COLORADO SCHOOL OF MINES
MECHANICAL ENGINEERING THERMAL-FLUID SYSTEMS

Effects of Modeling Approach and Microstructural Transport on Proton Exchange Membrane Fuel Cells

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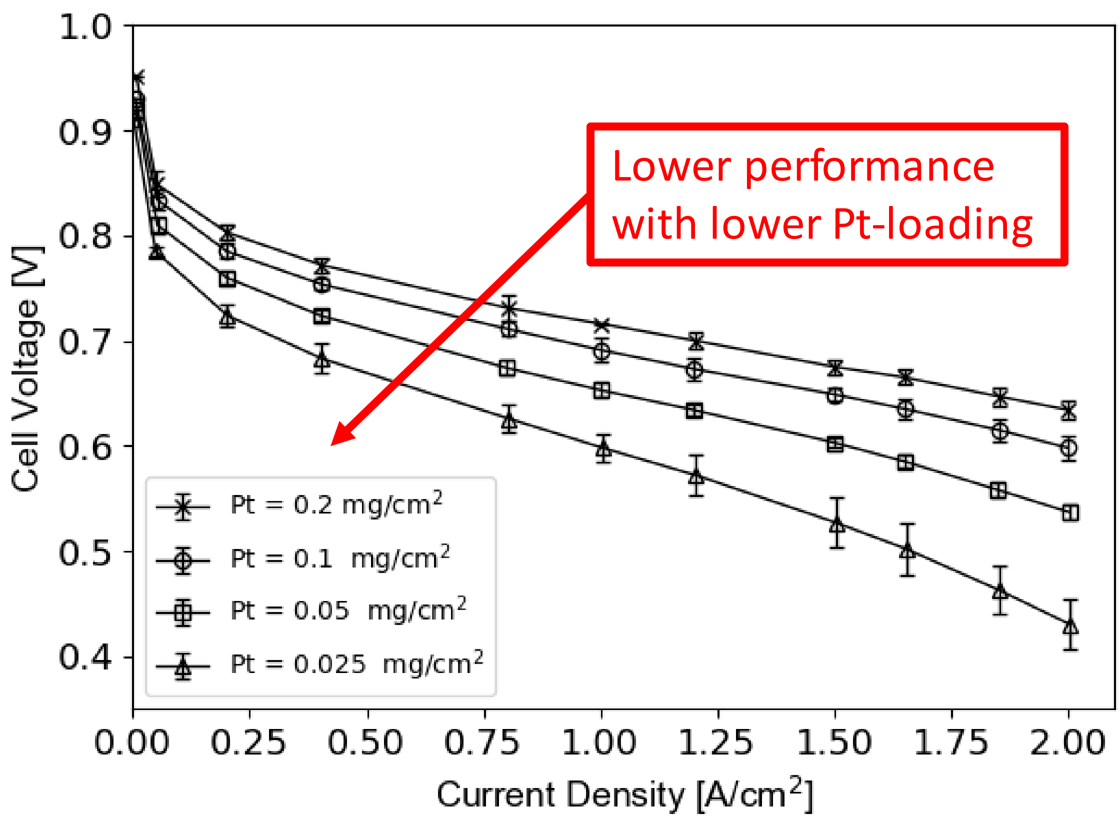
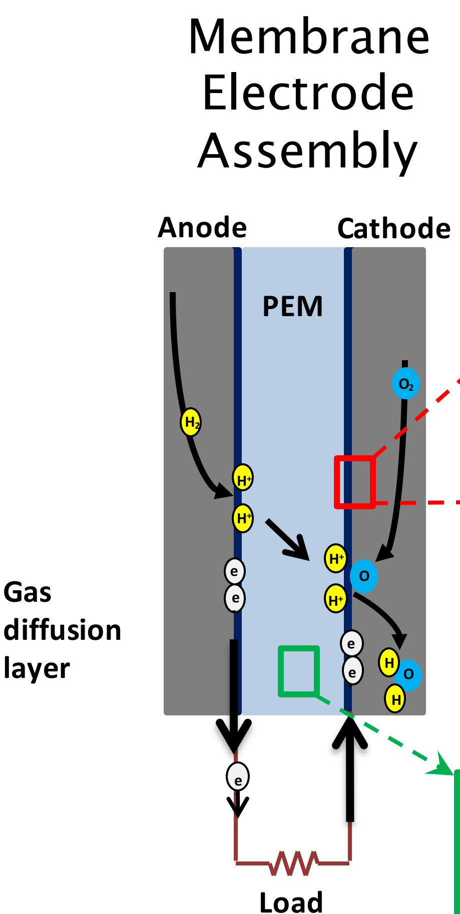
Performance of proton exchange membrane fuel cells (PEMFC) with low Pt loading

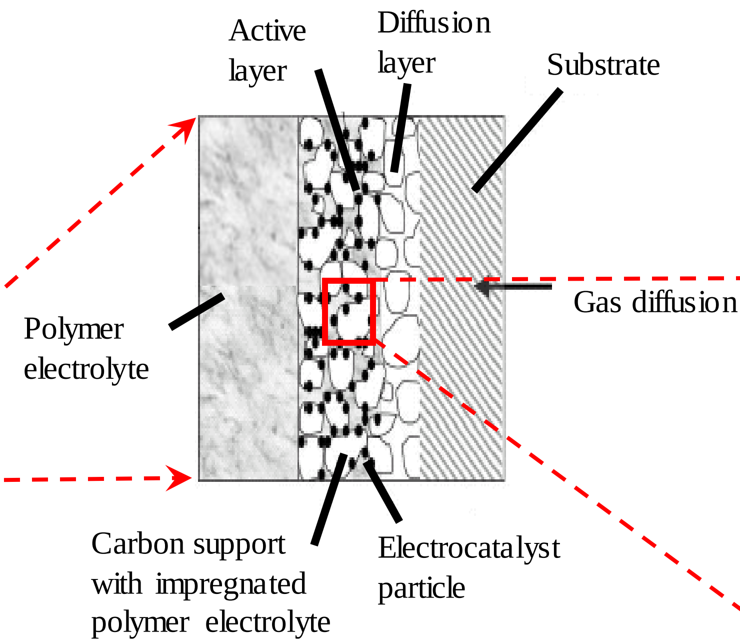
- **Motivation:**
  - DOE goal: 0.125 mg/cm^2 or 0.15 mg/kW by 2020
  - Unexplained losses with lower Pt loading
  - Complex structure-property relationships in electrolyte material
- **Approach:**
  - Development of PEMFC models
  - Thin film experiments on complex electrolyte



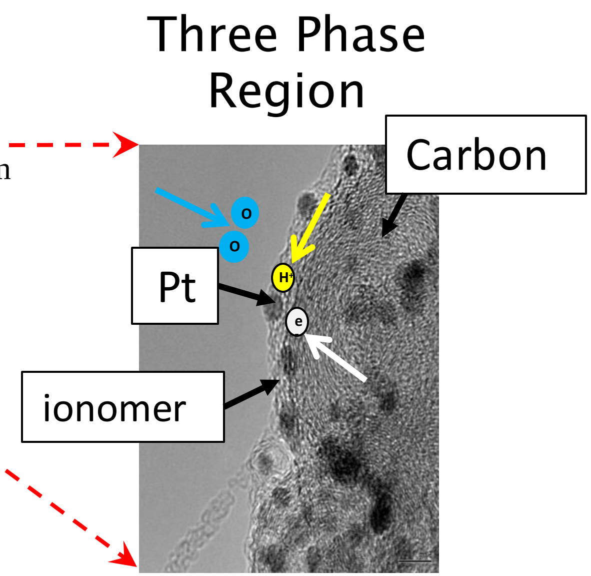
J. P. Owejan, J. E. Owejan, and W. Gu, "Impact of Platinum Loading and Catalyst Layer Structure on PEMFC Performance," *Journal of The Electrochemical Society*, vol. 160, no. 8, 2013.

Multi-scale overview of PEMFC systems: full cell, cathode, and catalyst layer structures





