

**POSITIONING THE REFERENCE ELECTRODE IN
POLYMER ELECTROLYTE MEMBRANE FUEL
CELLS (PEMFC) UNDER PRIMARY AND
SECONDARY CURRENT DISTRIBUTION
——SIMULATION WITH CFD-ACE+**

Zhenyu Liu, Jesse Wainright, Robert Savinell
E. B. Yeager Center for Electrochemical Sciences
Department of Chemical Engineering
Case Western Reserve University, Cleveland OH, 44106

OBJECT OF RESEARCH

- **Understand the influence of the cell geometry on the electrode polarization and current distribution.**
- **Examine the proper position of the reference electrode for the Polymer Electrolyte Membrane (PEM) fuel cell or other solid electrolyte electrochemical systems under primary and secondary current distribution.**
- **Solve the typical electrochemical reaction boundary condition, the Butler -Volmer equation, by commercial code: CFD-ACE+.**
- **Give suggestion on the electrodes and/or system design and measurement of the PEM fuel cell.**

FUEL CELL OVERVIEW

- Electrochemical energy converters
 - reactants stored externally, supplied as needed
 - Electrodes act as catalysts for reactions
- chemical energy \Rightarrow electricity
 fuel \Rightarrow hydrogen air \Rightarrow oxygen
 refuel, not recharge

Anode - Fuel Electrode - negative



Cathode - Air Electrode - positive



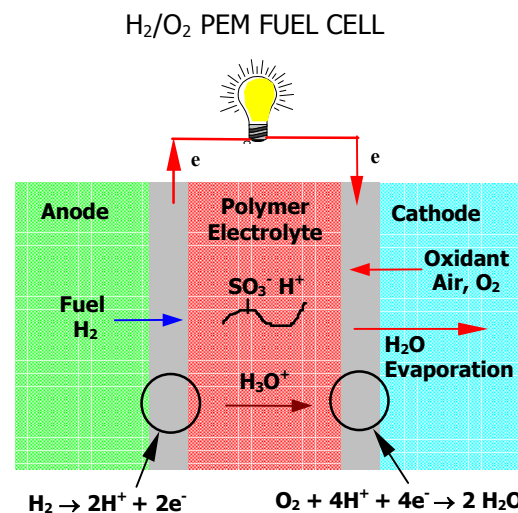
Polymer Electrolyte Membrane (PEM)

H⁺ conductor

separate reactants, electrodes

Current Collector

fine porosity for reactant distribution



Open Circuit Voltage \Rightarrow Thermodynamics (1.2V / cell)

Voltage under load \Rightarrow OCV - IR - reaction overpotentials - transport losses
current proportional to electrode area, voltage proportional to number of cells

WHAT IS A REFERENCE ELECTRODE?

- . **An electrode through which no current flows.**
- . **Provides a stable voltage reference.**
- . **Measurement of the cathode potential with respect to the reference allows the voltage losses at the cathode to be determined separately from the anode losses.**

HOW TO POSITION THE REFERENCE ELECTRODE IN A PEM FUEL CELL?

- The reference electrode can not be positioned between the electrodes.
- Membrane is very thin, typically between 25-175 micron. Therefore, tiny differences in the alignment of the two electrodes will significantly affect the polarization on both anode and cathode.
- The electrode misalignment is hard to eliminate in fabrication.
- The above difficulty can be solved by a proper design of the electrode geometry and a proper position for the reference electrode.

CURRENT DISTRIBUTION AND THE WAGNER NUMBER

The Primary current distribution: Only the IR (current x resistance) of the electrolyte is considered. The reaction overpotential (also called surface or activation overpotential) and the concentration overpotential are neglected.

The Secondary current distribution: Both the IR of the electrolyte and the reaction overpotential are considered, the concentration overpotential is neglected.

The Wagner number (Wa): a non-dimensional number, which is the ratio of kinetic resistance to the ohmic resistance.

