The Impact of Hydration Dynamics on the Control of a PEM Fuel Cell

Syed K. Ahmed
Donald J. Chmielewski

Department of Chemical and Environmental Engineering

Presented at the Annual Meeting of the AIChE: November 2006
Outline

- PEMFC Model
  - Mat. & Energy Balances and Electrochemistry
  - Membrane Model
- Controller Analysis
  - Feedback Control
  - Feedback/Feed-forward Control
Polymer Electrolyte Membrane Fuel Cell (PEMFC)

Generated power due to enthalpy released by the reaction:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

($\Delta H \sim 58 \text{ kcal/mole } H_2$)
Dynamic Model of PEMFC

- Parameters based on 1 kW scale.
- Humidified hydrogen feed
- Air cooling is assumed.
Material Balances in the Anode Gas

\[
V_{an} \frac{dC_{H_2}}{dt} = F_{an}^{in} C_{H_2,in} - F_{an} C_{H_2} - r_{H_2} A_{mem}
\]

\[
V_{an} \frac{dC_{H_2O}^{(an)}}{dt} = F_{an}^{in} C_{H_2O,in}^{(an)} - F_{an} C_{H_2O}^{(an)} - J_{H_2O}^{(an)} A_{mem}
\]

\[
F_{an} C = F_{an}^{in} C - (r_{H_2} + J_{H_2O}^{(an)}) A_{mem}
\]

Electrochemical Reaction Rate \(\rightarrow\) \(r_{H_2}\)

Flux of Water to the Membrane \(\rightarrow\) \(J_{H_2O}^{(an)}\)
Material Balances in the Cathode Gas

\[ V_{ca} \frac{dC_{O_2}}{dt} = F_{ca}^{in} C_{O_2,in} - F_{ca} C_{O_2} - r_{O_2} A_{mem} \]

\[ V_{ca} \frac{dC_{H_2O}}{dt} = F_{ca}^{in} C_{H_2O,in}^{(ca)} - F_{ca} C_{H_2O}^{(ca)} - J_{H_2O}^{(ca)} A_{mem} \]

\[ F_{ca} C = F_{ca}^{in} C - \left( r_{O_2} + J_{H_2O}^{(ca)} \right) A_{mem} \]

Electrochemical Reaction Rate ----> \( r_{O_2} \)

Flux of Water to the Membrane ----> \( J_{H_2O}^{(ca)} \)
Energy Balances
(Reaction Chamber Gases)

Cathode Chamber Gas

\[ V_{ca} \frac{dT_{ca}}{dt} = F_{ca}^{in} T_{ca}^{in} - F_{ca} T_{ca} + \left( \frac{UA}{\rho C_p} \right)_{ca} (T_{sol} - T_{ca}) \]

Anode Chamber Gas

\[ V_{an} \frac{dT_{an}}{dt} = F_{an}^{in} T_{an}^{in} - F_{an} T_{an} + \left( \frac{UA}{\rho C_p} \right)_{an} (T_{sol} - T_{an}) \]
Energy Balances
(Cooling Jacket and Solid Material)

Cooling Jacket Gas

\[ V_{jac} \frac{dT_{jac}}{dt} = F_{in} T_{in}^{in} - F_{jac} T_{jac} + \left( \frac{UA}{\rho C_p} \right)_{jac} (T_{sol} - T_{jac}) \]

Solid Material

\[ \left( \rho C_p \right)_{sol} V_{sol} \frac{dT_{sol}}{dt} = (UA)_{ca} (T_{ca} - T_{sol}) + (UA)_{jac} (T_{jac} - T_{sol}) + (UA)_{an} (T_{an} - T_{sol}) + Q_{gen} A_{mem} \]
Reaction, Heat & Power Rates

Electrochemical Reaction Rates:
(molar generation per area of membrane)

\[ r_{H_2} = -\frac{j}{2F} \quad r_{O_2} = -\frac{j}{4F} \]

Heat Generation Rate:
(per area of membrane)

\[ Q_{gen} = (-\Delta H_f, H_2O) r_{H_2} - P_e \]

Power Generation Rate:
(electrical energy generation rate per area of membrane)

\[ P_e = j \, E_{cell} \]
Electrochemistry

• Why we need it
  – Reaction rates depend on $j$, current
  – Heat Generation depend on current

• Need $E_{cell}$

\[ E_{cell} = E_{cell}(j) \]
Electrochemistry

\[ E_{\text{cell}} = E_{\text{ner}} - E_{\text{act}} - E_{\text{ohm}} - E_{\text{mt}} \]
Electrochemistry
(Ideal Voltage)

\[ E_{cell} = E_{ner} - E_{act} - E_{ohm} - E_{mt} \]

Nernst Potential:

\[ E_{ner} = E_o + \frac{RT_{sol}}{2F} \ln \left( \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) \]
Electrochemistry
(Kinetic Losses)

\[ E_{cell} = E_{net} - E_{act} - E_{ohm} - E_{mt} \]

