Performance Measurement of MEAs

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1. Measurement of MEA Performance
   i. Measurement of ECA
   ii. Measurement of ORR activity
   iii. Effect of RH and T on
        a) Performance/Activity
        b) Membrane resistance
        c) Catalyst Layer resistance

2. Current Status - PEMFC

3. Overview of Requirements & Testing
   i. Expected MEA operating environment
   ii. Electrolyte membrane target performance
   iii. Electrolyte membrane durability
   iv. Target cost of membrane
   v. Automotive fuel cell MEA degradation map
Measurement of MEA Performance
Fuel Cell Specification

Typical subscale cell used in testing of MEA performance and durability.
Cyclic Voltammograms - Issues

- N₂ Flow Rate at Cathode*
- Cell Temperature
- Cell RH

Effect of N\textsubscript{2} Flow Rates on CV

- High N\textsubscript{2} flow rates result in a shift of the H\textsubscript{2} onset towards positive potentials-leading to smearing of H\textsubscript{ads} peaks.
- Zero N\textsubscript{2} flow rate is recommended for ECA diagnostics.

H\textsubscript{2} Evolution Onset Shift


Effect of Cell Temperature on CV

Ph.D. Dissertation of M. Oudenhuijzen
“Support Effects in Heterogeneous Catalysis”,
Chapter 6, p.104 (2002).
Effect of RH - CV

Should one measure CVs at low or high RH to evaluate I-V performance at low RH?

Onset of oxide formation shifts positively as RH decreases.

Nissan, unpublished data.
Reproducibility and Utilization

ECA Measurement Conditions

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N2 Flow Rate / SLPM</td>
<td>0</td>
</tr>
<tr>
<td>Cell Temperature / °C</td>
<td>30</td>
</tr>
<tr>
<td>Voltage Scan Range / V</td>
<td>0.04 - 0.9</td>
</tr>
</tbody>
</table>

80% Utilization

Scatter in values of ORR activity reported in the literature.

**Reasons for Scatter**

- Catalyst Loading
- Surface Area
- Operating Conditions
- Protocol Used
  - Pre-conditioning
  - Intermediate-conditioning
  - Direction of Sweep

**Oxide Coverage**
Nissan Abstracts on Pt - Oxides : This meeting

214th Meeting of the Electrochemical Society
Honolulu, HI, 2008

Abstract 914
The Influence of Pt-oxide Coverage on the ORR Reaction Order in PEMFCs
M. Uchimura and S. Kocha

Abstract 919
MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components.
Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara

Abstract 1036
Simultaneous Electrochemical Measurement of ORR Kinetics and Pt Oxide Formation/Reduction
S. Sugawara, K. Tsujita, S. S. Kocha, K. Shinohara, S. Mitsushima and K. Ota,
Schematic of Measurement Protocols

Cell Temp. 80 °C, RH 100 %, P_{O2} : ~ 70 kPa
ORR Activity - Tafel Plots

Benchmarking data from different laboratories is difficult
ORR Activity – Modeling

Importance of Pt Oxide Film on ORR Kinetics


\[ i = nFKC_{O_2}(1 - \theta)\exp\left(-\frac{\beta F \eta}{RT}\right)\exp\left(-\frac{\gamma r \theta}{RT}\right) \]

Adsorbed oxygen species can

1. block the adsorption of O\textsubscript{2} on active Pt sites.
2. alter the adsorption energy of reaction intermediates.

Abstract 919

(214th Meeting of the Electrochemical Society, Honolulu, HI, 2008)

MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components.

Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara

Effect of oxide on activity was included and fitted to MEA ORR results.
Abstract 919
MEA Performance Modeling for Breakdown of Catalyst Layer Polarization Components, Y. Suzuki, S. Sugawara, N. Horibe, S. Kocha and K. Shinohara
Effect of RH

The key parameters that need to be measured to characterize high temperature/low RH membranes using MEAs in subscale fuel cells are the following:

- Catalyst Activity
- Membrane Resistance
- Catalyst Layer Resistance
Effect of RH: Activity

Kinetic reaction order:  < 1
ECA : Small effect
Tafel : Higher at lower RH
Activity: decreases at low RH below 50%

“Effect of Elevated Temperature and Reduced RH on ORR Kinetics for PEM Fuel Cells”
Effect of RH – IV Performance, HFR

HFR increases and performance decreases as RH decreases.
Ionomer resistance in the catalyst layer increases at lower RH.
Current Status - PEMFC
Current Status – Improved Stacks

*MEA (Membrane Electrode Assembly):* Double the power density is achieved through improved conductivity of the electrolyte layer within the MEA, where the main chemical reaction occurs, coupled with a more densely-packed cell structure.

