Mathematical Model of a Direct Methanol Fuel Cell

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Objective of HAPS
(Hybrid Advanced Power Sources)

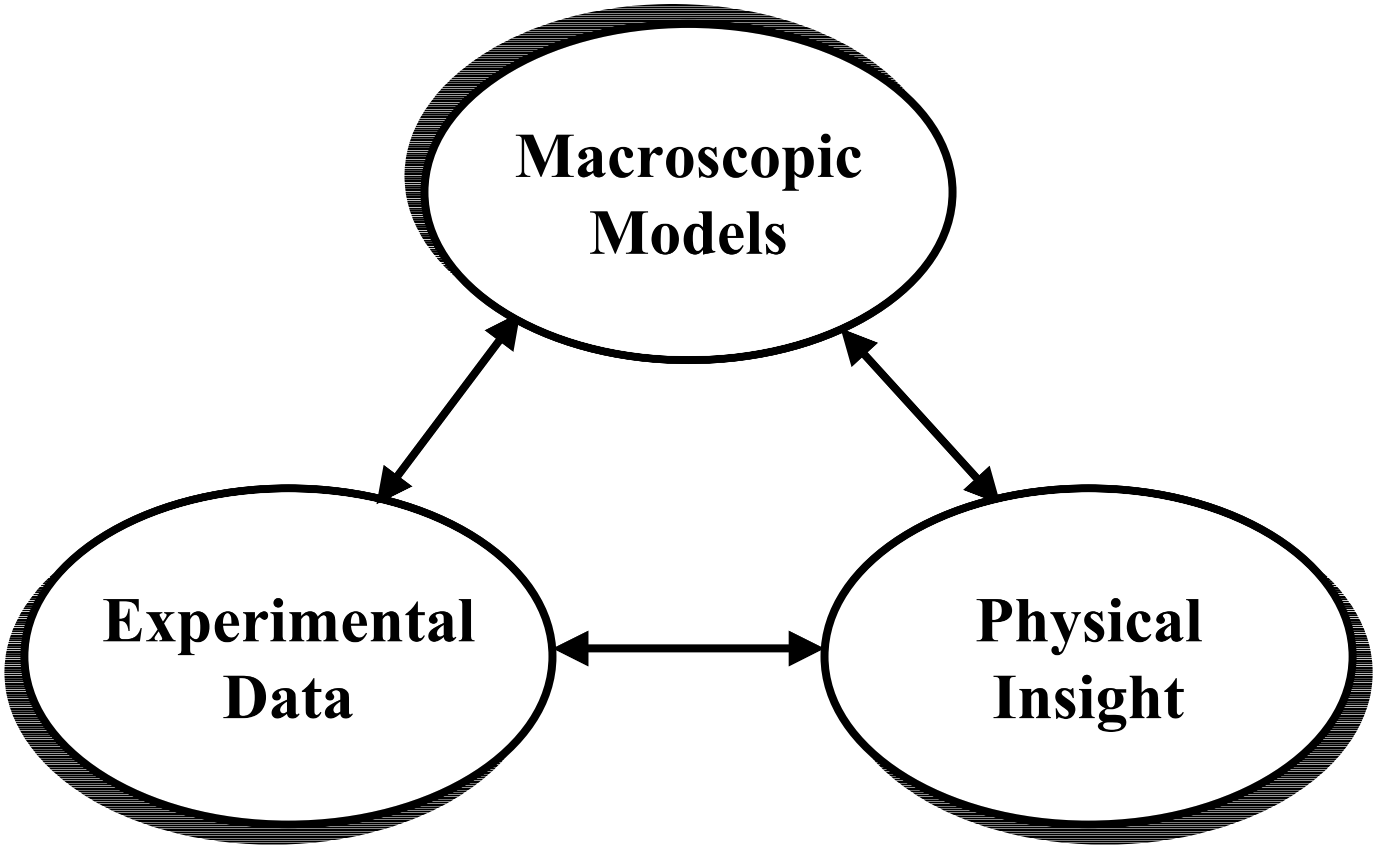
Develop design tools for rapid prototyping of hybrid advanced power sources

