Simulating Performance and Species Crossover in a Vanadium Redox Flow Battery using COMSOL Multiphysics

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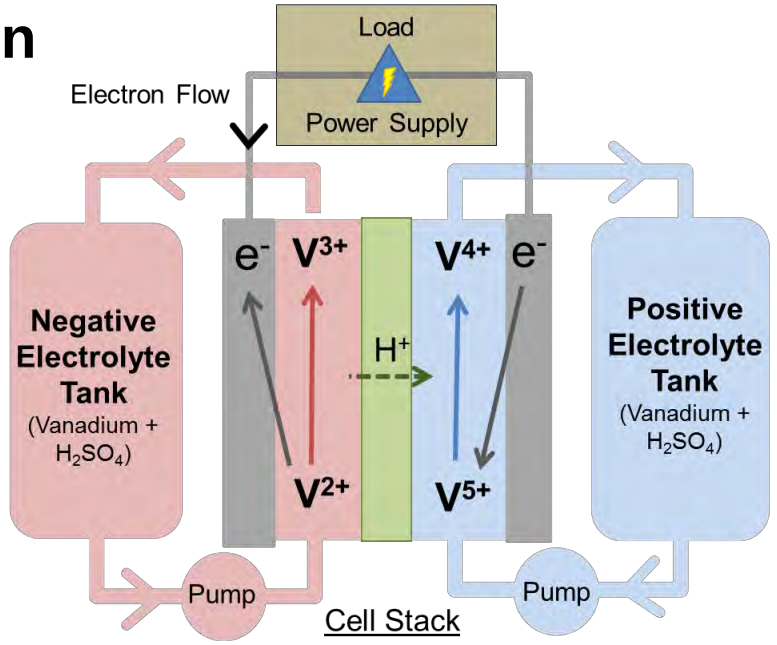

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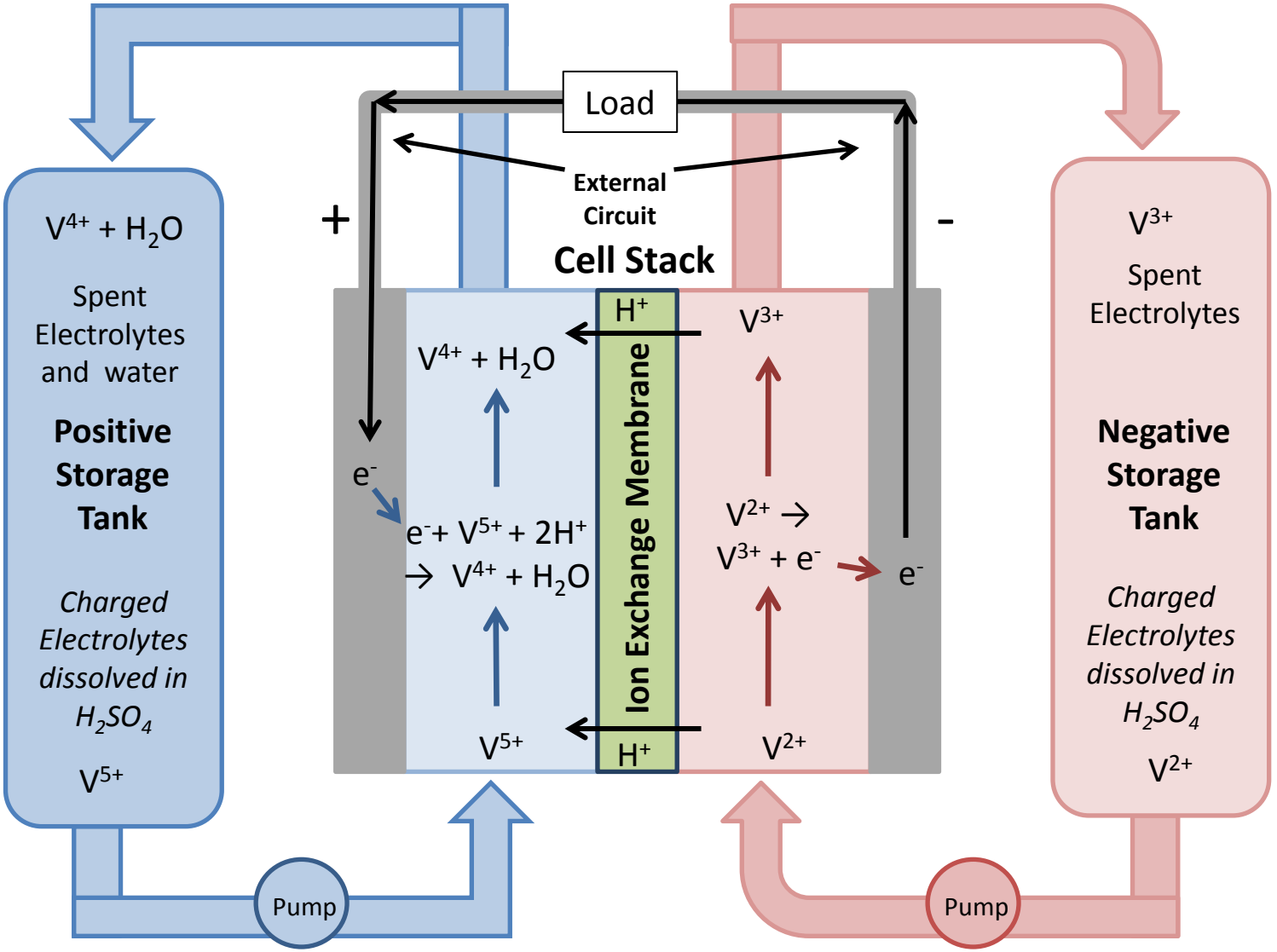
Vanadium Redox Flow Battery



Vanadium Redox Flow Battery

- **Advantages:**
  - Decoupled power and energy ratings
    - Power rating (kW) ~ Size of Cell
    - Energy rating (kWh) ~ Volume of Electrolyte
  - Large cycle life: 12,000+ cycles
  - Limited self-discharge
  - Low Maintenance
- **Disadvantages:**
  - Low energy and power density
    - Energy density: 20 – 35 Wh/L
    - Power density: 25 – 100 W/L

Motivation

Crossover is one of the key issues limiting the performance of vanadium redox flow batteries (VRFB)

- Less than 15 published models in the last 4 years

Majority modeling efforts: Macroscopic, 2-D, and transient models

- Poor experimental agreement
- Ideal membrane assumption *(no crossover)*

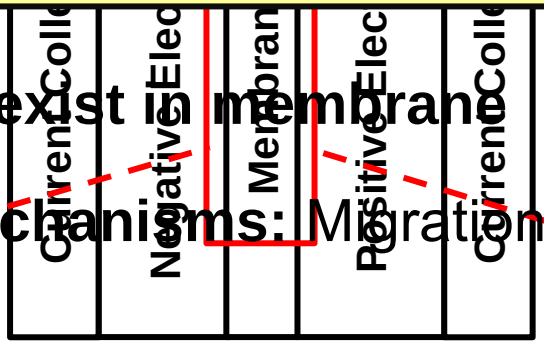
→ Restricted to **single charge/discharge cycle**

→ **Simplified** membrane performance

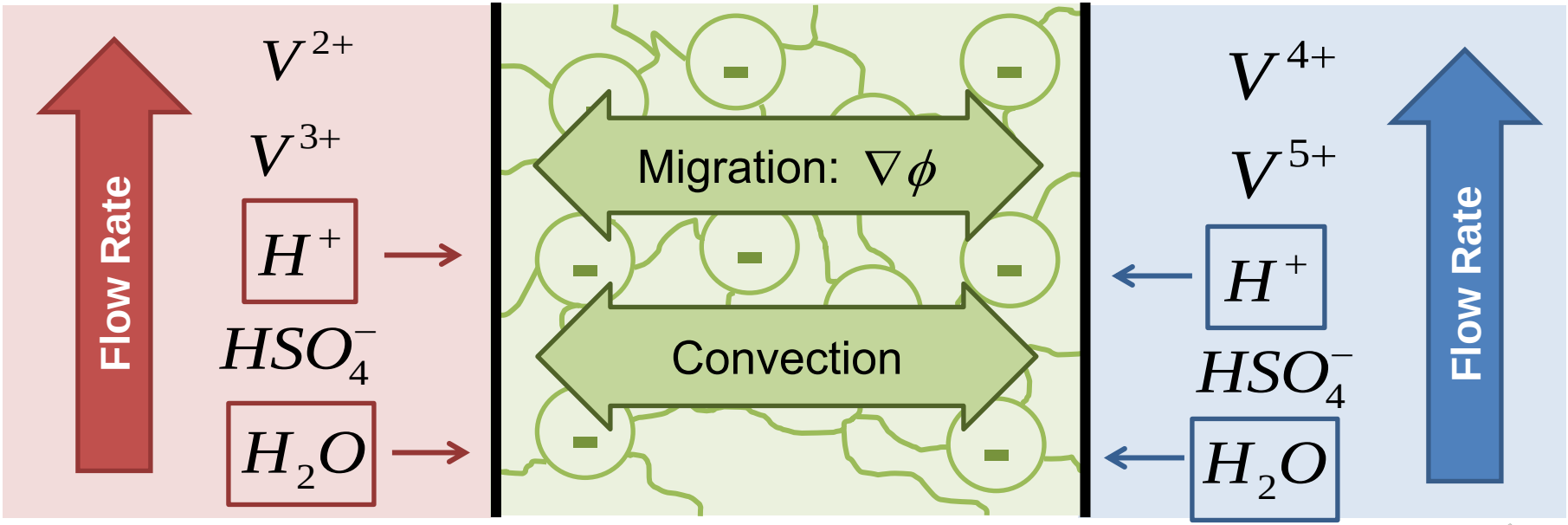
Current Modeling: Membrane

In the membrane, current modeling efforts assume single ion (hydrogen) transport

1. **Only H^+ and H_2O exist in membrane**
2. **Two transport mechanisms:** Migration and Convection only

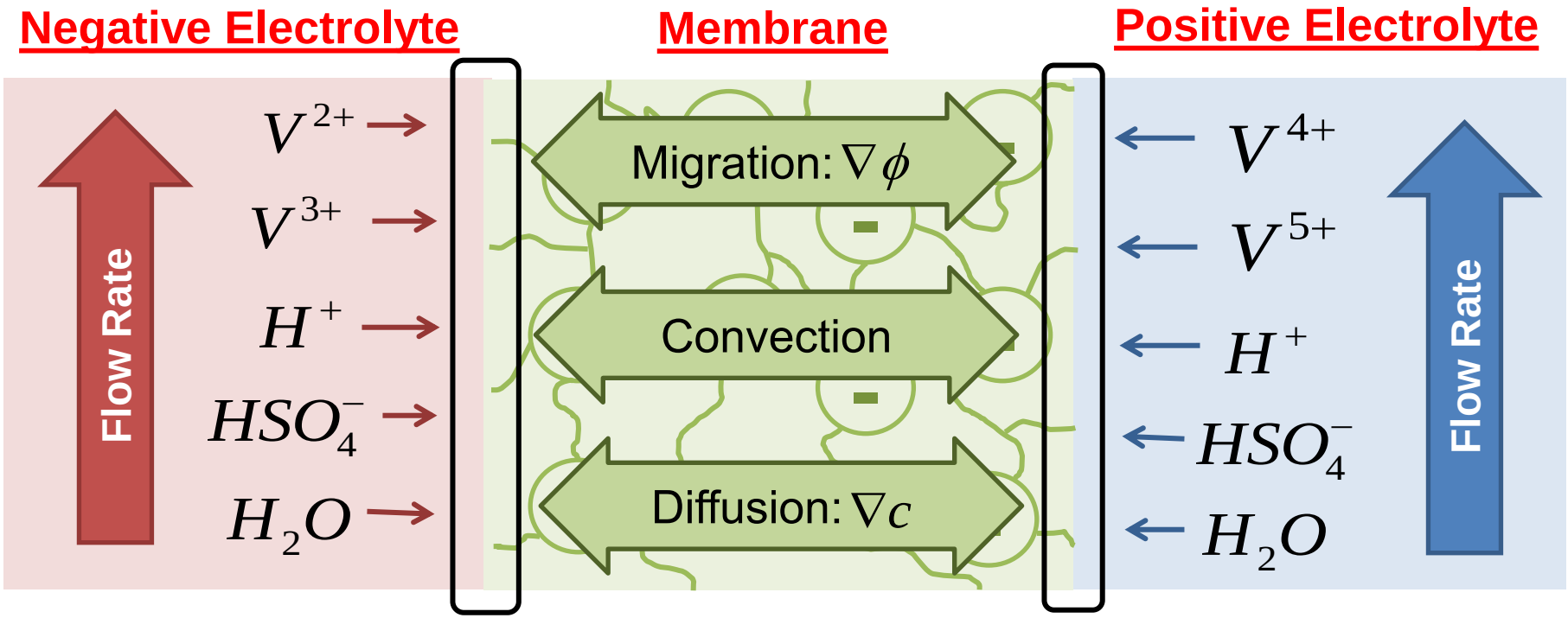


Negative Electrolyte | **Membrane** | **Positive Electrolyte**



Real Scenario: Membrane

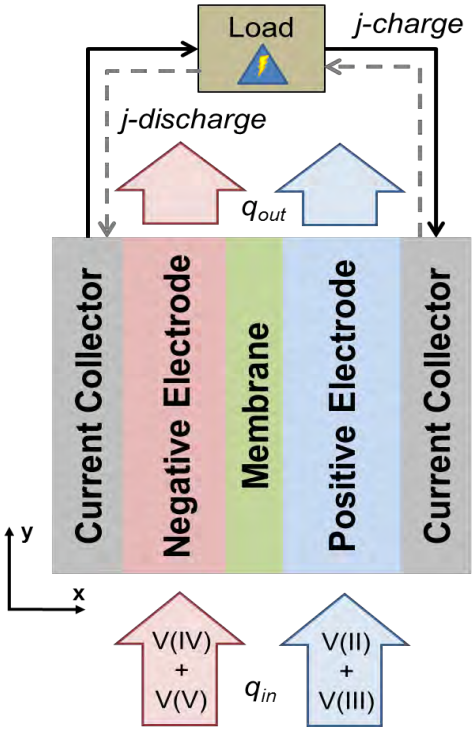
1. **All species in electrolytes exist in membrane**
2. **All transport mechanisms:** Migration, Diffusion, Convection
3. **Interfacial physics and side reactions**



Proper models should account for all these physics

Objective

Develop a comprehensive, 2-D, transient model which incorporates **the proper membrane physics** to accurately capture the crossover effect on charge/discharge cycling using **COMSOL**



