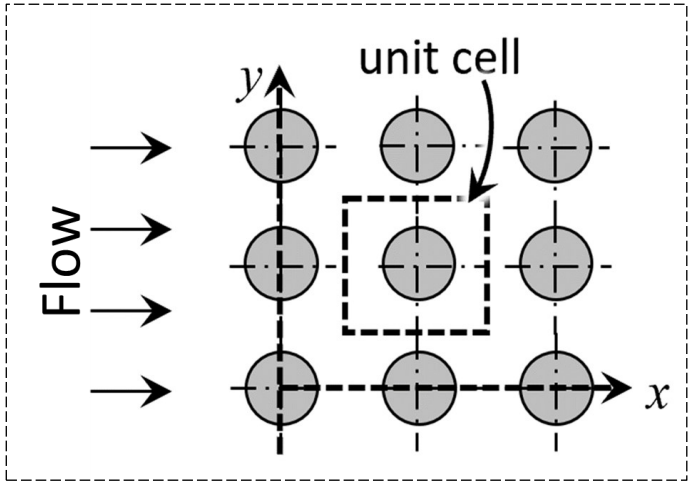
Gives
fractional deviation in
advection rate

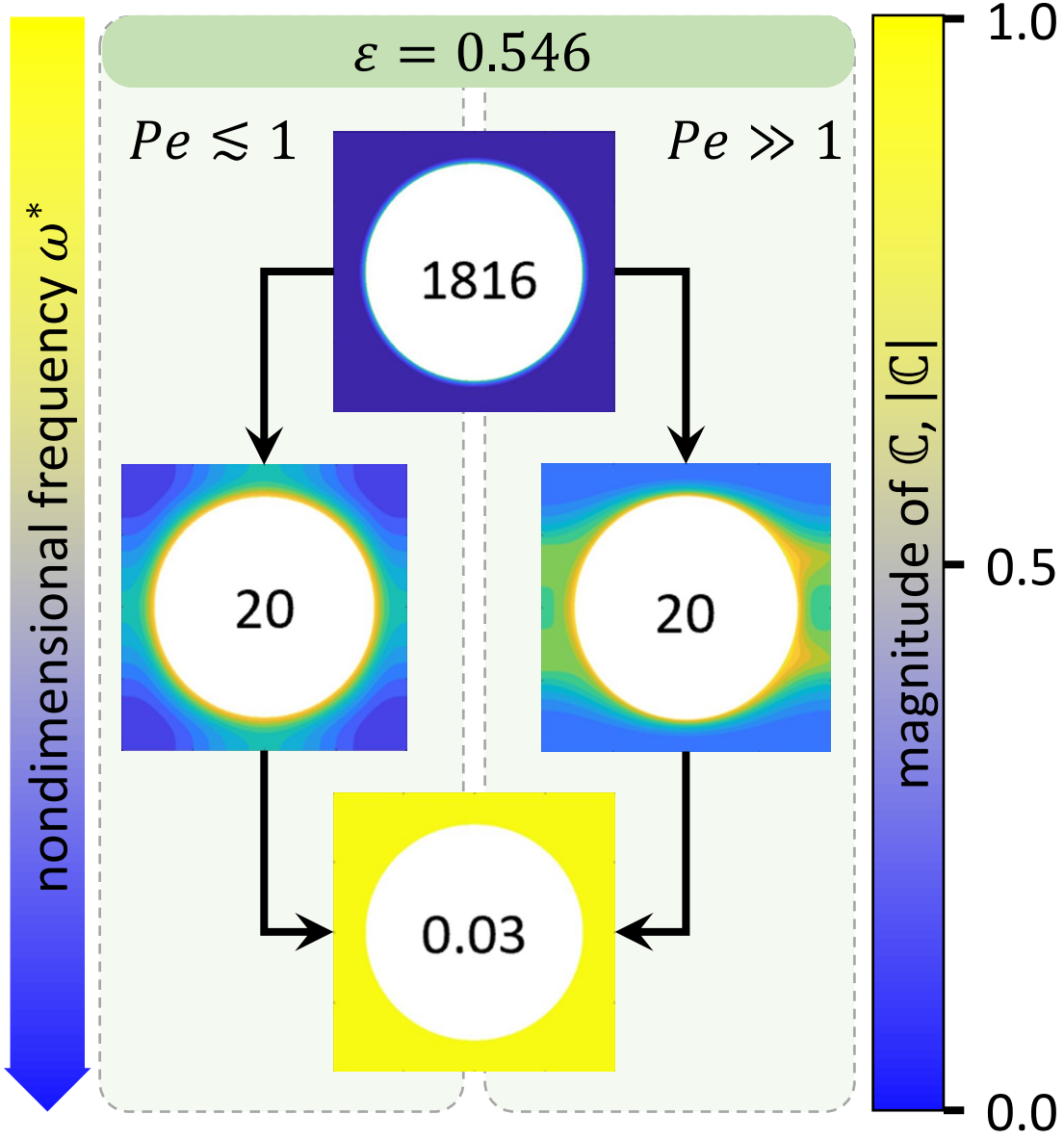


Porous electrode



Mimics carbon fiber electrode





