Electrochemical Modeling of PEM Fuel Cells

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Valentin Sulzer*, Jason Siegel, Peyman Mohtat, Vishal Srivastava, Karthik Duraisamy

University of Michigan

*vsulzer@umich.edu

Fuel Cell Power Control University of Michigan

CASLab

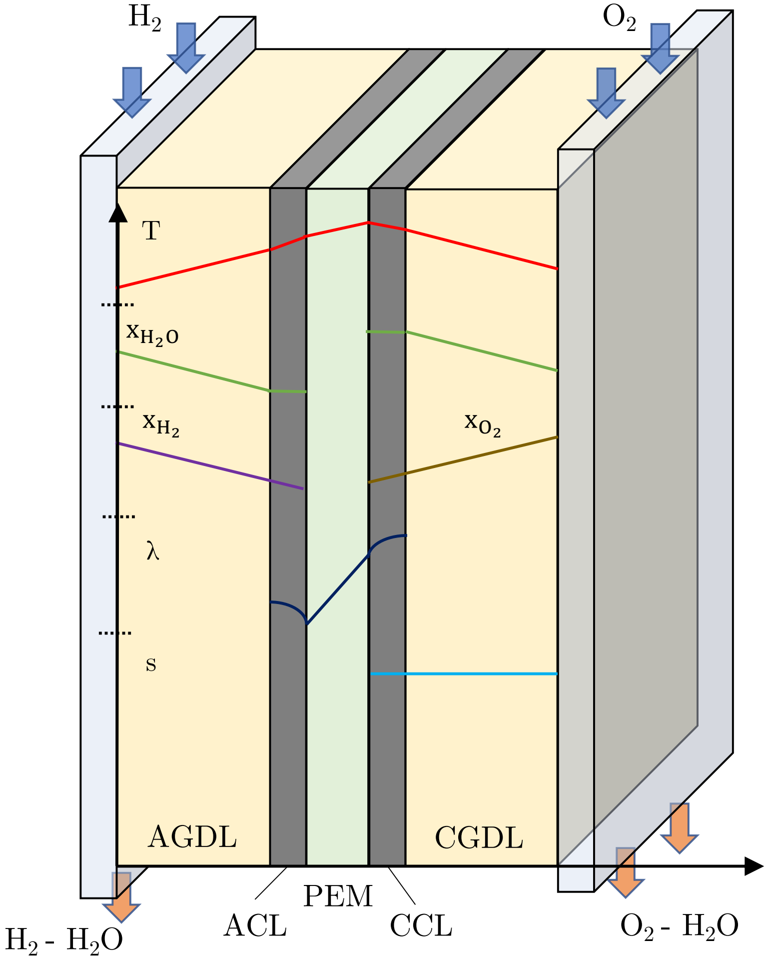
Understanding fuel cell behavior

- How do we understand the complex electrochemical phenomena occurring in fuel cells?
- Physical models can help but are often computationally expensive
- Reduced-order modeling gives efficient and accurate solutions of physical models
- Asymptotic analysis provides additional physical insights into dominant effects

Modeling approaches

Different approaches possible:

- Full 3D (serpentine channels)
- Full 2D (straight channels)
- 1D through-cell (lumped channels)
- 1D channel (lumped through-cell)
- 1+1D (decomposed through-cell and channel)



REDUCED-ORDER MODELING

Two-step approach

1. Non-dimensionalization
   – Identify scales
   – Prepare for asymptotically reduced-order models
   – Reduce stiffness (faster, more stable numerical solution)

2. Asymptotic analysis
   – Systematically derive reduced-order model based on dimensionless parameter scales
   – Retain same physical parameter values (unlike most other ROM methods)
   – Shown to work well for battery models (similar)

Nondimensionalization: basic principles

1. Example: membrane water

$$\frac{\epsilon_i}{V_m}\frac{\partial\lambda}{\partial\hat{t}} = -\frac{\partial\hat{N}}{\partial\hat{x}} + \hat{S}_{ad} + \frac{\hat{a}\hat{j}}{2F}$$

$$\hat{N} = -\hat{D}_\lambda\frac{\partial\lambda}{\partial\hat{x}} + \frac{n_d\hat{i}_p}{F}$$

$$\hat{S}_{ad} = \frac{\hat{k}_{ad}}{\hat{h}V_m}\left(\lambda_{eq} - \lambda\right)$$

2. Set

$$\hat{t} = \hat{\tau}\, t$$
$$\hat{x} = \hat{h}\, x$$
$$\hat{i}_p = \hat{I}\, i_p$$
$$\hat{j} = \frac{\hat{I}}{\hat{a}\hat{h}}\, j$$

$\hat{h}$: known
$\hat{I}$: known
$\hat{\tau}$: t.b.d.

