PEM Fuel Cell Diagnostics
as Design Tool

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Diagnosis

noun
Investigation or analysis of the cause or nature of a condition, situation or problem

Diagnostic(s)

noun
the art or practice of diagnosis
Purpose of Fuel Cell Diagnostics

Diagnostics in fuel cell development process
Knowledge:
materials
processes
interactions

requirements

design

model

Should it work?

fabricate

test

diagnostics

Does it work?
Purpose of Fuel Cell Diagnostics

- Diagnostics in fuel cell development process
- Diagnostics in control development process
Purpose of Fuel Cell Diagnostics

- Diagnostics in fuel cell development process
- Diagnostics in control development process
- Diagnostics in operation
**Generic Control Loop**

- **Controller** output signal to **control element**
- **Control element** manipulates a **fuel cell**
- **Fuel cell** processes variables and sends a measured value to a **measurement sensor/transmitter**
- **Measurement sensor/transmitter** measures a **process variable** and sends it to the **controller**
- **Controller** compares the measured value with a **set point** to determine an **error**
- **Controller** output signal manipulates the **fuel cell**
- **Fuel cell** affects the **process variable**
- **Process variable** is disturbed and affects the **controller**

**Key Terms:**
- Controller
- Control element
- Fuel cell
- Measurement sensor/transmitter
- Process variable
- Error
- Set point
- Disturbances
Fuel Cell Diagnostic Methods

- Observe
  (voltage/current, pressure drop, temperature)
Fuel Cell Diagnostic Methods

- Observe
  (voltage/current, pressure drop, temperature)
- Change a parameter and compare
**First fuel cell law:**
One cannot change only one parameter in a fuel cell — change of one parameter causes a change in at least two other parameters, and at least one of them has an opposite effect of the one expected to be seen.

Fuel cells: Problems at different scales
Fuel Cell Diagnostic Methods

- Observe
  (voltage/current, pressure drop, temperature)
- Change a parameter and compare
- Disturb and observe
  - Small disturbances
  - Large disturbances (exaggerate or accelerate)
Role of Diagnostics in Fuel Cell Control

- **Control element(s)**
- **Fuel cell**
- **Diagnose**
- **Measured values**
- **Controller output signal(s)**
- **Disturbances**
- **Manipulated variable(s)**
- **Process variable(s)**
- **Controller action signal**
- **Diagnosis**
- **Desired/expected state of health**
Purpose of Fuel Cell Diagnostics

- Diagnostics in fuel cell development process
- Diagnostics in control development process
- Diagnostics in operation
- Post mortem diagnostics
Cathegorization of Diagnostic Methods

- Online
- Offline
- Post mortem
Fuel Cell Diagnostic Methods

Electrochemical techniques
- Polarization curve
- Current interruption
- Electrochemical Impedance Spectroscopy
- Cyclic Voltammetry
- CO Stripping Voltammetry
- Linear Sweep Voltammetry

Species Distribution Mapping
- Pressure Drop Measurements
- Gas Composition Analysis
- Neutron Imaging
- Magnetic Resonance Imaging
- X-ray Imaging
- Optically Transparent Fuel Cells
- Embedded Sensors

Current Distribution Mapping
- Partial MEA
- Segmented Cells

Temperature Distribution Mapping
- IR Transparent Fuel Cells
- Embedded Sensors
Diagnostics as a design tool

- Polarization curve
- Polarization curve hysteresis
- Comparative polarization curves
- Current interrupt
- AC impedance spectroscopy
- Pressure drop
- Current density mapping
- Temperature mapping
- Flow visualization
- Neutron/X-Ray imaging
Fuel cell polarization curve

![Graph showing the relationship between cell potential (V) and current density (mA/cm²). The graph includes the theoretical (ideal) voltage, activation losses, resistance losses, and mass transport losses, along with the resulting V vs. i curve.](image)
Fuel cell polarization curve

- Normal polarization curve
- Mass transport problems
  - Flooding?
- Higher resistance
  - Drying?
- Higher activation losses
Data should be taken at multiple current or voltage points.