Modeling Domain

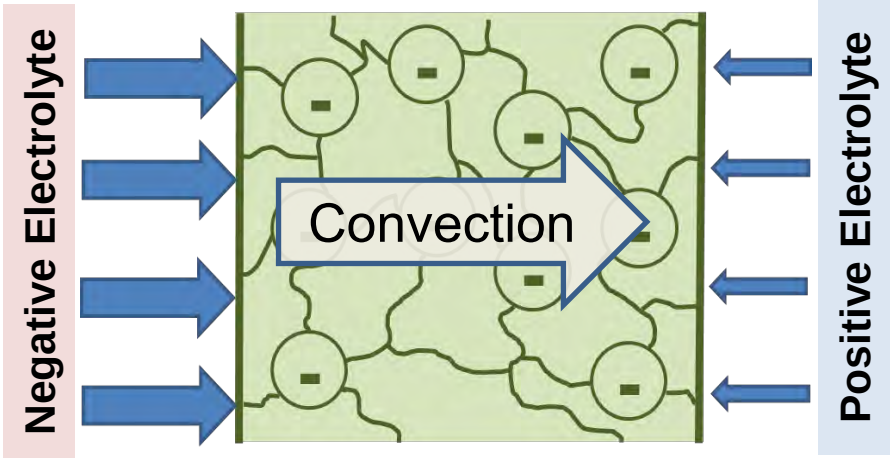
Main Components of Present Model

1) Membrane

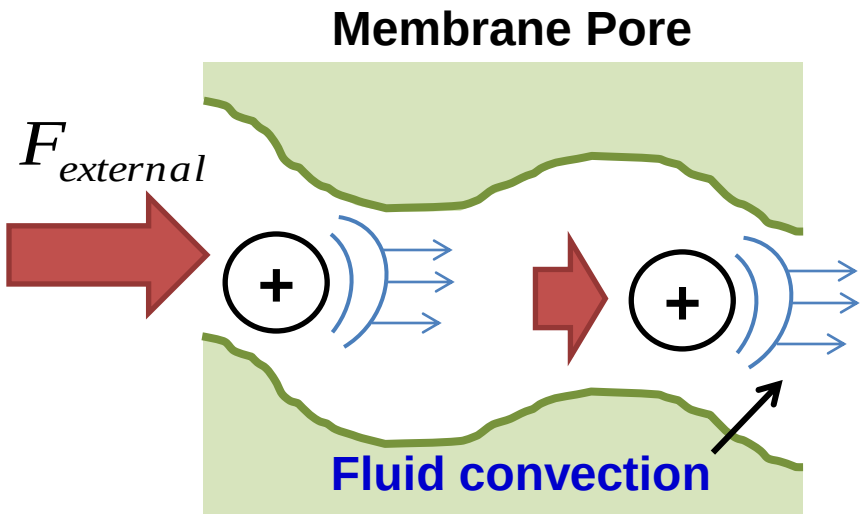
2) Membrane/Electrode Interface

3) Open Circuit Voltage

Formulation: Membrane Convection



1. Osmotic Pressure



2. Viscous Forces

Simplified Membrane: Migration Only

$$F_{external} = F\nabla\phi_l$$

Real Scenario: Migration & Diffusion

$$F_{external} = F\left(\nabla\phi_l + \nabla\phi_{diff}\right)$$

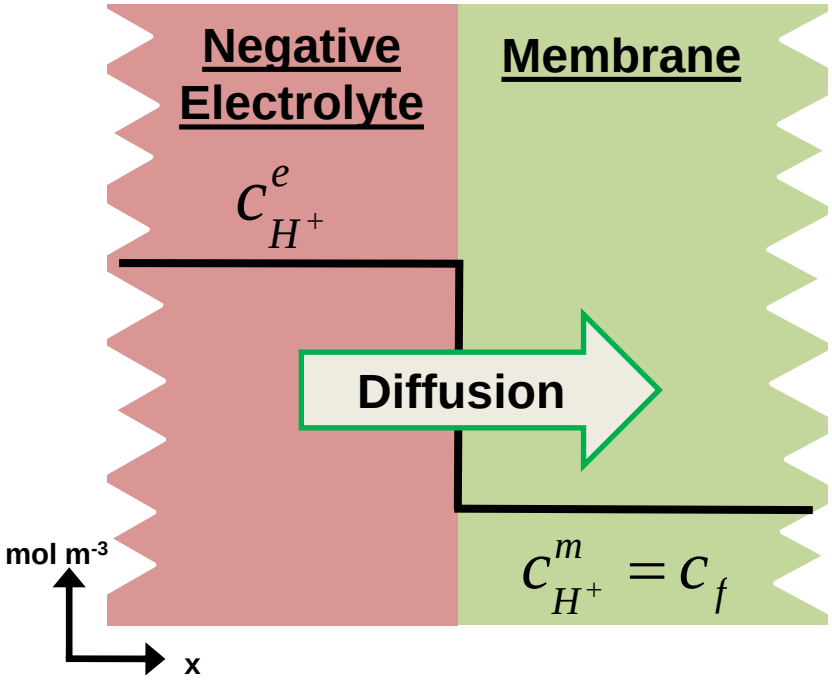
Effective diffusion potential

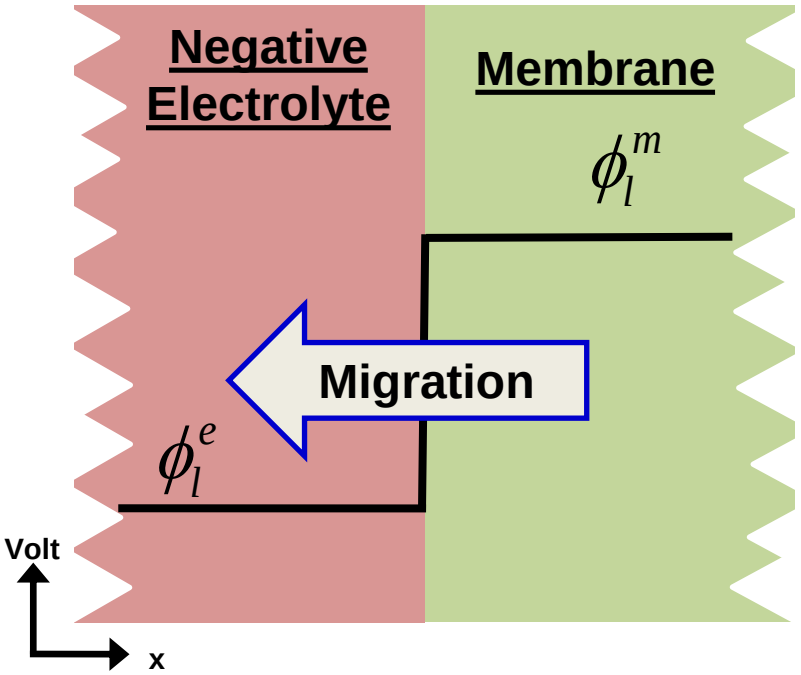
$$\nabla\phi_{diff} = \frac{\sum Diffusion\_Flux}{Liquid\_Conductivity}$$

$$= \frac{RT}{F}\frac{\sum_i z_i D_i \nabla c_i}{\sum_i z_i^2 D_i c_i}$$

Membrane|Electrolyte Interface

Membrane|electrolyte interface is key for proper coupling of electrode and membrane physics



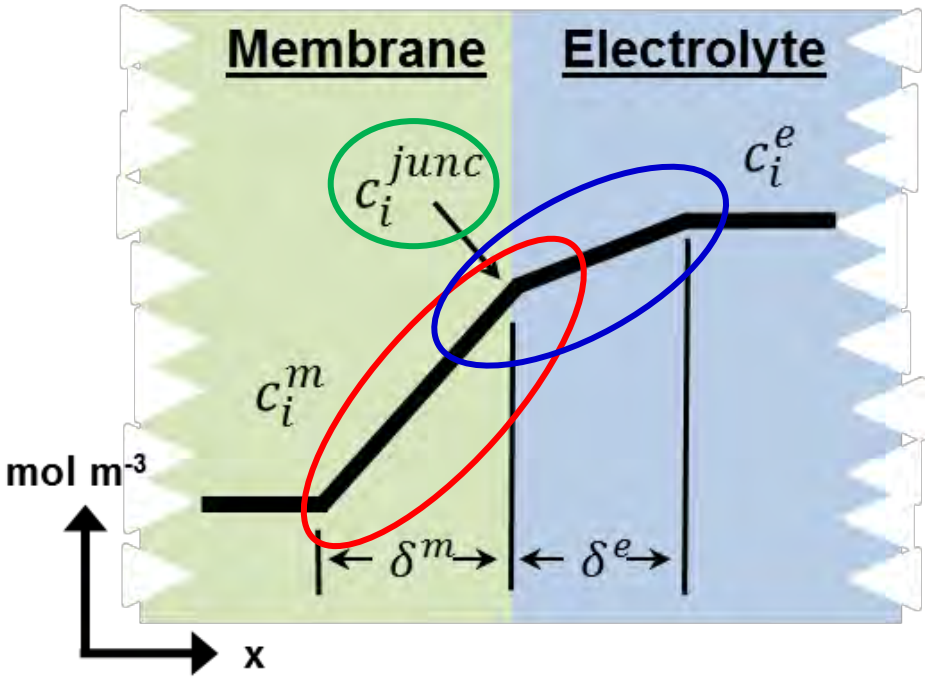


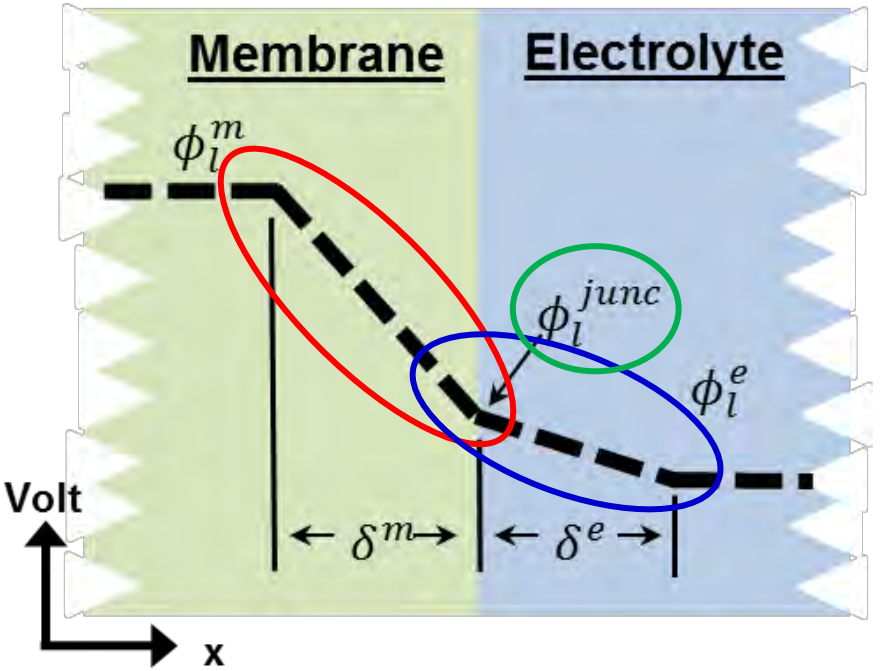
Proton gradient facilitates diffusion into membrane → Diffusion will violate electro-neutrality

Diffusion + Migration = Zero Net Charge Transfer

Interfacial Regions

- At interfacial region, concentration and potential change linearly





- **Two Regions**
  1. Electrolyte Region
  2. Membrane Region
- **Additional Variables**
  - Junction Concentration
  - Junction Potential