Thin films harder to study – less known

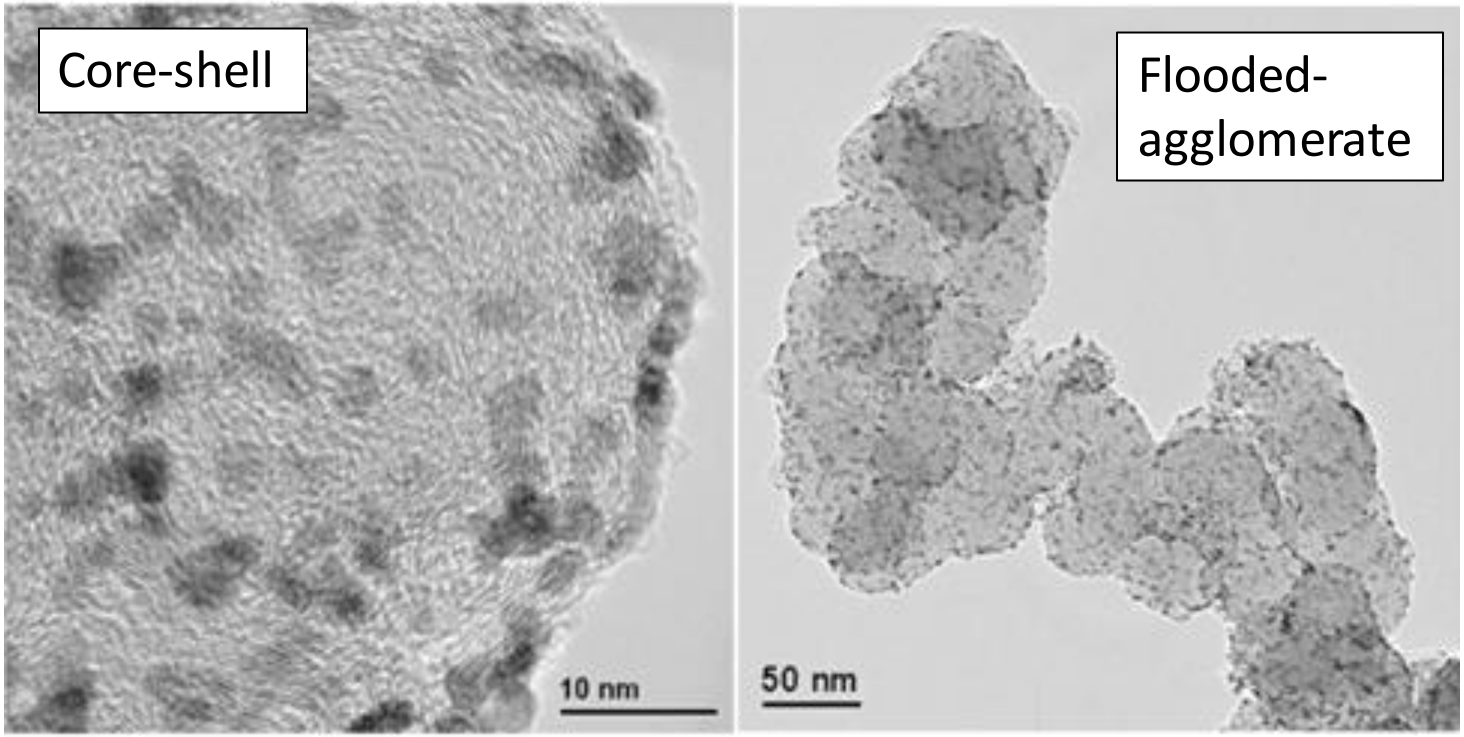


Well known properties and relationships with bulk Nafion

K. L. More, R. Borup, and K. S. Reeves, "Identifying Contributing Degradation Phenomena in PEM Membrane Electrode Assemblies Via Electron Microscopy," *ECS Transactions* **3(1)** pp. 717-733 2006 [doi:10.1149/1.2356192]

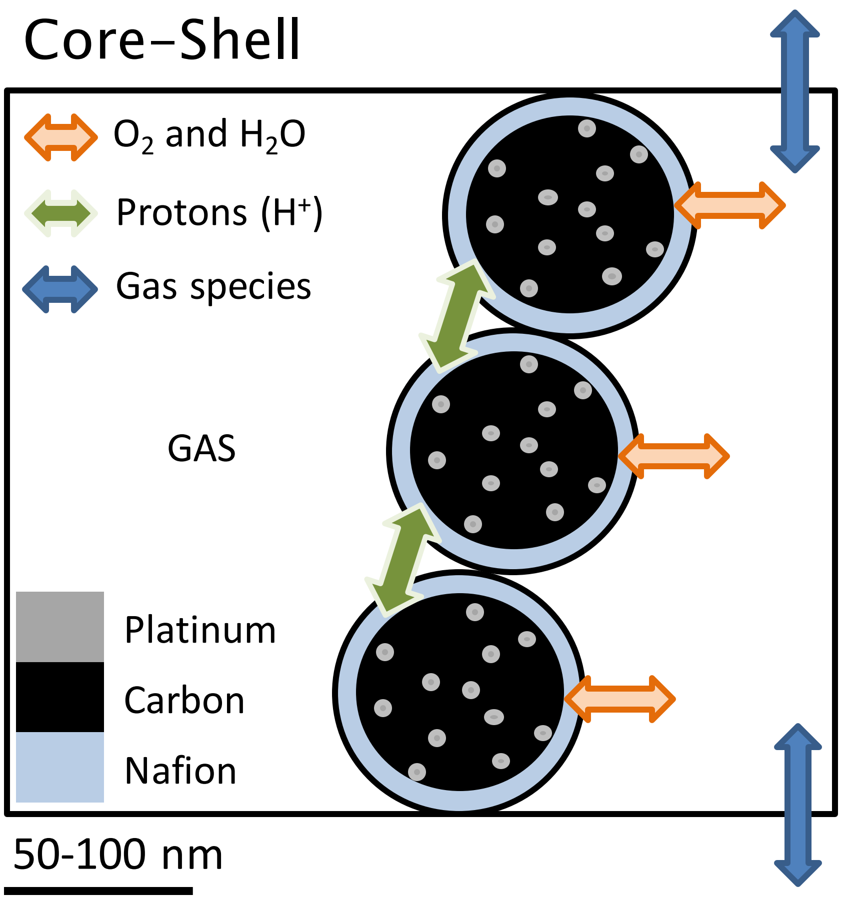
Observed catalyst layer microstructures within PEMFC cathodes

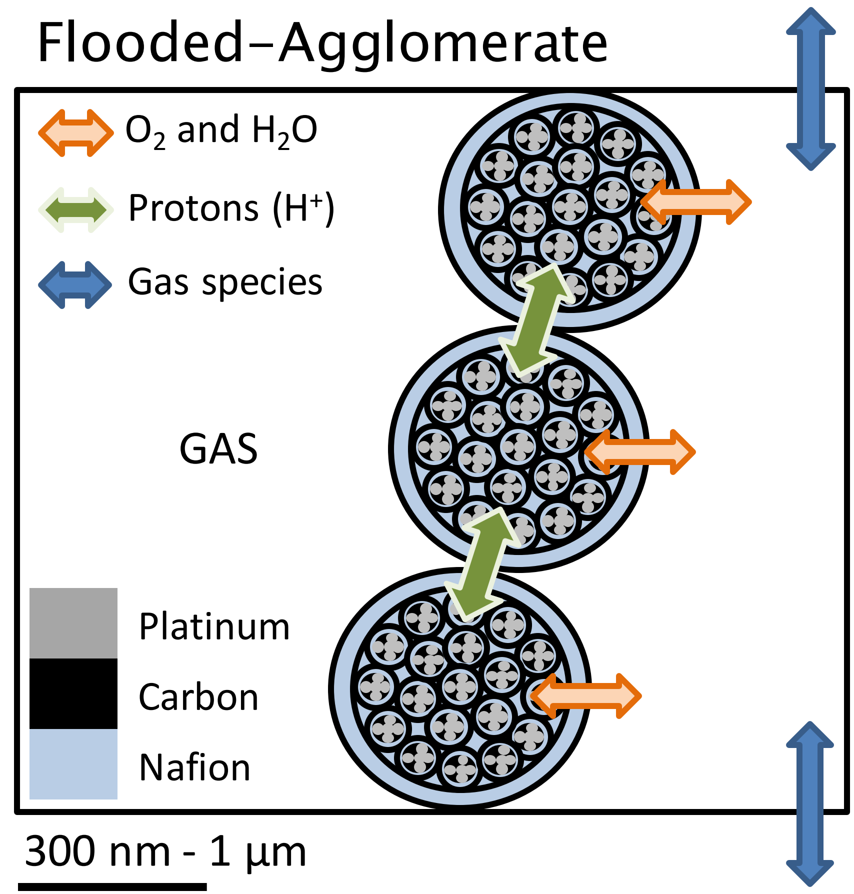
- Microstructure can be categorized as a cluster of particles or single particle depending on scale



[1]

Differences in PEMFC catalyst layer models: microstructures, domains, and transport





PEMFC model assumptions

1. Isothermal and steady-state
2. Water is in equilibrium between Nafion and gas phases
3. Fast electron transport, i.e., uniform Pt/C potential
4. No local potential gradients in radial Nafion shells
5. Uniform microstructure throughout the catalyst layer

Governing equations for PEMFC models

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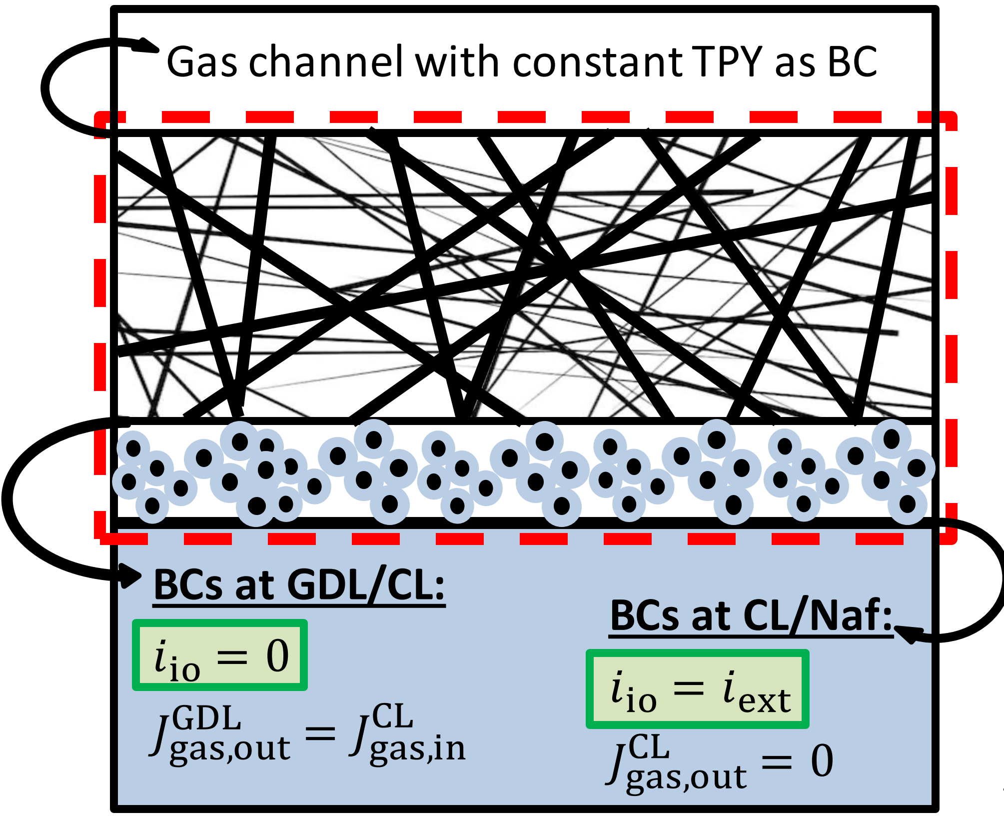


