DEGRADATION AND RELIABILITY MODELLING OF POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELLS

Michael Fowler
mfowler@uwaterloo.ca
OUTLINE

- Introduction to Fuel Cell Technology
- Endurance Run of a Single Cell
- Reliability of Fuel Cells
- Voltage Degradation in PEM Fuel Cells
- Modelling of PEM Fuel Cell Degradation
- Conceptual Reliability Analysis of PEM Fuel Cell Stack
SURVEY OF FUEL CELL DEVELOPERS

• “For continuous use products, one game changer may be accelerated testing of the fuel cell. There are currently no accurate models for forecasting failure modes, which is why our products are fairly short lived. We base their lifetime on actual data we have”

WHY FUEL CELLS FOR POWER GENERATION

- High Efficiency
- Low Environmental Burden and Emissions
- High Reliability
- Flexibility of Design
- Easily Refuelled

BARRIERS TO MARKET ACCEPTANCE OF FUEL CELLS

- Cost
- Endurance and reliability
- Refuelling infrastructure and ‘supply chain’ are not in place
- Public Perception of hydrogen
GOALS

• Identify key failure modes associated with PEM fuel cells
• Develop a Generalized Steady State Electrochemical Degradation Model with ageing or voltage degradation terms
• Develop a conceptual model for fuel cell stack reliability
FUEL CELL OPERATION

Hydrogen

Electrolyte

Catalyst

Bipolar plate

Water vapor (and excess air)

Oxygen (or air)

electr. consuming device
**PEM FUEL CELL SYSTEM**

Fuel: Natural Gas, Synthesis gas, landfill gas, distillate, methanol, propane

Fuel Processor and Gas Clean-up

Air
Exhaust

Hydrogen Rich Gas
Water

Fuel Cell Stack

Power Conditioner
DC
AC Power

Co-generation
Exhaust
Energy
FUEL CELL HARDWARE
FUEL CELL TEST STATION
Ideal and Actual Fuel Cell Voltage/Current Characteristics

Theoretical EMF or Ideal Voltage (open circuit voltage)

- Region of Ohmic Polarization (Resistance Loss)
- Region of Activation Polarization (Reaction Rate Loss)
- Region of Concentration Polarization (Gas Transport Loss)

Higher Efficiency
Larger Cell

Total Loss
VOLTAGE DEGRADATION CURVE
FOR A SINGLE PEM CELL
(Operated at 80°C, 0.4 amp cm², 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)
Voltage Performance at End of Life

Voltage (Volts at 0.4 Amps/cm²) vs. Age (Hours)
**RELIABILITY JARGON**

- **Durability** - ability to resist permanent change in performance over time, i.e. degradation *or irreversible degradation*. This phenomena is related to *ageing*.

- **Reliability** - The ability of an item to perform the required function, under stated conditions, for a period of time. Combination of degradation, and failure modes that lead to catastrophic failure.

- **Stability** - recoverable function of efficiency, voltage or current density decay *or reversible degradation*. 

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Failure of the plate
Smooth, unbroken and even carbon fibres on gas diffusion layer.

Polymer and impregnation and no debris can be seen.
ENDURANCE TESTED MEA

Polymer Deposit Seen through-out Electrode

Debris seen in various Location. Likely seal oxidation products.
Seal Oxidation
SCORCHING ALONG THE EDGE
SCORCHING
SUMMARY OF OBSERVED FAILURE

Tear on Disassembly

Oxidation of Seals can be seen on MEA

Discolouration on Edge

Flow Path can be seen imprinted on carbon cloth. More pronounced when wet.

Tear or Burn-through on the edge of active region
FMEA OF A FUEL CELL

• Plate
  – Cracking
  – Scorching
  – Change in the Plate which will impact the MEA
    • Dimensional changes (warping, erosion, misalignment)
    • Contamination or debris released

• Seal Failure

• MEA
  – Pinhole Formation
  – Shorting
  – Degradation of Voltage
VOLTAGE DEGRADATION

• Voltage Degradation will be the main factor governing the ‘life’ of the stack itself (*i.e.* time in service, performance and reliability at end of life)

• Degradation must be accommodated for in control systems

• Will be important in Life Cycle Analysis (especially the Life Cycle Costing)
DEGRADATION FAILURE MODES
(leading to degradation of performance or *durability*)

- **Kinetic or activation loss in the anode or cathode catalyst** – Loss of Apparent Catalytic Activity
- **Ohmic or resistive increases in the membrane or other components** – Loss of Conductivity
- **Decrease in the mass transfer rate of in the reactants flow channel or electrode** – Loss of Mass Transfer Rate of Reactants
VOLTAGE DEGRADATION MODES

- Conductivity Loss
- Loss of Apparent Catalytic Activity
- Loss of Rate of Mass Transport
- BOL