*Cell Structure:* A more densely-packed cell structure is achieved through the replacement of the carbon separator with a new thin metal separator. The separator functions to break down the hydrogen, oxygen and cooling water necessary for the chemical reaction. A specific coating applied to the separator helps improve conductivity and prevents chemical corrosion, leading to increased efficiency and durability throughout the fuel cell stack’s life-cycle.

*Electrode:* Higher durability electrode material results in a 50% reduction of the platinum required compared to the previous generation. This in turn, provides a significant breakthrough in the cost of these components.

*Stack size and cost:* The combined improvements in the cell result in double the power density, which enables a downsizing of the fuel cell stack size by one-third and significant cost reduction, without sacrificing performance. Compared to the previous generation, the new generation stack’s power output is increased 1.4 times from 90kW to 130kW, which can power larger vehicles. Stack size is reduced by 25% to 68L from 90L, which allows for improved packaging flexibility.

Need further improvements in terms of a HTM-MEA that operates at high T and low RH to achieve PEMFC system cost targets.

Not Enough!
Overview of Requirements & Testing
The Fuel Cell Commercialization Conference of Japan (FCCJ) has worked with three automobile manufacturers in Japan to define the target performance, durability, and cost of fuel cells for transportation application, and in January 2007 produced a booklet describing them. This article provides an overview of these target values and highlights the durability parameters specifically required in the automotive application in relation to the current knowledge of degradation mechanisms of fuel cells. On the basis of this information, FCCJ has proposed a methodology for testing membrane-electrode assemblies (MEAs) as an approach to the evaluation of materials for the two most important components: electrolyte membranes and electrode catalysts.
### Operating Environment & Target Performance

#### Table 1. Expected MEA (membrane-electrode assembly) operating environment[1]

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>Cell operating temperature (includes start-up) (coolant outlet temperature)</td>
<td>−30 to 90 °C</td>
<td>−30 to 100 °C</td>
<td>−40 to &lt;120 °C</td>
</tr>
<tr>
<td>Operation condition</td>
<td>2</td>
<td>Operation gas inlet: lower limit of RH</td>
<td>40%</td>
<td>30%</td>
<td>Nonhumidified</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Operating gas outlet pressure (atm&lt;sub&gt;abs.&lt;/sub&gt;)</td>
<td>1.4</td>
<td>1.2</td>
<td>~1.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Operation gas stoichiometry</td>
<td>Air</td>
<td>1.5</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
<td>1.3</td>
<td>~1.0 (no recirculation)</td>
</tr>
</tbody>
</table>

#### Table 2. Electrolytic membrane target performance[1]

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation function</td>
<td>1</td>
<td>Membrane resistance (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>&lt;0.15</td>
<td>&lt;0.10</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low temperature region&lt;sup&gt;a&lt;/sup&gt; −20 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>High temperature region</td>
<td>90 °C</td>
<td>100 °C</td>
<td>120 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High humidity (95% RH)</td>
<td>&lt;0.0125</td>
<td>&lt;0.0125</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low humidity (30% RH)</td>
<td>&lt;0.08</td>
<td>&lt;0.05</td>
<td>&lt;0.0125</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Gas permeability at 80 °C, 95% RH (cm&lt;sup&gt;3&lt;/sup&gt;/(cm&lt;sup&gt;2&lt;/sup&gt; s kPa))</td>
<td>Oxygen</td>
<td>(1–9) × 10&lt;sup&gt;−8&lt;/sup&gt;</td>
<td>(1–9) × 10&lt;sup&gt;−9&lt;/sup&gt;</td>
</tr>
<tr>
<td>Structural function</td>
<td>3</td>
<td>Glass transition temperature (softening point)</td>
<td>&gt;130 °C</td>
<td>&gt;140 °C</td>
<td>&gt;160 °C</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Volumetric swelling rate at 100 °C boiling of pure water</td>
<td>Measure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> The samples should be prepared as follows; first, well humidified in the room temperature, then lowering the temperature to −20 °C while keeping the samples in sealed condition.
## Membrane Durability