- A combination of batteries, capacitors and fuel cell

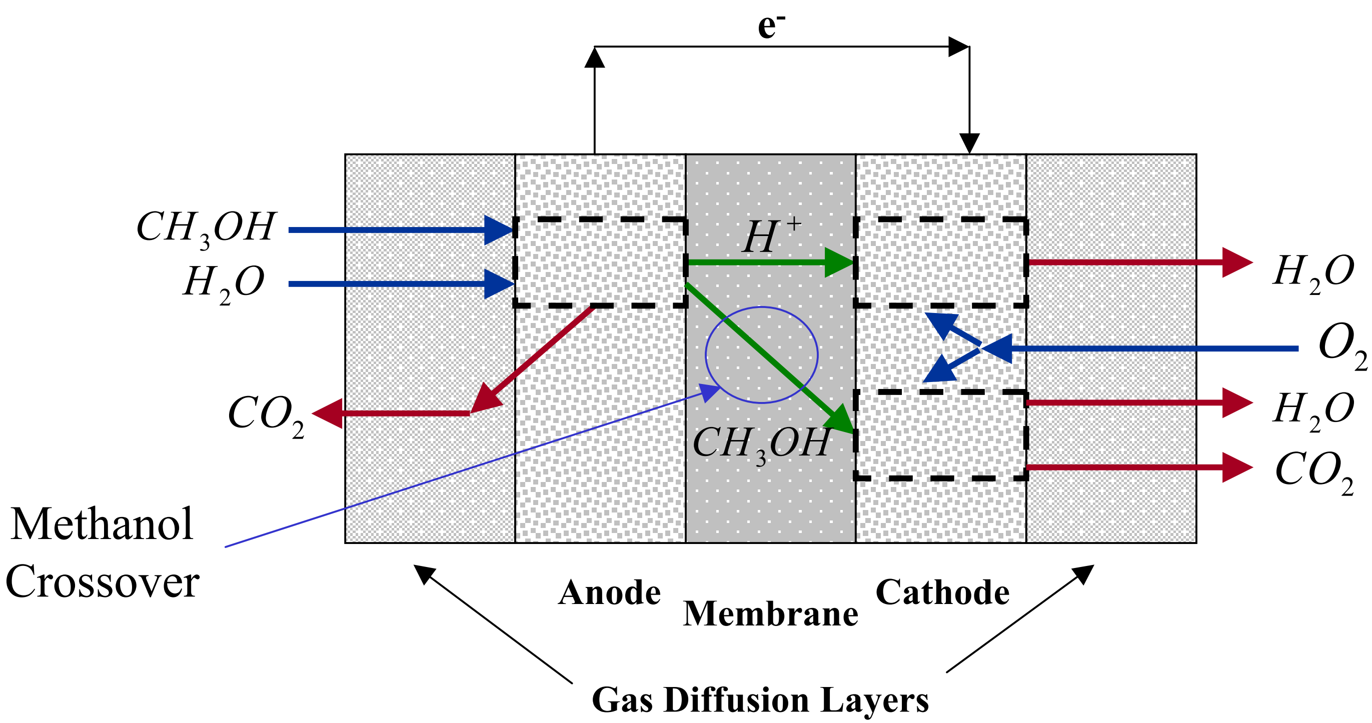
DMFC Modeling Tasks

- Develop robust cell models that can predict voltage, methanol crossover, and water management as a function of temperature and methanol concentration.
- Develop system-level models within our Virtual Test Bed (VTB) to optimize hybrid power systems
- Integrate key features of the cell model into the computational fluid dynamics environment to study scale-up issues related to stack configuration, flow field design, etc.

Analysis Approach



DMFC Schematic



$$Anode: \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$Cathode: \quad 6H^+ + 6e^- + \frac{3}{2}O_2 \rightarrow 3H_2O$$

Methanol Crossover

Reduces DMFC efficiency

- Mixed potential effect
  - ➢The methanol that comes into contact with the cathode reduces the voltage of the cathode.
- Fuel consumption
  - ➢The methanol that comes into contact with the cathode reacts with oxygen to produce heat rather than electric power.

Reducing Methanol Crossover

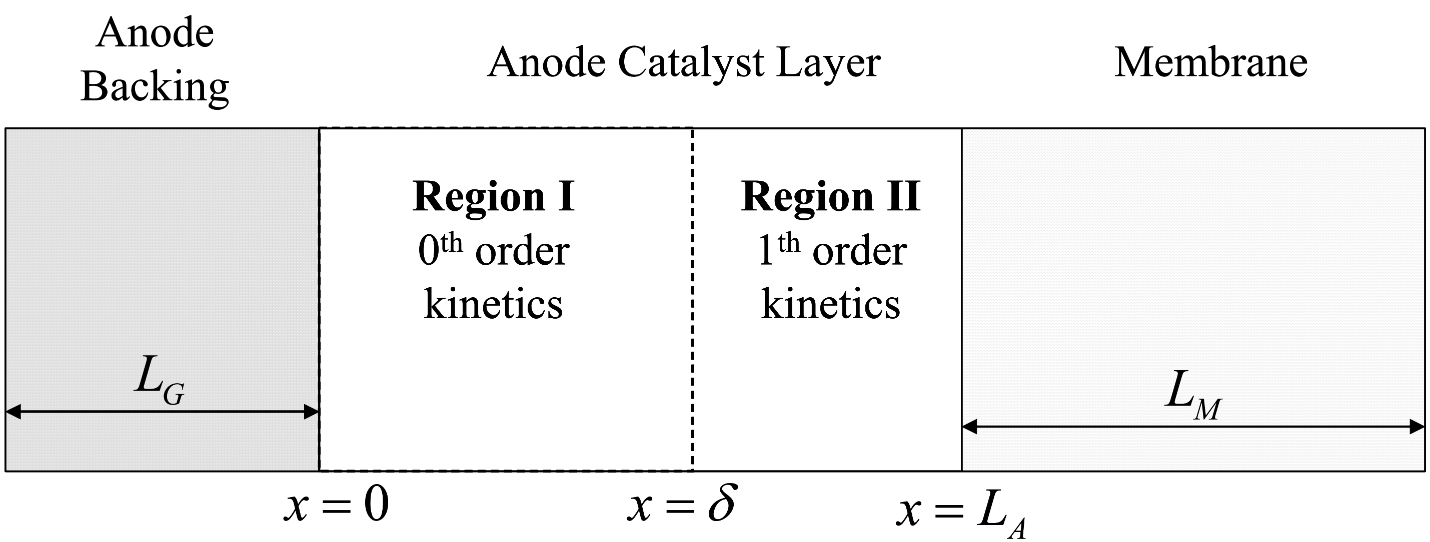
- Control the methanol feed to the anode.
- Use of thicker and more diffusional resistive MEA (membrane electrode assembly) components.