Typical points would be open circuit and 5 or 6 points between 600 mV/cell and 850 mV/cell,

15 minutes dwell at each point

The data from the last five (5) minutes should be averaged and then plotted as average current versus average voltage.
Polarization curve sweep
PEM Fuel cell transient response

Qiangu Yan, J. Power Sources, Vol 161, 2006, pp 492–502
Unitized Regenerative Fuel Cell Cyclic Operation

> 100 LEO cycles

Elapse Time (hr)

Cell Voltage/Differential Pressure

Fuel Cell 40 min  Electrolysis 60 min

Presented at IECEC, Portsmouth, VA, August 12, 2003
Passive Self-Breathing Micro PEM Fuel Cell

after 120 min significant difference in between structures visible
closed current collectors result in higher voltages
higher differences with higher current densities
voltage difference for pin-hole structure smaller at 400 mA/cm² → reduced concentrations?
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Polarization curve at cell temperature 80°C
anode/cathode humidifier temperatures 80/60°C
hydrogen/air, 30 psig, H2 stoich 1.5, air stoich 5.0
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Comparative polarization curves

Fig. 5 For air operation, in Ballard Mark 5E hardware, the kinetic benefit of a PtCr alloy cathode is masked by mass transport losses. The comparative performance of the PtCr alloy and a pure Pt cathode electrocatalyst is shown using air, helox (21% O₂ in helium) and O₂ as oxidants and H₂ as fuel. The MEAs (< 1 mg Pt cm⁻²) are based on catalysed substrates bonded to Nafion 115 membrane electrolyte. The cell is operated at 80°C, in hydrogen/air, helox, oxygen, 308/308 kPa, 1.5/2, 2, 10 stoichiometry, full internal membrane humidification.

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Current interrupt method for measurement of fuel cell resistance

- Digital oscilloscope
- Fuel cell
- Load

Voltage graph:
- Cell voltage before current interrupt
- Immediate rise in voltage, $\Delta V_R$
- Slow rise to OCV, $\Delta V_{act}$
- OCV

Diagram:
- Switch activating fuel cell, followed by load
- Time of current interrupt
- Voltage graph with time axis indicating immediate and slow voltage changes
Current interrupt method for measurement of fuel cell resistance

Cell voltage before current interrupt

Immediate rise in voltage, $\Delta V_R$

extrapolated straight lines

discrete points

ringing effect

OCV

Time of current interrupt

voltage

time
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Electrochemical Impedance Spectroscopy

- Each of the losses has their own rate (time constant)
- Apply an AC stimulus (on top of DC) and observe consequent AC result (amplitude and phase)
- Deconvolute the impedance associated with each process.

\[ Z(\omega) = \frac{E(\omega)}{i(\omega)} \]
Electrochemical Impedance Spectroscopy

Set-up

Freq. Response Analyzer

Gen. $V_{AC}$ $I_{AC}$

Load

Voltage Sense Leads ($V_{DC} + V_{AC}$)

Main Cell Leads ($I_{DC} + I_{AC}$)

Fuel Cell
Fuel Cell Equivalent Circuit

Key: GDL = gas diffusion layer, dl = double layer, ct = charge transfer, a = anode, c = cathode.
Two ways of showing the same results:
Nyquist and Bode plots
Fuel Cell EIS – Typical Results

HF Resistance
The high, medium and low-frequency features of PEFC EIS

In a H₂/O₂ (air) fuel cell, the spectra often have **three features**, which are denoted as high-frequency, medium-frequency, and low-frequency.