The expression of Wa:

$$W_a = \frac{RT\kappa}{nFli_0} \quad \text{For small reaction overpotential (<25mV)}$$

$$W_a = \frac{RT\kappa}{nFli_{avg}} \quad \text{For large reaction overpotential (>120 mV)}$$

GOVERNING EQUATION

The current in the membrane is due to the motion of the protons:

$$N_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i + v c_i$$

$$i = F \sum_i z_i N_i$$

The proton is uniformly distributed within the membrane, and there is no convection, therefore:

$$i = -\kappa \nabla \Phi \quad \text{Ohm's law}$$

where $\kappa = F^2 \sum_i z_i^2 u_i c_i$ the conductivity

The material balance within the membrane reduces to the Laplace equation at steady state:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \Rightarrow \nabla^2 \Phi = 0$$

BOUNDARY CONDITIONS

To simplify the simulation, the potential of the anode at OCV is set to 0V. That is: $\Phi = 0$, where Φ is the potential at the electrode surface.

The electrochemical reaction at the cathode-membrane interface is another Boundary condition. For the Primary current distribution, there is no overpotential, so the Boundary condition at the cathode is:

$$\Phi = V_{output} \quad V_{output} \text{ is the output potential (user input)}$$

The Butler-Volmer Equation describes the boundary condition for the secondary current distribution:

$$i = -\kappa \left(\frac{\partial \Phi}{\partial n} \right)_B = i_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta \right) - \exp\left(\frac{\alpha_c F}{RT} \eta \right) \right]$$

$$\eta = OCV - IR - V_{output}$$

i_0 : the exchange current density

OCV, i_0 : user input

SIMPLIFY THE SECONDARY CURRENT DISTRIBUTION BOUNDARY CONDITION

At small overpotential (overpotential < 25mV) or large overpotential (overpotential > 120mV), the Butler-Volmer Equation can be reduced to the linear or Tafel approximation respectively, and obtain:

$$\Phi = V - \frac{RT\kappa}{nFli_0} \cdot \left(\frac{\partial\Phi}{\partial N}\right)_B \quad \text{For linear approximation}$$