Model Development

Based on recent models in the literature:

J.P. Meyers and J. Newman, "Simulation of the direct methanol fuel cell: II. Modeling and data analysis of transport and kinetic phenomena", *J. Electrochem Soc.*, **149**, A718-A728 (2002).

Z.H. Wang and C. Y. Wang, "Mathematical modeling of liquid-feed direct methanol fuel cells", *J. Electrochem. Soc.*, **150**, A508 (2003).

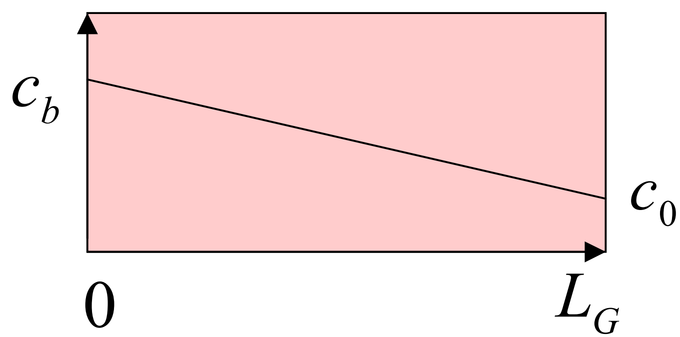


Anode Backing

Governing Equation

$$D_G \frac{d^2 c_G}{dx^2} = 0 \qquad \Rightarrow \qquad D_G \frac{(c_b - c_o)}{L_G} = \frac{I}{6F} + N_{MeOH}$$

Concentration Profile



Membrane

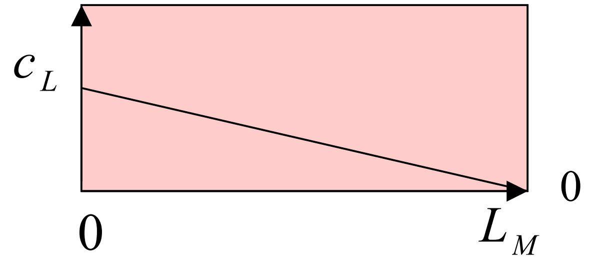
Methanol Flux

$$N_{MeOH} = -D_M \frac{dc_M}{dx} + \xi_{MeOH} \frac{I}{6F}$$

Governing Equation

$$D_M \frac{d^2 c_M}{dx^2} = 0 \quad \Rightarrow \quad D_M \frac{c_L}{L_M} = \frac{\xi I}{6F} + N_{MeOH}$$

Concentration Profile



Anode Catalyst Layer

Governing Equation

$$D_A \frac{d^2 c}{d x^2} = \frac{j}{6F}$$

Current

Tafel kinetics: $j = aI_0 e^{\frac{\alpha_a \eta_a F}{RT}}$

Wang & Wang: $I_0 = I_{0,ref}\left(\frac{c}{c_{tr}}\right)^m \qquad m = \begin{cases} 0; & c \ge c_{tr} \\ 1; & c < c_{tr} \end{cases}$

$$D_A \frac{d^2 c}{dx^2} = \frac{aI_{0,ref}}{nF}\left(\frac{c}{c_{tr}}\right)^m e^{\frac{\alpha_a \eta_a F}{RT}}$$

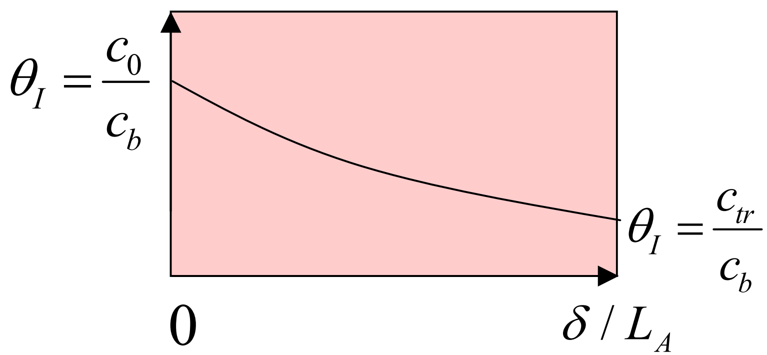
ACL (Region I)

Governing Equation

$$\frac{d^2\theta_I}{d\chi^2} = A_I$$

$$\theta_I = \frac{c_I}{c_b} \qquad \chi = \frac{x}{L_A} \qquad A_I = \frac{L_A^2 a I_{0,ref}}{c_b D_A n F} e^{\frac{\alpha_a \eta_a F}{RT}}$$