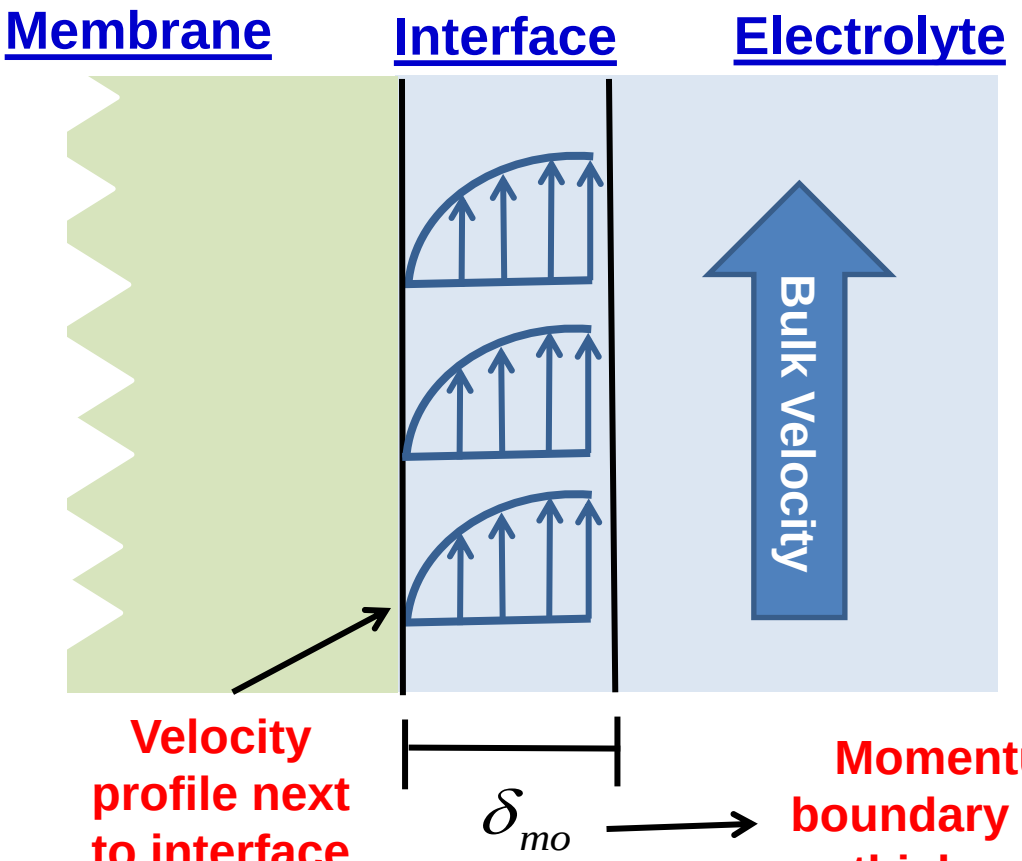
Interfacial Thickness

- **Electrode:**

  interfacial thickness = diffuse boundary layer thickness $\left(\delta^e\right)$

- **Membrane:** $\delta^e = \delta^m$

  interfacial thickness = electrode interfacial thickness



Electrode Interfacial Thickness

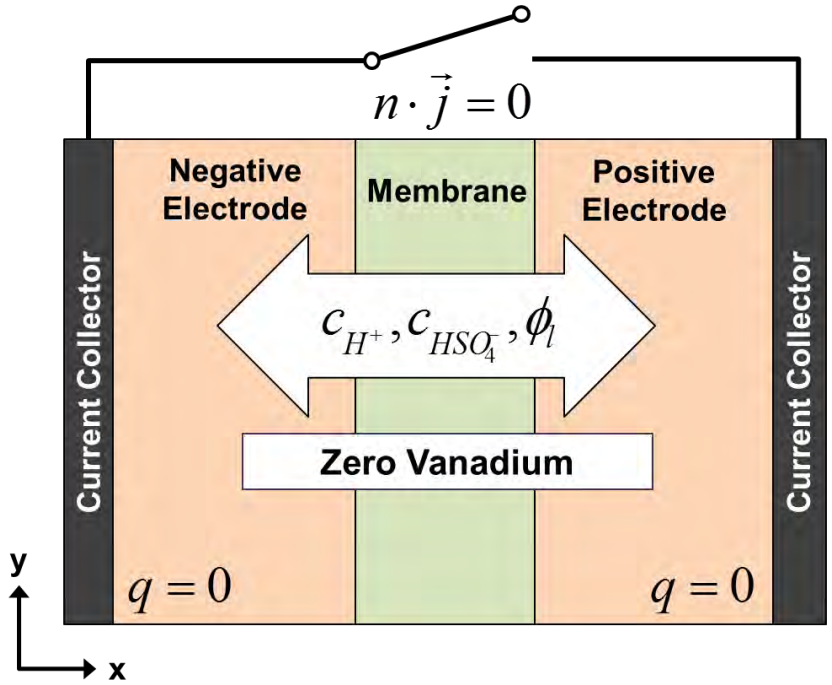
$$\delta^e = \delta_{mo}\left(\frac{D_{avg}^{eff}\rho}{\mu}\right)^{1/3}$$

Verification: Interfacial Case Study

- Verification at **Equilibrium** Conditions
- Does simulated potential jump equal the Donnan Potential?

$$\Delta\phi^D_{sim} = \phi^m - \phi^e \qquad \Delta\phi^D_{sim} \stackrel{?}{=} \Delta\phi^D_{theory} \qquad \Delta\phi^D_{Theory} = \frac{RT}{F}\ln\left(\frac{c^e_{H^+}}{c^m_{H^+}}\right)$$

- **Approach**: Develop a simplified case study & solve for **equilibrium**

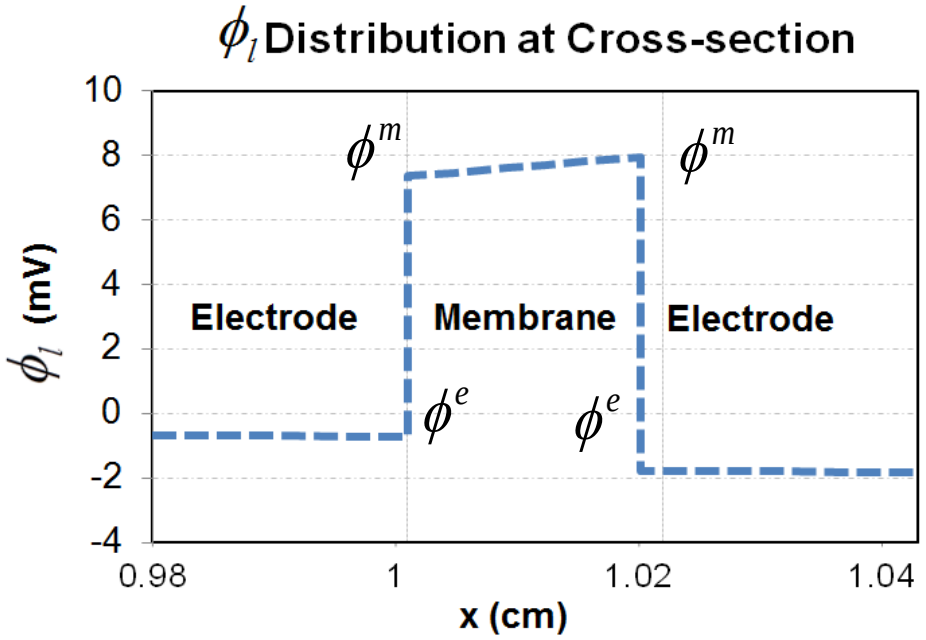


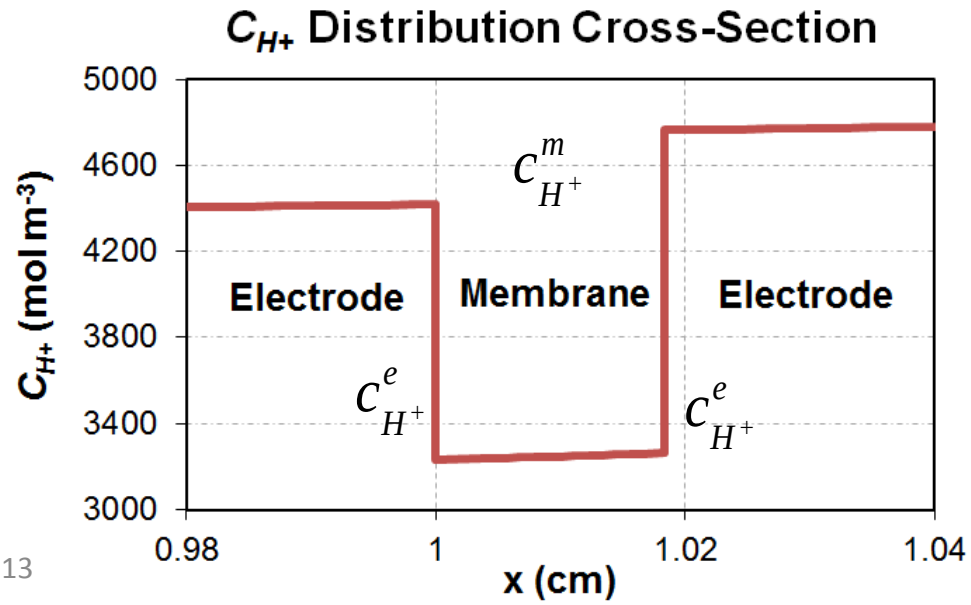
$$\frac{dE_{cell}}{dt} = 0$$ ← **Equilibrium condition in cell**