Charge neutrality

Diffusion

Reaction terms

Advection

- **Gas diffusion layer (GDL):**

$$\frac{\mathrm{d}\rho_k}{\mathrm{d}t} = \frac{\sum J''_k}{\Delta y}$$

$$J''_k = \boxed{-\frac{\epsilon}{\tau^2} D_{\mathrm{av}} \rho_{\mathrm{av}} \frac{\mathrm{d}Y_k}{\mathrm{d}y}} - \boxed{\frac{K_g}{\mu} \rho_{k,\mathrm{av}} \frac{\mathrm{d}P}{\mathrm{d}y}}$$

- **Catalyst layer (CL):**

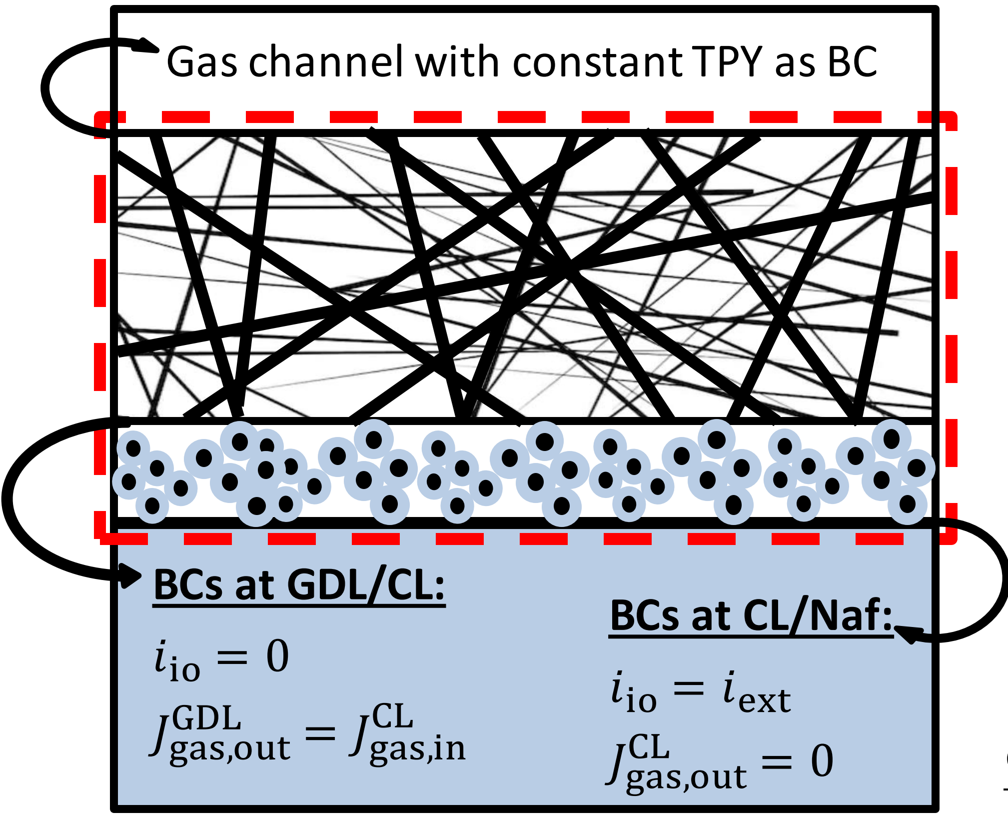
$$\boxed{\frac{\mathrm{d}\Phi_{\mathrm{dl}}}{\mathrm{d}t} = \frac{i'''_{\mathrm{dl}}}{C_{\mathrm{dl}} A'''_{\mathrm{dl}}}}$$

$$\boxed{i'''_{\mathrm{dl}} = \nabla i_{\mathrm{io}} - i_{\mathrm{Far}} A'''_{\mathrm{Pt}} \qquad i_{\mathrm{io}} = -\sigma_{\mathrm{io,eff}} \nabla \Phi}$$

$$\frac{\mathrm{d}\rho_{\mathrm{gas},k}}{\mathrm{d}t} = \frac{\sum J''_k}{\Delta y} + \boxed{\dot{s}''_{\mathrm{rxn1},k} A'''_{\mathrm{rxn1}}}$$

$$\frac{\mathrm{d}\rho_{\mathrm{naf},k}}{\mathrm{d}t} = \boxed{D_{\mathrm{eff}} \left(\frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\rho_k}{\mathrm{d}r} \right) \right)} + \boxed{\sum \dot{s}''_{\mathrm{rxn},k} A'''_{\mathrm{rxn}}}$$

Governing equations for PEMFC models



Dependent on Nafion properties

- **Gas diffusion layer (GDL):**

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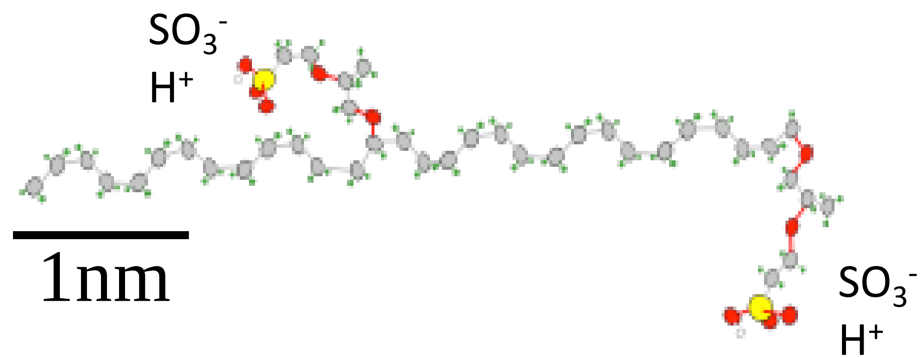
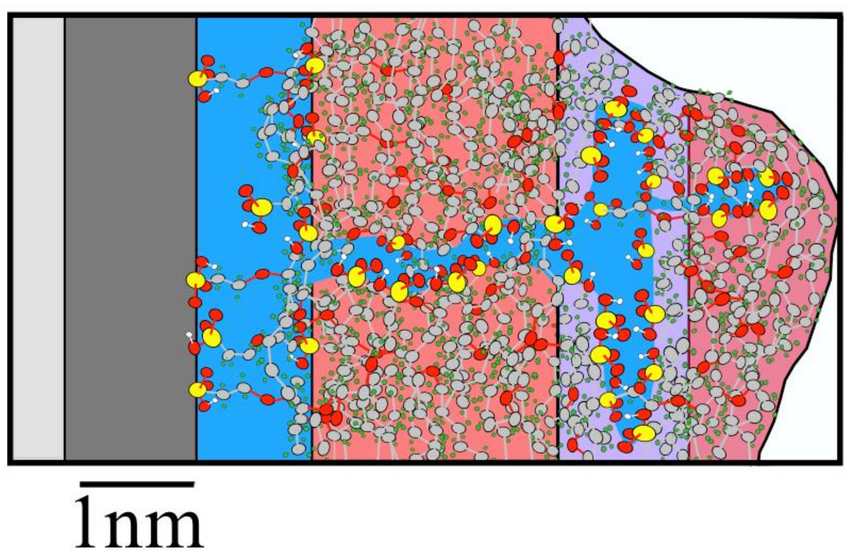
Nafion structure-property relationships are influenced by multiple factors

- Structure-property dependencies:
  - Temperature
  - Relative humidity
  - Substrate
  - Thickness