- **High-frequency** – internal ohmic resistance and the contact capacitance in the granular electrode structure.
- **Medium-frequency** – charge transfer (kinetic) resistance.
- **Low-frequency** – mass transport resistance.
Advantages and limitations of EIS for fuel cells

- Studying the entire frequency response can give information on:
  - Interfacial charge transfer resistance
  - Ohmic losses
    - Electronic
    - Ionic conductivity of electrolyte membranes
  - Oxidant and fuel mass transport resistance
  - Double-layer capacitance
  - Water management
  - Adsorption processes

- Measurement is relatively fast (slower than current interrupt).
- Applicable across the whole current-voltage operating range.
- Does not perturb the system (much) (cf. current interrupt).
- Simple equivalent circuits can be used for analysis.
Advantages and limitations of EIS for fuel cells

Relatively sophisticated instrumentation required.

- Care must be taken with the measurement and the interpretation of the data.
- Robust EIS measurements must show:
  - **Linearity** – the AC signal must be low enough to ensure that the electrochemical response is linear. I.e. response from the system must be a linear function of the applied perturbation for meaningful mathematical analysis.
    \[ \Delta V = \Delta i R \]
  - For a non-linear system, the change in current is not proportional to the voltage change
    \[ \Delta V \neq \Delta i R \]
  - In practice we use small signals (ca. 10 mV) to ensure that the system behaves approximately linearly.
    - Small signals lead to lower accuracy
    - In practice we have to consider a trade-off between linearity and accuracy.
Comparison with Current Interrupt

<table>
<thead>
<tr>
<th>Electrochemical Impedance Spectroscopy</th>
<th>Current Interrupt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Advantages</strong></td>
</tr>
<tr>
<td>Provides information on the various losses in a fuel cell.</td>
<td>Rapid measurement.</td>
</tr>
<tr>
<td>No significant perturbation to fuel cell.</td>
<td>Low cost.</td>
</tr>
</tbody>
</table>

**Disadvantages**

For high current systems a load is required that has the ability to accept ac input and operate over the bandwidth of the measurement.

High cost instrumentation required.

Difficult to apply to all cells in a stack simultaneously.

**Disadvantages**

Significant perturbation to fuel cell.

Requires interruption of the fuel cell current delivery.

Current must be flowing for measurement to be taken (cannot measure at open circuit conditions).

Low signal-to-noise when measuring at low current density.
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Current density mapping with segmented cell

Segmented bipolar plates

- local current density measurement
  - dynamic > 2000 measurement /s
- local temperature measurement
- local electrochemical impedance spectroscopy (EIS)

4 mm
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Temperature Mapping with iR Camera

![Diagram of a fuel cell with labeled parts: Screws, Barium fluoride, Anode end plate, Anode polar plate, MEA, Cathode polar plate, Cathode end plate.]
Temperature Mapping with iR Camera
Segmented fuel cell with separate temperature control

smallest sensor on the market
Sensirion SHT 71
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Flow Visualization

Interdigitated Flow Field

Straight Channels

X Liu, et al. Water flooding and two-phase flow in cathode channels of proton exchange membrane fuel cells, Journal of Power Sources,
Optical measurements of water partial pressure
Visualization of oxygen partial pressure


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Real time detection of liquid water inside an operating fuel cell
neutrons can ‘see’ water in fuel cells

normalization of images: water distribution map

original radiography  

100 mm

ratio:
water filled cell/empty cell

water distribution
Liquid water distribution in PEMFC by neutron imaging at Penn State University

Synchrotron X-Ray Radiography

High-resolution Soft X-ray Radiography

(a) Current collector, X-rays, CCM (CL & PEM), GDL, O₂, H₂

(b) 12 mm, 1 mm, Channel, Rib, 2 mm, 0.8 mm, Gas inlet/outlet, Active area

P. Deevanhxay, Electrochemistry Comm., 2012
http://dx.doi.org/10.1016/j.elecom.2012.05.028,
Conclusions

- Diagnostics – important aspect of fuel cell R&D

- Limited number of diagnostic methods applicable for fuel cell control purposes

- Definition of optimum performance must include life time

- In order to achieve optimum performance diagnostics is crucial for prognostics and health management
More information about PEM fuel cells:

Frano Barbir
PEM Fuel Cells: Theory and Practice
Elsevier/Academic Press, 2005
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