Characterization of Water Management in PEM Fuel Cells with Microporous Layer Using Electrochemical Impedance Spectroscopy

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Water management in PEM fuel cell

FLOODED

DRY

Hydrogen + Water + Oxygen → Water + membrane + catalyst + porous transport layer

Hydrogen

Oxygen

Water

Fuel Cell Research Centre
Microporous Layer (MPL)

Porous Transport Layer (PTL) (Gas Diffusion Layer)
Catalyst Coated Membrane (CCM)
Proton Exchange Membrane (PEM)

porous carbon backing
microporous layer
catalyst layer
Positive effects of MPL:

- reduces cathode flooding

- improves catalyst utilization

- Reduces variability in cell performance

Polarization curves for PEMFCs without MPL and with MPL on anode and cathode sides. Error bars represent standard deviation within batch of identically built cells.

Theories explaining MPL effect

Hydrophobic characteristic of the MPL forces water from cathode towards FFP reducing flooding

Proposed in:
Theories explaining MPL effect

MPL facilitates water back diffusion providing better humidification of membrane and catalyst layers

Proposed in:
Theories explaining MPL effect

MPL makes open pathways for gaseous oxygen to be transported to catalyst layer

Proposed in:
Approaches to examine proposed mechanisms

Flow visualization

Approaches to examine proposed mechanisms

**Electrochemical Impedance Spectroscopy (EIS)**

Setup 1 or Setup 2

\[ I = V * R_s \]

- Impedance analyser
- Resistance \( R_s \)
- Electronic load
- PEM fuel cell

High-current impedance

Low-current impedance

EIS enabled potentiostat or potentistat + impedance analyser
EIS response of PEM fuel cell
Mid-frequency arc: charge transfer resistance

Effect of current density on EIS response

\[ R_{ct} = \left( \frac{\partial \eta}{\partial i} \right)_{T} = - \frac{2.303RT}{\alpha F} \frac{1}{i} \]

Low-frequency arc: mass-transport resistance

Effect of cathode gas on EIS response

High-frequency arc: membrane resistance


Diameter of high-frequency arc found to be consistent with the resistance calculated from the known geometry and conductivity of the Nafion membrane

EIS response of PEM fuel cell: arc assignment

**polarization curve**

- **i = 0.21 A cm⁻²**

**Z' / Ω cm²**

- **-0.2**
- **-0.1**
- **0.0**
- **0.1**
- **0.2**
- **0.3**
- **0.4**
- **0.5**
- **0.6**

**Z'' / Ω cm²**

- **-0.2**
- **-0.1**
- **0.0**
- **0.1**
- **0.2**
- **0.3**
- **0.4**
- **0.5**
- **0.6**

**Total cell resistance (R_{cell})**

- **600 Hz**
- **60000 Hz**
- **12 Hz**
- **3 Hz**
- **0.1 Hz**

**In-series resistance** (FFP, endplates, cables etc.)

- **Membrane resistance**

- **Cathode charge-transfer resistance**

- **Cathode mass-transport resistance**
Effect of MPL on PEMFC EIS response

Impedance diagrams for PEMFC with (2,3) and without (1) MPL fed with H₂/Air. Current density – 0.21 A cm⁻².
Effect of MPL: influence of current density

- Without MPL
- With MPL

Current densities:
- 0.3 A cm$^{-2}$
- 0.7 A cm$^{-2}$
Equivalent circuit fitting

Randles circuit:

\[ Z'' / \Omega \text{ cm}^2 \]

\[ Z' / \Omega \text{ cm}^2 \]
Effect of current density on cathode charge-transfer and Warburg resistances

Without MPL

With MPL

$R_{ct}$

$R_w$

$R_{ct} + R_w$

$i / \text{mA cm}^{-2}$

$R / \Omega \text{cm}^2$
Time constants for oxygen transport process

Experimentally determined:

Table I. Summary of EIS-determined parameters for cells with and without an MPL (average values of the parameters are reported).