3. Substitute

$$\epsilon_i\frac{\partial\lambda}{\partial\hat{t}} = \frac{\partial}{\partial x}\left(\frac{\hat{D}_\lambda\hat{\tau}V_m}{\hat{h}^2}\frac{\partial\lambda}{\partial x} - \frac{\hat{I}\hat{\tau}V_m}{F\hat{h}}n_d i_p\right) + \frac{\hat{k}_{ad}\hat{\tau}}{\hat{h}}\left(\lambda_{eq} - \lambda\right) + \frac{\hat{I}\hat{\tau}V_m}{F\hat{h}}\frac{j}{2}$$

4. Choose timescale to balance one of the terms; here

$$\hat{\tau} = \frac{F\hat{h}}{\hat{I}V_m} \approx 1s$$

5. Finally

$$\epsilon_i\frac{\partial\lambda}{\partial t} = \frac{\partial}{\partial x}\left(D_\lambda\frac{\partial\lambda}{\partial x} - n_d i_p\right) + k_{ad}\left(\lambda_{eq} - \lambda\right) + \frac{j}{2}$$

$$D_\lambda = \frac{\hat{D}_\lambda\hat{\tau}V_m}{\hat{h}^2};\ \mathrm{k}_{\mathrm{ad}} = \frac{\hat{k}_{ad}\hat{\tau}}{\hat{h}}$$

Parameter groupings

Dimensionless through-cell model

$$0 = \frac{\partial}{\partial x}\left(\sigma_{\mathrm{e}}\frac{\partial \phi_{\mathrm{e}}}{\partial x}\right) - j,$$

$$0 = \frac{\partial}{\partial x}\left(\sigma_{\mathrm{p}}\frac{\partial \phi_{\mathrm{p}}}{\partial x}\right) + j,$$

$$\rho c_{\mathrm{p}}\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_{\mathrm{T}}\frac{\partial T}{\partial x}\right) + \theta_{\mathrm{ad}}k_{\mathrm{ad}}(\lambda_{\mathrm{eq}} - \lambda) + \theta_{\mathrm{ec}}\gamma_{\mathrm{ec}}(c_{\mathrm{H_2O}} - c_{\mathrm{sat}})$$
$$+ \sigma_{\mathrm{e}}\left(\nabla\phi_{\mathrm{e}}\right)^2 + \sigma_{\mathrm{p}}\left(\nabla\phi_{\mathrm{p}}\right)^2 + j\eta - \theta_{\mathrm{r}}(1+\Theta T)\frac{j}{2},$$

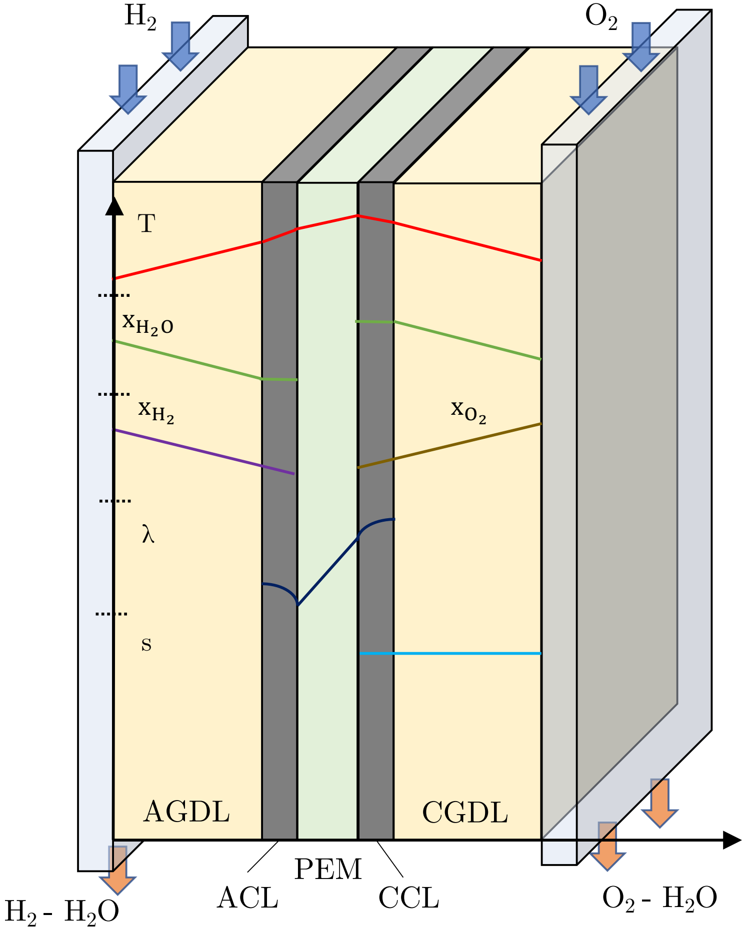
$$\varepsilon_{\mathrm{i}}\frac{\partial \lambda}{\partial t} = \frac{\partial}{\partial x}\left(D_{\lambda}\frac{\partial \lambda}{\partial x} - n_{\mathrm{d}}i_{\mathrm{p}}\right) + k_{\mathrm{ad}}(\lambda_{\mathrm{eq}} - \lambda) + r_{\mathrm{H_2O}},$$