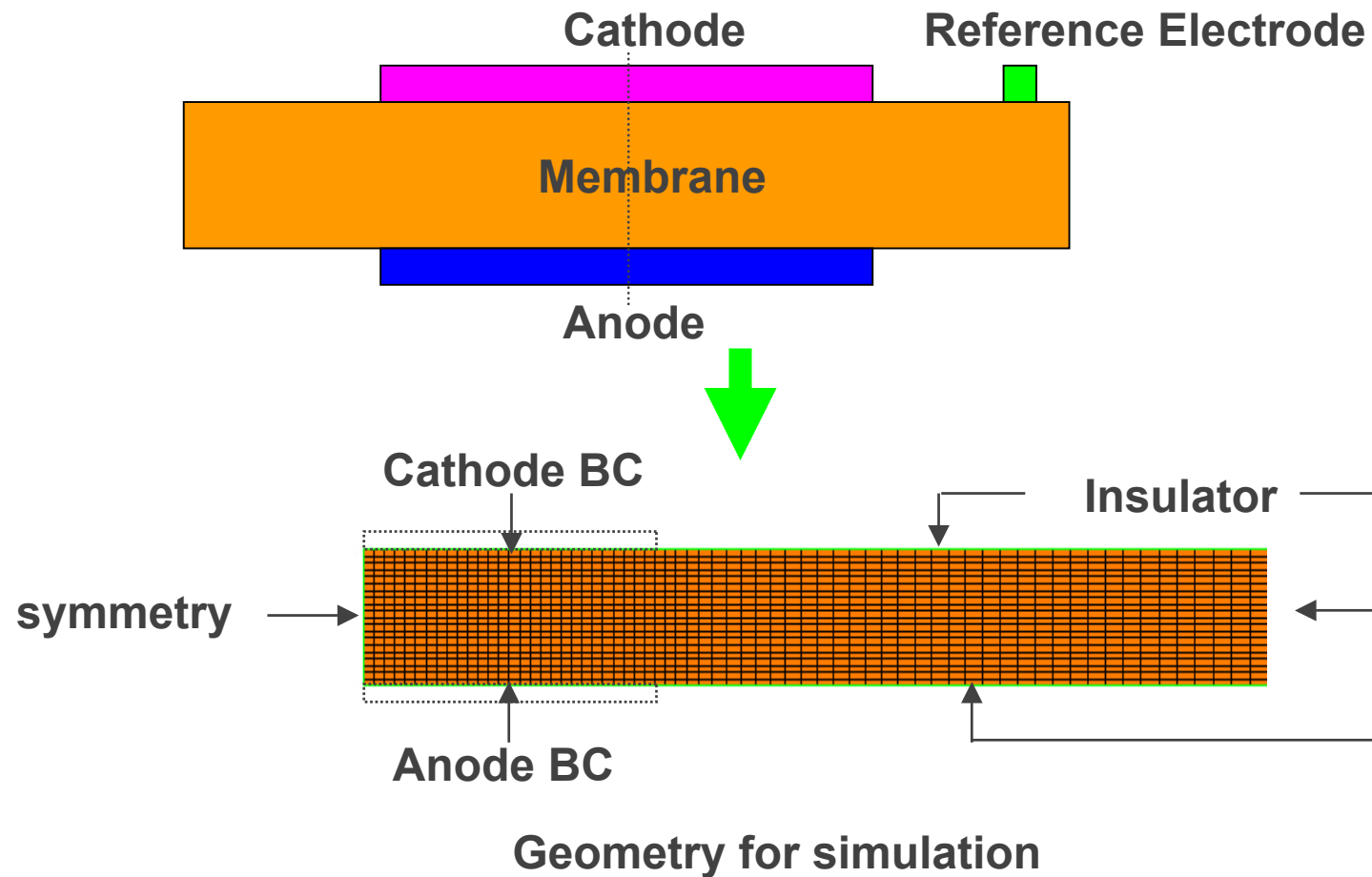
$$\Phi = V - \eta_0 - \frac{RT}{nFi_{avg}} \frac{\kappa}{l} \frac{d\Phi}{dN} \quad \text{For Tafel approximation}$$

The corresponding Wagner number is:

$$Wa = \frac{RT\kappa}{nFli_0} \quad \text{For small reaction overpotential (<25mV)}$$

$$Wa = \frac{RT\kappa}{nFli_{avg}} \quad \text{For large reaction overpotential (>120 mV)}$$

GEOMETRY



CFD-ACE SOLVER AND BOUNDARY CONDITIONS

Use the user scalar module to solve the problem:

Reduce the general transport equation:

$$\frac{\partial \rho \phi}{\partial t} + \nabla \cdot (\rho \vec{V} \phi) = \nabla \cdot (D \nabla \phi) + S_{\phi}$$

to the Laplace equation.

General Boundary Condition Equation:

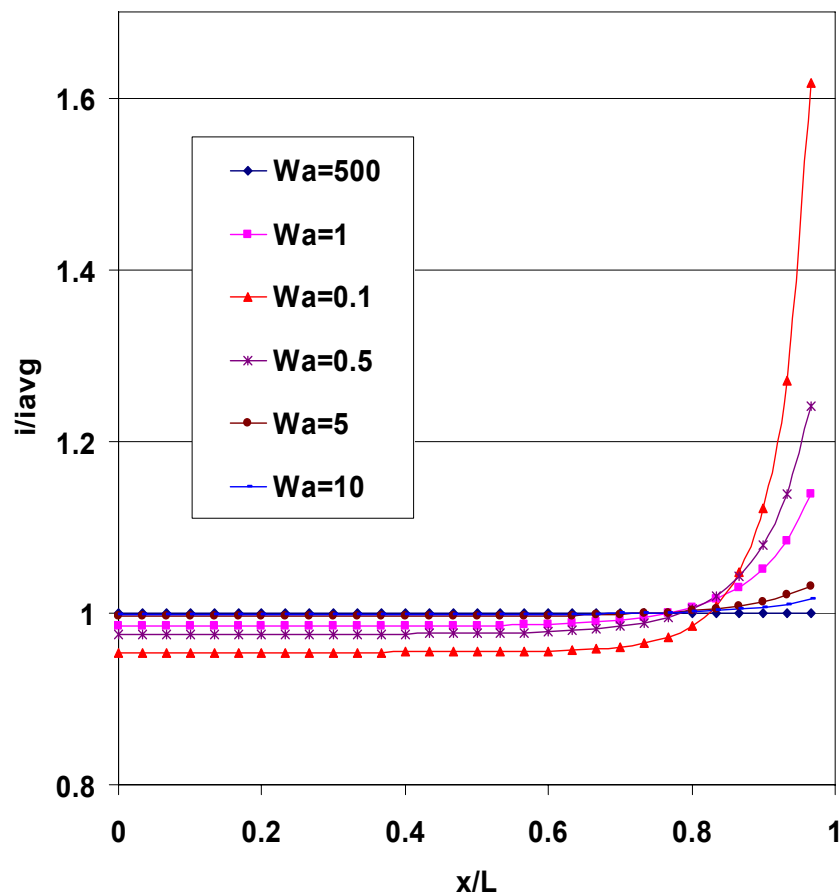
$$a \left(\frac{d\phi}{dn} \right)_B + b \phi = c$$

For the primary current distribution and the linear or Tafel approximation of secondary current distribution, the above general boundary condition can be directly applied.

The other way to solve the secondary current distribution boundary condition is by writing a user subroutine for the Butler-Volmer equation, which is a flux type boundary condition.

SECONDARY CURRENT DISTRIBUTION AT PLANAR ELECTRODE

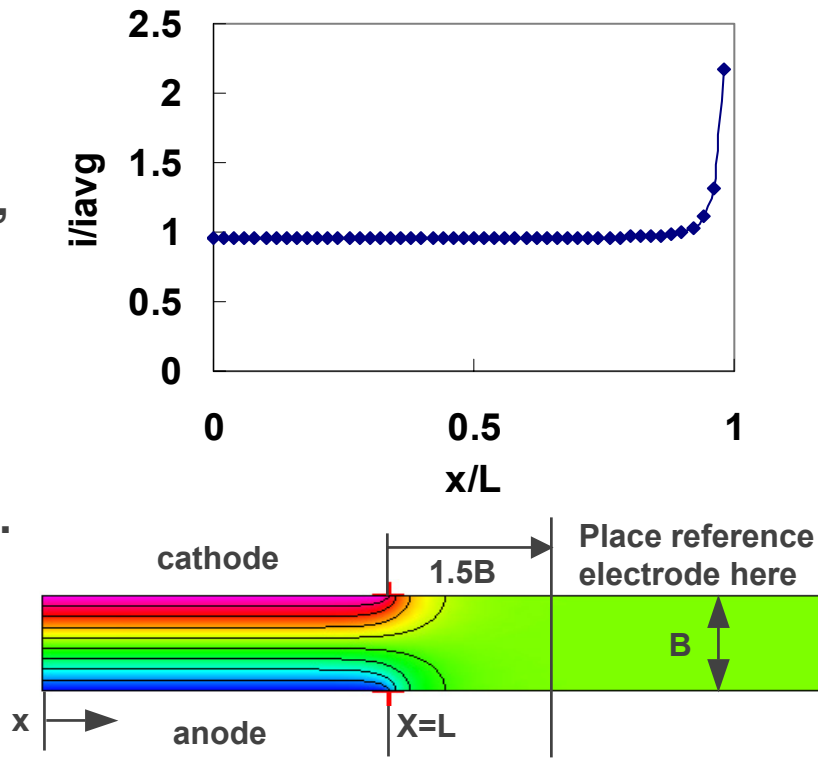
Simulation results show the effect of the kinetic resistance and the ohmic resistance on the current distribution along the electrode. Large kinetic resistance tends to make the current distribution uniform as shown by the plot for large Wagner numbers.