Simplifications

- Static cell
- Zero current
- Sulfuric acid only

Verification: Interfacial Case Study





Directly from simulated potentials

$$\Delta\phi^D_{sim} \approx \phi^m - \phi^e$$

Error of Comparison

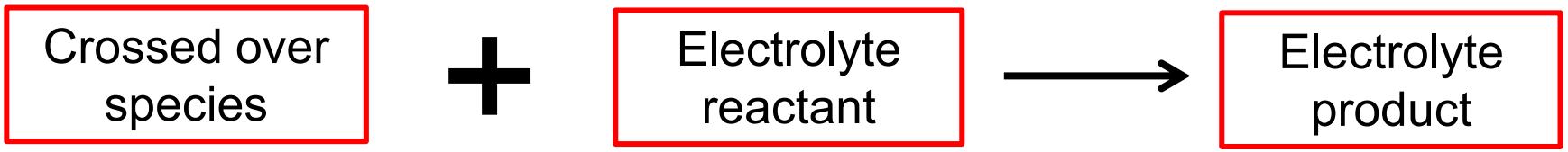
0.35% to 0.61%

$$\Delta\phi^D_{Theory} = \frac{RT}{F}\ln\left(\frac{c^e_{H^+}}{c^m_{H^+}}\right)$$

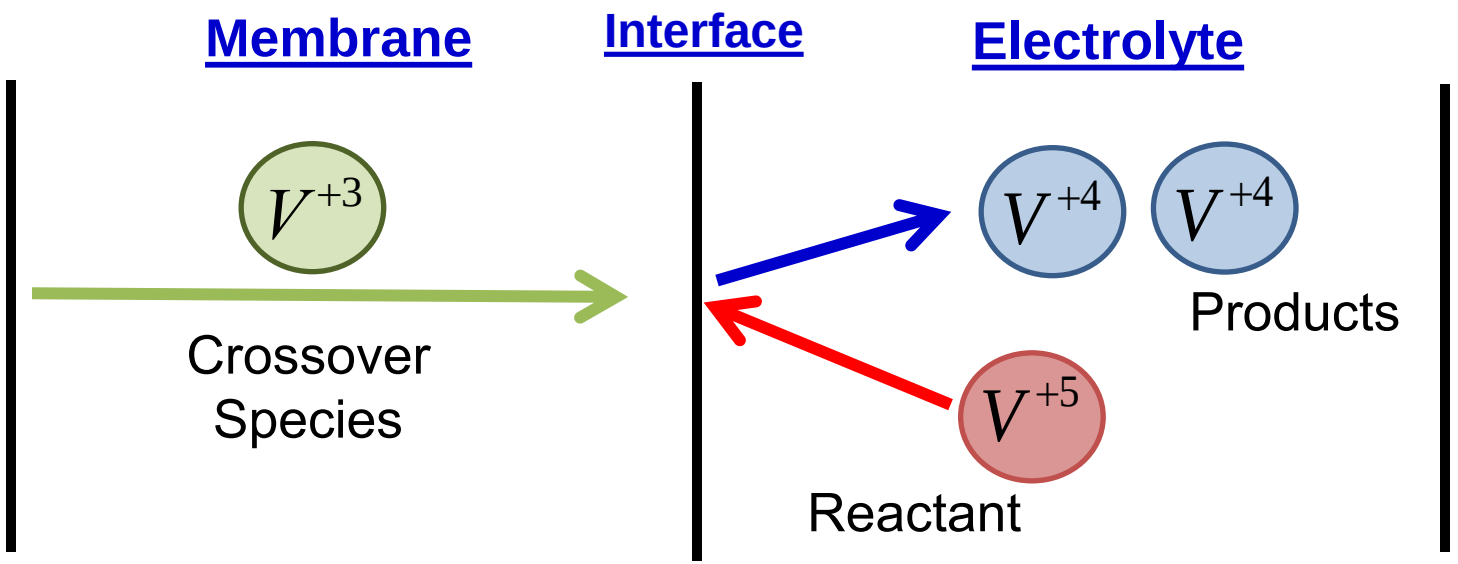
Computed from simulated concentrations

Formulation: Crossover

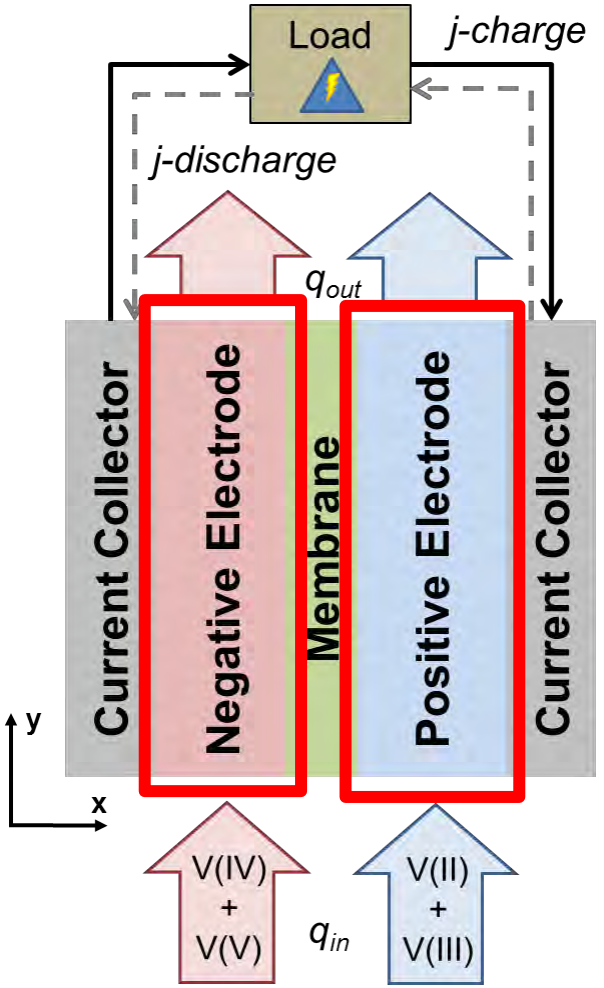
- Instantaneous side reactions in the electrolyte interfacial region



- Vanadium species (V^{+2}, V^{+3}, V^{+4}, V^{+5}) crossing over through the membrane **initiate side reactions**.



Open Circuit Voltage & Electrode Structure



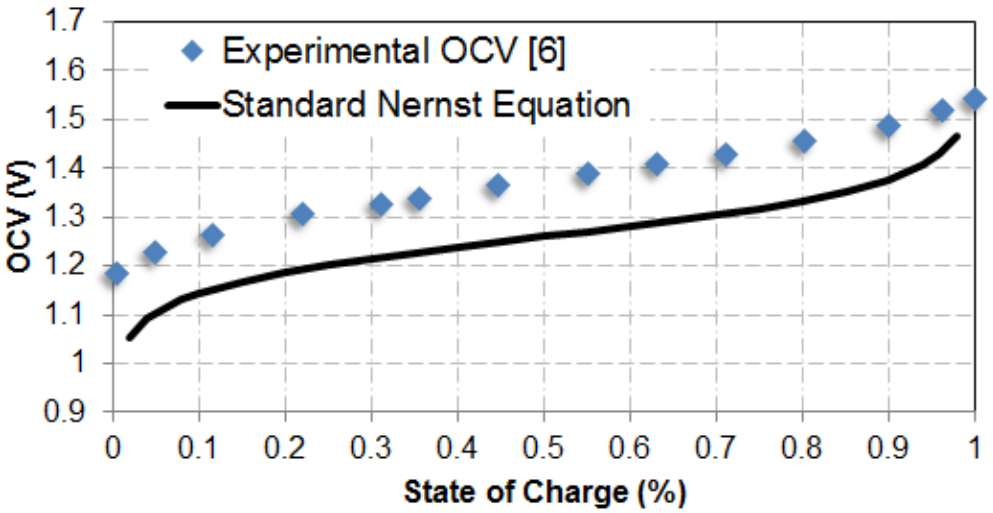
Modeling Domain

Open Circuit Voltage

Common Issue:

– Observed discrepancy between theoretical and experimental voltage

• e.g., **130 to 140 mV** difference between predicted and measured VRB performance



Reason for Deviation:

– Originates from inaccuracy of calculated OCV in models

- Typical implementation of the Nernst equation does not account for all electrochemical phenomena

Standard Nernst Equation:

$$E = E_0 + \frac{RT}{nF} \ln\left(\frac{c_{VO_2^+} \cdot c_{V^{2+}}}{c_{VO^{2+}} \cdot c_{V^{3+}}} \right)$$