$$\upsilon_{\mathrm{m}}\varepsilon_{\mathrm{g}}\frac{\partial c_{\mathrm{H_2O}}}{\partial t} = \frac{\partial}{\partial x}\left(D^{\mathrm{eff}}_{\mathrm{H_2O}}\frac{\partial c_{\mathrm{H_2O}}}{\partial x}\right) - k_{\mathrm{ad}}(\lambda_{\mathrm{eq}} - \lambda) - \gamma_{\mathrm{ec}}(c_{\mathrm{H_2O}} - c_{\mathrm{sat}}),$$

$$\upsilon_{\mathrm{m}}\varepsilon_{\mathrm{g}}\frac{\partial c_{\mathrm{H_2}}}{\partial t} = \frac{\partial}{\partial x}\left(D^{\mathrm{eff}}_{\mathrm{H_2}}\frac{\partial c_{\mathrm{H_2}}}{\partial x}\right) - \frac{j}{2},$$

$$\upsilon_{\mathrm{m}}\varepsilon_{\mathrm{g}}\frac{\partial c_{\mathrm{O_2}}}{\partial t} = \frac{\partial}{\partial x}\left(D^{\mathrm{eff}}_{\mathrm{O_2}}\frac{\partial c_{\mathrm{O_2}}}{\partial x}\right) + \frac{j}{4},$$

$$\upsilon_{\mathrm{V}}\varepsilon_{\mathrm{l}}\frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(D_{\mathrm{s}}\frac{\partial s}{\partial x}\right) + \gamma_{\mathrm{ec}}(c_{\mathrm{H_2O}} - c_{\mathrm{sat}}),$$



Dimensionless through-cell model

$$0 = \frac{\partial}{\partial x}\left(\sigma_e \frac{\partial \phi_e}{\partial x}\right) - j,$$

$$0 = \frac{\partial}{\partial x}\left(\sigma_p \frac{\partial \phi_p}{\partial x}\right) + j,$$

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k_T \frac{\partial T}{\partial x}\right) + \theta_{ad} k_{ad}(\lambda_{eq} - \lambda) + \theta_{ec}\gamma_{ec}(c_{H_2O} - c_{sat})$$
$$+ \sigma_e (\nabla\phi_e)^2 + \sigma_p (\nabla\phi_p)^2 + j\eta - \theta_r(1+\Theta T)\frac{j}{2},$$

$$\varepsilon_i \frac{\partial \lambda}{\partial t} = \frac{\partial}{\partial x}\left(D_\lambda \frac{\partial \lambda}{\partial x} - n_d i_p\right) + k_{ad}(\lambda_{eq} - \lambda) + r_{H_2O},$$

$$\upsilon_m \varepsilon_g \frac{\partial c_{H_2O}}{\partial t} = \frac{\partial}{\partial x}\left(D^{eff}_{H_2O} \frac{\partial c_{H_2O}}{\partial x}\right) - k_{ad}(\lambda_{eq} - \lambda) - \gamma_{ec}(c_{H_2O} - c_{sat}),$$

$$\upsilon_m \varepsilon_g \frac{\partial c_{H_2}}{\partial t} = \frac{\partial}{\partial x}\left(D^{eff}_{H_2} \frac{\partial c_{H_2}}{\partial x}\right) - \frac{j}{2},$$

$$\upsilon_m \varepsilon_g \frac{\partial c_{O_2}}{\partial t} = \frac{\partial}{\partial x}\left(D^{eff}_{O_2} \frac{\partial c_{O_2}}{\partial x}\right) + \frac{j}{4},$$

$$\upsilon_V \varepsilon_l \frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(D_s \frac{\partial s}{\partial x}\right) + \gamma_{ec}(c_{H_2O} - c_{sat}),$$

large **small**

- Electron conductivity large (~uniform electron potential)
- Thermal conductivity large (~uniform temperature)
- Gas diffusivities large (~uniform gas concentrations)
- Evaporation/condensation large
- Fast gas time constants (quasi-steady)
- Liquid water transport slow