Boundary Conditions



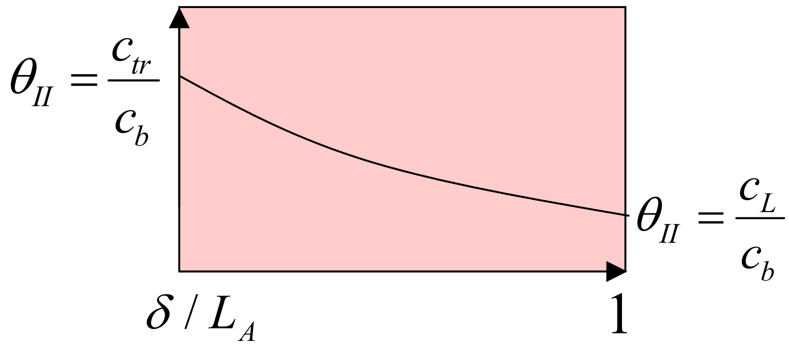
ACL (Region II)

Governing Equation

$$\frac{d^2\theta_{II}}{d\chi^2} = A_{II}\theta_{II}$$

$$\theta_{II} = \frac{c_{II}}{c_b} \qquad \chi = \frac{x}{L_A} \qquad A_{II} = \frac{L_A^2 a I_{0,ref}}{c_{tr} D_A n F} e^{\frac{\alpha_a \eta_a F}{RT}}$$

Boundary Conditions



Anode Catalyst Layer

Concentration Profile

– Region I

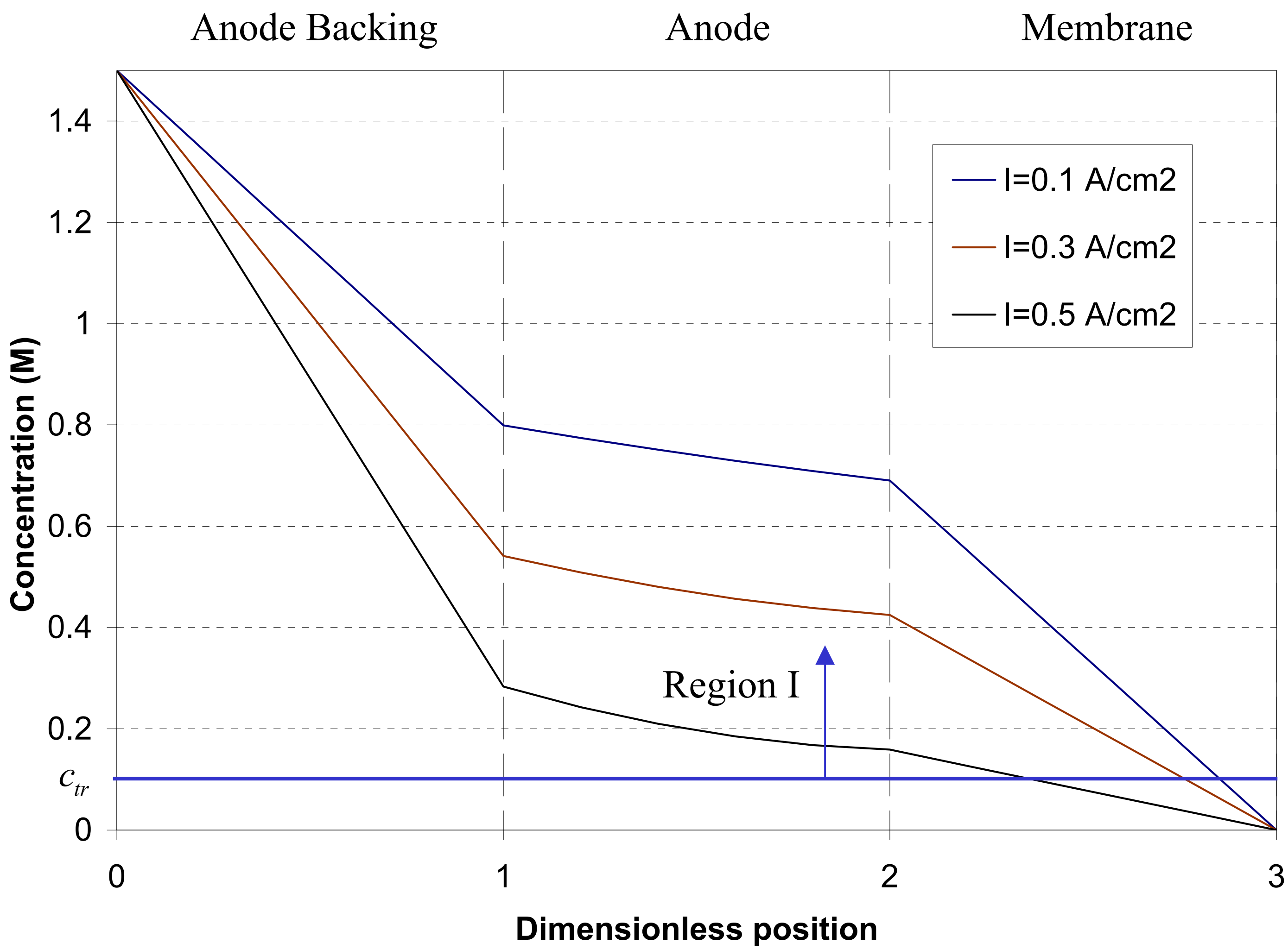
$$\theta_I = \frac{A_I}{2}\chi^2 + \left(\frac{c_L - c_0}{c_b} - \frac{A_I}{2}\right)\chi + \frac{c_0}{c_b}$$