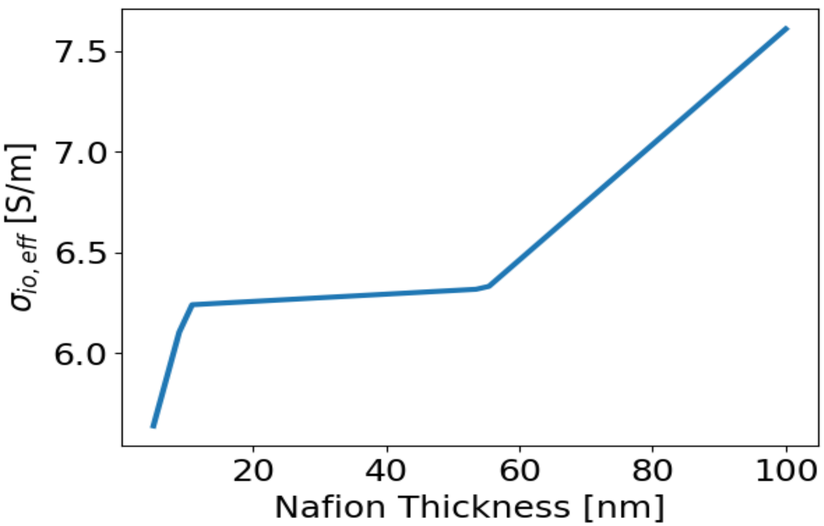
- Literature shows:
  - Water absorption
  - Surface interactions
  - Confinement
  - Lamellae



[2]

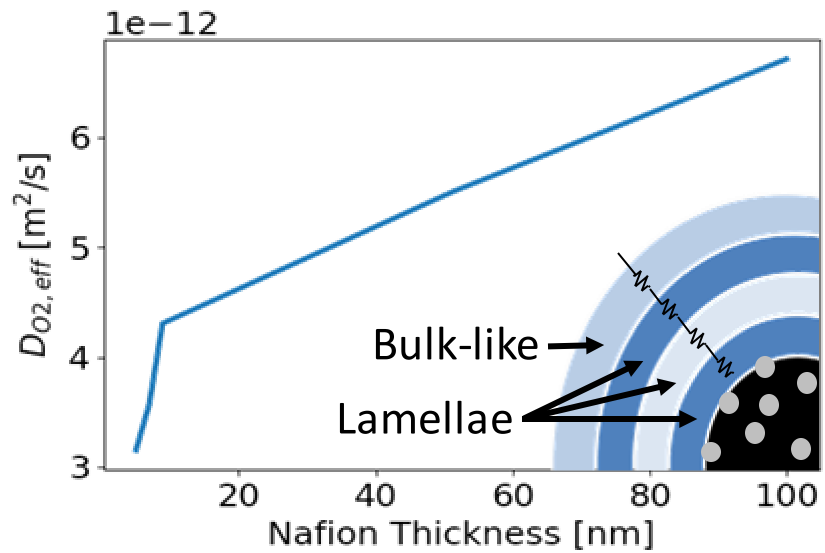
Structure-property relations: an approach to determine relevant CL transport

- Ionic Conductivity (σ_{io})
  - Triple interpolation from data taken with varied thicknesses, temperature, and relative humidity



D. K. Paul, R. McCreery, and K. Karan, "Proton Transport Property in Supported Nafion Nanothin Films by Electrochemical Impedance Spectroscopy," *Journal of The Electrochemical Society*, vol. 161, no. 14, 2014.

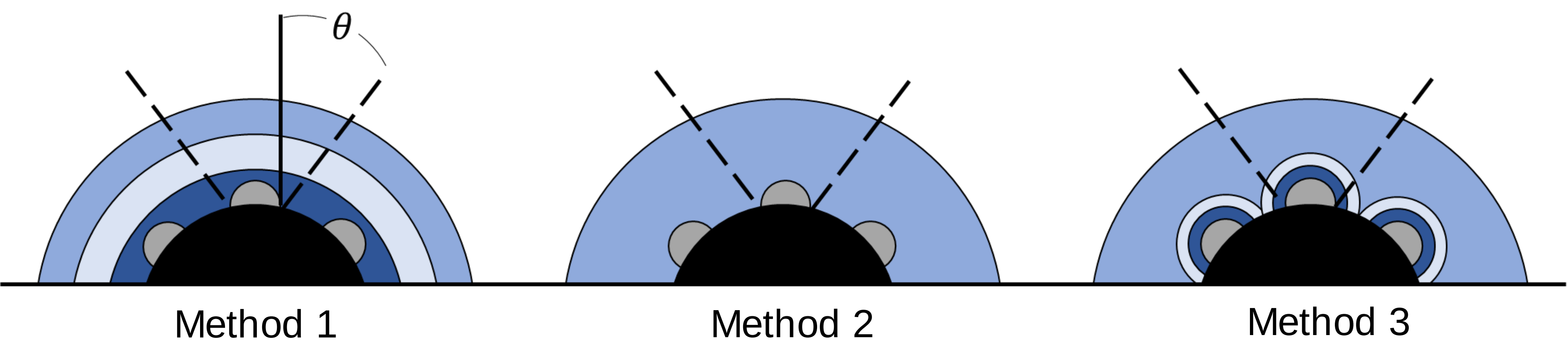
- Diffusion Coefficient (D_{O2})
  - Series resistor network
  - Weight layers by H_2O and scaling based on NR data



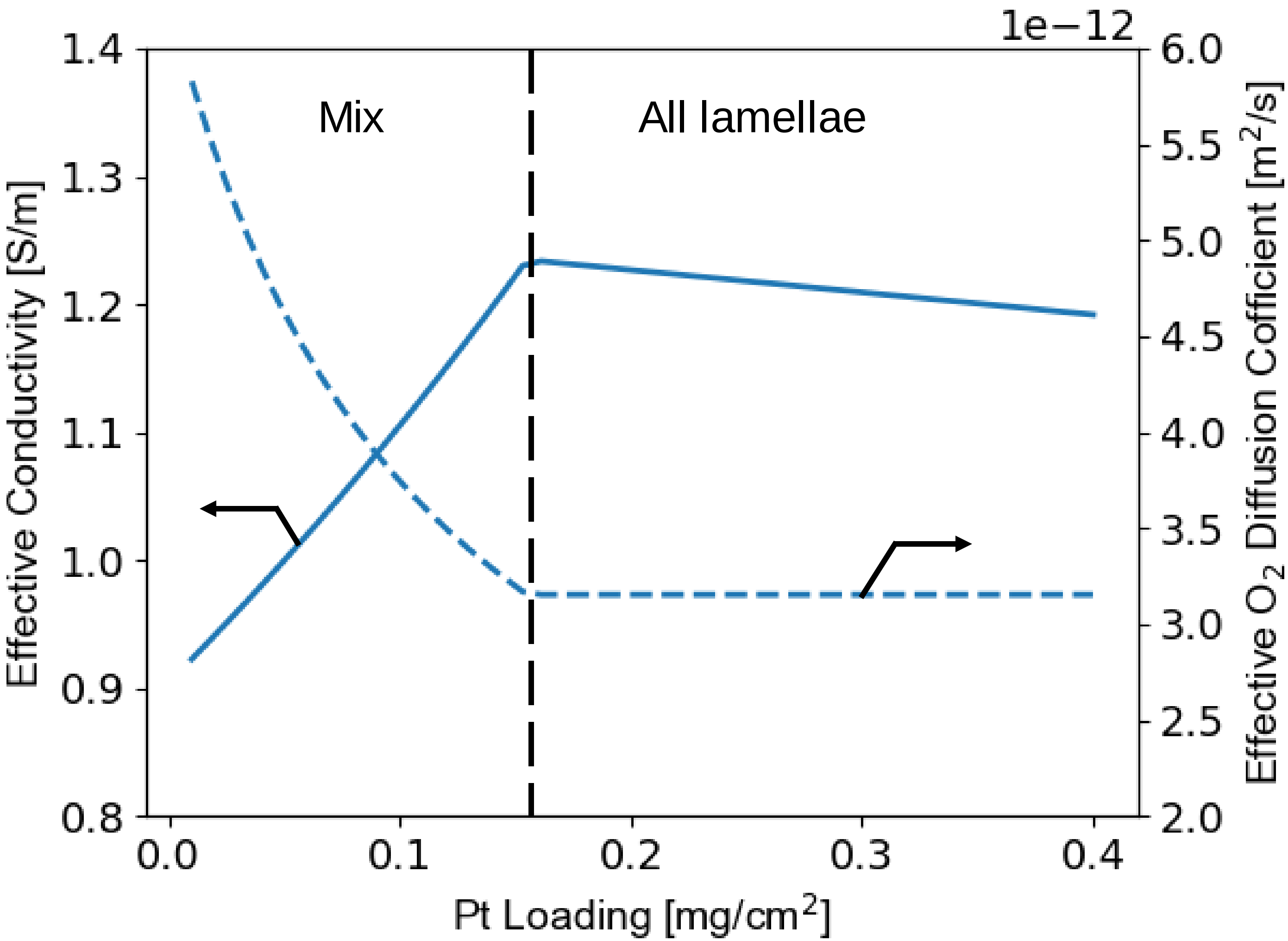
S. C. DeCaluwe, A. M. Baker, P. Bhargava, J. E. Fischer, and J. A. Dura, "Structure-property relationships at Nafion thin-film interfaces: Thickness effects on hydration and anisotropic ion transport," *Nano Energy*, vol. 46, pp. 91–100, 2018.