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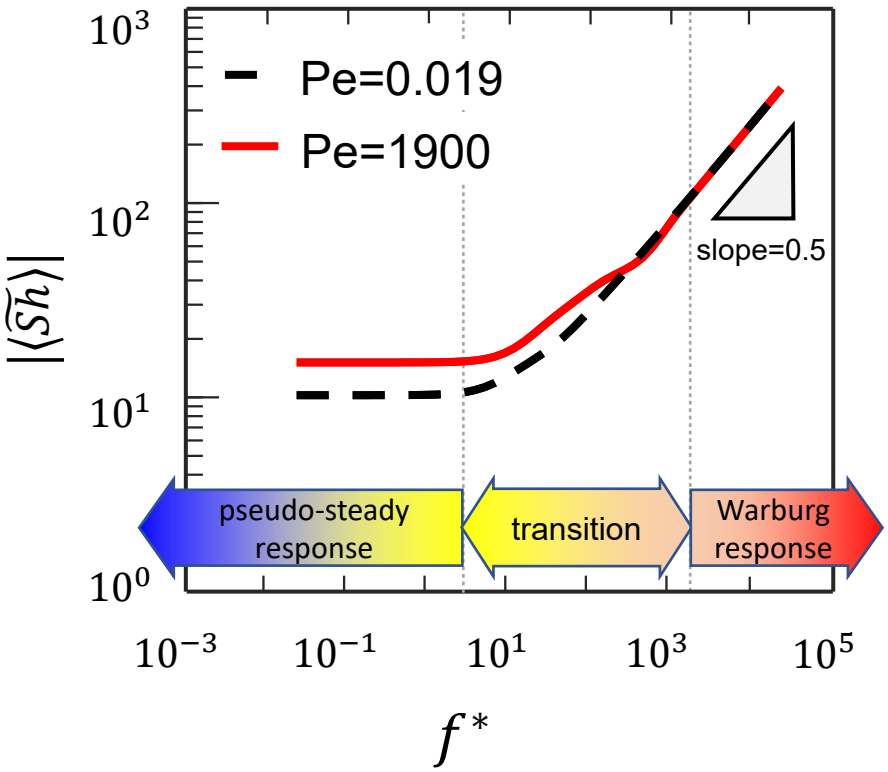
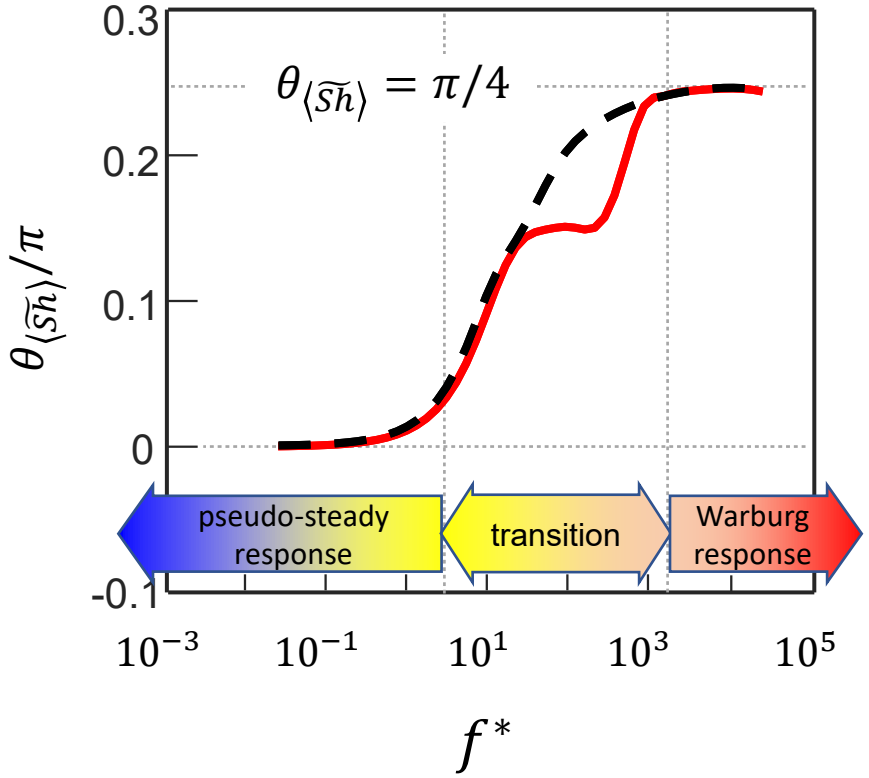
Volume averaged coefficient - Diffusion