– Region II

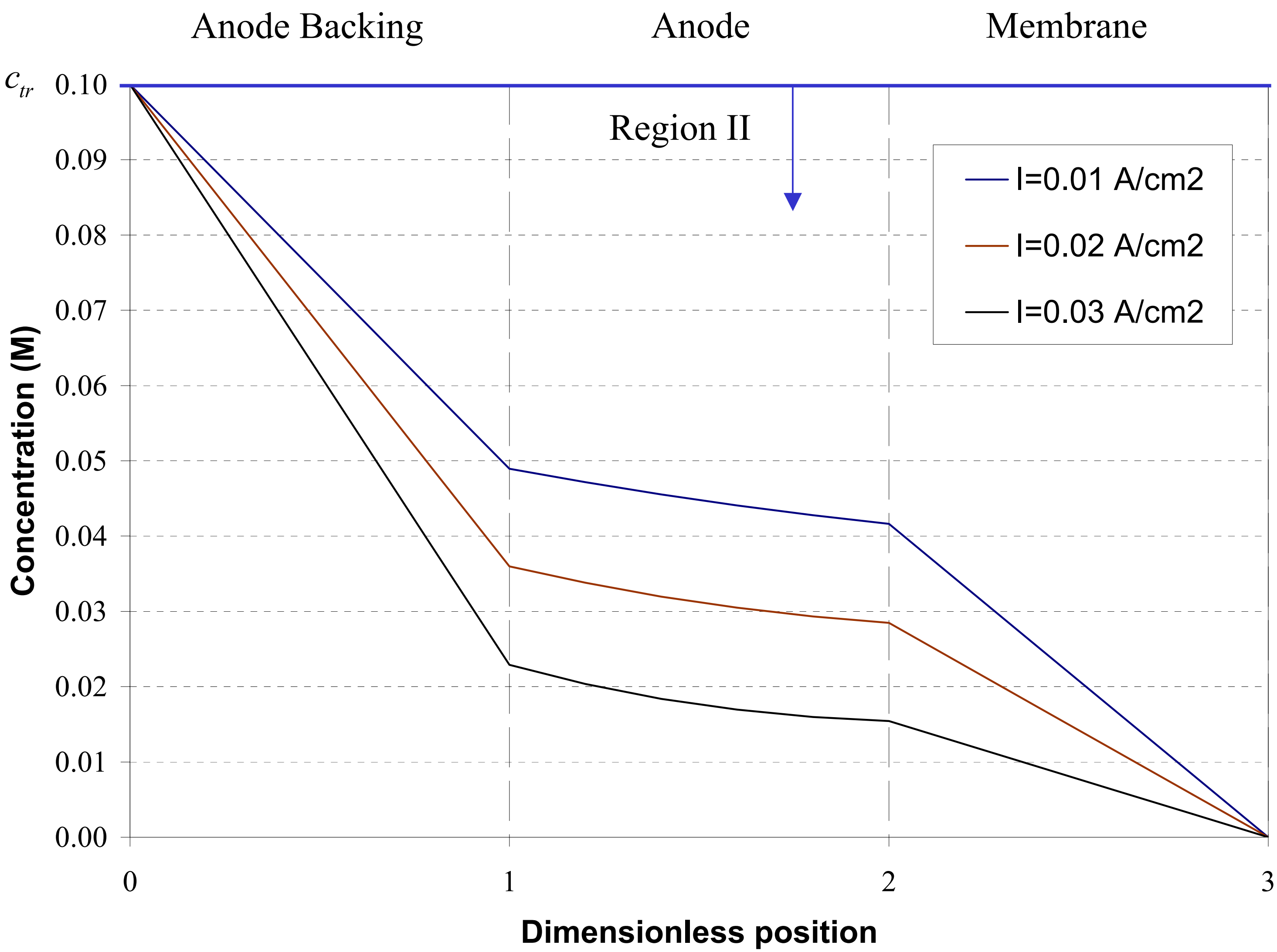
$$\theta_{II} = C_1 e^{\sqrt{A_{II}}\chi} + C_2 e^{-\sqrt{A_{II}}\chi}$$

$$C_1 = \frac{c_0}{c_b} - \frac{c_L - c_0 e^{\sqrt{A_{II}}}}{c_b\left(e^{-\sqrt{A_{II}}} - e^{\sqrt{A_{II}}}\right)} \qquad C_2 = \frac{c_L - c_0 e^{\sqrt{A_{II}}}}{c_b\left(e^{-\sqrt{A_{II}}} - e^{\sqrt{A_{II}}}\right)}$$

