Modeling, simulation and characterization of atomic force microscopy measurements for ionic transport and impedance in PEM fuel cells

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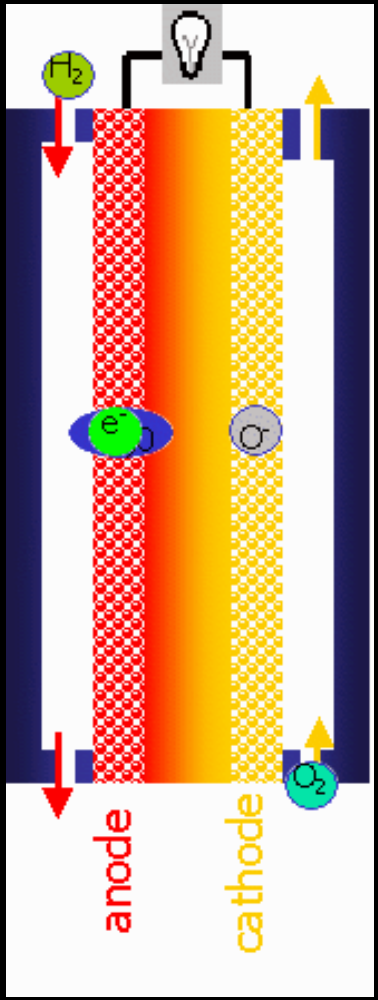
Broad scope of research

- Modeling of ionic transport in proton exchange membrane fuel cells
- Electrostatic atomic force microscope imaging
- Simulation of impedance spectroscopy measurements

Background
fuel cell membranes

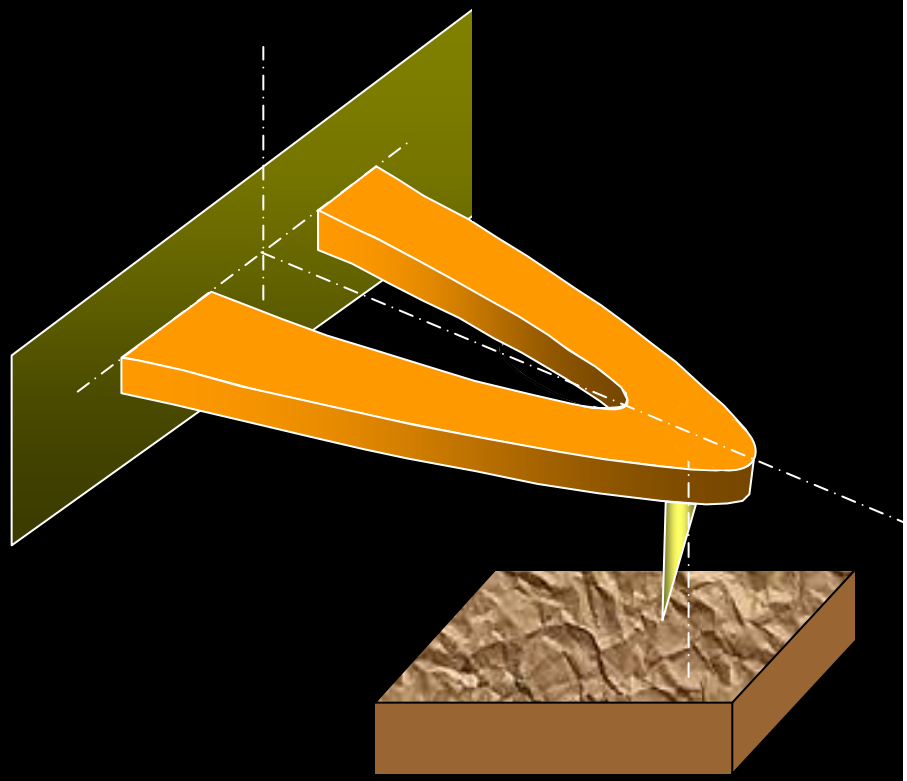
- Local variations in ion concentration in the Nernst diffusion layer at the membrane surface in proton exchange membrane fuel cells (PEMFC) under current load conditions are poorly understood and may significantly influence mass transport across the membrane.

- Increased understanding of the ion behavior at the Nernst diffusion layer of the membrane surface could enable new classes of solid polymer fuel cell membranes with increased mass transport.