Spectral Sherwood number: $\langle \widetilde{Sh} \rangle(\omega) \equiv \left(\frac{b}{D}\right) \frac{\langle \vec{j} \rangle_s}{\bar{c}_s - \langle \bar{c} \rangle} = \frac{-\langle \partial \mathbb{C} / \partial n^* \rangle}{1 - \langle \mathbb{C} \rangle}$

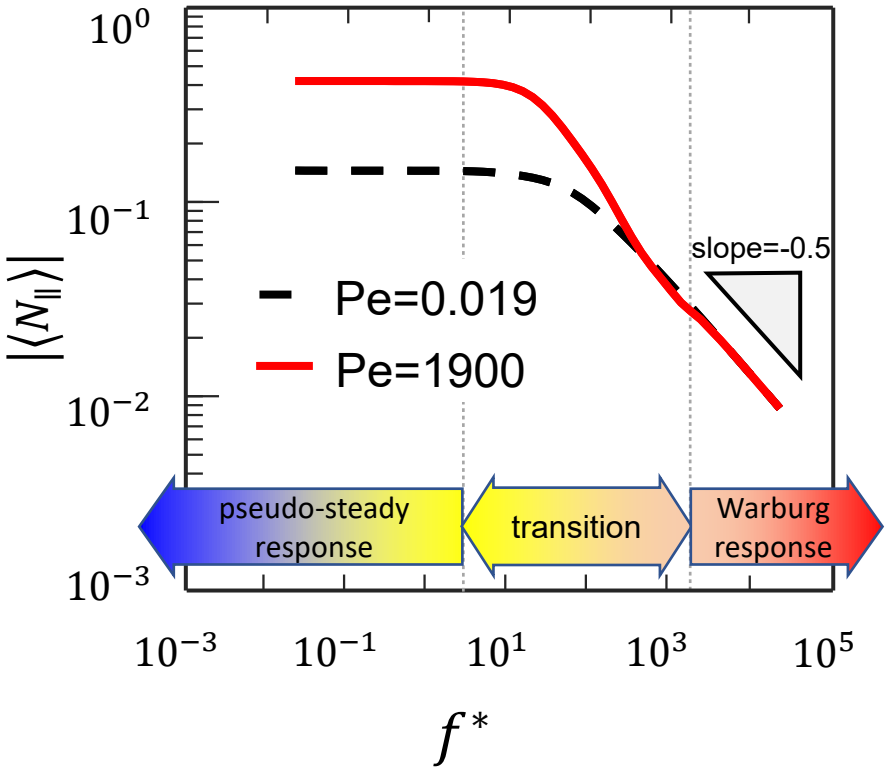


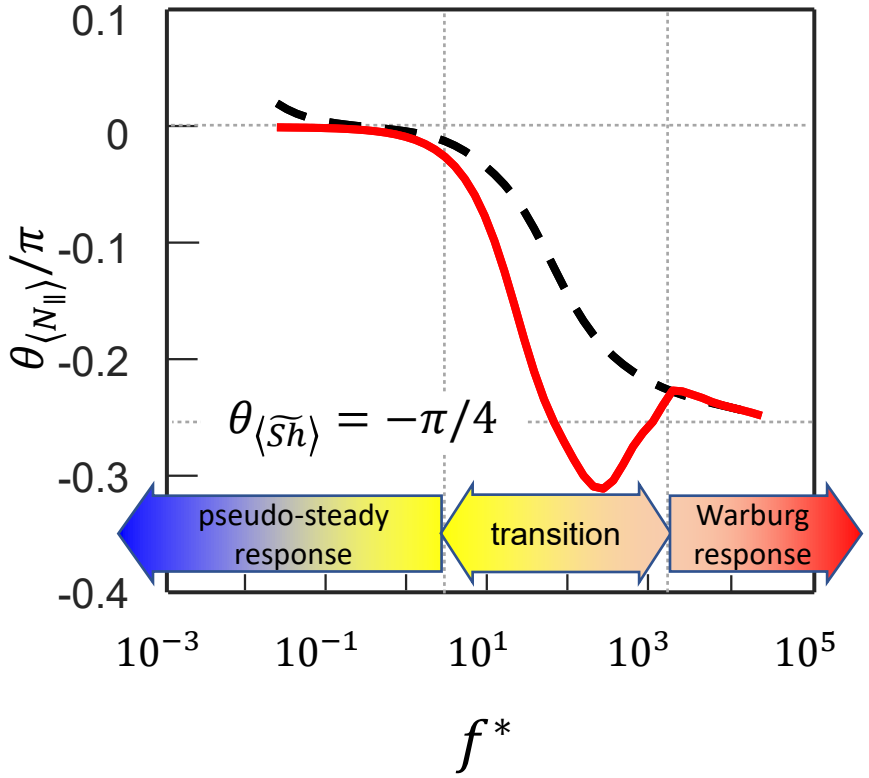


Volume averaged coefficient - advection

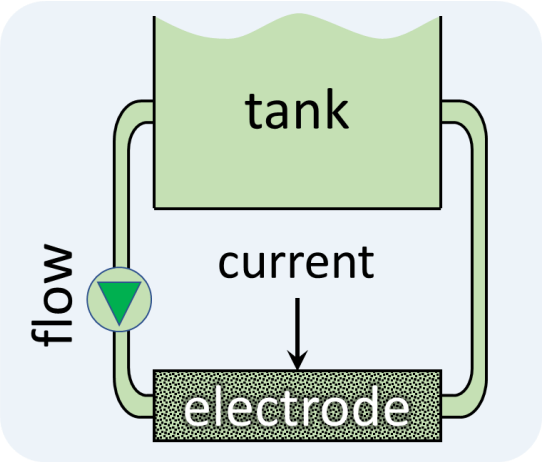