PRIMARY CURRENT DISTRIBUTION

Case: Identical and perfectly aligned electrodes

For the primary potential and current distribution, with identical and aligned electrodes, the reference electrode should be placed 1.5 times gap away from the edge of the electrode; the potential measured is midway between the two electrodes. (Reference electrode can be placed on either side of membrane)



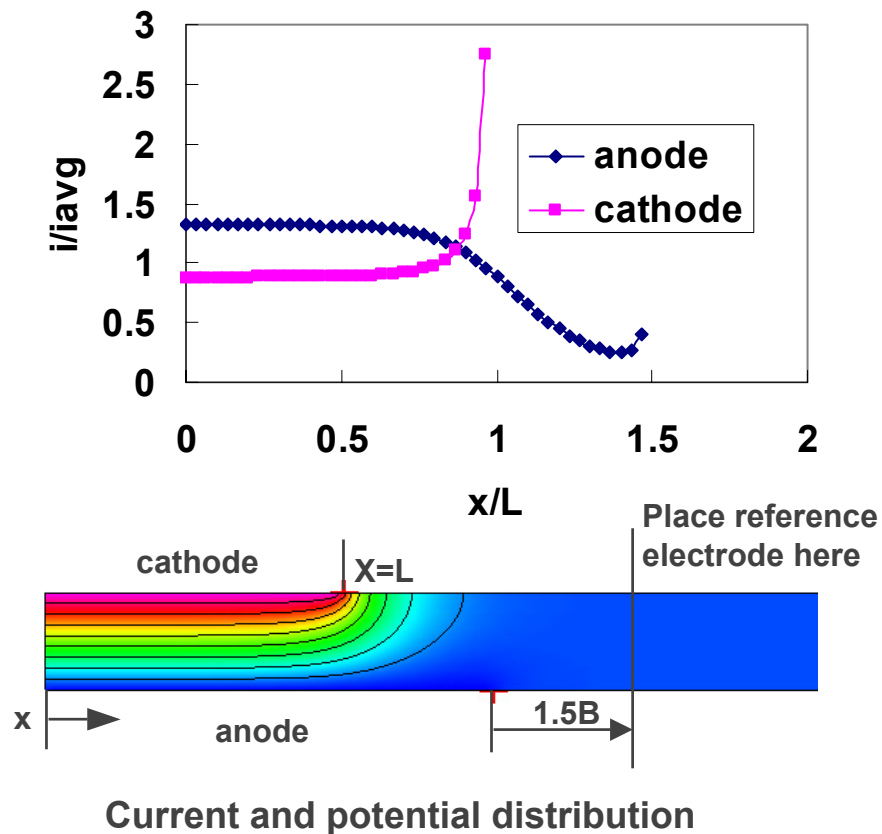
Current and potential distribution

PRIMARY CURRENT DISTRIBUTION

Case: anode oversize cathode

When the anode is oversized more than 1.5 times the gap in relation to the cathode, and if the reference electrode is placed at a distance $1.5B$ beyond the larger electrode edge, then the potential measured is that of the larger anode.

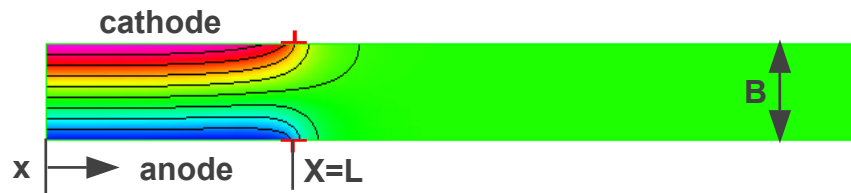
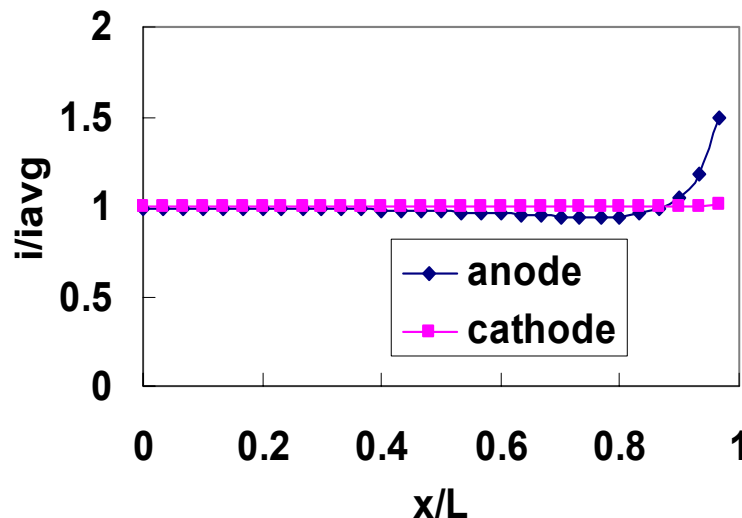
(Reference electrode can be placed on either side of membrane)



SECONDARY CURRENT DISTRIBUTION

Case: Identical and perfectly aligned electrodes

If the anode W_a is small relative to the cathode W_c , and if the reference electrode is placed some distance beyond the electrodes, the potential measured is to the value somewhere between the anode and cathode, closer to the anode with smaller W_a , but the exact position is not known. (therefore, it is difficult to know the exact potential measured with the reference electrode)

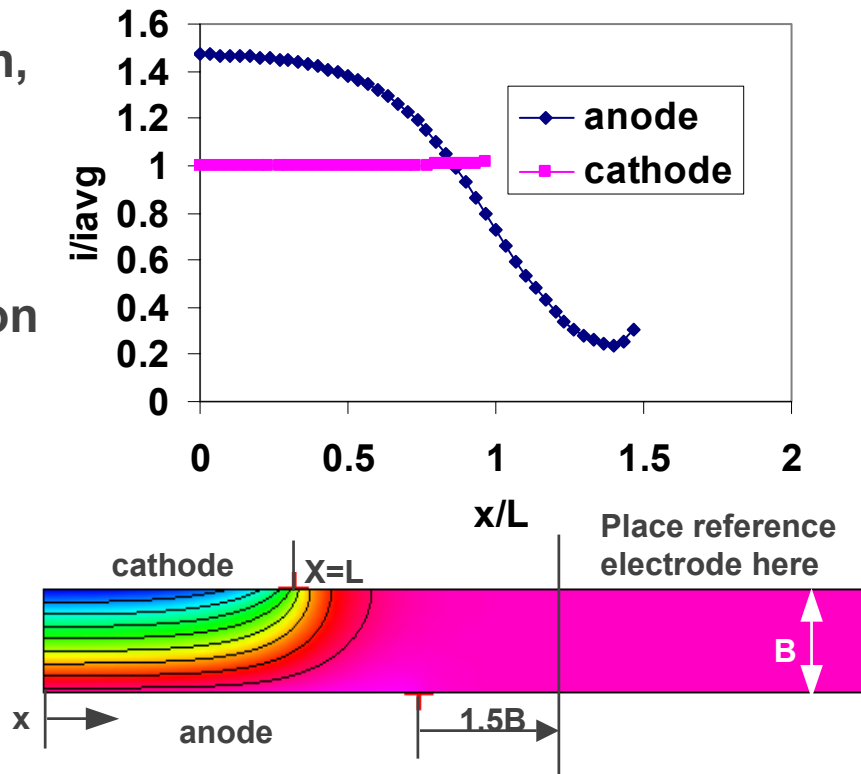


Current and potential distribution (different kinetic factors on both electrodes. W_a (anode): 0.1; W_c (cathode): 25)