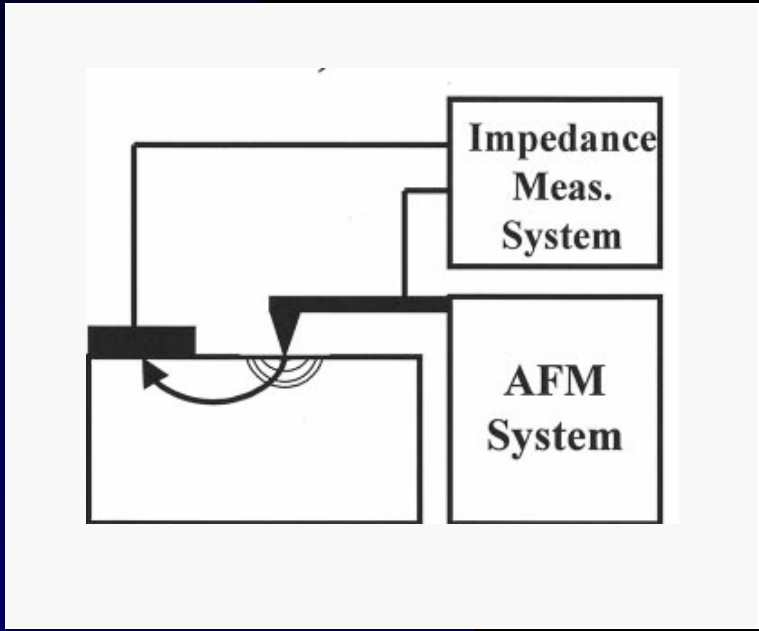


Background
electrostatic force microscopy

- Long-range electrostatic forces between a sample and a noncontact AFM tip is used to extract surface potential or capacitance images
- Since fuel cell membrane charge characteristics may be inhomogeneous, imaging these variations could prove crucial to understanding the functionality of membranes.
- Our research is aimed to provide a better understanding of the relationship between the image obtained and the charge distributions present on the membrane.