Advective-flux transfer function

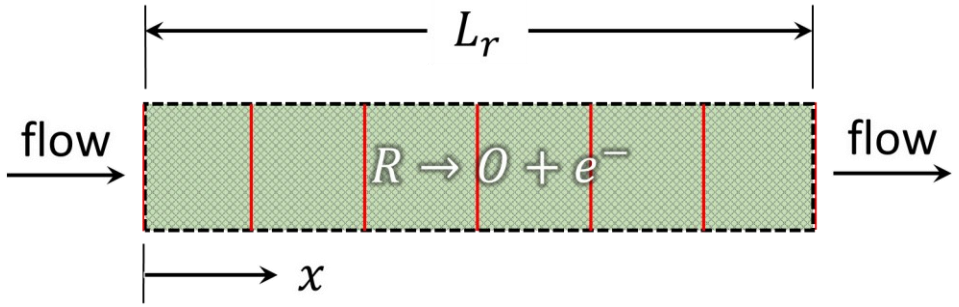
$$\langle \boldsymbol{N} \rangle \equiv \left(\frac{\varepsilon}{|\boldsymbol{u}_s|} \right) \frac{\langle \overline{\boldsymbol{W}} \rangle}{\bar{c}_s - \langle \bar{c} \rangle}$$





Frequency dependent up-scaled transport





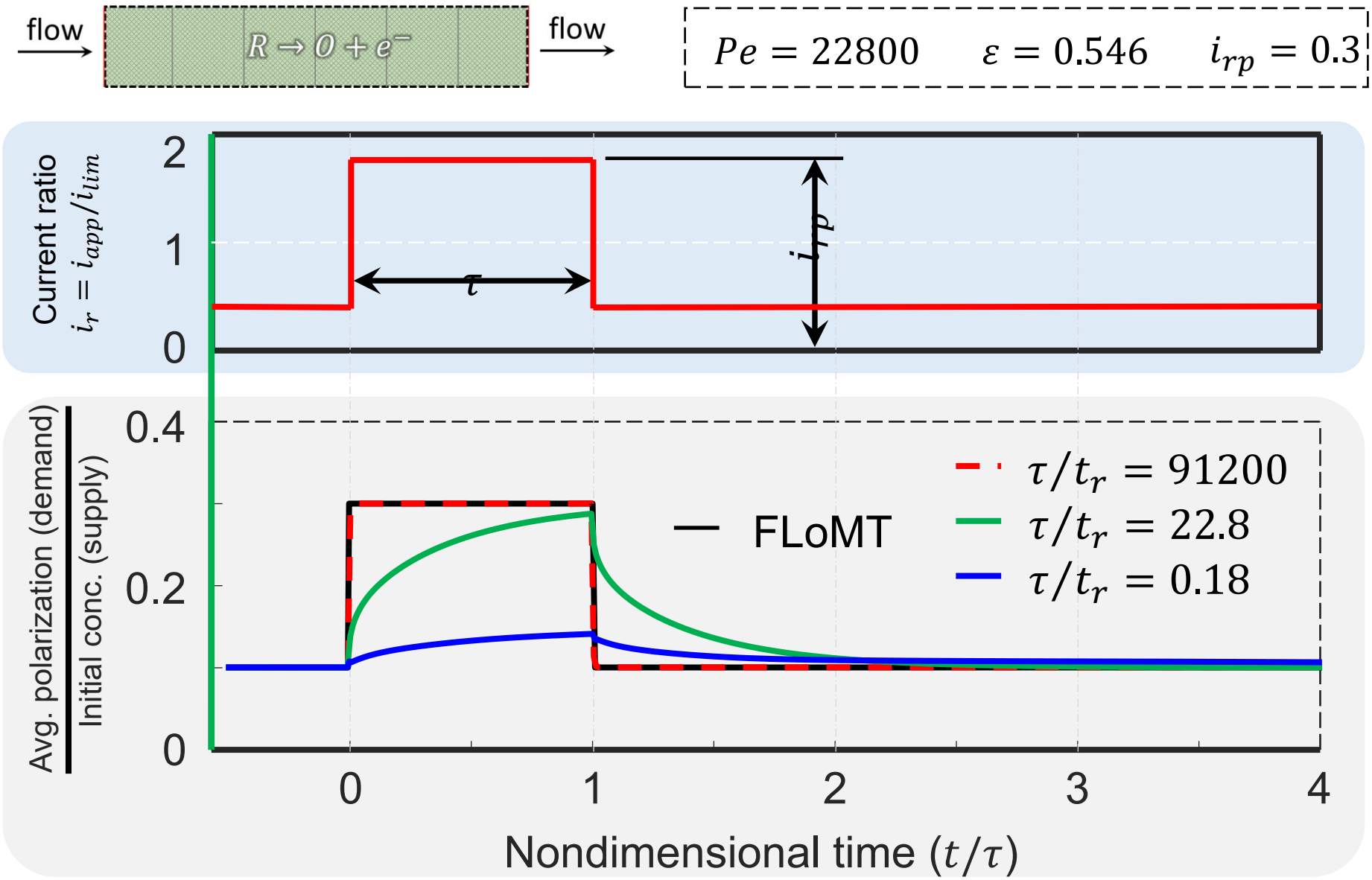
1-D upscaled model using porous electrode theory