Submodel for physically-based transport properties within CL Nafion

- Method 1: lamellae – data (σ_{io}) and series resistor network (D_{O2})
- Method 2: no lamellae – weight by bulk-like water fraction
- Method 3: mix of lamellae (on Pt) and no lamellae (on C)

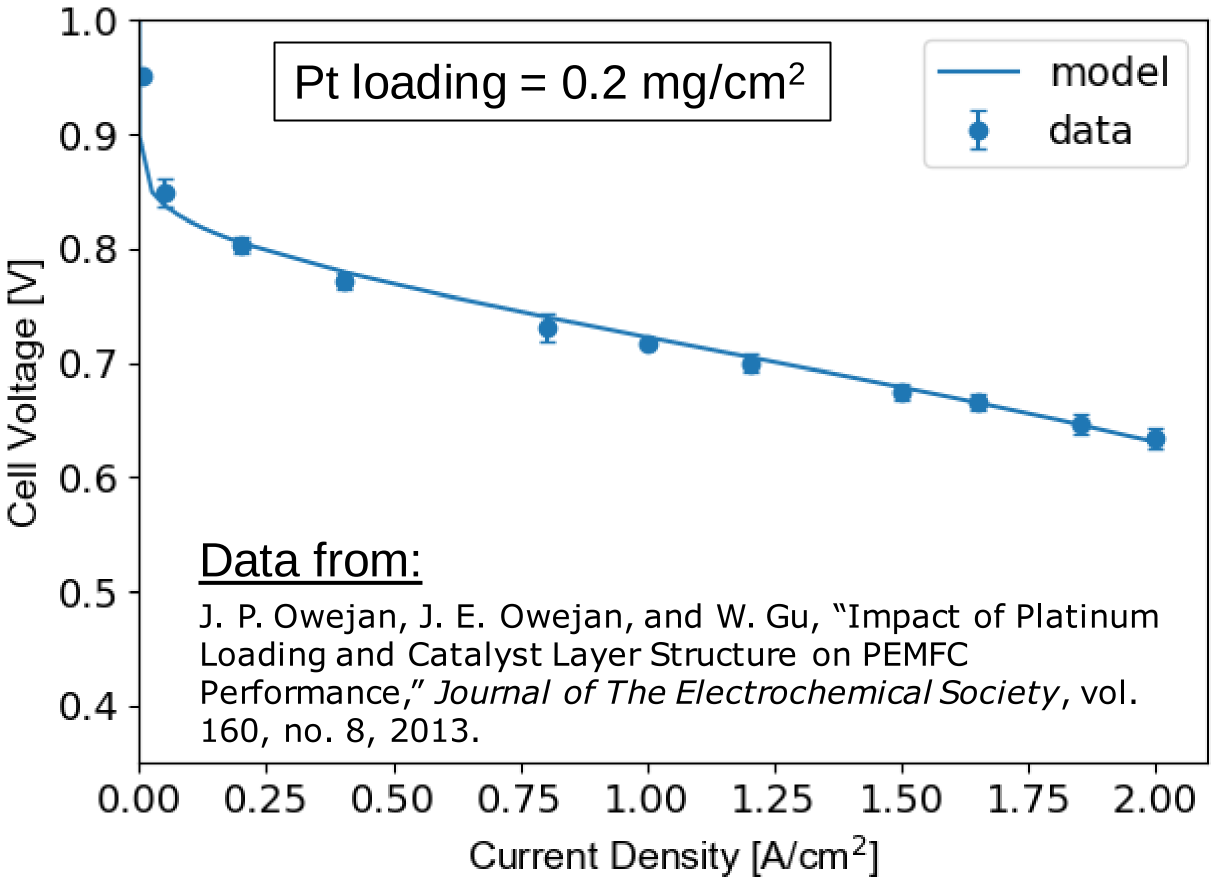


Mixed-based approach captures transport property effects as Pt loading changes



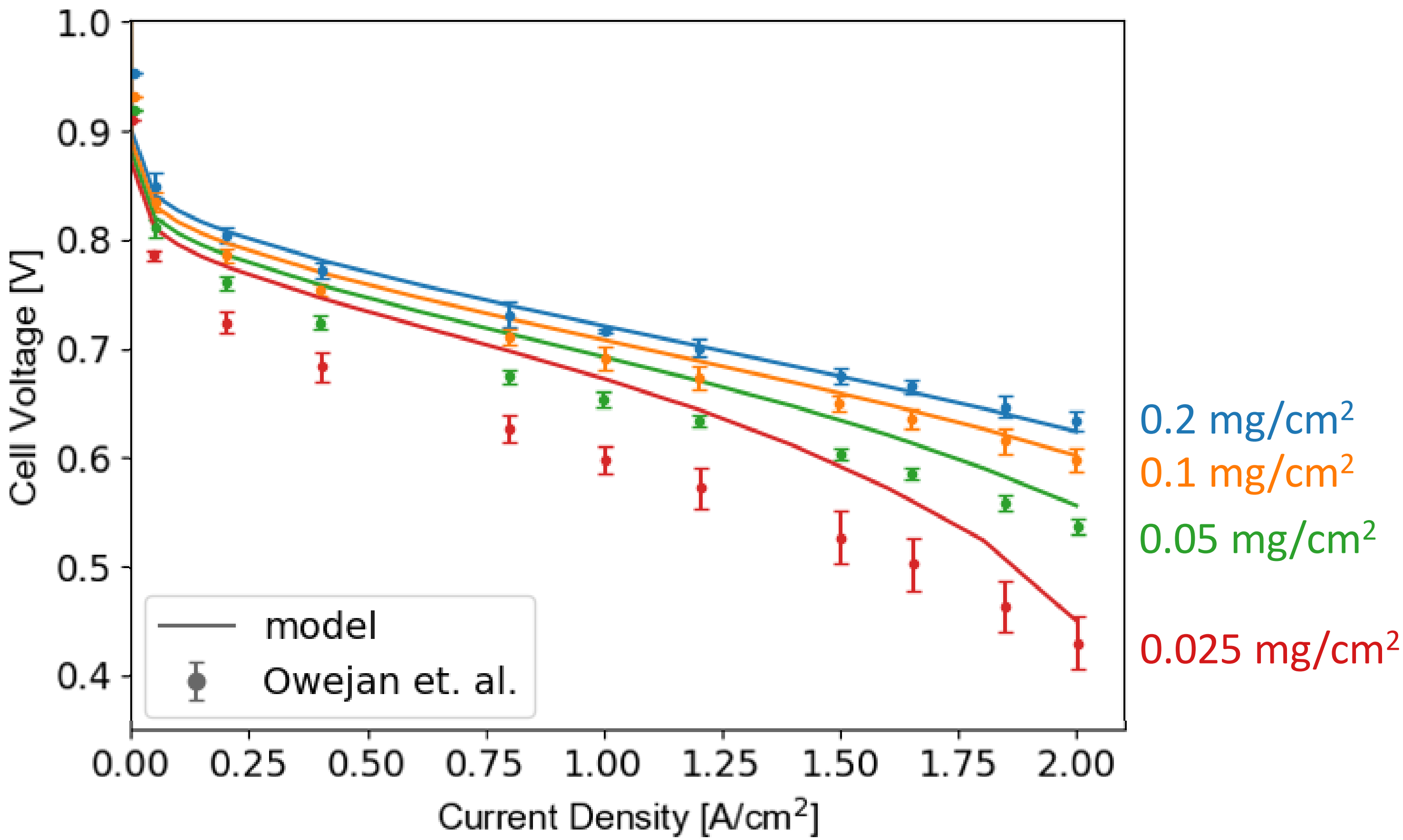
Validation of PEMFC core-shell model at higher Pt loading

- Crude fitting by adjusting the membrane resistance and Butler-Volmer exchange current density shows good agreement