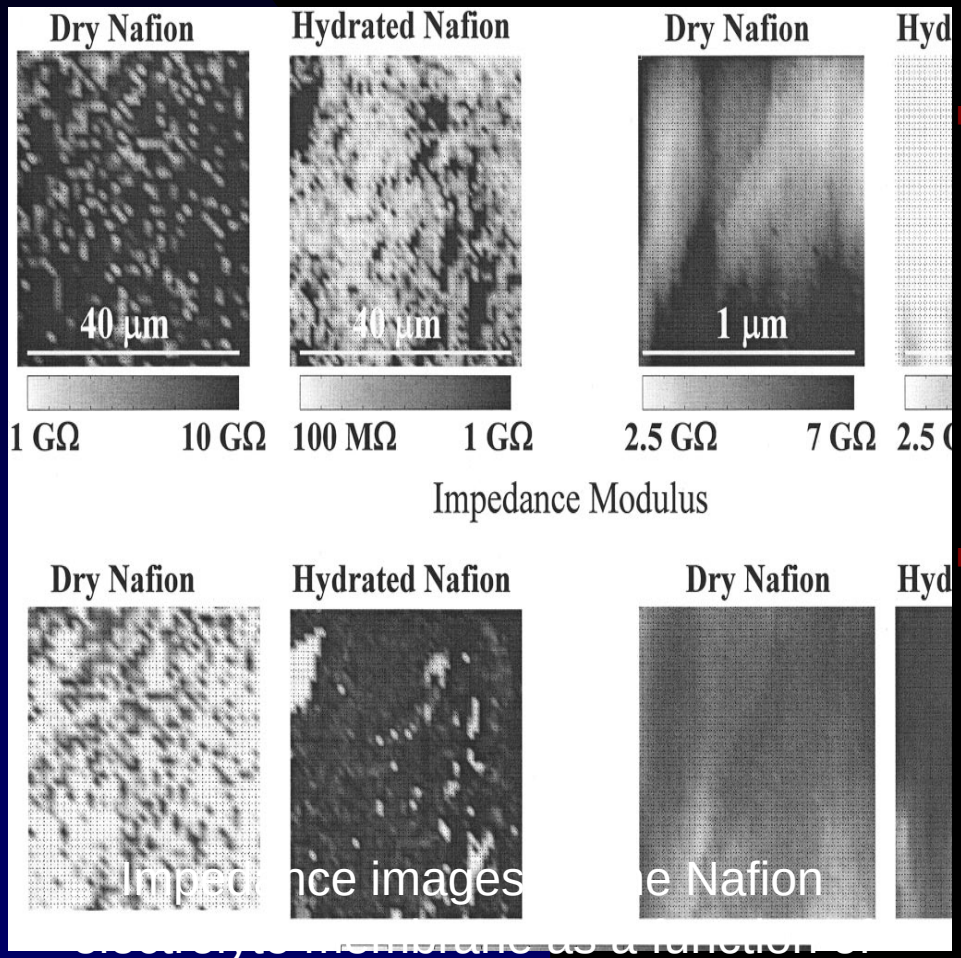
Background
impedance spectroscopy



Impedance measured between AFM tip and bulk electrode – spreading resistance ensures local characterization

- Nanometer scale visualization and measurement of impedance – quantifying the response of a material to an applied varying voltage – is valuable for a wide variety of materials investigations, including fuel cell systems.
- Prinz et al. have introduced an atomic force microscope-based impedance imaging technique with < 100 nm resolution

Background
impedance spectroscopy



Impedance images of the Nafion electrolyte membrane as a function of humidity (O'Hayre et al.)

- Factors contributing to "electrochemical" impedance imaging results for ionic materials are poorly understood.
- Modeling the physical processes involved in the impedance measurement could greatly enhance the usefulness of this technique.

Broad scope of research

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- Electrostatic atomic force microscope imaging
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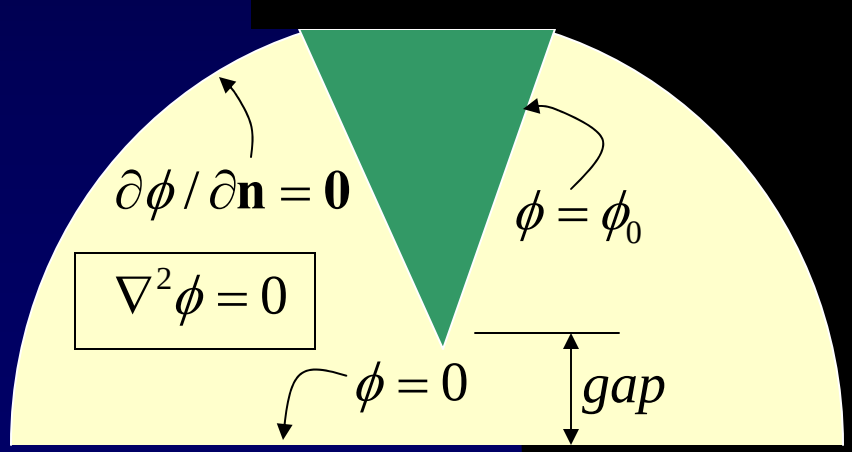
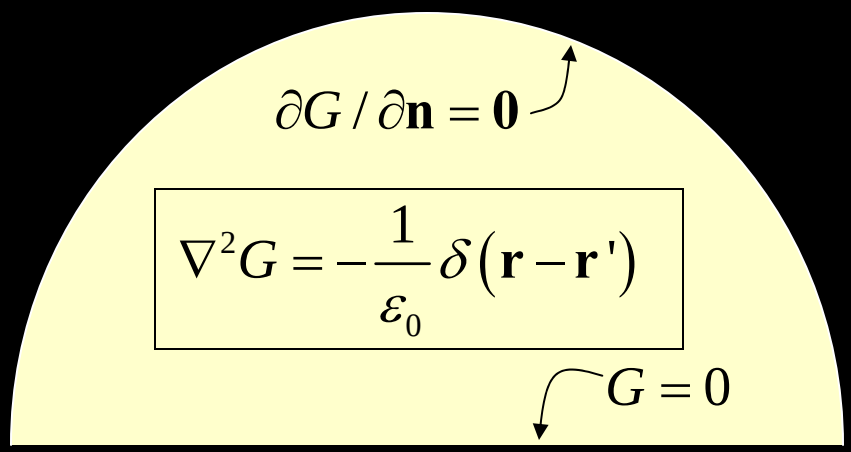
Electrostatic atomic force microscope imaging

- A starting point: consider the electrostatic force acting on a conductive tip above a conductive plane. We are developing:
- A novel analytical (Green's function) approach to determining the electrostatic force by solving for the charge distribution based on realistic tip geometry
- Direct numerical simulation using the finite element method