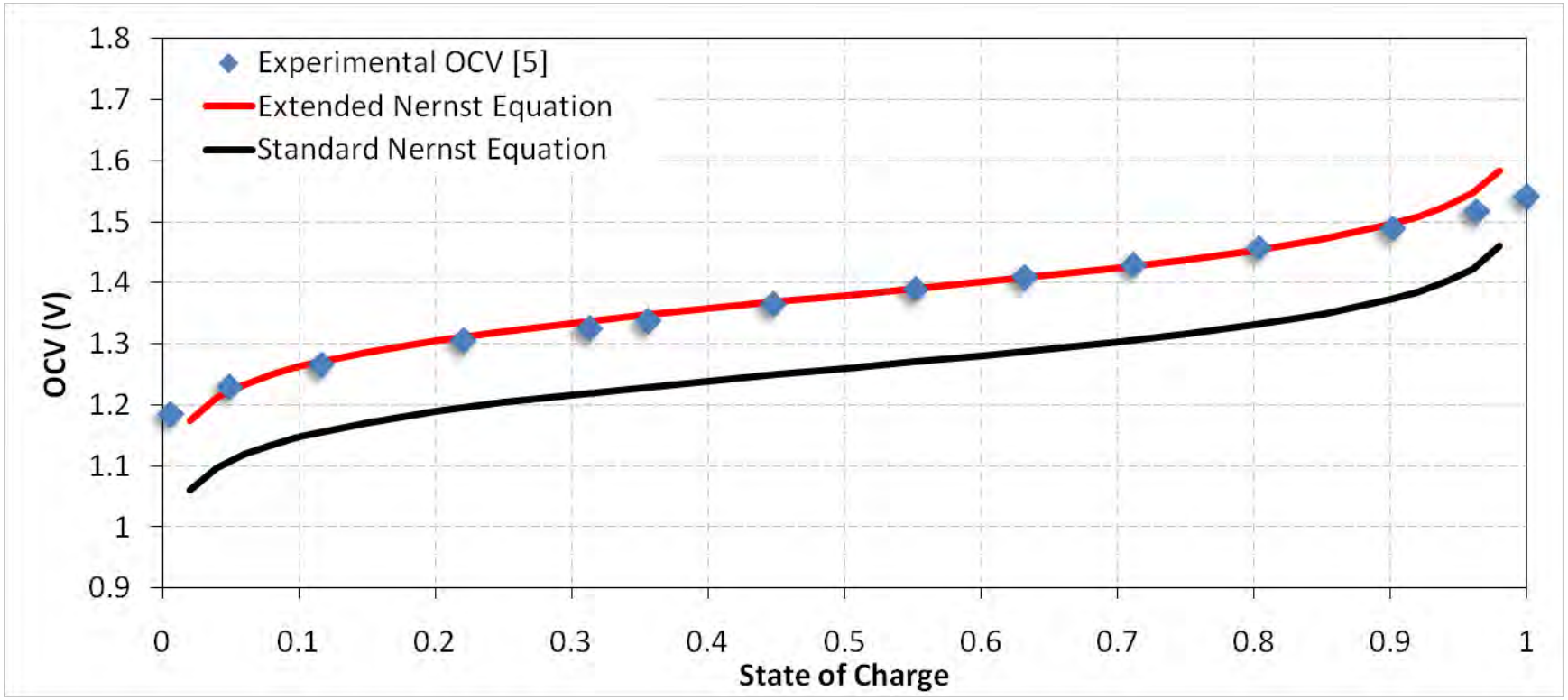
Knehr, K. W. and Kumbur, E. C., Electrochemistry Communications, **13** (2011) 342

Extended Nernst Equation

Donnan Potential

Proton Contribution

$$E = E_0 + \frac{RT}{nF}\ln\left(\frac{c_{VO_2^+}\cdot c_{V^{2+}}}{c_{VO^{2+}}\cdot c_{V^{3+}}}\right) \longrightarrow E = E_0 + \frac{RT}{F}\ln\left(\frac{c_{VO_2^+}\cdot c_{V^{2+}}\cdot c_{H^+}^{+}\cdot \left(c_{H^+}^{+}\right)^2}{c_{VO^{2+}}\cdot c_{V^{3+}}\cdot c_{H^+}^{-}}\right)$$



Initial concentrations: Negative - 2M V^{3+} and 6M H^+

Positive - 2M VO^{2+} and 4M H^+

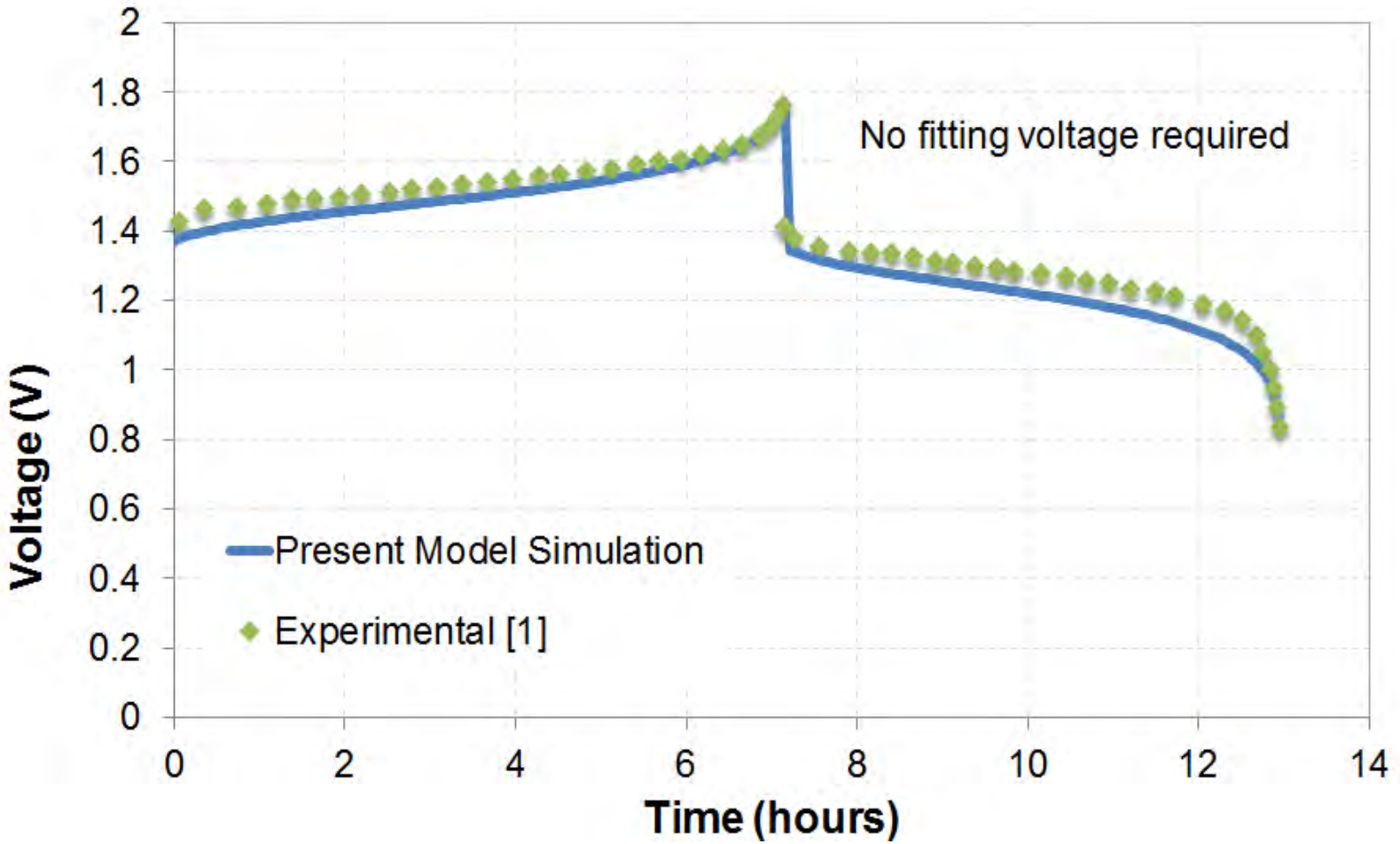
Knehr, K. W. and Kumbur, E. C., Electrochemistry Communications, **13** (2011) 342