$$\varepsilon \frac{\partial \langle c_i \rangle}{\partial t} + \nabla \cdot \boldsymbol{u}_s \langle c_i \rangle - |\boldsymbol{u}_s| \nabla \cdot \mathcal{F}^{-1}\{\langle \boldsymbol{N} \rangle (\bar{c}_{s,i} - \langle \bar{c} \rangle_i)\} = \frac{aD_i}{s_i b} \mathcal{F}^{-1}\{\langle \widetilde{Sh} \rangle (\bar{c}_{s,i} - \langle \bar{c} \rangle_i)\}$$

Accounts for instantaneous deviation of advection rate

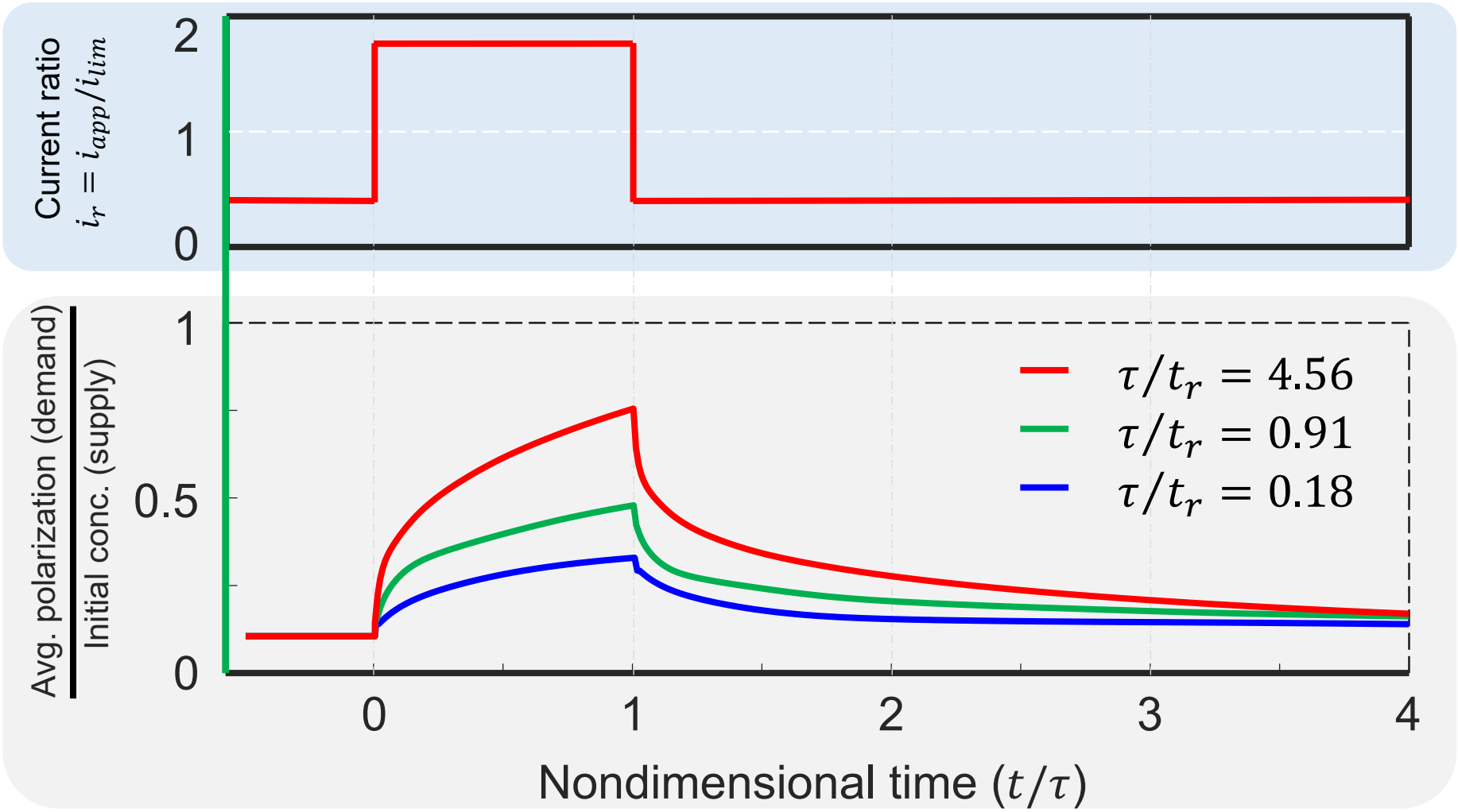
Accounts for the instantaneous reaction rate