Electrostatic atomic force microscope imaging

- Given the electrostatic potential distribution on the AFM tip and the sample surface/bulk
- Solve for the electrostatic potential ϕ
- Calculate the charge distribution on the tip, the system capacitance and tip-sample force





Electrostatic atomic force microscope imaging

- Use of Green's theorem gives:

$$\iint_{S_{tip}} G(\mathbf{r},\mathbf{r}')\sigma(\mathbf{r})dS(\mathbf{r}) = \phi_0$$

$$\sigma(\mathbf{r}) = \varepsilon_0 \frac{\partial \phi}{\partial n}(\mathbf{r})$$

$$C = \frac{\iint_{S_{tip}} \sigma(\mathbf{r})dS(\mathbf{r})}{\phi_0}$$

- C Capacitance
- σ Charge density
- ϕ_0 Potential
- G Green's function

Electrostatic atomic force microscope imaging

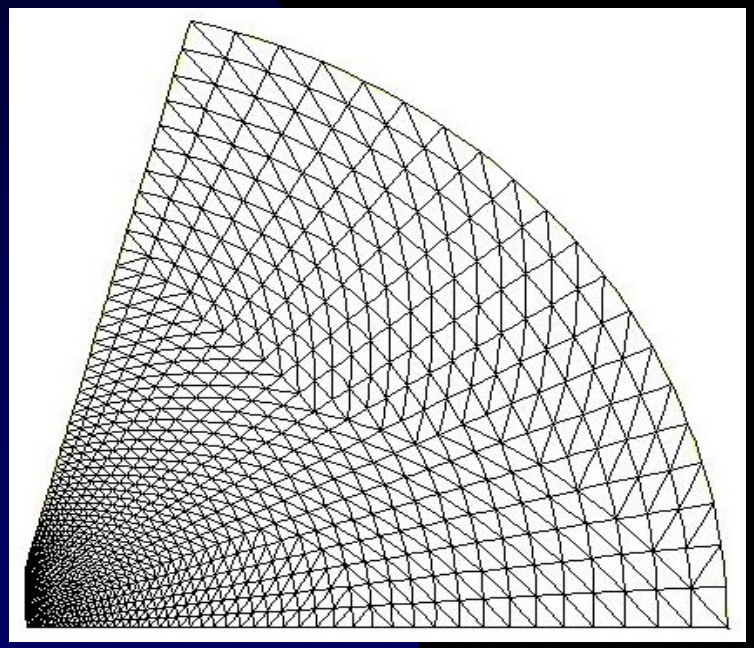
- Semi-analytical solution via scale-independent variational principle:

$$\hat{C} = \frac{\left[\iint_{S_{tip}} \hat{\sigma}(\mathbf{r}')dS(\mathbf{r}') \right]^2}{\iint_{S_{tip}} \iint_{S_{tip}} dS(\mathbf{r})dS(\mathbf{r}')\hat{\sigma}(\mathbf{r}')G(\mathbf{r},\mathbf{r}')\hat{\sigma}(\mathbf{r})}$$

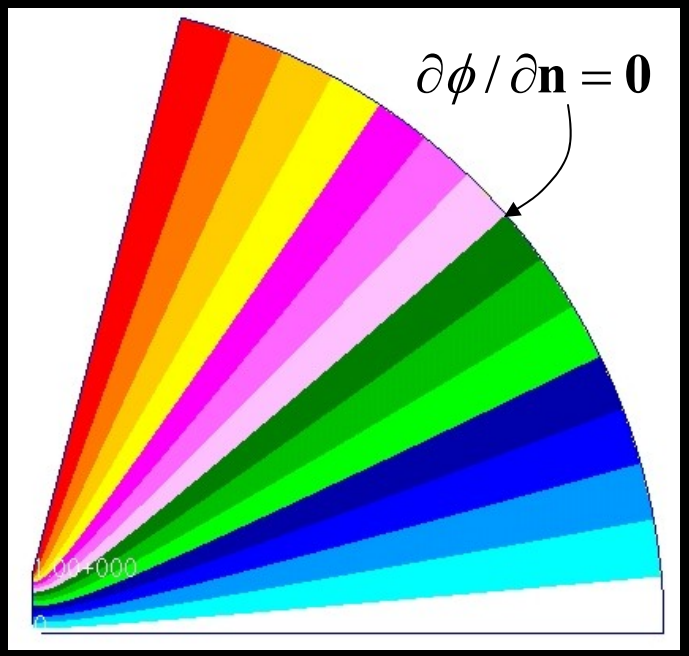
$$\delta\hat{C} = \frac{d}{d\varepsilon}\hat{C}\left(\hat{\sigma} + \varepsilon\delta\hat{\sigma}\right)\Big|_{\varepsilon=0} = 0 \quad \Leftrightarrow \quad \begin{array}{l} \hat{\sigma} = \sigma \\ \hat{C} = C \end{array}$$