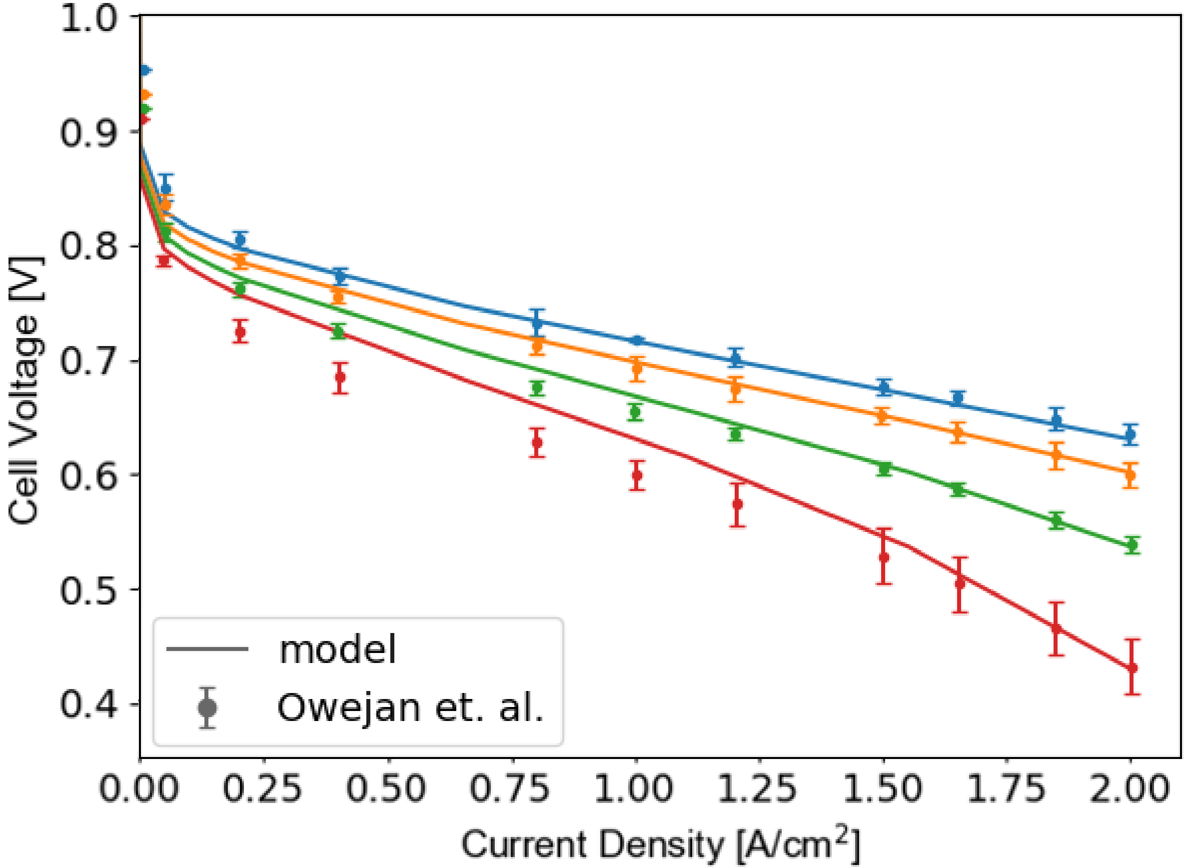


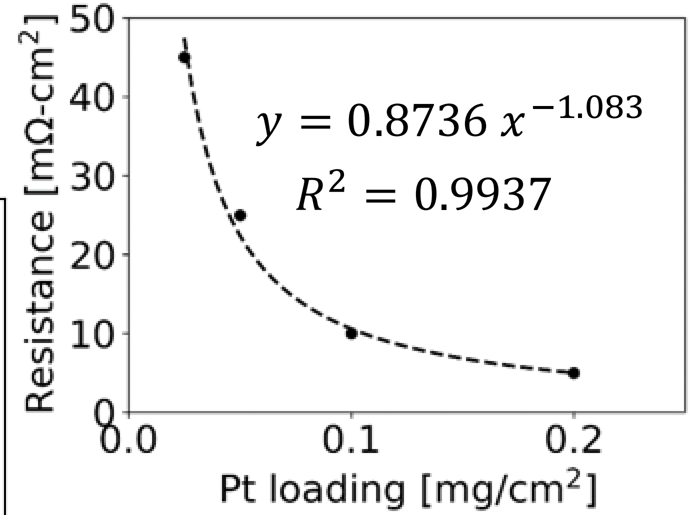
Core-shell model at lower Pt loadings does not capture activation overpotentials

- Reasonable adjustments made to the solubility, capture angle (θ), exchange current density (i_o), and membrane resistance (R_{Naf})



Adding an additional resistance term improves core-shell fits at high currents





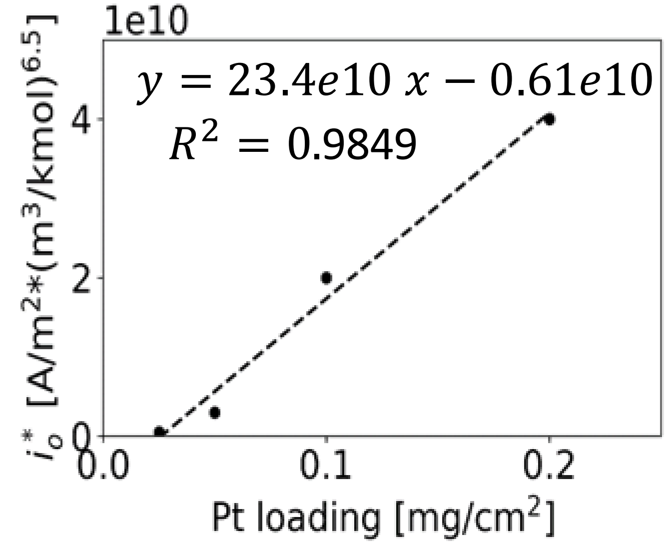
0.2 mg/cm^2

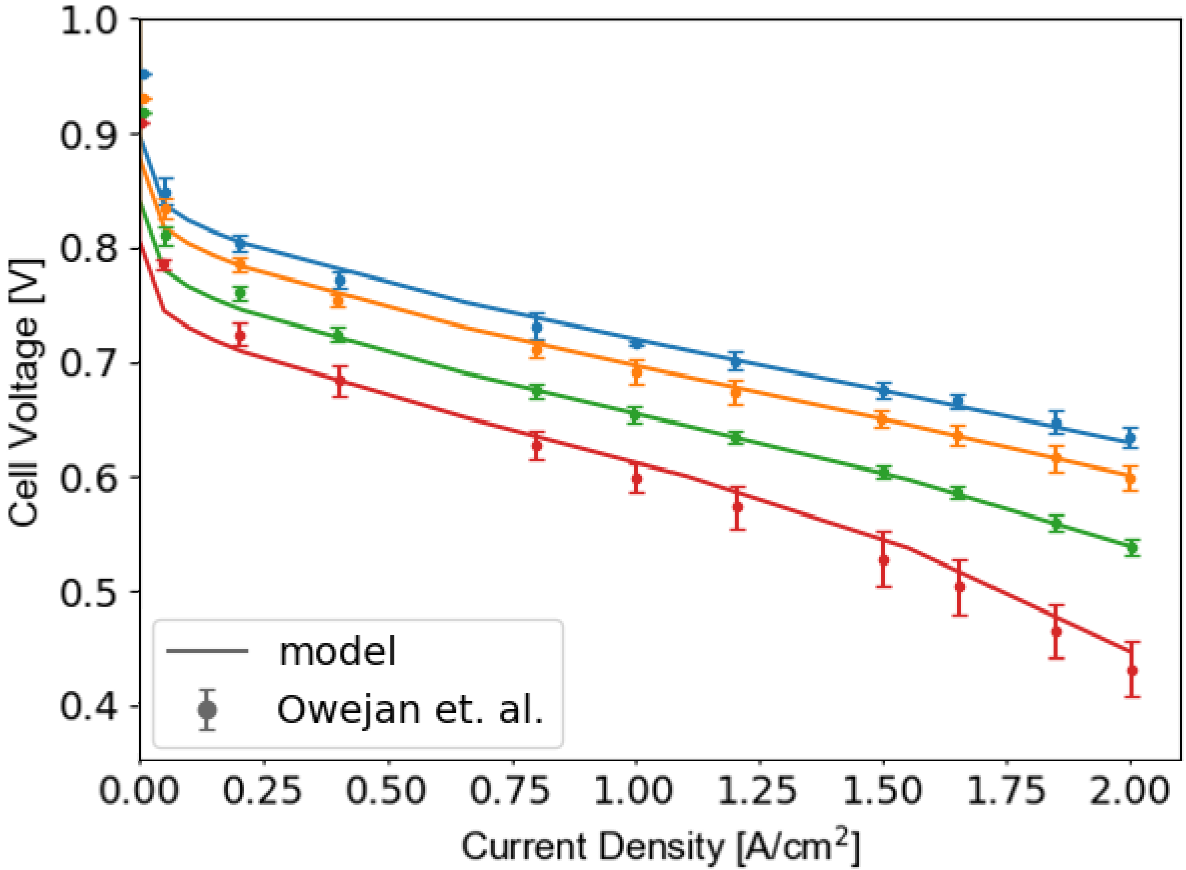
0.1 mg/cm^2

0.05 mg/cm^2

0.025 mg/cm^2

Hand fitting the kinetics at low Pt loadings provides improvement in core-shell model