Average polarization - reactant demand



Average polarization (over-limiting operation)

$Pe = 22800$ $\varepsilon = 0.546$ $i_{rp} = 1.2$



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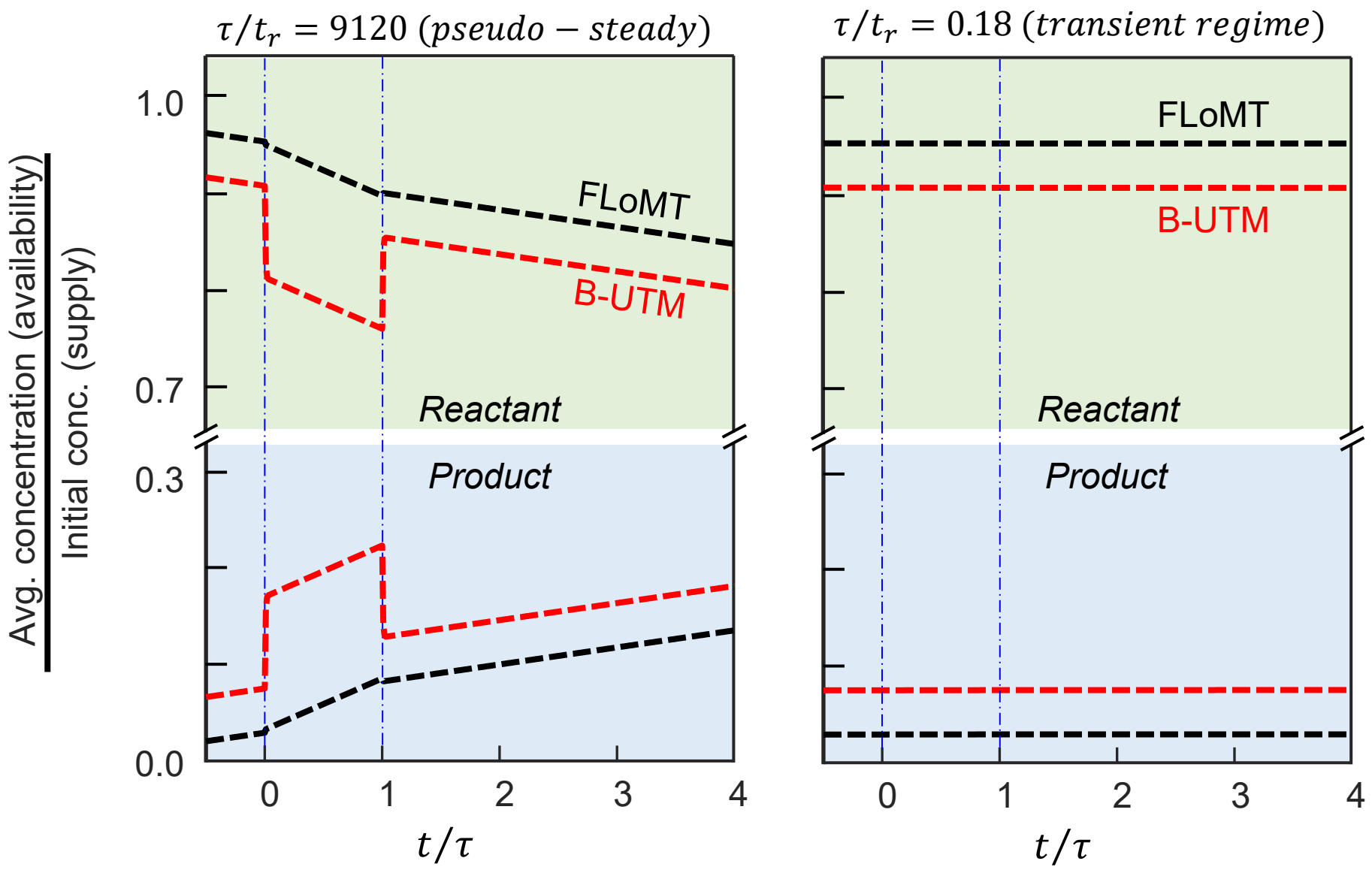
Average concentration - reactant availability