Activation Loss:

\[ E_{act} = \frac{1}{\alpha} \frac{RT_{sol}}{2F} \ln\left( \frac{j}{j_o} \right) \]

Exchange Current Density:

\[ j_o = j_o^o \left( \frac{C_{O_2}^{(ca)}}{C_{O_2}^o} \right)^\gamma \]
Electrochemistry
(Loss Due to Ionic Resistance)

\[ E_{cell} = E_{ner} - E_{act} - E_{ohm} - E_{mt} \]

**Ohmic Loss:**

\[ E_{ohm} = IR = j\left(\frac{t_{mem}}{\sigma}\right) \]

Membrane Thickness: \( t_{mem} \)  
Ionic Conductivity: \( \sigma \)
Electrochemistry
(Mass Transfer Losses)

\[ E_{cell} = E_{ner} - E_{act} - E_{ohm} - E_{mt} \]

Mass Transfer Loss:

\[ E_{mt} = \left(1 + \frac{1}{\alpha}\right) \frac{RT_{sol}}{2F} \ln \left( \frac{j_L}{j_L - j} \right) \]

Limiting Current Density:

\[ j_L = 2F K_{mt} C^{(ca)}_{O_2} \]

Mass Transfer Coefficient:

\[ K_{mt} = D^{(ca)}_{GDL} / t_{GDL} \]
Outline

➢ PEMFC Model
  • Mat. & Energy Balances and Electrochemistry
  • Membrane Model

➢ Controller Analysis
  • Feedback Control
  • Feedback/Feed-forward Control
Hydration Model for MEA

Anode
In
\((H_2, H_2O)\)

Anode
Exhaust

Cathode
Air in

Cathode
Exhaust

Solid Material

Current Collector

MEA

\(H_2\)

\(H_2O\)

\(O_2\)

\(N_2\)

\(H_2O\)
Hydration Model for MEA
Water Transport in the Membrane

ELECTRO-OSMOTIC DRAG

DIFFUSION
Water Transport in the Membrane

Water Flux Mechanisms:

\[ J_{\text{diff}} = -D_e \frac{\partial C_{H_2O}^{(mem)}}{\partial z} \]

\[ J_{\text{drag}} = \xi \frac{j}{F} \]
Hydration Model for MEA

Equations of Change:

\[
\frac{\partial C_{H_2O}^{(mem)}}{\partial t} = - \frac{\partial J_{H_2O}^{(mem)}}{\partial z}
\]

\[
J_{H_2O}^{(mem)} = J_{\text{diff}} + J_{\text{drag}} = -D \frac{\partial C_{H_2O}^{(mem)}}{\partial z} + \frac{j}{F} \xi
\]
Hydration Model for MEA

Equations of Change:

\[
\frac{\partial C_{H_2O}^{(mem)}}{\partial t} = - \frac{\partial J_{H_2O}^{(mem)}}{\partial z}
\]

\[
J_{H_2O}^{(mem)} = J_{\text{diff}} + J_{\text{drag}} = -D \frac{\partial C_{H_2O}^{(mem)}}{\partial z} + \frac{j}{F} \xi
\]
Hydration Model for Membrane

\[ \frac{\partial C^{(\text{mem})}_{H_2O}}{\partial t} = D_e \frac{\partial^2 C^{(\text{mem})}_{H_2O}}{\partial z^2} \]

Boundary Conditions

\[ -D_e \frac{\partial C^{(\text{mem})}_{H_2O}}{\partial z} + \frac{j}{F} \xi - J^{(an)}_{H_2O} = 0 \quad \text{at} \quad z = 0 \]

\[ -D_e \frac{\partial C^{(\text{mem})}_{H_2O}}{\partial z} + \frac{j}{F} \xi + J^{(ca)}_{H_2O} + r_{H_2O} = 0 \quad \text{at} \quad z = \delta_m \]
Concentration Profiles

\[ C_{(an)} H_2O \]

\[ C_{(mem)} \]

\[ \hat{C}_o \]

\[ C_{H_2O} (0) \]

\[ C_{H_2O} (z) \]

\[ C_{(ca)} H_2O \]

\[ \tau_a \]

\[ \tau_m \]

\[ \tau_c \]
Water Fluxes Into the Membrane

\[ J^{(an)}_{H_2O} = k^{(an)}_{gdl} \left[ C^{(an)}_{H_2O} - \hat{C}^{(an/mem)}_{H_2O} \right] \]

\[ J^{(ca)}_{H_2O} = k^{(ca)}_{gdl} \left[ C^{(ca)}_{H_2O} - \hat{C}^{(mem/ca)}_{H_2O} \right] \]
Water Vapor at Membrane Surface

\[ a_{an,\text{mem}} = a_{an,\text{gas}} \quad a_{ca,\text{mem}} = a_{ca,\text{gas}} \]
Water Vapor at Membrane Surface

\[ a_{an,\text{mem}} = a_{an,\text{gas}} \quad a_{ca,\text{mem}} = a_{ca,\text{gas}} \]