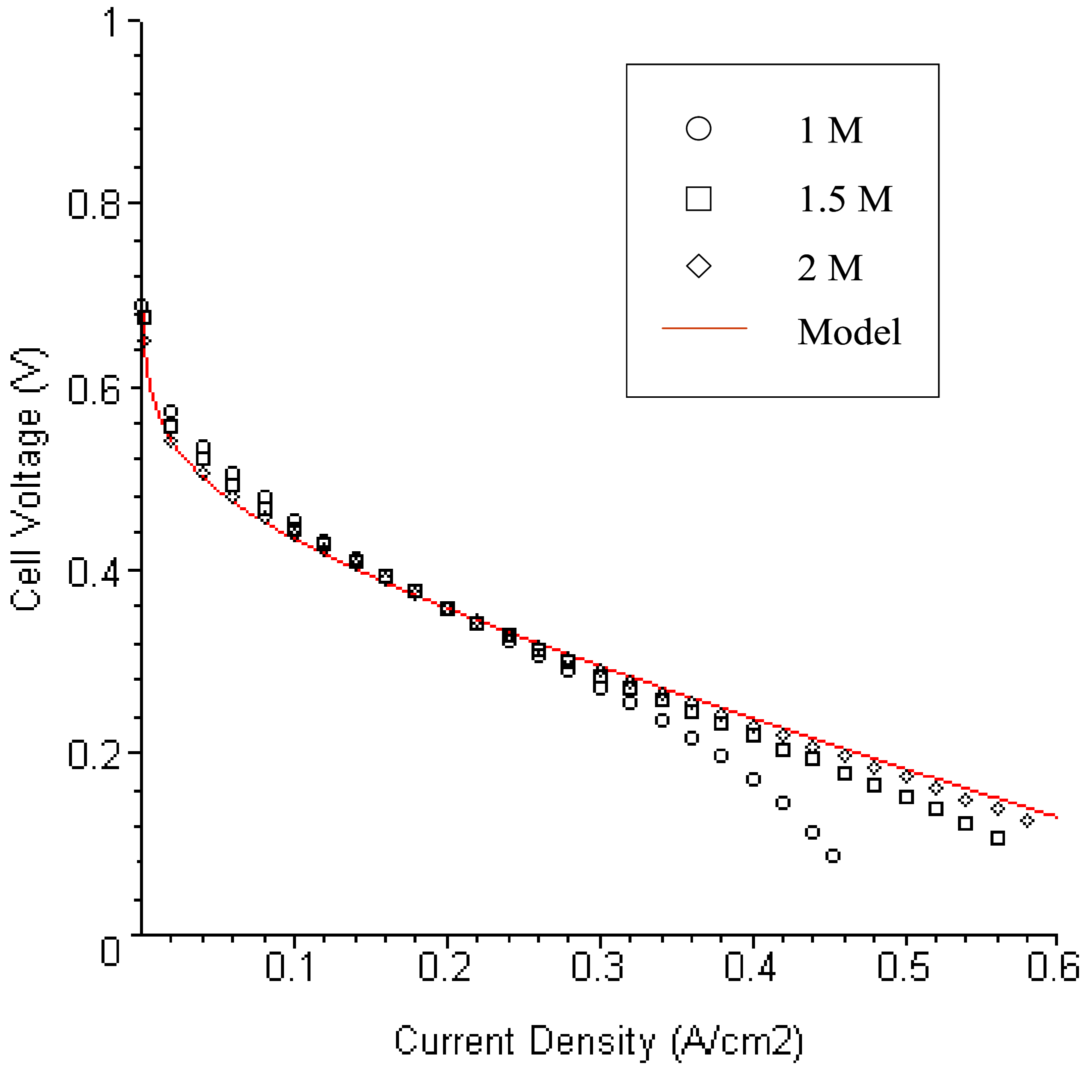
Model Predictions (1.5 M MeOH)