Validation

Operating Conditions

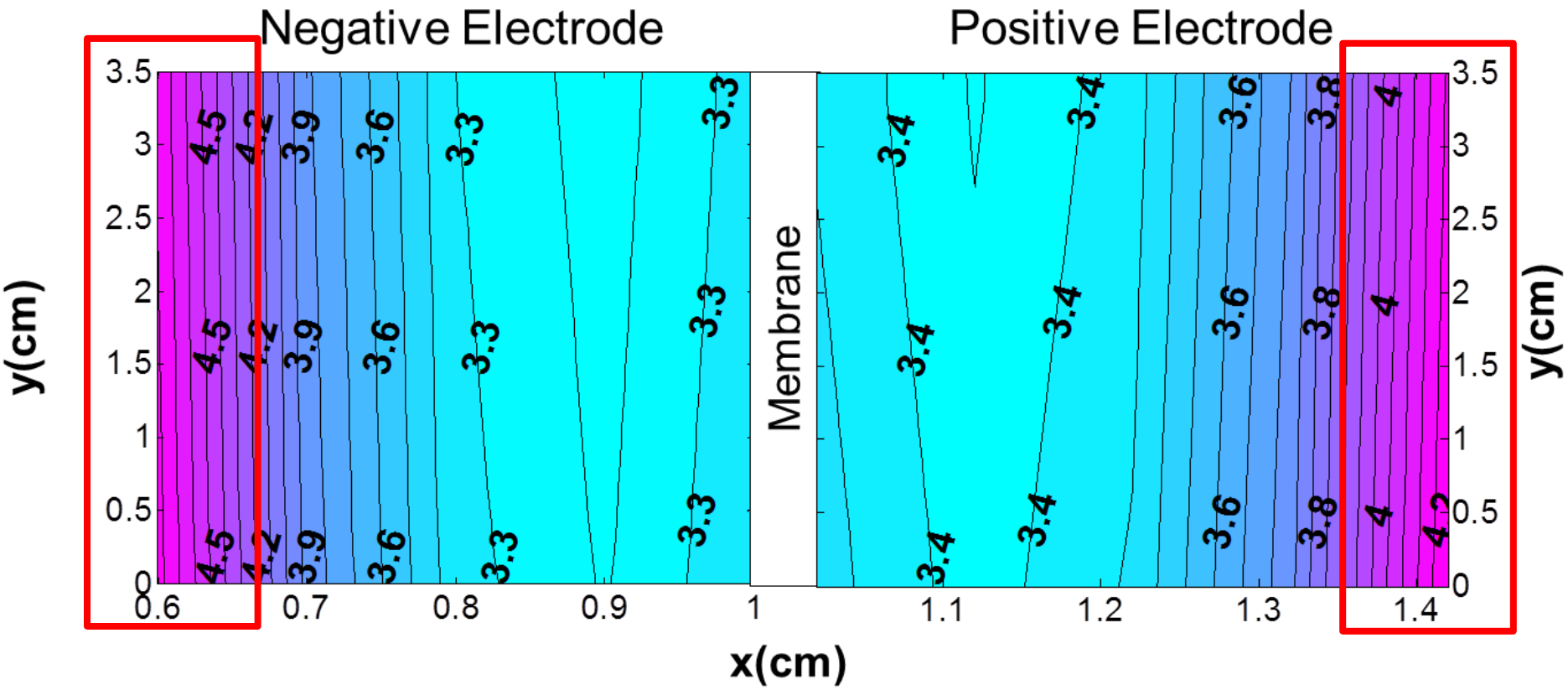
Half-cell volume: 30 mL **Current: 0.4 A**

Vanadium concentration: 1.5 M **Cell size: 5 cm^2**



P. Qian et. Al.., J. Power Sources, **175** (2008) 613

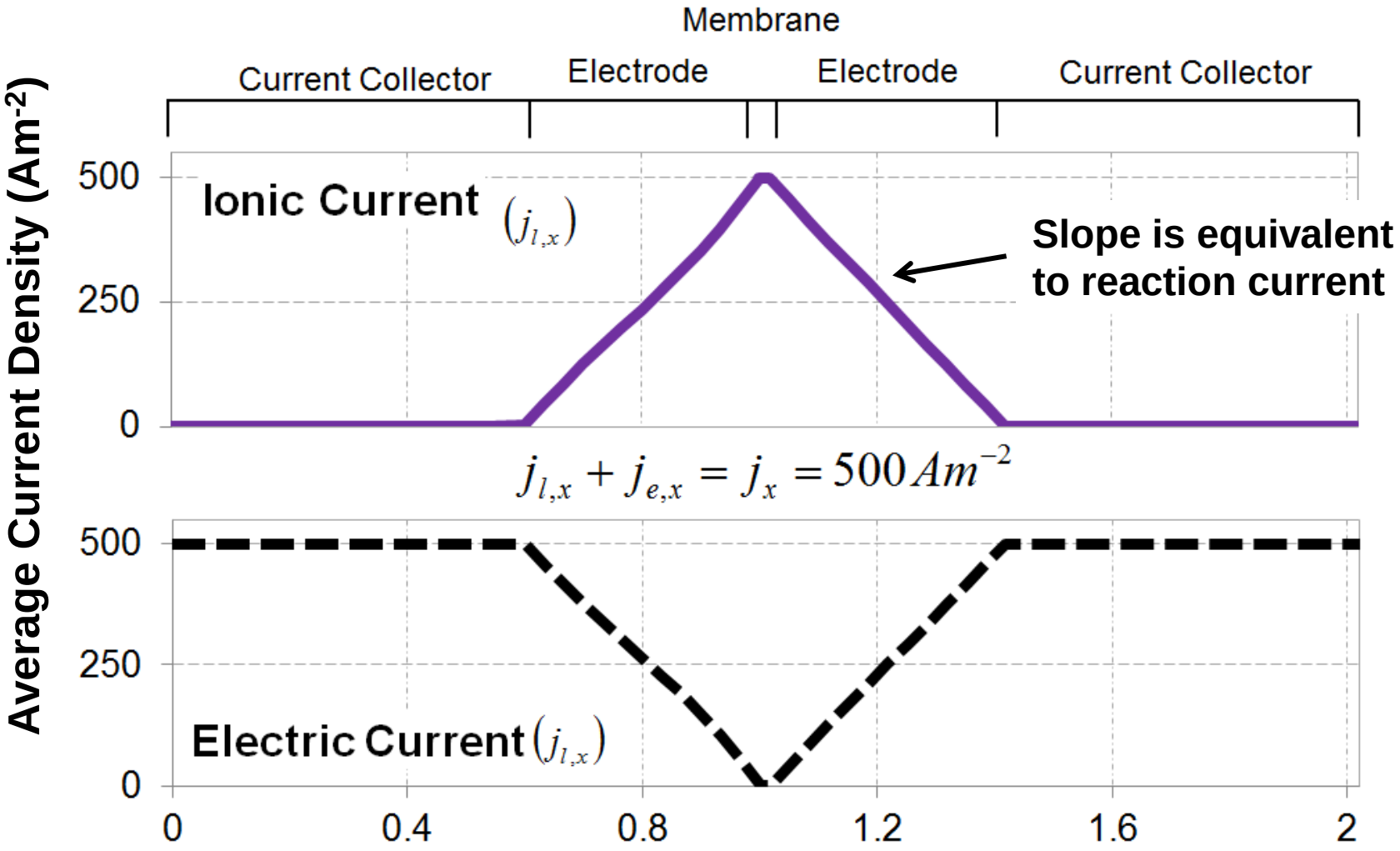
Results: Reaction Current Density



Current (A m^{-2}): Charging at 50% state of charge

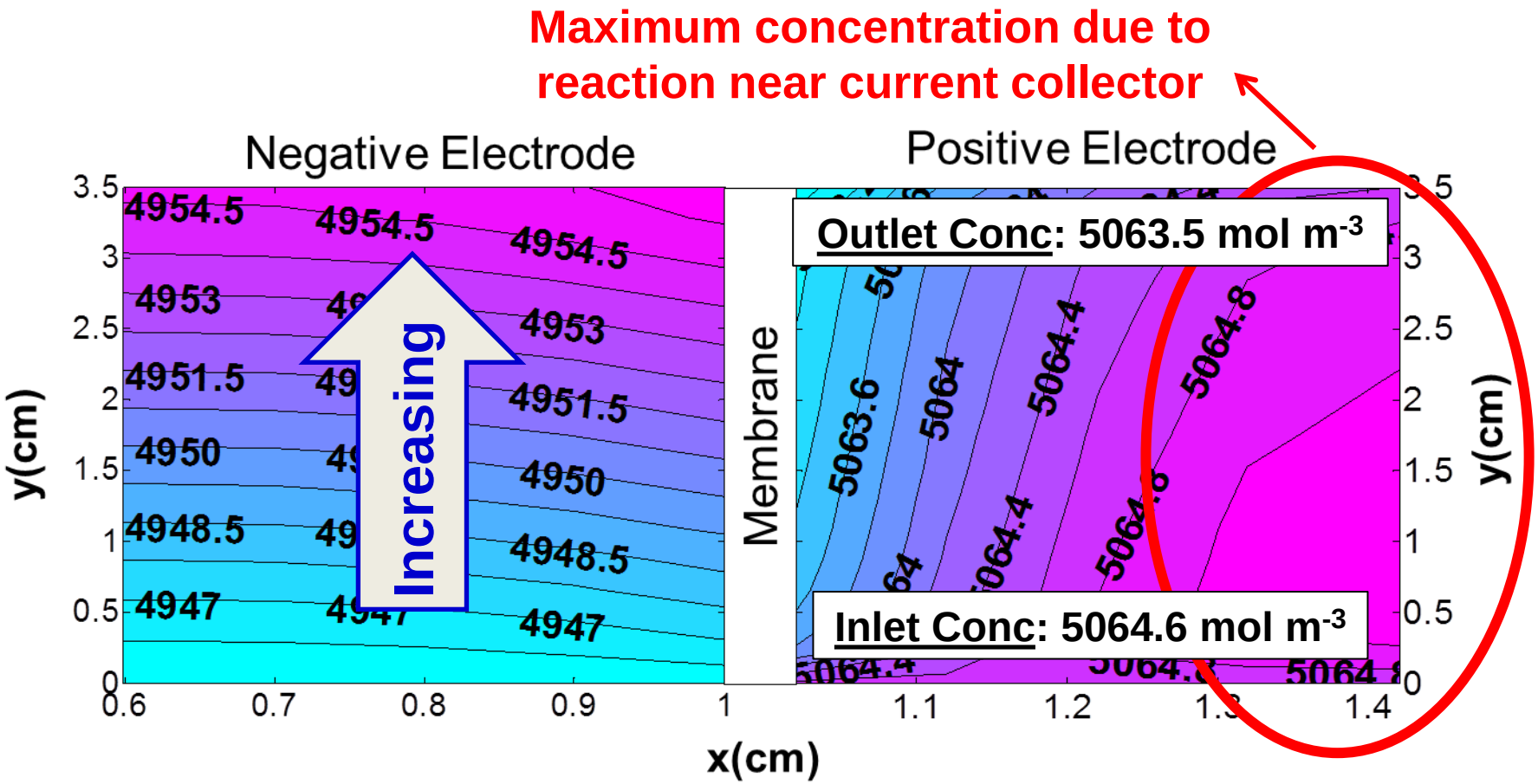
Reaction is concentrated near current collector