### Table 3. Electrolytic membrane durability

<table>
<thead>
<tr>
<th>Category</th>
<th>No.</th>
<th>Test item</th>
<th>Evaluation item</th>
<th>2010</th>
<th>2015–2020</th>
<th>2020–</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Remaining IEC</td>
<td>&gt;90%</td>
<td>&gt;95%</td>
<td>&gt;95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Remaining ion conductivity</td>
<td>&gt;90%</td>
<td>&gt;95%</td>
<td>&gt;95%</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Hot water tolerance</td>
<td>Remaining tensile strength and strain</td>
<td>&gt;90%</td>
<td>&gt;95%</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>Material stability</td>
<td></td>
<td></td>
<td>Ion dissolution (F⁻, SO₄²⁻)</td>
<td>Measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Assumed remaining rates after 1000 h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Chemical tolerance</td>
<td>H₂O₂ gas exposure test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Freeze tolerance</td>
<td>Freeze/thaw cyclic test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>–30 to 80°C, dry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structural stability</td>
<td>4</td>
<td>Moisture tolerance</td>
<td>Humidity cycle test 0</td>
<td>Gas leak (breakage)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(dry) to 100% RH, at 80°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Creep tolerance</td>
<td>Compressive creep test 95°C</td>
<td>Measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>in distilled water/95% RH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tensile creep test</td>
<td></td>
<td></td>
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</tbody>
</table>

### Table 4. Target cost of electrolytic membrane

<table>
<thead>
<tr>
<th>No.</th>
<th>Production level</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 000 000 m²/year</td>
<td>$10/m²</td>
</tr>
</tbody>
</table>
**Membrane Durability - Map**

<table>
<thead>
<tr>
<th>Part</th>
<th>Degradation</th>
<th>Estimated factor</th>
<th>Evaluation mode (measured items)</th>
<th>Necessary mechanism/technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Gas leak by membrane break</td>
<td>Mechanical stress by expand/shrink</td>
<td>Dry/wet cycle (gas leak)</td>
<td>Crack formation/propagation mechanism</td>
</tr>
<tr>
<td></td>
<td>Crossover increase by membrane thinning</td>
<td>Electrolyte decomposition by $\text{H}_2\text{O}_2$, OH radical (promotion by impurity) and Pt band</td>
<td>OCV hold (hydrogen crossover)</td>
<td>Radical formation mechanism, electrolyte decomposition process, and suppression/chemical and thermally stable polymer structure</td>
</tr>
<tr>
<td></td>
<td>Proton transport decrease by sulfonate acid drop</td>
<td>Thermal decomposition by local heat spot</td>
<td>High temperature and low humidity operation measure sulfonic acid</td>
<td></td>
</tr>
<tr>
<td>Ionomer</td>
<td>ECA reduction by larger Pt diameter</td>
<td>Electrochemical dissolution and deposition</td>
<td>Potential cycle (0.6/0.9 V) (ECA)</td>
<td>Mechanism of Pt dissolution/deposition, countermeasure</td>
</tr>
<tr>
<td></td>
<td>ECA reduction by Pt loss</td>
<td>Electrochemical dissolution</td>
<td>Potential cycle (0.9/1.3 V) (ECA)</td>
<td>Design criteria for Pt alloy</td>
</tr>
<tr>
<td></td>
<td>ECA reduction by catalyst migration</td>
<td>Carbon support corrosion by high potential</td>
<td>High fuel utilization operation (ECA)</td>
<td>Durable catalyst support (carbon alternate)</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Activation decrease due to catalyst poisoning</td>
<td>Impurities in air or fuel</td>
<td>Impurity gas test ($\text{H}_2/\text{O}_2$, overpotential)</td>
<td>Possible recovery process on FCV system</td>
</tr>
<tr>
<td></td>
<td>Activation decrease by alloy dissolution</td>
<td>Electrochemical dissolution</td>
<td>Potential cycle (0.6/0.9 V) ($\text{H}_2/\text{O}_2$, Overpotential)</td>
<td>Design criteria for Pt alloy</td>
</tr>
</tbody>
</table>

Figure 2. Automotive fuel cell MEA degradation map.\(^{[1]}\)
END