Activity in Membrane:

\[ \frac{C_{H_2O}^{(\text{mem})}(0)}{N_s} = \lambda(a_{an,\text{mem}}) \quad \frac{C_{H_2O}^{(\text{mem})}(\delta_{\text{mem}})}{N_s} = \lambda(a_{ca,\text{mem}}) \]

\[ \lambda(a) = 0.0043 + 17.81a - 39.85a^2 + 36.0a^3 \]
Water Vapor at Membrane Surface

\[ a_{an,mem} = a_{an,\text{gas}} \quad a_{ca,mem} = a_{ca,\text{gas}} \]

Activity in Membrane:

\[ \frac{C_{\text{H}_2\text{O}}^{(\text{mem})}(0)}{N_s} = \lambda(a_{an,\text{mem}}) \quad \frac{C_{\text{H}_2\text{O}}^{(\text{mem})}(\delta_{\text{mem}})}{N_s} = \lambda(a_{ca,\text{mem}}) \]

\[ \lambda(a) = 0.0043 + 17.81a - 39.85a^2 + 36.0a^3 \]

Activity in Gas:

\[ \hat{C}_{\text{H}_2\text{O}}^{(\text{an/\text{mem})}} = \frac{a_{an,\text{gas}}p_{\text{vap}}(T_{\text{sol}})}{RT_{\text{sol}}} \quad \hat{C}_{\text{H}_2\text{O}}^{(\text{mem/\text{ca}})} = \frac{a_{ca,\text{gas}}p_{\text{vap}}(T_{\text{sol}})}{RT_{\text{sol}}} \]
Steady-State Water Content

\[ \lambda = \frac{\text{H}_2\text{O}/\text{SO}_3^-}{\text{cm}^2} \]

- 0.6 A/cm²
- 0.4 A/cm²
- 0.2 A/cm²

Length Across PEM (cm)
Dynamic Model of PEMFC

- Parameters based on 1 kW scale.
- Humidified hydrogen feed.
- Air cooling is assumed.
Membrane Conductivity

$$\sigma(\lambda(z)) = 0.005193*\lambda(z) - 0.00326$$
Electrochemistry
(Loss Due to Ionic Resistance)

\[ E_{cell} = E_{ner} - E_{act} - E_{ohm} - E_{mt} \]

Ohmic Loss:

\[ E_{ohm} = IR = j \left( \int_{0}^{t_{mem}} \frac{dz}{\sigma(z)} \right) \]

Ionic Conductivity:
\[ \sigma(\lambda(z)) = 0.005193*\lambda(z) - 0.00326 \]
Outline

- PEMFC Model
  - Mat. & Energy Balances and Electrochemistry
  - Membrane Model

- Controller Analysis
  - Feedback Control
  - Feedback/Feed-forward Control
Current Set-Point Tracking

Transportation Applications

Current \( j^{(sp)} \) Controller \( MV \) PEMFC

\( j \)
Current Controller
Current Controller
Current Controller

Current Density (A/cm²)

Cell Voltage (V)
Current Controller
Current Controller
Current Controller

Water Content in the Membrane at the Cathode GDL

\[ \lambda = \frac{\text{H}_2\text{O}}{\text{SO}_3} \]
Water Fluxes Into the Membrane
Current Controller

Solid Temperature (°C)

[Graph showing solid temperature rising from 80°C to approximately 140°C over a range of 0 to 200 units on the x-axis.]
Current/Temperature Controller

Current Controller

PI

PEMFC

$E_{cell}$

$j$

$F_j$

$T^{s(sp)}$

$T^s$

$j^{(sp)}$

$T_s$
Current/Temperature Controller

Current Density (A/cm²)

0 500 1000 1500 2000
Current/Temperature Controller

Solid Temperature (°C)

0 500 1000 1500 2000

79 80 81 82 83 84
Current/Temperature Controller

Exiting Flowrate of Anode Gas (cm$^3$/s)

Exiting Flowrate of Cathode Gas (cm$^3$/s)
Current/Temperature Controller

- Exiting Flowrate of Anode Gas (cm^3/s)
- Exiting Flowrate of Cathode Gas (cm^3/s)
- Cathode - Oxygen Mole Fraction
Feed-forward Controller

- Feed-forward Controller
- Current Controller
- PEMFC
- PI

Signals:
- $j^{(sp)}$
- $T^{s(sp)}$
- $E_{cell}$
- $F_{j}$
- $F_{o}^{c}, F_{o}^{a}$
- $T^{s}$
Feed-forward Controller
Feed-forward Controller

Current Density (A/cm²)

Power Density (W/cm²)
Feed-forward Controller
Feed-forward Controller
Water Content by the Cathode GDL

![Graph showing water profile at t=-9.9767](image)
Feed-forward Controller
Conclusion

• What is the Impact of Hydration Dynamics on the Fuel Cell?

• Fuel cell is unpredictable and a better controller needs to be attached
Acknowledgements

Argonne National Laboratory

Department of Chemical & Environmental Engineering, IIT