Asymptotic analysis: basic principles

1. Dimensionless equation

$$\epsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D(c)}{\epsilon}\frac{\partial c}{\partial x}\right) - j$$

2. Asymptotic expansion ($\epsilon \ll 1$)

$$c = c^0 + \epsilon c^1 + \cdots$$
$$j = j^0 + \epsilon j^1 + \cdots$$
$$D = D^0 + \epsilon D^1 + \cdots$$

3. Substitute

$$\epsilon \frac{\partial}{\partial t}(c^0 + \epsilon c^1 + \cdots)$$
$$= \frac{\partial}{\partial x}\left(\frac{(D^0 + \epsilon D^1 + \cdots)}{\epsilon}\frac{\partial}{\partial x}(c^0 + \epsilon c^1 + \cdots)\right)$$
$$- (j^0 + \epsilon j^1 + \cdots)$$

4. Match orders of ϵ.

a) O($1/\epsilon$):

$$0 = \frac{\partial}{\partial x}\left(D^0 \frac{\partial c^0}{\partial x}\right)$$

So $c^0 = c_{ch}$ (value at the boundary)

b) O(1):

$$0 = \frac{\partial}{\partial x}\left(D^0 \frac{\partial c^1}{\partial x}\right) - j^0$$

Linear equation: easy to solve for c^1

Reduced-order fuel cell model

	Full Model	Linearized model
Membrane water content	Nonlinear diffusion-drag-reaction	Nonlinear diffusion-drag-reaction
Water vapor	Nonlinear diffusion	Single ODE
Oxygen and hydrogen	Nonlinear diffusion	Closed-form solution (steady-state)
Electric potentials (voltage)	Ohm’s law + Butler-Volmer	Closed-form solution
Thermal	Full energy balance	Single ODE
Liquid water saturation	Unsaturated flow	Closed-form solution
Channel concentrations	Nonlinear diffusion-convection	Convection only