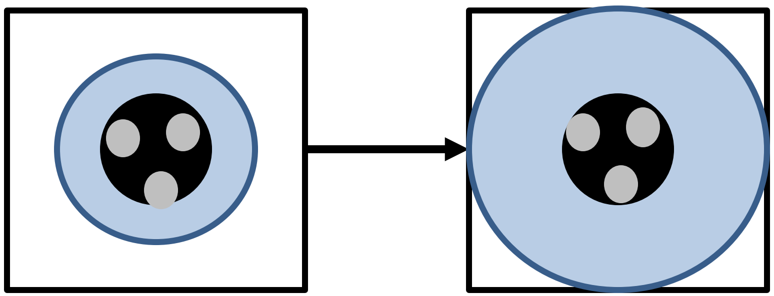
0.2 mg/cm^2

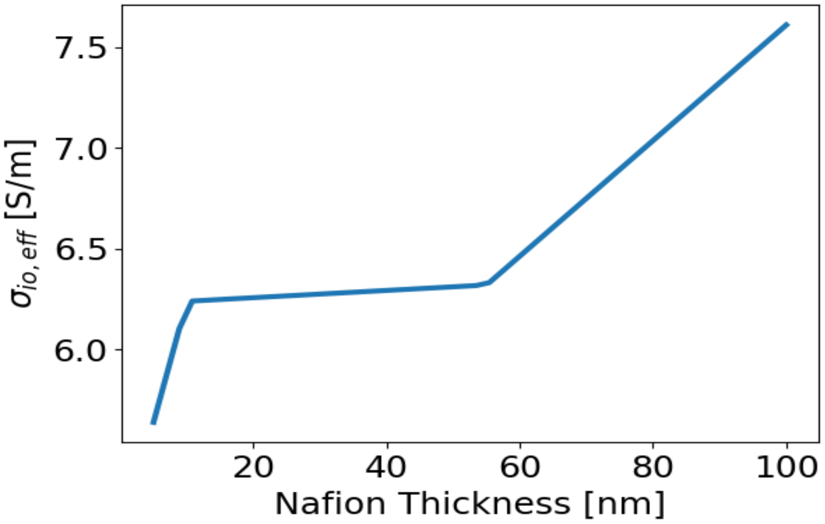
0.1 mg/cm^2

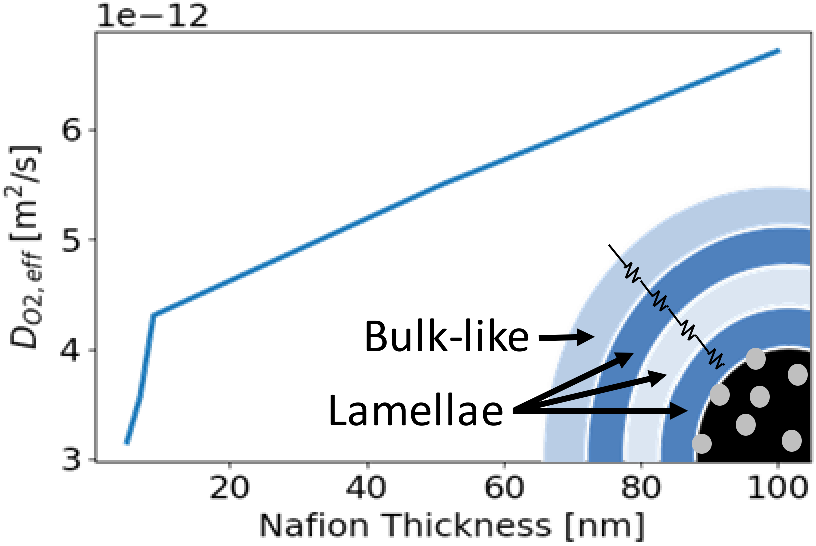
0.05 mg/cm^2

0.025 mg/cm^2

How does the Nafion thickness impact cell performance in core-shell model?







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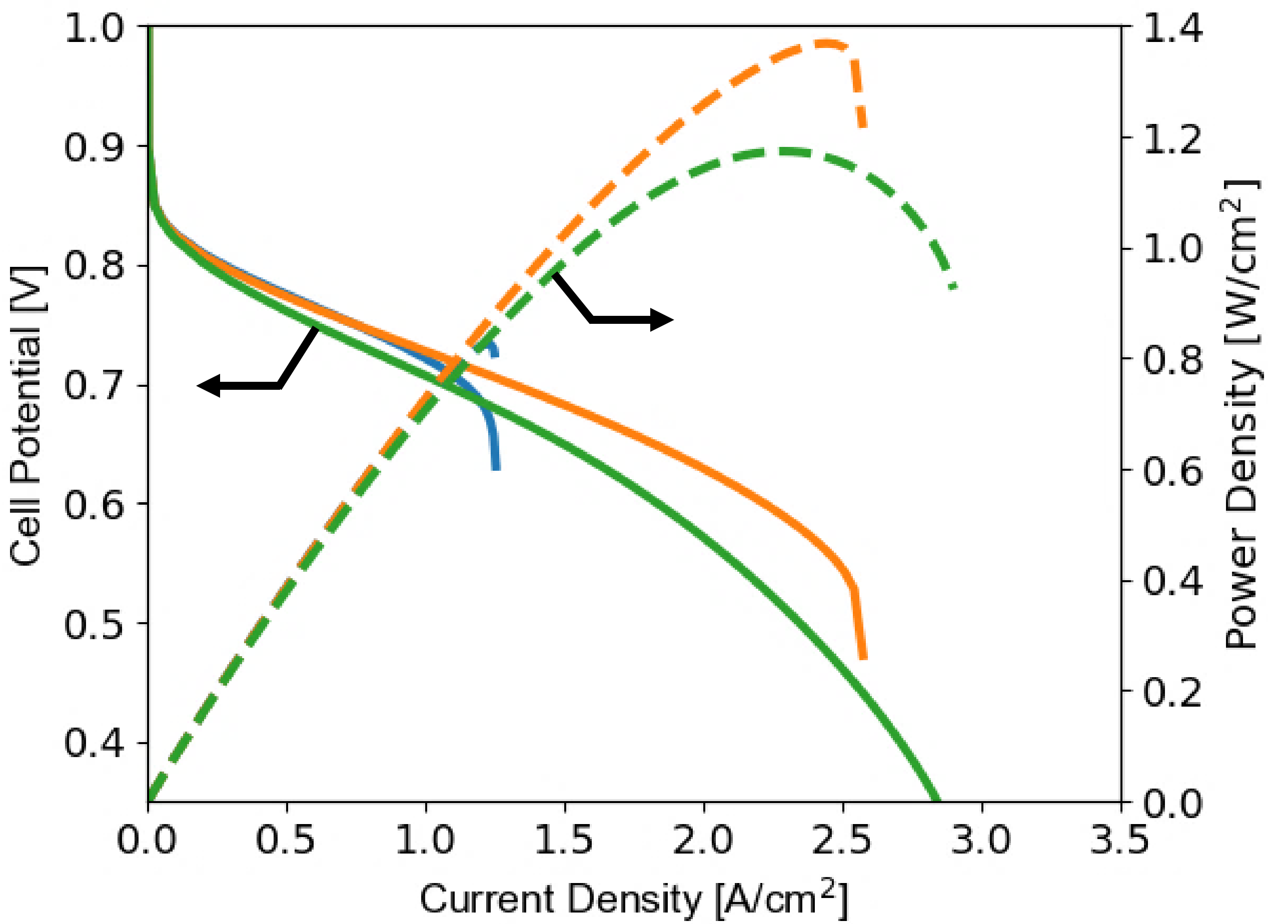
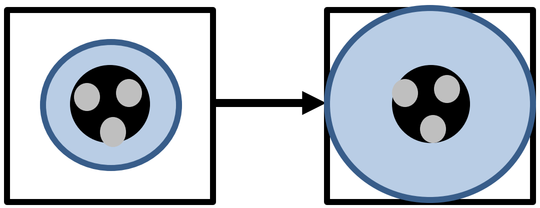
Thicker Nafion shells can outperform thinner ones at relevant currents