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VOLTAGE DEGRADATION CURVE
FOR A SINGLE PEM CELL
(Operated at 80°C, 0.4 amp cm², 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)
ACTIVITY TERM $k_{\text{cell}}$
(from the GSSEM) OF A SINGLE CELL
(Operated at 80°C, 0.4 amp cm$^2$, 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)
RESISTANCE INCREASE CURVE OF A SINGLE CELL
(Operated at 80°C, 0.4 amp/cm², 30 psig/30 psig, H2/Air – stoichiometric ratios 1.2/2)
SIMULATION OF A SINGLE CELL USING THE GSSEDLM

- Potential (Volt) vs. Current Density (Amp/cm²)
- Power (Watts) vs. Current Density (Amp/cm²)

- BOL
- 1500 Hours
- 3000 Hours
- 4500 Hours
- 6000 Hours
RELIABILITY ANALYSIS

- Must account for stochastic behaviour of cells
- Includes a Degradation Model’, (durability) where ‘Failure’ is degradation to below threshold value for specific parameter (e.g. voltage, efficiency, power) Catastrophic failure of the MEA
- Goal of the analysis is to allow an understanding of the impact of design (e.g. redundancy - increase loading of catalyst) and operation changes (e.g. limitation of operating states) on EOL performance
RELIABILITY ANALYSIS

- Will require some type of ‘Degradation Model’, which allows reliability to be function of degradation evaluation (durability)
- ‘Failure’ is degradation to below threshold value for specific parameter (e.g. voltage, efficiency, power)
- Should account for stochastic behaviour of cells
- Catastrophic failure of the MEA
- Goal of the analysis is to allow an understanding of the impact of design (e.g. redundancy - increase weight of catalyst) and operation changes (e.g. limitation of operating states) on EOL performance
STACK AGING MODEL

(100 CELLS – 100 cm²)

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MODELLING OF STOCHASTIC BEHAVIOUR

Simulation 100 Cell Stack
50.56 cm² Area, 3atmg, H₂/Air SR 1.2/2

Variability in 110 cell Stack
Normalized Variability of a Single Cell
OPERATION WITH MEA FAILURE AND RENEWAL

100 Cell Stack, 100 cm², MTTF 6430 hours
MTTF – MEAN TIME TO FAILURE

Operation Time In Hours * 1000

Values in 10^4 - 3

Mean = 4879.75
REN RENEWAL RATE VARIATION

Weibull 4330 hour MEA
Charateristic Life
Weibull 6330 hour
Characteristic Life
Normal 4330 Mean
MEA MTTF
90% Confidence
Normal 6430 hour Mean
MTTF
No MEA Replacement
VARIATION IN DEGRADATION RATES

Operating Time (hours)

Voltage (volts at 1amp cm$^{-2}$)

- Half Conductivity Decay Rate
- Half the Activity Decay Term
- Double Activity Decay Term
- Double Conductivity Decay Rate
- 90% Confidence Region

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MAJOR CONTRIBUTIONS OF THIS WORK

- Identification of key failure modes associated with PEM fuel cells
- Development of GSSEDAM, modelling the performance of a cell with operating age
- Develop a conceptual model for fuel cell stack reliability.
Acknowledgement / References

• **NSERC, National Defence, Support of the Electrochemical Power Sources Group at RMC.**

• **Key References for Further Information:**
  


# Measurement Error

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DETERIORATION CAN NOT BE AVOIDED

• **intrinsic reactivity** (thermodynamic, chemical and physical instability), including material corrosion and degradation

• **manufacturing irregularities and design flaws**

• **reactant contaminants** (including those contaminants that may leach from the reactant storage and delivery systems)

• **abusive handling**

• **defect propagation**
Instrument Error

$y = 0.0004x + 3.0897$

![Graph showing the relationship between Internal Resistance and Age (Hours)].

- **Series1**
- **Linear (Series1)**

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PEM MODEL DEVELOPMENT

\[ V_{\text{Cell}} = E_{\text{Nernst}} + \eta_{\text{act, a}} + \eta_{\text{act, c}} + \eta_{\text{ohmic}} \]

\[ E_{\text{Nernst}} = 1.229 \times 10^{-5} (T - 29815) + 4.308 \times 10^{-5} \cdot T (\ln p^*_H + \frac{1}{2} \ln p^*_O) \]

\[ \eta_{\text{act, c}} = \frac{1}{\alpha_c} \left[ -10.36 \cdot 10^{-6} \cdot \Delta G_e + 8.62 \cdot 10^{-5} \cdot T (12.863 + \ln A + \ln k' + (1 - \alpha_c) \ln c^*_o - \ln i) \right] \]

\[ \eta_{\text{act, a}} = -\frac{\Delta G_{ec}}{2F} + \frac{RT}{2F} \ln (4F \cdot A \cdot k^*_a \cdot c^*_H) - \frac{RT}{2F} \ln i \]
TOTAL ACTIVATION OVERVOLTAGE

\[ \eta_{\text{act}} = \xi_1 + \xi_2 \cdot T + \xi_3 \cdot T \left[ \ln(c_{O_2}^*) \right] + \xi_4 \cdot T \left[ \ln(i) \right] \]

\[ \xi_1 = -\frac{\Delta G_{\text{ec}}}{2F} - \frac{\Delta G_e}{\alpha_c nF} \]

\[ \xi_2 = \frac{R}{nF\alpha_c} \ln \left[ k_c^0 (c_{H^+}^{*})^{(1-\alpha_c)} (c_{H_2O}^*)^{\alpha_c} \left( k_d^0 \right)^{n\alpha_c} \right] + \frac{R}{F} \ln \left( n2F^{3/2} \right) + \left( \frac{R}{2F} + \frac{R}{\alpha_c nF} \right) \ln(A) + \frac{R}{2F} \ln(c_{H_2}^*) \]

\[ \xi_2 = k_{\text{cell}} + 0.000197 \cdot \ln(A) + 4.3 \times 10^{-5} \cdot \ln c_{H_2}^* \]

\[ \xi_3 = \frac{R(1-\alpha_C)}{\alpha_C nF} \]

\[ \xi_4 = -\left( \frac{R}{2F} + \frac{R}{\alpha_c nF} \right) \]
TOTAL OHMIC OVERVOLTAGE

\[ \eta_{ohmic} = \eta_{ohmic}^{\text{electronic}} + \eta_{ohmic}^{\text{proton}} \]
\[ = -i(R^{\text{electronic}} + R^{\text{proton}}) \]
\[ = -i \cdot R^{\text{internal}} \]

\[ R^{\text{proton}} = \frac{r_M l}{A} \]

\[ r_M = \frac{181.6 \left[ 1 - 0.03 \left( \frac{i}{A} \right) + 0.062 \left( \frac{T}{303} \right)^2 \left( \frac{i}{A} \right)^{2.5} \right]}{\lambda - 0.634 - 3 \left( \frac{i}{A} \right) \exp \left( 3.25 \left[ \frac{T - 303}{T} \right] \right)} \]
AGEING PARAMETERS

\[ \xi_2 = k_{DR} \times \frac{Age}{T} + k_{cell} + 0.000197 \cdot \ln A + 4.3 \times 10^{-5} \cdot \ln c^{*}_{H_2} \]

- proposed ageing rate \( k_{DR} \) of is \(-0.055 \ \mu \text{V/hr}\)

\[ ?_{age} = ?^° + ?_{DR} \times \text{Age} \]

- \(-0.0007 \ \text{hr}^{-1} \) for \( \lambda_{DR} \)
- term related to the loss of mass transport of reactants (not developed in this work)
SINGLE CELL DEGRADATION

H₂/AIR  30 psig/30psig 80°C

Potential (Volts)

Current Density (mA/cm²)

600 hour Data
SR 1.15/3
λ 12.3
Epsilon² 0.00303

227 hour Data
SR 1.15/2
λ 7.5
Epsilon² 0.00320

600 hour Data
SR 1.15/2.0
λ 14.4
Epsilon² 0.00301

600 hour data
High stoic ratio - 600 hour data
BOL Data

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LOSS OF APPARENT CATALYTIC ACTIVITY

- Catalyst sintering (catalyst migration or ripening)
- Loss of catalytic or electrolyte material
- Low levels of contaminants binding to active sites
  - Contaminants from reactants (including dust)
  - Contaminants leached from fuel cell components
- Poor water management may contribute to effectiveness of catalytic sites (flooding and dehydration) or simply the presence of liquid water
- Degradation of Nafion in contact with active sites
- Carbon Corrosion
LOSS OF APPARENT CATALYTIC ACTIVITY
LOSS OF CONDUCTIVITY

- Low levels of cation contamination reducing the proton conductivity (this cause may be accelerated by high hydration levels as the water acts as a source and pathway for contaminants)
- Changes to electro-osmotic drag properties
- Changes to the water diffusion characteristics of the membrane
- Corrosion of the plates leading to increased contact resistance
- Thermal or hydration cycling leading to mechanical stress cycling resulting in delamination of the polymer membrane and catalyst
LOSS OF CONDUCTIVITY

Graph showing the loss of conductivity over time with varying current densities and potential (voltage) levels.
LOSS OF MASS TRANSFER RATE

- Swelling of polymer materials in the active catalyst layer changing water removal characteristics
- Compaction of the gas diffusion layer due to mechanical stresses
- Surface chemistry changes in the gas diffusion layer making water removal more difficult
- Carbon Corrosion
LOSS OF MASS TRANSFER
RATE OF REACTANTS

Current Density (A/cm²)

Potential (Voltage)

Power (watts)

BOL  1000 Hours  2000 Hours  3000 Hours  4000 Hours  5000 Hours