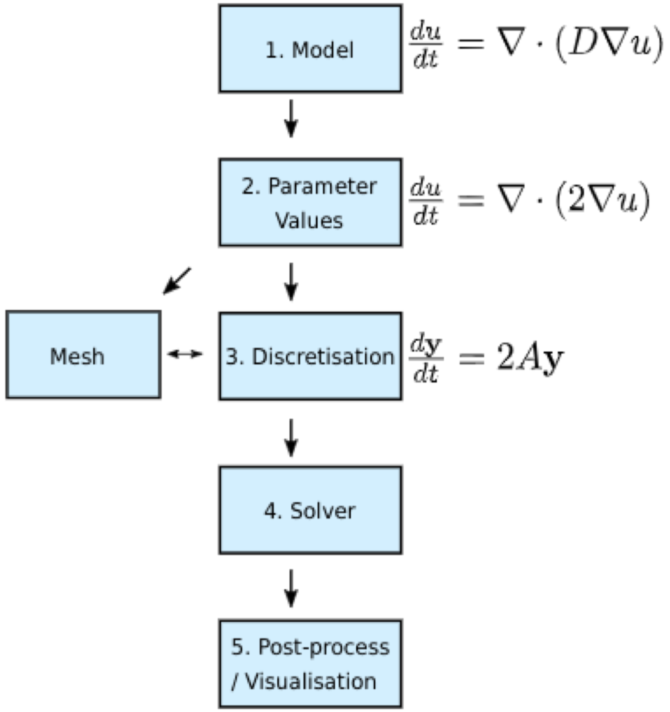
SIMULATION RESULTS

Numerical method

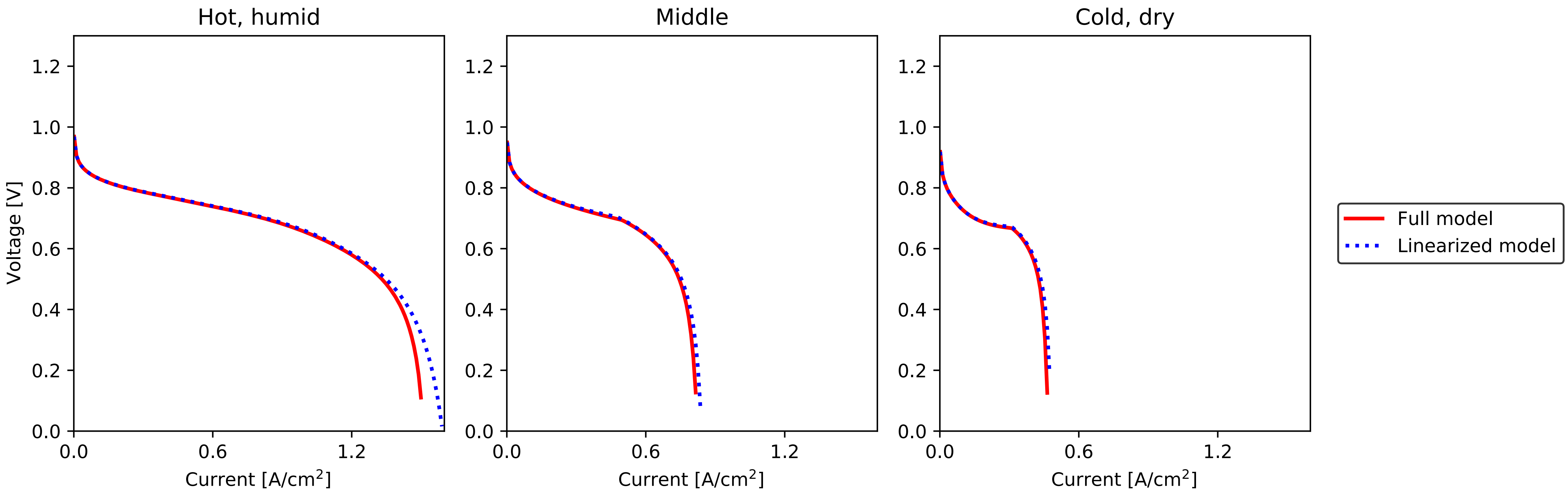
- Models implemented using PyBaMM framework

- Method of Lines:
  – Finite Volume spatial discretization
  – Use IDA (SUNDIALS) to solve resulting DAE system