SECONDARY CURRENT DISTRIBUTION

Case: anode oversize cathode

For hydrogen fuel cell application, (anode, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, $W_a \cong 0.1$; cathode, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$, $W_c \cong 25$). If anode is oversized more than 1.5 times gap in relation to cathode, and if the reference electrode is placed at a distance $1.5B$ beyond anode, then the potential measured is that of anode. (Reference electrode can be placed on either side of membrane)

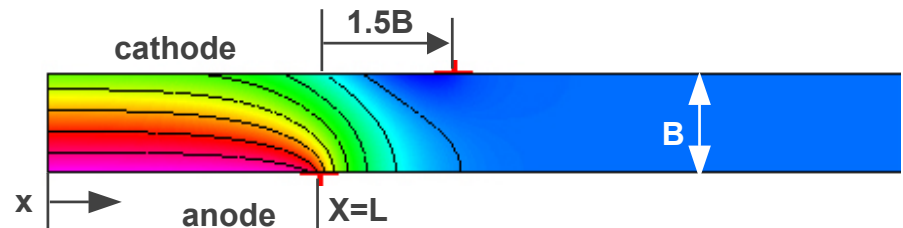
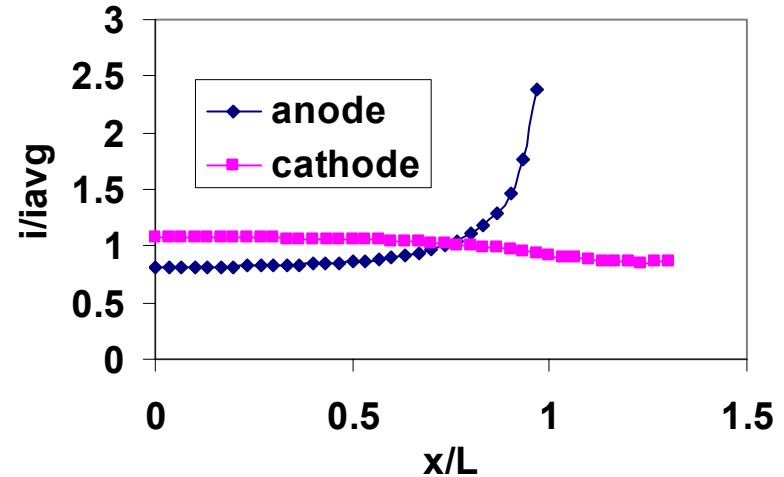


Current and potential distribution (condition for hydrogen fuel cell, W_a (anode): 0.1; (cathode):25)

SECONDARY CURRENT DISTRIBUTION

Case: cathode oversize anode

For hydrogen fuel cell application, (anode, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, $W_a \cong 0.1$; cathode, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$, $W_a \cong 25$). If the cathode oversizes the anode, the potential distribution along the electrodes are not uniform. Therefore, it is not possible to know what potential corresponds to that measured by the reference electrode.



Current and potential distribution
(condition for hydrogen fuel cell, W_a
(anode): 0.1; (cathode):25)

SUGGESTION ON CELL GEOMETRY

- For PEM fuel cell, the electrode with fast electrochemical reaction, usually the anode, should be designed to be larger (1.5 times the electrolyte thickness) than the opposite electrode, usually the cathode. The reference electrode can be positioned 1.5 times the electrode thickness, and the potential measured is that of the larger electrode, i.e. the anode.
- The design of a larger cathode (assume the cathode has slow reaction rate) is not suggested. In such case, the potential distribution is non uniform along the electrodes, and there is no way to know which potential is being measured with the reference electrode.

ACKNOWLEDGMENT

The research work is being advised by:

**Professor Robert F. Savinell (Advisor), Dr. Jesse Wainright
(Department of Chemical Engineering, Case Western Reserve
University)**

**Dr. Weiwei Huang (Energizer Coach)
(Eveready Battery Company, Inc.)**

The research work is sponsored by Eveready Battery Company