Electrostatic atomic force microscope imaging

- Finite element results for potential
- Need Dirichlet-to-Neumann radiation condition



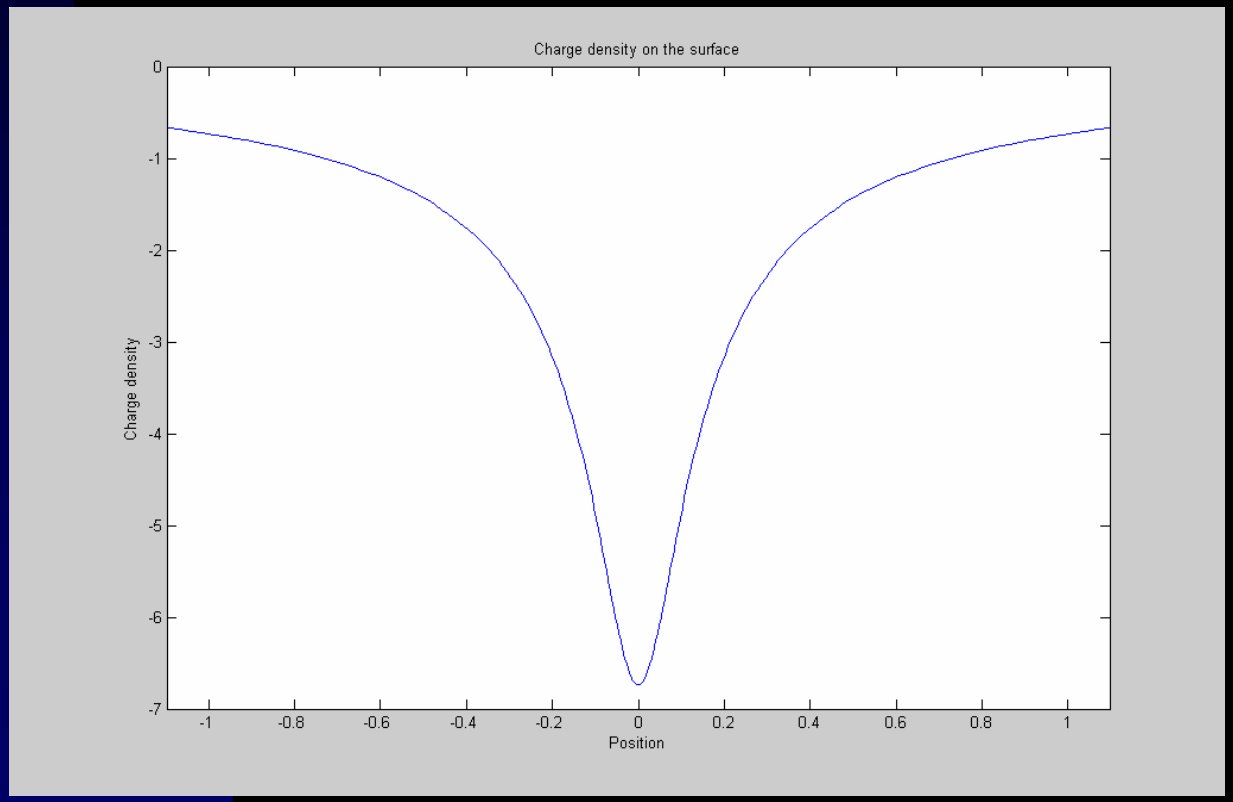
Mesh



Potential field

Electrostatic atomic force microscope imaging

- Finite element results for charge density on tip surface



Electrostatic atomic force microscope imaging

- Computation of capacitive force
- Based on the Maxwell stress tensor

$$F_j = \varepsilon_0 \int_S \left[\frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} - \frac{1}{2} \delta_{ij} \frac{\partial \phi}{\partial x_k} \frac{\partial \phi}{\partial x_k} \right] n_i \, dS$$

Broad scope of research

- Modeling of ionic transport in proton exchange membrane fuel cells
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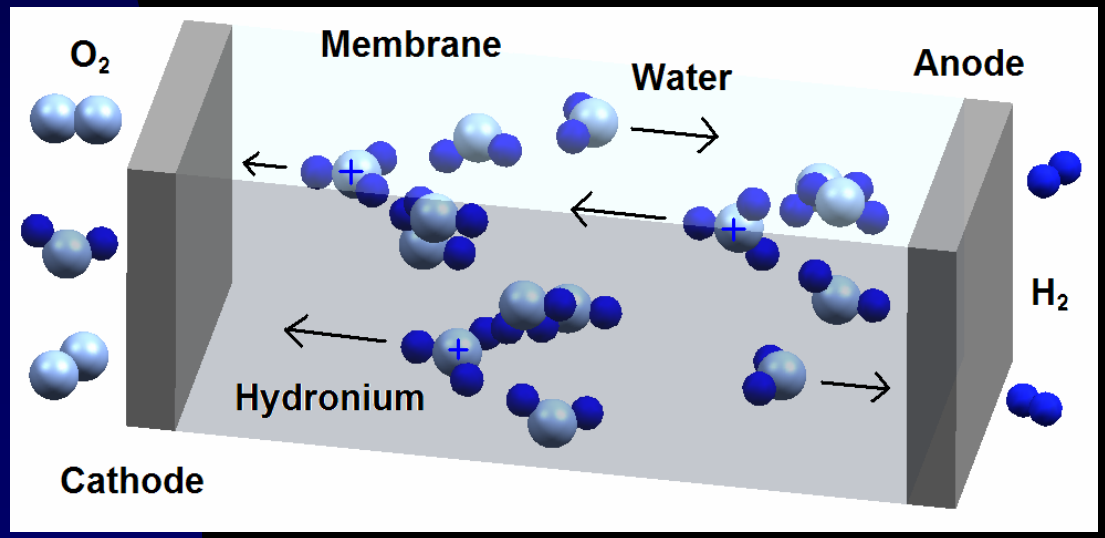
Modeling ionic transport in fuel cell membranes

- Ionic mass transfer in ion-selective membranes is not fully understood
- Local concentration changes in the Nernst diffusion layer influences mass transfer behavior of membrane
- Transient and steady state transport modeling are needed



Modeling ionic transport in fuel cell membranes

- Mathematical model

Mass balance with Nernst-Planck model (drift-diffusion)

$$\frac{\partial c}{\partial t} = -\nabla \cdot \left(-D\nabla c - c\frac{Dq}{kT}\mathbf{E} \right)$$

Charge conservation

$$-\nabla \phi = \mathbf{E}, \qquad \nabla \cdot \mathbf{E} = \left(c - c_0 \right) \frac{q}{\varepsilon_0 \varepsilon_r}$$

No-flux boundary condition

$$\mathbf{J} = -D\nabla c - c\frac{Dq}{kT}\mathbf{E} = 0$$

Modeling ionic transport in fuel cell membranes

- 1-d non-dimensional c-E steady-state PEMFC model
- Finite difference (Jeremy Cheng and David Barnett)

Drift-diffusion

$$\left(\frac{c_{j-1}-2c_j+c_{j+1}}{\Delta x^2}\right)-\lambda\left[E_j\left(\frac{c_{j+1}-c_{j-1}}{2\Delta x}\right)+c_j\left(\frac{E_{j+1}-E_{j-1}}{2\Delta x}\right)\right]=0$$

Poisson's equation

$$E_{j+1}-E_{j-1}=\beta\sum_i^j\left(c_i-c_{i-1}-2\right)\left(\frac{\Delta x}{2}\right)$$

Non-dimensional parameters

$$\beta=\frac{Lc_0q^*}{E_0\varepsilon_0\varepsilon_r}\approx 4.2e7,\qquad \lambda=\frac{q^*E_0L}{kT}\approx 3$$