PyBaMM



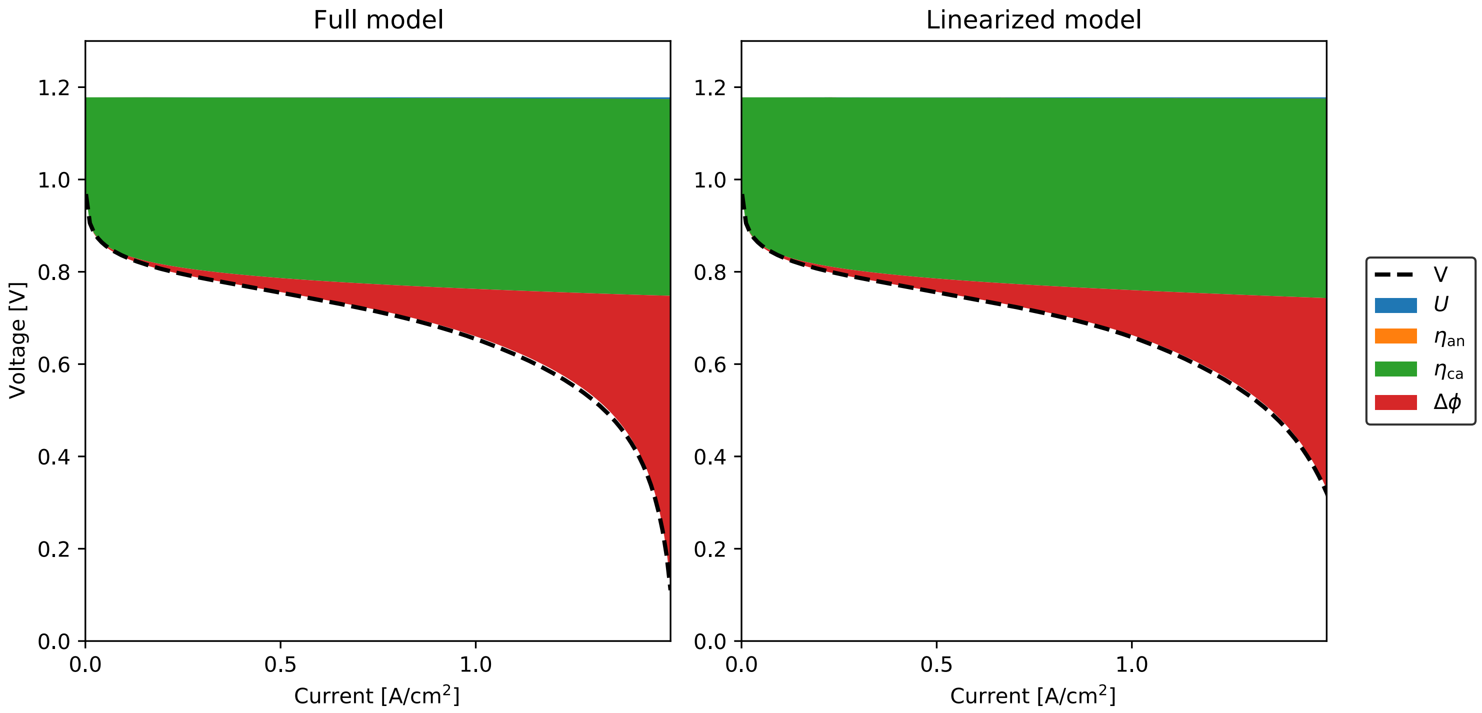
Polarization curves



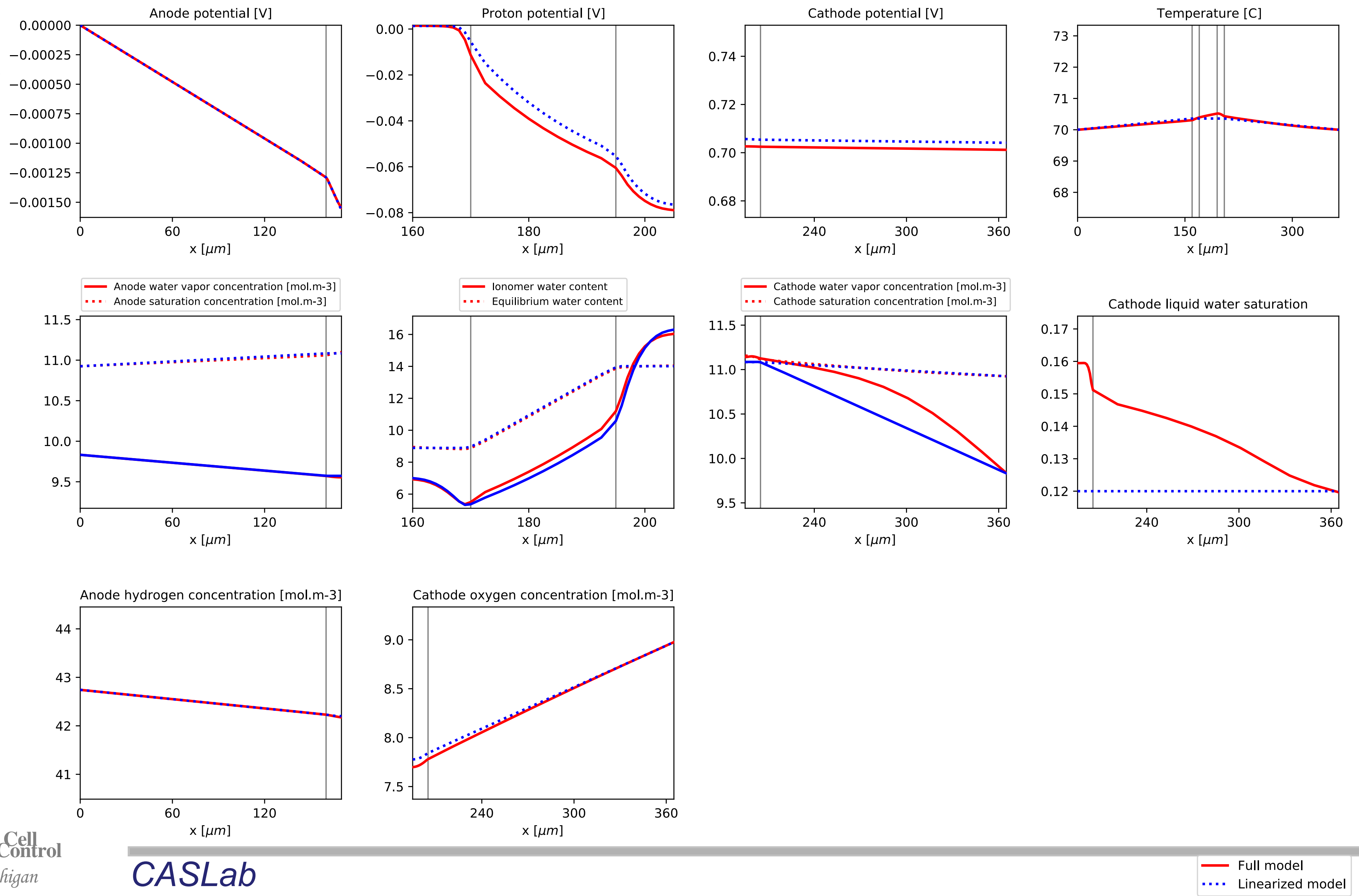
Voltage decompositions

$$V = U - \underbrace{\frac{\mathrm{I}F}{RT i_0^{\mathrm{an}} h_{\mathrm{ACL}}}}_{\eta^{\mathrm{an}}} - \underbrace{\frac{F}{2RT(1-\beta^{\mathrm{ca}})} \log\left(\frac{\mathrm{I}}{i_0^{\mathrm{ca}} h_{\mathrm{CCL}}}\right)}_{\eta^{\mathrm{ca}}} - \underbrace{\frac{\mathrm{I}F}{RT} f(\sigma_{\mathrm{p}}, i_0^{\mathrm{an}})}_{\Delta\phi}$$