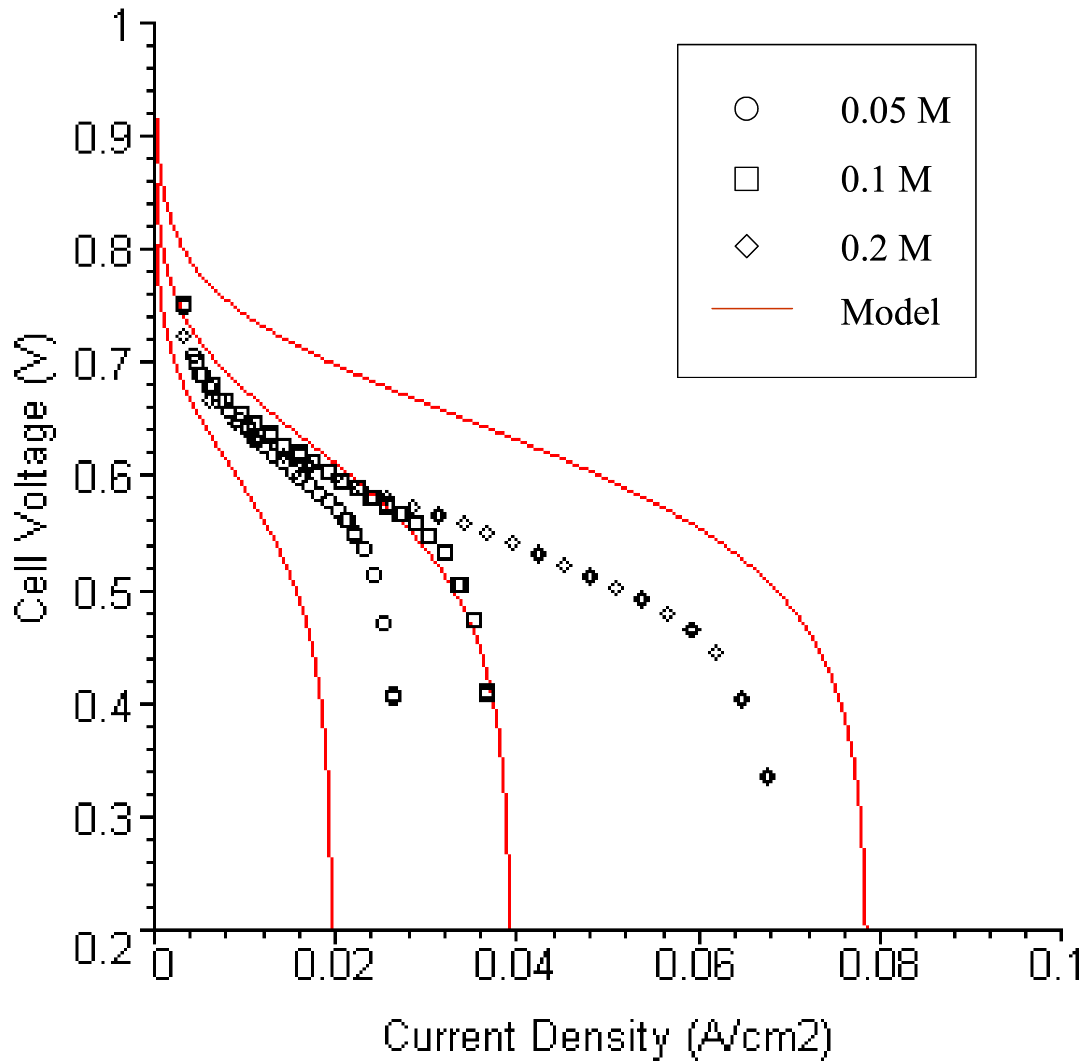
Model Predictions (0.1 M MeOH)



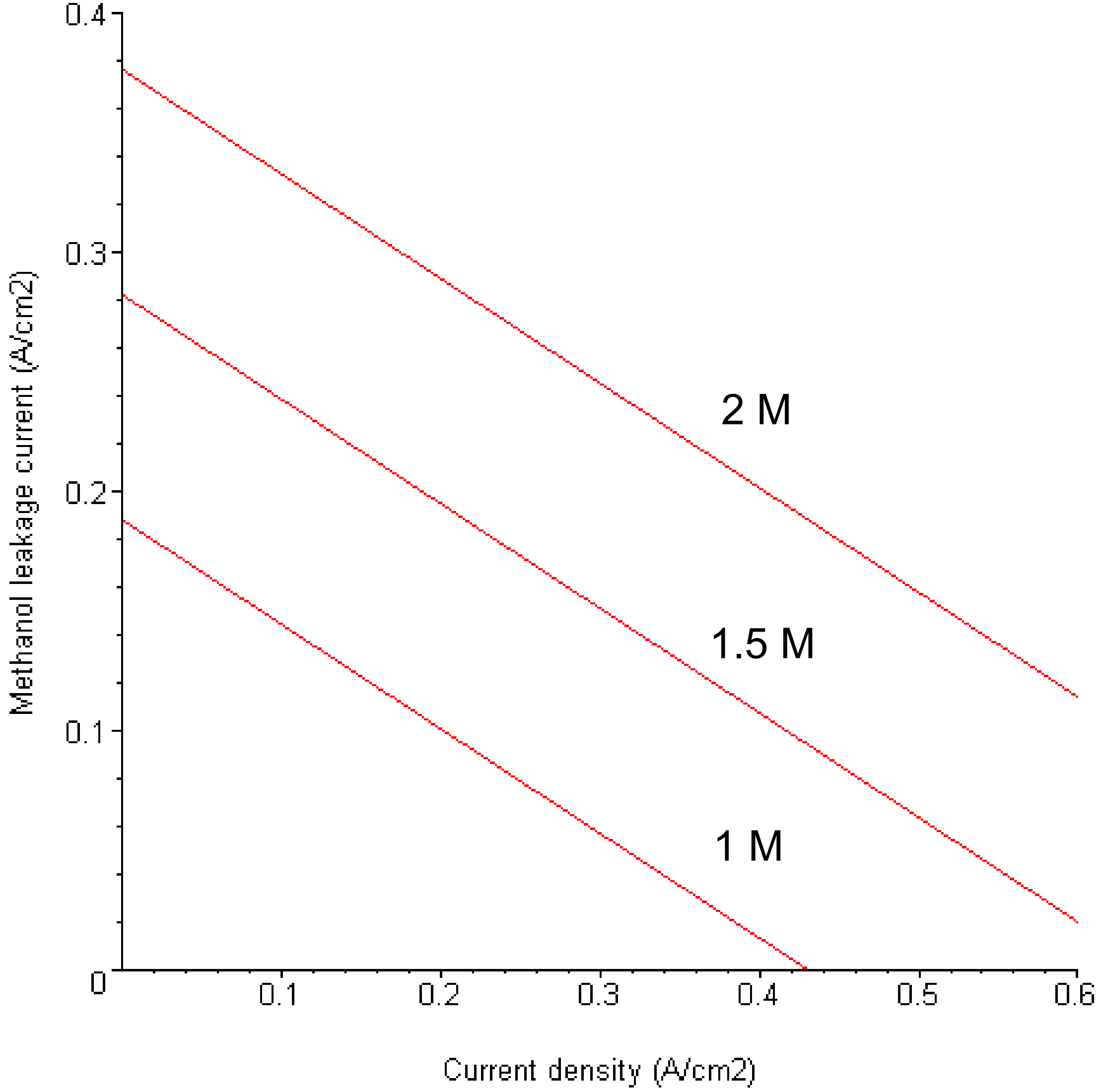
Polarization Curves at 70°C in Pt-Ru (Region I)



