Accelerated Stress Tests in PEM Fuel Cells: What can we learn from it?

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Presentation Overview

• Introduction

• Examples of PEMFC durability and degradation issues

• In-situ diagnostic techniques

• Spatial diagnostics

• Accelerated stress tests

• Closing remarks / summary
Many PEM fuel cell advances applicable to PEM electrolysis

Some related areas between the PEM fuel cell and PEM electrolysis:
- Electrolysis anode has similar requirements to PEMFC anode in cell reversal (fuel starvation)
- More durable and less expensive PEM membranes required
- 2-phase PEMFC cathode/flow field similar to 2-phase PEM electrolysis anode/flow field
- PEMFC anode/flow field similar to PEM electrolysis cathode/flow field
- Bipolar stacked flat plate approach similar in both cases
- Air bleed on PEMFC anode for reformate compared with $O_2$ cross-over to PEM electrolysis cathode
- Diagnostics and failure / durability testing similar for the PEM fuel cell and PEM electrolysis
- Etc, etc
Lifetime Issues

• Operational conditions, materials and design affect fuel cell lifetime

• Some key operational areas include:
  – Low humidification
  – High/excess humidification
  – Low reactant flows
  – High temperature
  – Low temperature
  – Fuel composition
  – Current density
  – etc
Failure Modes (Low Humidity)

Low humidity

- Dehydration
- Resistance increase
- Increases cross-over
- Membrane pinhole development

Low humidity and hot spots can lead to failures such as shorting and membrane holes (gas crossover detection by IR)

Failure Modes (Flooding)

Flooding
- High current issue
- Mass transport issues
- Purging required
- Cell design important

Cell Temperature = 75°C

Inlet Reactants
- DPT oxidant
- DPT fuel

Temperature (°C) vs. Time (s)
Effect of Cell Design for Water Management on Degradation


- **Isothermal operation, Mk5 single cell,**
  - air/H₂, 2/1.5 stoichiometry, 3.04/3.04 atma,
  - internal humidifier, 80 C, 0.538 Acm⁻²

- **Operation with a temperature rise,**
  - Mk513 8 cell stack, air/H₂,
  - 2/1.5 stoichiometry, 3.04/3.04 atma,
  - internal humidifier, 75 C coolant inlet,
  - 85 C coolant outlet, 1.076 Acm⁻²

- **1 µV/h**

- **60 µV/h**
Failure Modes (Low Reactant Stoichiometry)

Normal reaction:
\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

In absence of H\(_2\) and depending on potential:
\[ H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^- \]
\[ (E^{\circ}_{25^\circ C} = -1.23 \text{ V vs. NHE}) \]

\[ C + 2H_2O \rightarrow CO_2 + 2H^+ + 4e^- \]
\[ (E^{\circ}_{25^\circ C} = -0.21 \text{ V vs. NHE}) \]

Currents consumed generating $O_2$ and $CO_2$ for fuel cell undergoing fuel starvation
Enhanced water supply at anode sustains water electrolysis during fuel starvation reversal.
Extended fuel starvation reversal at 200 mA / cm² with different catalyst compositions and structures

Degradation of carbon catalyst support and other carbon components during fuel starvation

- When Pt anode catalyst is supported on carbon, degradation can occur due to loss of catalyst support.
- In addition to the $O_2$ evolution reaction, C oxidation can occur:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

Average stack performance recovery vs time spent in fuel starvation reversal
In-Situ PEM Cell Diagnostics for Durability and Degradation

• Ideal approach should target:
  – As many failure modes as possible
  – Be specific to as many components as possible
    • Flow field
    • Membrane
    • Electrodes
    • Etc
  – Very low invasiveness
  – Low cost
  – Provide accelerated insight into mechanism(s), i.e., predict longer term issues
Reference Electrodes

Anodic and Cathodic Component Overpotentials

Anodic and Cathodic Overpotential Ratios (effect of different operating conditions)

$\eta / \eta_0$

- Activation
- Ohmic
- Concentration
- Mass Transport
In-Situ Half Cell Electrochemistry for Electrode/Catalyst Evaluation

Example CVs after Lifetime Testing

PtRu Anode after 50 hours operation
PtRu Anode after >5000 Hour Operation

E (mV vs H₂ electrode)

CO Stripping Voltammetry for Catalyst Surface Area

(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-)
Impedance Analysis for Failure / Degradation Analysis