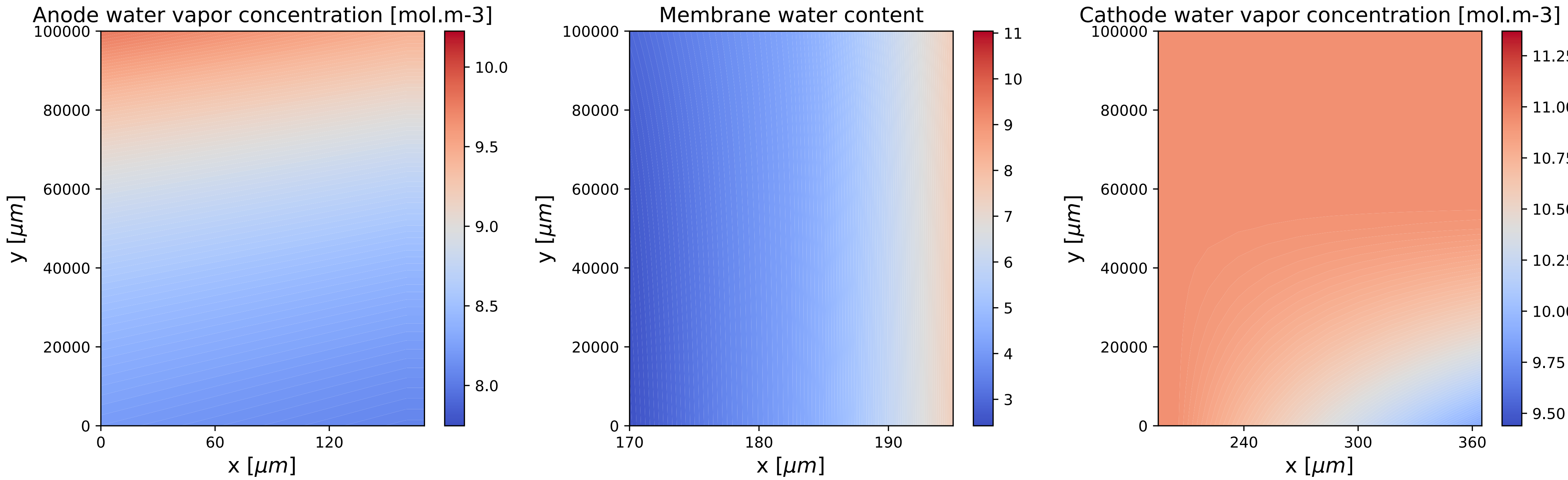
$$f(\sigma_{\mathrm{p}}, i_0^{\mathrm{an}}) = \frac{1}{a\bar{\sigma}_{\mathrm{p,cl}}^{\mathrm{an}} \tanh(a h_{\mathrm{ACL}})} + \int_{x=x_{\mathrm{ACL}}}^{x=x_{\mathrm{PEM}}} \frac{1}{\sigma_{\mathrm{p}}} \,\mathrm{d}x + \int_{x=x_{\mathrm{PEM}}}^{x=x_{\mathrm{CCL}}} \frac{1-(x-x_{\mathrm{PEM}})}{\sigma_{\mathrm{p}} h_{\mathrm{CCL}}} \,\mathrm{d}x$$



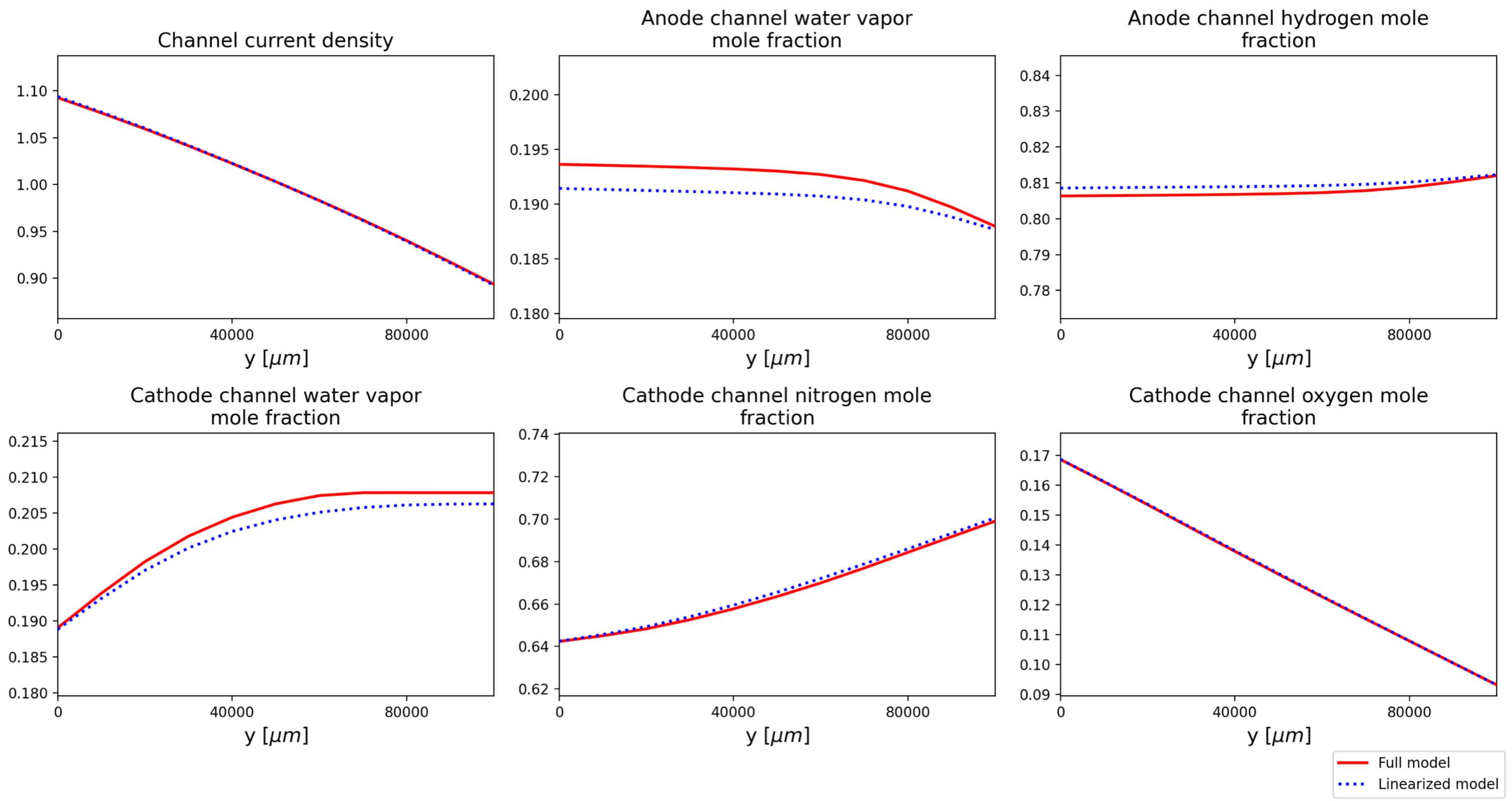
One-dimensional results



Two-dimensional results



Two-dimensional results



Model performance

	1D model		1+1D model	
	States	Solve time (s)	States	Solve time (s)
Full model	230	1.40	4740	232
Linearized model	33	0.13	780	3.37

Simulating constant-current operation for 100 seconds.
Simulation with 10 grid points in each through-cell domain (50 total) and 20 grid points in each channel.
Solved using CasADi, with absolute and relative tolerances of 1e-6, on a laptop with a 2.3 GHz 8-Core Intel Core i9 processor

Conclusions

- Reduced-order modeling (from asymptotic analysis) provide efficient and accurate solutions for PEMFC models

- Simplified model give additional insight
  - Closed-form expressions for most variables, but:
  - Membrane water transport is very important and must be fully resolved

- Next step: use these models to learn missing physics

Acknowledgments

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