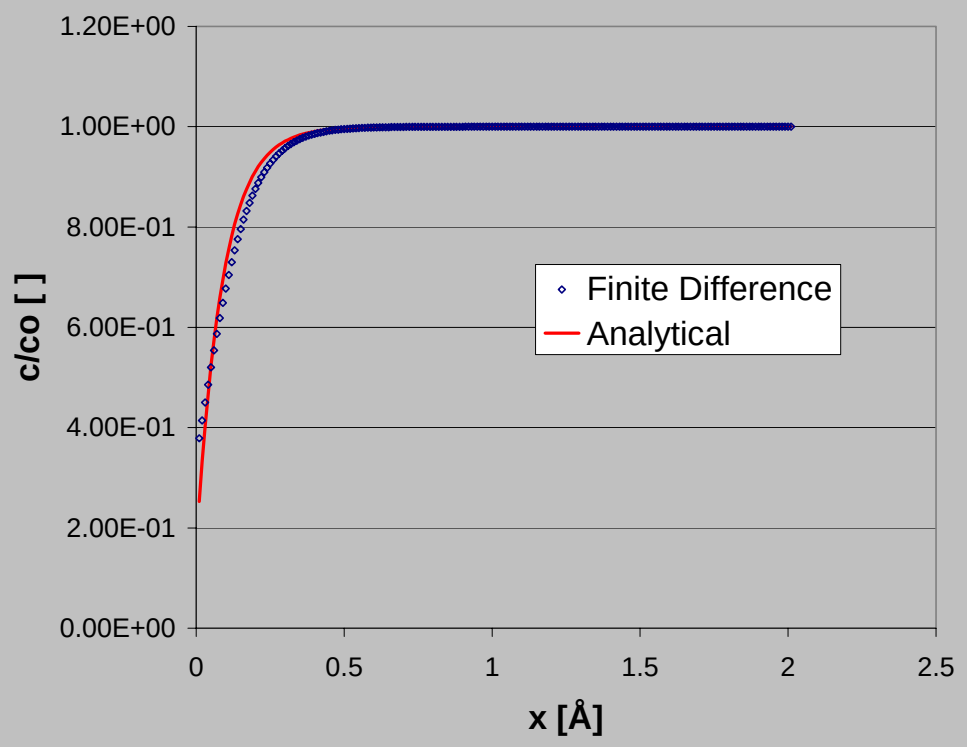
Modeling ionic transport in fuel cell membranes

- Detecting the Nernst boundary layer in 100 nm membrane

$$\vec{j} = -D\nabla c + \frac{Dqc\vec{E}}{kT} = 0$$

$$\nabla \cdot \vec{E} = \frac{(c - c_0)q}{\varepsilon_0 \varepsilon_r}$$

$$c = c_0 \varepsilon_0 \lambda \frac{\sinh q(\frac{1}{2} - \frac{x}{l})}{\sinh q}$$



Modeling ionic transport in fuel cell membranes

- Variational c-ϕ coupled form of BVP

$$0 = \int_\Omega w c,_t \, d\Omega + \int_\Omega w,_i \, D c,_i \, d\Omega + \int_\Omega w,_i \frac{Dq}{kT} c \phi,_i \, d\Omega$$

$$0 = -\int_\Omega v,_i \, \phi,_i \, d\Omega + \int_\Omega v \frac{q}{\varepsilon} c d\Omega - \int_\Omega v c' d\Omega + \int_{\Gamma_h} v \phi,_n \, d\Omega$$

- Finite element approximation

$$\begin{bmatrix} \mathbf{M}_1 & 0 \\ 0 & 0 \end{bmatrix} \frac{d}{dt} \begin{Bmatrix} \mathbf{c} \\ \boldsymbol{\varphi} \end{Bmatrix} + \begin{bmatrix} \mathbf{K}_1 & \mathbf{K}_2(c) \\ \mathbf{K}_3 & \frac{q}{\varepsilon} \mathbf{M}_3 \end{bmatrix} \begin{Bmatrix} \mathbf{c} \\ \boldsymbol{\varphi} \end{Bmatrix} = \begin{Bmatrix} \mathbf{0} \\ \mathbf{F} \end{Bmatrix}$$

Next steps

- Atomic force microscope imaging
  - Surface and/or bulk trapped charge distributions
  - Compute capacitive forces
  - Extend to 3-d
  - Application to experiments
- Modeling ionic transport in fuel cell membranes
  - Consider boundary layer effects in time-varying electric fields
  - Extend to 2-d and 3-d models (finite element approach)
  - Fully nonlinear coupled problem