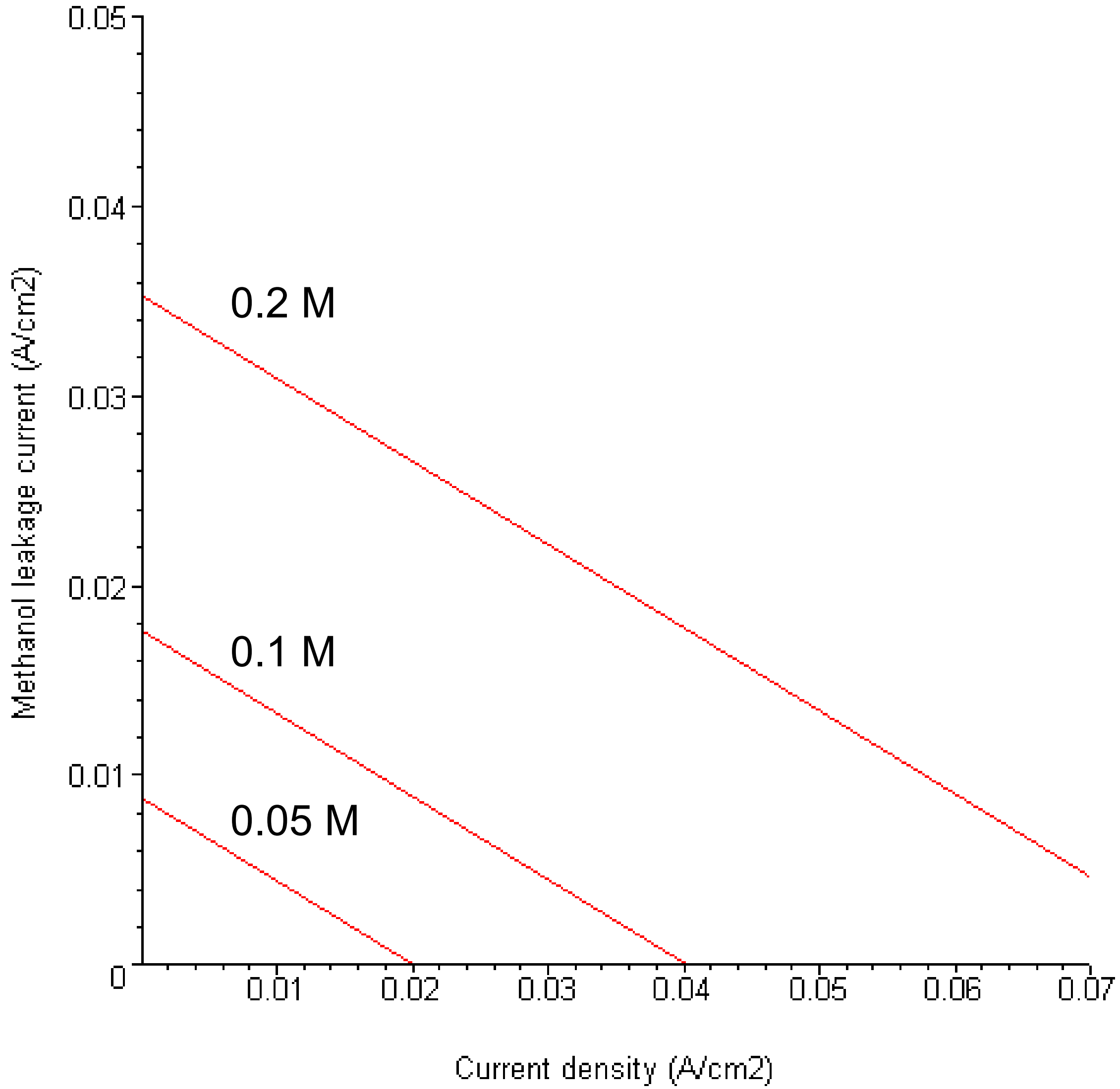
Polarization Curves at 70°C in Pt-Ru (Region II)



Methanol Leakage Current (Region I)



Methanol Leakage Current (Region II)



Summary

- We have developed robust cell models that can predict voltage, methanol crossover, and water management as a function of temperature and methanol concentration.
- Additional model validation is needed of I-V curves and methanol crossover to justify transport parameters and kinetic expression.
- These are being integrated into system-level models within our Virtual Test Bed (VTB) to optimize hybrid power systems

Acknowledgements

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