Results: Current Density



Able to track variations in current density throughout the cell

Results: Hydrogen Proton Distribution

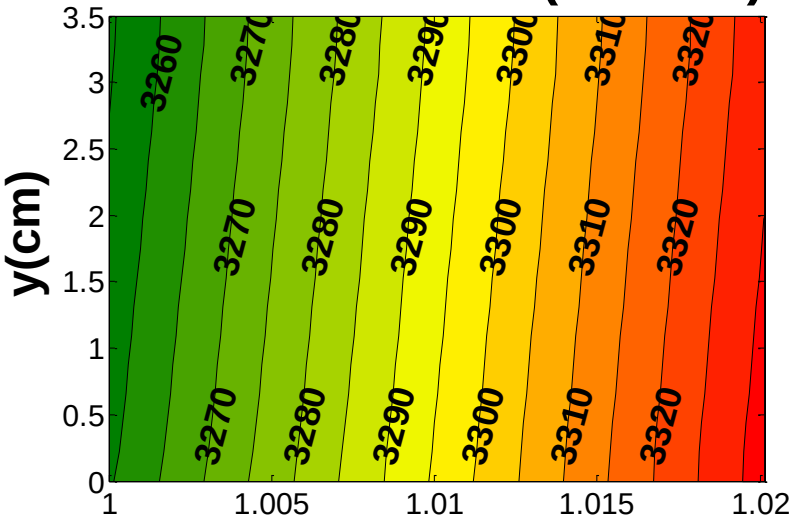


Concentration (mol m^{-3}): Charging at 50% state of charge

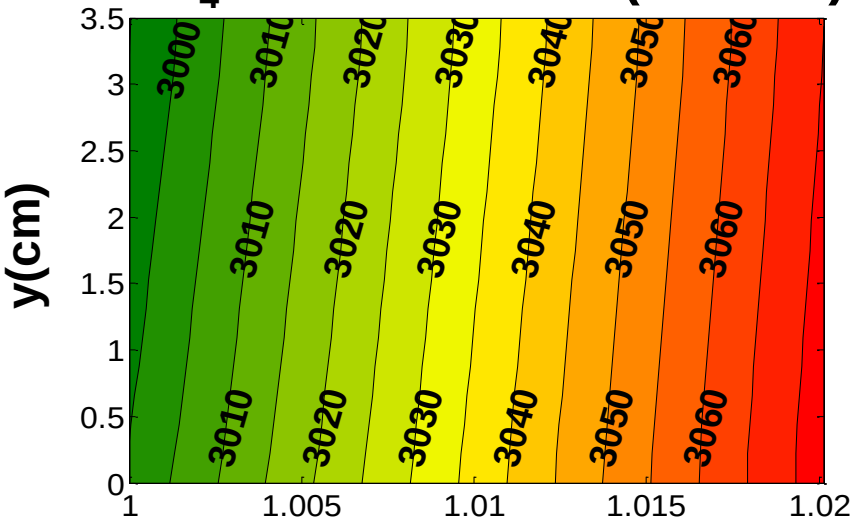
H^+ transport across the membrane is higher than the production in the electrode caused by the reaction

Results: Distributions in Membrane

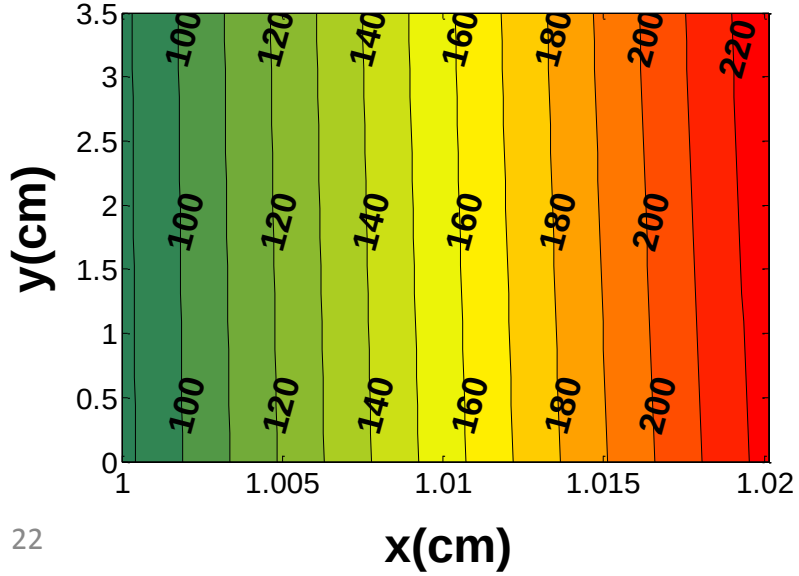
H^+ Concentration (mol m^{-3})



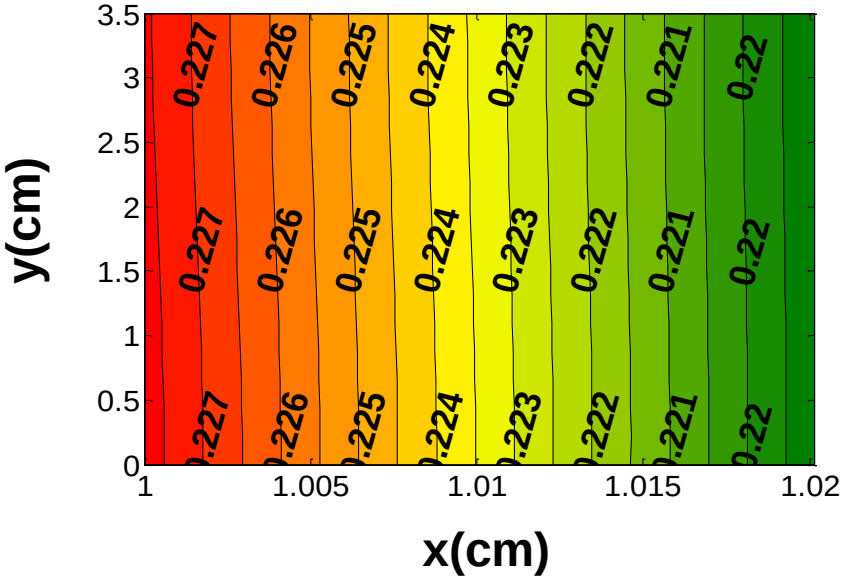
HSO_4^- Concentration (mol m^{-3})



V^{4+} Concentration (mol m^{-3})



Liquid Potential (V)



Results: Membrane Concentration

V^{4+} Flux in membrane (mol m^{-2} s^{-1})

	Net Flux	% convection	% diffusion	% migration
Charging	-8.28 x 10^{-5}	**94.8%**	2.7%	2.5%
Discharging	7.42 x 10^{-5}	**101.1%**	-4.3%	3.2%

H^{+} Flux in membrane (mol m^{-2} s^{-1})

	Net Flux	% convection	% diffusion	% migration
Charging	-6.72 x 10^{-3}	26.0%	8.0%	**66.0%**
Discharging	6.65 x 10^{-3}	25.4%	-5.2%	**79.8%**

10^2 greater than vanadium flux

Migration of protons generates electro-osmotic convection which governs direction of vanadium flux in the membrane

Conclusions

- A new model is developed to account for multi-ionic transport through the membrane
- A framework for the membrane|electrolyte interface was defined to couple the species transport in the membrane with the electrode
- Simulated results agreed well with experimental data without the need for a fitting voltage (via use of extended Nernst equation)
- The model can predict transient performance and spatial distributions of species concentration, potentials, reactions in the membrane and electrode

Ongoing Work

- Extensive experimental validation
- Parametric study of extended charge/discharge cycles
- Performance simulations for multiple membrane materials and electrode microstructures

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