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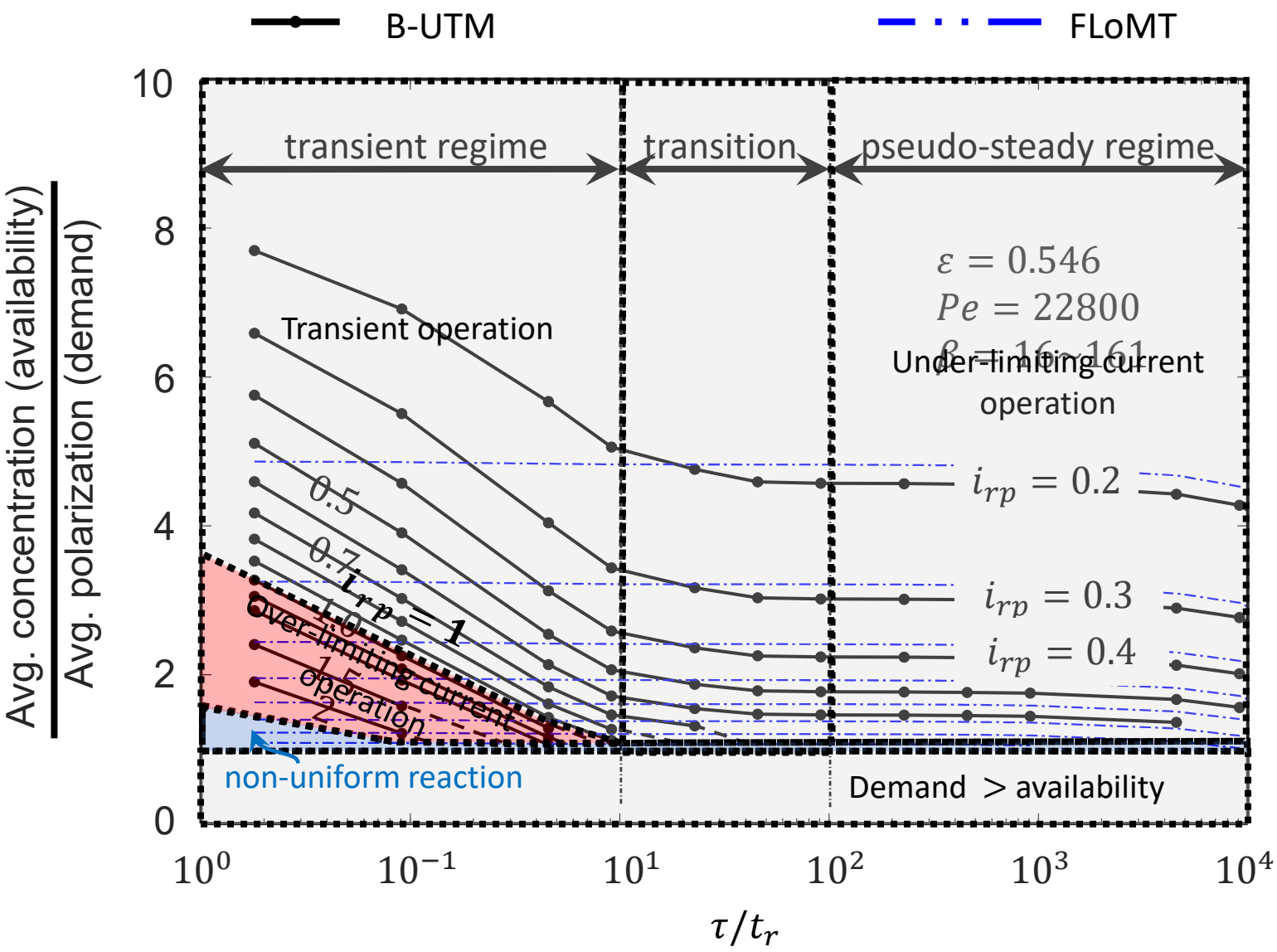
Non-dimensional maps of operational space