Low Humidity Failure Mode

Flooding Failure Mode

\[ j = 0.1 \text{ A cm}^{-2}, \quad T_{\text{stack}} = 70^\circ\text{C} \]

\[ j = 0.2-0.5 \text{ A cm}^{-2}, \quad T_{\text{stack}} = 70^\circ\text{C} \]

Performance Losses from Tri-Oxidant Polarization
(O₂ (21%)/N₂, O₂ (21%)/He, O₂(100%)) : D (O₂/He) / D(O₂/N₂) ~ 3; D(O₂ )D(O₂/N₂ )~ 7

Multi-component gas analysis (experimental and theoretical analysis)
2-Phase Flow Analysis in PEM Based Cells

• Diagnostic tools to understand two-phase flow and flow distributions in PEMFC flow fields
• Provides better solutions for water management in PEMFCs
• This approach can be applied to PEM electrolysis

H₂O (l) = 1/2O₂ + 2H⁺ + 2e⁻

Anode Purge Diagnostic based on Anode Water Removal

In-Situ Characterization and Diagnostics at UBC

– Challenges by regions or components
  • Spatial resolution
  • Concurrent techniques
    – impedance, electrochemical techniques
    – anode water removal, transient operating conditions, etc
  • High throughput (combinatorial analysis)
    – Material performance and degradation
Spatially resolved current distribution mapping in an operating fuel cell using segmented cells

UBC Fuel Cell:
4 x 4 segmentation over 50 cm²

Spatially resolved current distribution mapping in an operating fuel cell using fully isolated subcells

Effect of Failure Mode Conditions on Sensing Electrodes (example for sensing external to active area)

Accelerated Fuel Cell Testing and Product Life

Voltage cycling

- voltage, current density
- temperature
- humidification
- reactant concentration
- catalyst loading
- Etc, etc

Accelerated Stress Parameters

- nominal stress (extrapolated)
- accelerated stress (experimental)
Transient Testing for Accelerated Performance Degradation  
(e.g., cell voltage reversal testing)

**Performance Degradation vs. Time Spent in Reversal**

Each cycle: 30 x 10 sec reversal pulses at 200 mA/cm²

- **Baseline**
- **40/20 Pt/Ru/Shaw in PTFE**

**Baseline Catalyst**

**Cell Reversal Tolerant Catalyst**

Average Voltage (V)

Time (min)
Accelerated Spatially Resolved Stress Testing

• Gradients in operating conditions allow accelerated testing because of enhanced sensitivity in some regions
• A variety of *in situ* characterization techniques can be applied and spatially determined
• Dynamic/transient spatially resolved measurements
  – Water transport
  – Current density, etc

![Diagram of a grid with labels: reference electrode, anode segment, and electrolyte.](image)
Parameter Change as a Result of In-plane Gradients

Dimensionless oxygen concentration, temperature, and relative humidity profiles across a PEMFC flow field, $x$ = dimensionless distance

Increased Sensitivity with Lower Reactant Concentration

Cell inlet reactant concentration decreased

Mass Transport Loss and Sensitivity Increases

Effect of stoichiometry on concentration gradient

Sensitivity Increases
Increased sensitivity to operating parameters

H2 Stoichiometry Sensor Cell Response

Voltage response of other cells in stack

Sensor cell voltage response

4 runs, different rates of flow change

Early detection of out of range operating conditions or degradation

Summary

• Many diagnostics and failure/durability testing methods for the PEM fuel cell are applicable to PEM electrolysis
• In-situ PEM cell diagnostics can have low invasiveness and provide specific component and mechanistic information
• More sensitive operating conditions and transients can be used to provide accelerated test information
• Spatially resolved measurements can provide an important accelerated test platform for
  – operating conditions
  – component materials and designs
Wilkinson Electro/Photo-Chemical Research Group (since 2004)

• Fuel Cell and Battery Research
  – New materials and new approaches
  – Technology simplification
  – New catalysis approaches
  – Failure modes, durability, and accelerated testing methods

• Clean Energy Research
  – Electrochemical approaches to clean energy and clean water
  – CO₂ reduction and solar fuels
  – Hydrogen production and storage
    • Photochemical & Photo-electrochemical hydrogen production
    • Advanced electrolysis
    • Metal and chemical hydrides

• Water treatment

Sources of Funding:
• NSERC
• NRC
• CMC
• PICS
• CRC
• CFI
• WED
• Industry
Thank You!
Questions?

“We have not inherited this world from our parents, but we have it on loan from our children”

- Native British Columbia Haida Quote