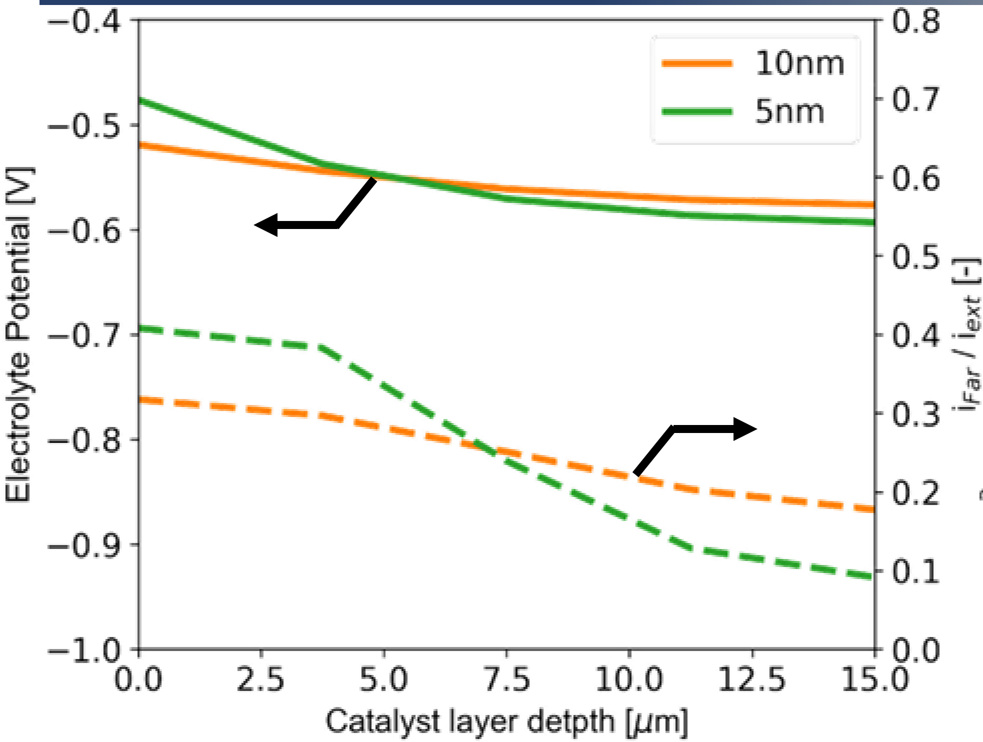
Pt loading = 0.2 mg/cm²

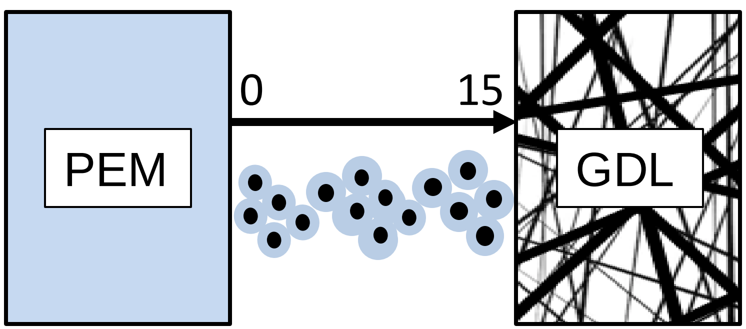


Constant A'''_{Pt} and A'''_{C} with changing CL porosity



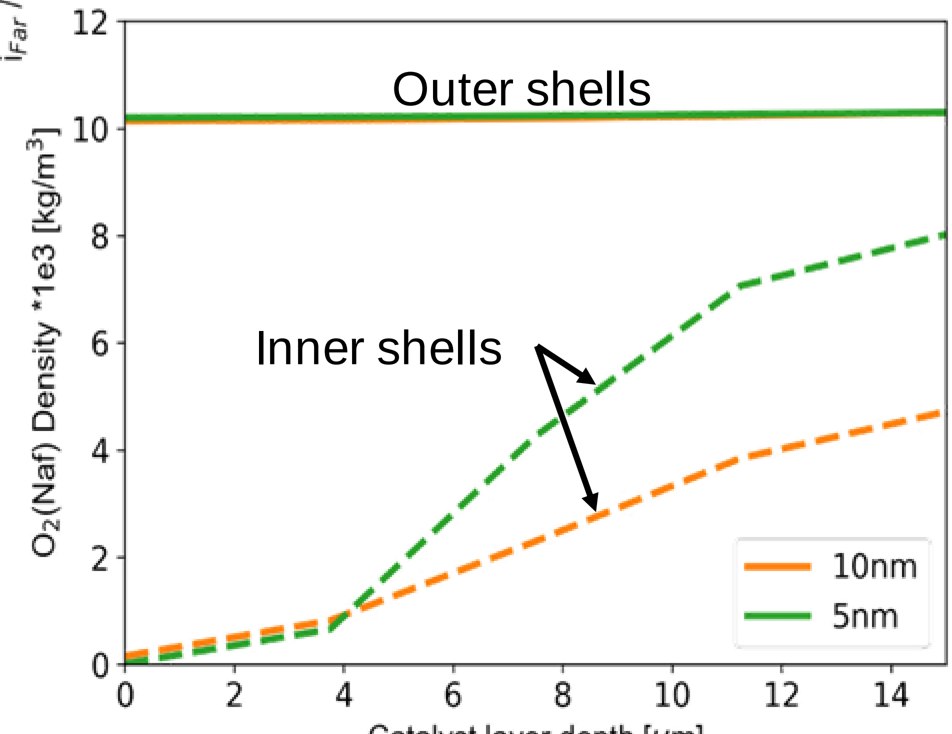
Thinner shells require a larger overpotential near the PEM interface





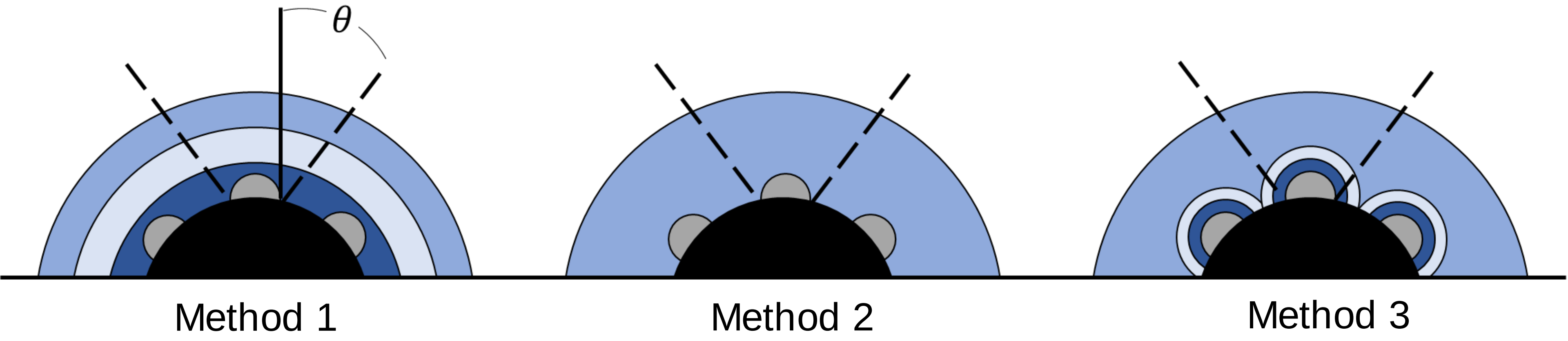
Current = 2.2 A/cm^2

Pt loading = 0.2 mg/cm^2



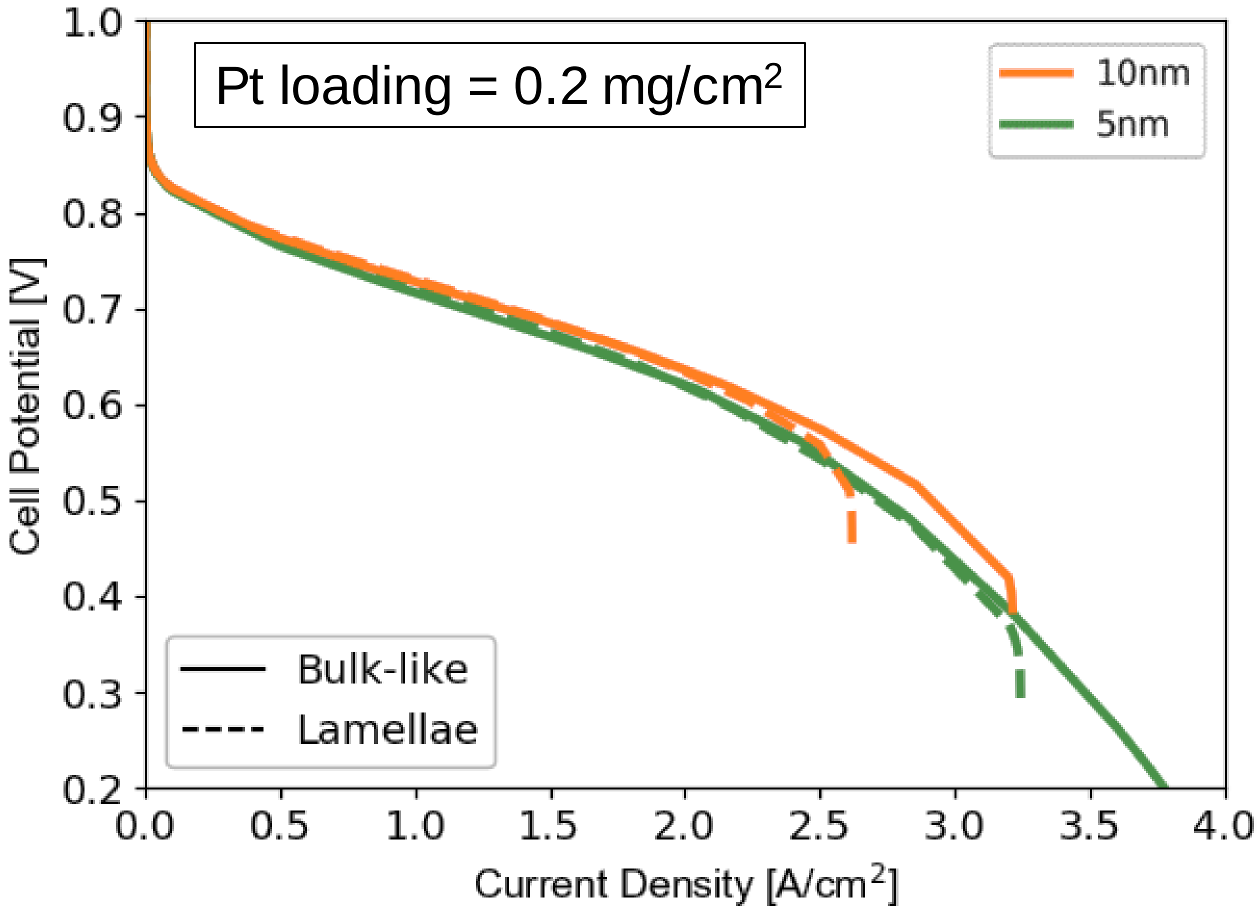
How do the different transport models affect predicted polarization curves?

- Method 1: lamellae – data (σ_{io}) and series resistor network (D_{O2})
- Method 2: no lamellae – weight by bulk-like water fraction
- Method 3: mix of lamellae (on Pt) and no lamellae (on C)



Bulk-like method outperforms others for core-shell model due to higher D_{O2}

- The different transport property models primarily influence limiting current with bulk-like having the best performance



Conclusions

- Low Pt loading
  - Current core-shell model does not capture activation overpotentials
- Thickness-dependent transport properties
  - Thicker Nafion shells in the CL may improve cell performance
- Physically-based scaling of transport properties
  - Transport losses are captured well in the core-shell model, but are overpredicted in flooded-agglomerates

Next steps

- Incorporate more complex surface chemistry at Pt interface
- Remove model assumptions about water transport
- Look at other modeling microstructures (e.g. multi-diameter core-shell or multi-scale core-shell with agglomerate)
- Neutron reflectometry (NR) experiments to capture species gradients across Nafion and calculate transport properties

Questions?

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- Thank you!

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References

- [1] C. He, S. Desai, G. Brown, and S. Bollepalli, “PEM Fuel Cell Materials: Costs, Performance, and Durability Issues,” *The Electrochemical Society*, pp. 41–44, 2005.
- [2] S. C. DeCaluwe, “Early Career Research Program: Flow-through Neutron Reflectometry – an in operando sample environment for active polymer interface studies.”