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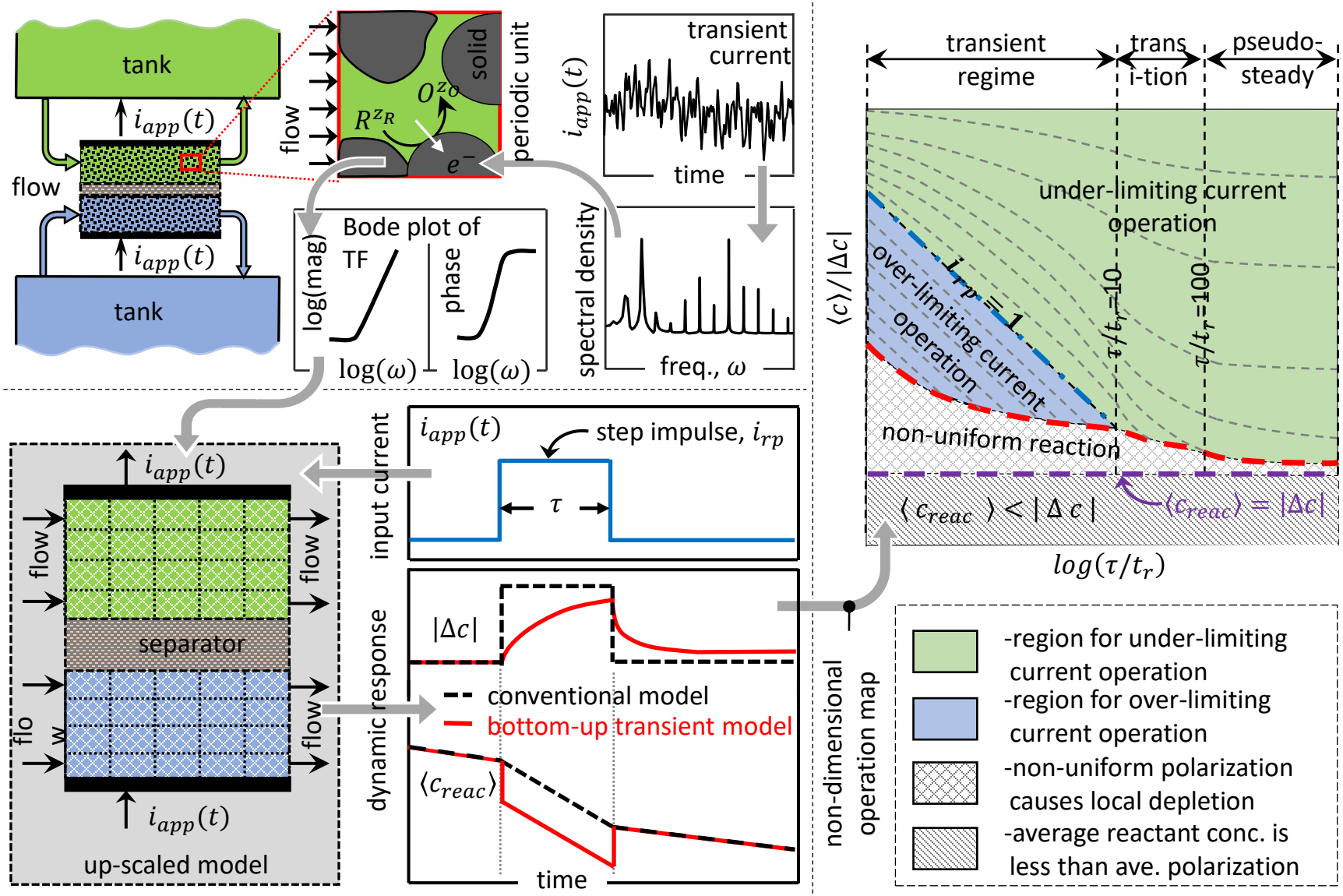
Reviewing the theory briefly



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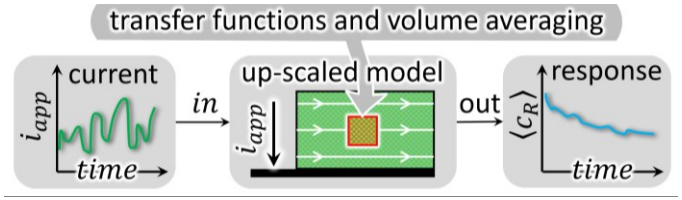
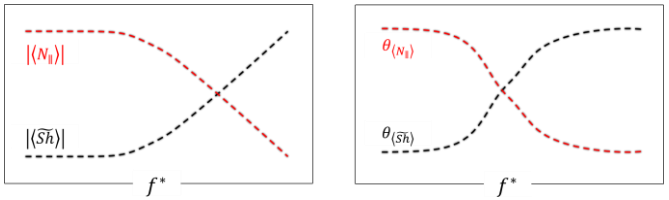
Conclusions

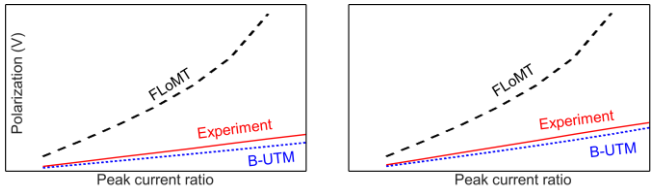
A bottom-up multi-scale theory is developed which can capture transient response of FBs.

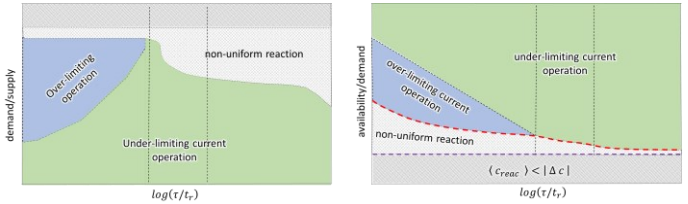




Volume averaged TFs enable direct upscaling.

Compared to FLoMT, B-UTM predictions are significantly close to experimental observations.





Over-limiting current is possible for short period of time.