<table>
<thead>
<tr>
<th>$i$ mA/cm$^2$</th>
<th>$R_{\Omega}$ Ω cm$^2$</th>
<th>$R_{ct}$ Ω cm$^2$</th>
<th>$R_{int}$ Ω cm$^2$</th>
<th>$L^2/D$ s</th>
<th>$R_{\Omega}$ Ω cm$^2$</th>
<th>$R_{ct}$ Ω cm$^2$</th>
<th>$R_{int}$ Ω cm$^2$</th>
<th>$L^2/D$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.017</td>
<td>0.215</td>
<td>0.069</td>
<td>0.329</td>
<td>0.015</td>
<td>0.359</td>
<td>0.015</td>
<td>0.359</td>
</tr>
<tr>
<td>400</td>
<td>0.017</td>
<td>0.194</td>
<td>0.077</td>
<td>0.239</td>
<td>0.015</td>
<td>0.255</td>
<td>0.015</td>
<td>0.255</td>
</tr>
<tr>
<td>500</td>
<td>0.017</td>
<td>0.189</td>
<td>0.090</td>
<td>0.172</td>
<td>0.015</td>
<td>0.236</td>
<td>0.015</td>
<td>0.236</td>
</tr>
<tr>
<td>600</td>
<td>0.017</td>
<td>0.182</td>
<td>0.120</td>
<td>0.136</td>
<td>0.015</td>
<td>NA$^a$</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>700</td>
<td>0.017</td>
<td>0.173</td>
<td>0.136</td>
<td>0.110</td>
<td>0.015</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>800</td>
<td>0.017</td>
<td>0.157</td>
<td>0.246</td>
<td>0.098</td>
<td>0.016</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>900</td>
<td>0.017</td>
<td>0.153</td>
<td>0.347</td>
<td>0.096</td>
<td>0.016</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

$^a$NA = not analyzed.

Theoretically predicted:

Table II. Estimated time constants for various oxygen-transport processes.

<table>
<thead>
<tr>
<th>Transporting phase</th>
<th>PTL (g)</th>
<th>MPL (g)</th>
<th>Cathode layer (g)</th>
<th>Cathode layer (w)</th>
<th>Cathode layer (agg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (m)</td>
<td>Gas-filled pore</td>
<td>Gas-filled pore</td>
<td>Gas-filled pore</td>
<td>Water film in cathode layer</td>
<td>Ionomer in cathode layer</td>
</tr>
<tr>
<td>$D$ (m$^2$/s)</td>
<td>$300 \times 10^{-6}$</td>
<td>$3 \times 10^{-5}$</td>
<td>$35 \times 10^{-6}$</td>
<td>$50 \times 10^{-9}$</td>
<td>$200 \times 10^{-9}$</td>
</tr>
<tr>
<td>Volume fraction of transporting phase</td>
<td>0.56</td>
<td>0.2</td>
<td>0.2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>$D_{eff}$ (m$^2$/s)$^a$</td>
<td>$1.26 \times 10^{-6}$</td>
<td>$4.93 \times 10^{-6}$</td>
<td>$2.68 \times 10^{-8}$</td>
<td>$2.00 \times 10^{-9}$</td>
<td>$2.83 \times 10^{-10}$</td>
</tr>
<tr>
<td>$L^2/D_{eff}$ (s)</td>
<td>$1.15 \times 10^{-2}$</td>
<td>$1.83 \times 10^{-4}$</td>
<td>$4.57 \times 10^{-4}$</td>
<td>$1.25 \times 10^{-6}$</td>
<td>$1.41 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$ $D_{eff} = D \times$ (volume fraction of transporting phase$^{15}$).
MPL effect models

Model A: MPL promotes water back diffusion

Expected effects:
• Increased amount of water in cathode catalyst layer
• Reduced membrane resistance
• Reduced water content in cathode PTL

observed

Model B: MPL forces water to FFP

Expected effects:
• Reduced amount of water in cathode catalyst layer
• Increased water content in cathode PTL

not observed

Proposed in:

Prepared in: