Improving durability of PEMFC by reducing the impact of operating conditions on electrode degradation

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Optimization of Low Loading Electrode

- Down-select MEA components such as catalyst, GDL, membrane etc.
- 2-3 rounds of design of experiments to optimize electrode performance to generate SOA MEA

<table>
<thead>
<tr>
<th>Item</th>
<th>Units</th>
<th>2020 Targets</th>
<th>2020 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$/kW_{net}</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Q/ΔT</td>
<td>kW/°C</td>
<td>1.45</td>
<td>1.45 1.94</td>
</tr>
<tr>
<td>V at 0.8 V</td>
<td>mA/cm²</td>
<td>300</td>
<td>0.44 0.30</td>
</tr>
<tr>
<td>PD at 670 mV</td>
<td>mW/cm²</td>
<td>1000</td>
<td>1000 1275</td>
</tr>
<tr>
<td>Durability</td>
<td>Hours @ &lt; 10% V loss</td>
<td>5000</td>
<td>*5000  *2000</td>
</tr>
<tr>
<td>Mass activity</td>
<td>A/mg_{PGM} at 0.9 V</td>
<td>&gt; 0.44</td>
<td>0.65 0.65</td>
</tr>
<tr>
<td>PGM Content</td>
<td>g/kW rated mg/cm²_{MEA}</td>
<td>0.125</td>
<td>0.10 0.125</td>
</tr>
</tbody>
</table>

**Electrode Durability**: Conduct voltage cycling study on state-of-art MEA and map the operating conditions to minimize power degradation rate.
Multi-factor Design of Experiments
Test Protocol – 20 Run DoE

Test factors

<table>
<thead>
<tr>
<th>Cell Temp (°C)</th>
<th>RH (%)</th>
<th>Upper Potential (mV)</th>
<th>Upper Potential Hold time (s)</th>
<th>Test Stand</th>
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<tbody>
<tr>
<td>55</td>
<td>40</td>
<td>850</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>75</td>
<td>70</td>
<td>900</td>
<td>3</td>
<td>B</td>
</tr>
<tr>
<td>95</td>
<td>100</td>
<td>950</td>
<td>5</td>
<td>C</td>
</tr>
</tbody>
</table>

Constant Test Parameters:

- Lower Potential: 0.6 V
- Lower Potential Hold Time: 1 sec
- Ramp rate: 0.35 V/s
- Environment: H₂/N₂

- 50cm² MEA
- Selection of MEAs with Pt loading within +/- 2%
## Test Protocol

<table>
<thead>
<tr>
<th>Run Order</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Upper Potential (V)</th>
<th>Hold Time (s)</th>
<th>Stand</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95</td>
<td>100</td>
<td>0.85</td>
<td>1</td>
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<tr>
<td>2</td>
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<td>40</td>
<td>0.95</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>95</td>
<td>40</td>
<td>0.95</td>
<td>5</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>55</td>
<td>100</td>
<td>0.85</td>
<td>5</td>
<td>A</td>
</tr>
<tr>
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<td>75</td>
<td>70</td>
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<td>3</td>
<td>A</td>
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<tr>
<td>6</td>
<td>55</td>
<td>100</td>
<td>0.85</td>
<td>1</td>
<td>B</td>
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<tr>
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<td>100</td>
<td>0.85</td>
<td>5</td>
<td>B</td>
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<tr>
<td>8</td>
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<td>0.90</td>
<td>3</td>
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<tr>
<td>9</td>
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<td>0.95</td>
<td>1</td>
<td>B</td>
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<tr>
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<tr>
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<td>0.85</td>
<td>1</td>
<td>C</td>
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<tr>
<td>12</td>
<td>95</td>
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<td>0.95</td>
<td>5</td>
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<tr>
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<td>70</td>
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<td>3</td>
<td>C</td>
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<td>100</td>
<td>0.95</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>15</td>
<td>55</td>
<td>40</td>
<td>0.85</td>
<td>5</td>
<td>C</td>
</tr>
<tr>
<td>16</td>
<td>55</td>
<td>100</td>
<td>0.95</td>
<td>5</td>
<td>D</td>
</tr>
<tr>
<td>17</td>
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<td>0.85</td>
<td>5</td>
<td>D</td>
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<tr>
<td>18</td>
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<td>40</td>
<td>0.85</td>
<td>1</td>
<td>D</td>
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<td>100</td>
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<td>1</td>
<td>D</td>
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<tr>
<td>20</td>
<td>75</td>
<td>70</td>
<td>0.90</td>
<td>3</td>
<td>D</td>
</tr>
</tbody>
</table>

**Individual Test Parameters**

**20 Voltage Cycle Waveform used in DOE**
Test Protocol

**Low-P Dry:** 80 °C, 32% RH, 150 kPa_{abs}

**Low-P Wet:** 80 °C, 100% RH, 170 kPa_{abs}

**High-P Wet:** 93.5 °C, 100% RH, 250 kPa_{abs}

30k x2 (60k total)

20 Voltage Cycle Waveform used in DOE
• BOL test-to-test variations within ± 4 mV in High-P-Wet conditions
• Impact of Test stand variations on experimental results is expected to be small
Clear trend between ECA Loss and Voltage Loss is observed
- Benign conditions show very little ECA, mass activity, and performance loss
- No data for 3333 (last case) after 60k cycles due to severe performance loss

Note:
- Labels are ordered as T, RH, UP, and HT (reading bottom to top on X-axis)
- 1, 2, and 3 represent the test factor level
• Clear trend between ECA Loss and Voltage Loss is observed
• Benign conditions show very little ECA, mass activity, and performance loss

Note:
• Labels are ordered as T, RH, UP and HT (reading bottom to top on X-axis)
• 1, 2 and 3 represent the test factor level
ECA vs Voltage Loss

Vertical lines represent 10% voltage loss from BOL
ECA vs Voltage Loss

- Vertical lines represent 10% voltage loss from BOL
- ~20% ECA Loss at Low Pressure Conditions
- ~50% ECA Loss at High Pressure Conditions
Ex-situ Post-Mortem Analysis
Material Analysis

- Largely minimal changes from BOL in benign to moderate conditions
- Significant Pt movement towards membrane under severe operating conditions

- Most samples show small variation in mean particle size diameter
- Samples with large performance losses show significant bimodal distribution
Statistical Model
Statistical Model

- Half-normal plot identifying the significant test factors that impact ECA loss (after 60k cycles)
- Factors with higher score and coefficients represent the significant factors
- **UP, RH and T** along with their interactions RH:UP and T:RH were found to be the statistically significant factors

**Statistical Model:**

- ECA Loss (m$^2$/gPt) = (-0.69789 - 0.0138*T - 0.26655*RH + 2.171011*UP + 0.000649*(T*RH) + 0.277891*(RH*UP))$^2$
- V Loss (mV/kCycle) = exp( 2.649229 - 0.01459*T - 0.21813*RH - 4.18264*UP + 0.000394*T*RH + 0.236053*RH*UP) – 0.5
Predicted Operating conditions to limit losses

- Based on both ECA Loss vs. V Loss data from this DOE and performance model.
- To achieve target 10% V Loss or lower (@ 150 Kpa condition), less than 20% ECA Loss should be maintained at end of test (EOT).
- For 10% VLoss @ 250 Kpa condition, less than ~ 55% ECA loss should be maintained at EOT.
Degradation Model
PtO Model

- Single equations to calculate the rate of change in PtO coverage, no fast and slow slope
- The model coefficients are solved for based on PtCo electrode data
- Addition of equation for build up of PtO₂

\[
\text{PtO} + \text{H}_2\text{O} \leftrightarrow \text{PtO} + 2\text{H}^+ + 2\text{e}^- \quad (1)
\]
\[
i_{\text{PtO}} = k_{\text{PtO}} \left[ (1 - \theta_{\text{PtO}} - \theta_{\text{PtO}_2}) \text{RH} e^{\frac{23210\alpha_1}{T}(E - E^0(\text{PtO}))} e^{\frac{\omega_{\text{PtO}}\theta_{\text{PtO}}}{RT}} - \theta_{\text{PtO}} c_{H^+}^0 e^{\frac{23210(1-\alpha_1)}{T}(E - E^0(\text{PtO}))} e^{\frac{-\omega_{\text{PtO}}\theta_{\text{PtO}}}{RT}} \right]
\]
\[
\text{PtO} + \text{H}_2\text{O} \leftrightarrow \text{PtO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (2)
\]
\[
i_{\text{PtO}_2} = k_{\text{PtO}_2} \left[ \theta_{\text{PtO}} \text{RH} e^{\frac{23210\alpha_2}{T}(E - E^0(\text{PtO}_2))} e^{\frac{\omega_{\text{PtO}}\theta_{\text{PtO}_2}}{RT}} - \theta_{\text{PtO}_2} c_{H^+}^0 e^{\frac{23210(1-\alpha_2)}{T}(E - E^0(\text{PtO}_2))} e^{\frac{-\omega_{\text{PtO}}\theta_{\text{PtO}_2}}{RT}} \right]
\]

Parameters that changes with temperature

- \( E^0(\text{PtO}) = E^{00}(\text{PtO}) + \frac{\Delta E}{\Delta T} (T - 353) \)
- \( k_{\text{PtO}} = k_{\text{PtO}}^0 e^{\frac{\Delta H_{\text{PtO}}}{T}} \left( \frac{1}{298} \right) \)
- \( k_{\text{PtO}_2} = k_{\text{PtO}_2}^0 e^{\frac{\Delta H_{\text{PtO}_2}}{T}} \left( \frac{1}{298} \right) \)

Parameters that changes with RH

\[
C_{H^+} = \frac{1}{558.4 + 18 \lambda}
\]

\[
X_{\text{PtO}} = \theta_{\text{PtO}} + \theta_{\text{PtO}_2}
\]

Equations to get \( \theta_{\text{PtO}} \) and \( \theta_{\text{PtO}_2} \)

\[
\theta_{\text{PtO}}^{\text{new}} = \theta_{\text{PtO}}^{\text{old}} + \Delta \frac{i_{\text{PtO}} - i_{\text{PtO}_2}}{0.9942 A_{\text{Pt}} L_{\text{Pt}}}
\]
\[
\theta_{\text{PtO}_2}^{\text{new}} = \theta_{\text{PtO}_2}^{\text{old}} + \Delta \frac{i_{\text{PtO}_2}}{0.9942 A_{\text{Pt}} L_{\text{Pt}}}
\]

Srikanth Arisetty et. Al. 2015 ECS Trans. 69 273
Oxide based corrections for ECA

- Damage factor (DamECA(t)) for ECA is calculated as a function of oxide current (i_{PtO/PtO2}) and oxide coverage (θ_{PtO/PtO2})
- ECA loss can be calculated from Damage factor
- Temperature and RH are intrinsically integrated into the oxide coverage and oxide current
- Coefficients are calculated by fitting model to the 20-run doe data

\[
DamECA(t) = \int_{t=0}^{T} (i_{PtO}^{n2} \theta_{PtO}^{n1} + i_{PtO2}^{n4} \theta_{PtO2}^{n3}) dt
\]

ECA:

\[
A_{Pt}(t) = A_{Pt}(t = 0) e^{-k_{z}DamECA(t)}
\]

Damage Factor:

\[
ECA predictions Steps:
\]

- Drive cycle simulations \(\rightarrow i_{PtO/PtO2}\) and \(θ_{PtO/PtO2}\)
- Calculate Damage factor
- Calculate ECA loss over time

Srikanth Arisetty et al 2015 ECS Trans. 69 273
Degradation Model

<table>
<thead>
<tr>
<th>UPL</th>
<th>Temperature</th>
<th>RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>0.875</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>0.85</td>
<td>65</td>
<td>40</td>
</tr>
<tr>
<td>0.825</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Using previous approach, 60-run full parametric DOE was run
- UPL and Temperature limits were imposed for the entire cycle
- RH values were varied only for the 1st part of the cycle (wet), while the 2nd part was kept at 40%RH for all cycles

Table P.7, https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_myrdd_fuel_cells.pdf
Degradation Model

<table>
<thead>
<tr>
<th>UPL</th>
<th>Temperature</th>
<th>RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
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</tr>
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<td>0.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Using previous approach, 60-run parametric DOE simulations were run
- UPL and Temperature limits were imposed for the entire cycle
- RH values were varied only for the 1st part of the cycle (wet), while the 2nd part was kept at 40%RH for all cycles

Table P.7, https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_myrdd_fuel_cells.pdf
Degradation Model - Results

• Contour maps show the estimated ECA ($m^2/gPt$) after 5000 hrs
• Minimum ECA limited to 14 $m^2/gPt$
Contour maps show the estimated ECA ($\text{m}^2/\text{gPt}$) after 5000 hrs.

- Minimum ECA limited to 14 $\text{m}^2/\text{gPt}$
- Highlighted areas represent optimal zone of operation for fixed UPL.
Drive Cycle Testing
### Drive Cycle Tests (H₂-Air)

<table>
<thead>
<tr>
<th>Test</th>
<th>Max Cycle Potential (V)</th>
<th>Max. Temperature (°C)</th>
<th>Max. RH (%)</th>
<th>Run Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Drive Cycle</td>
<td>-</td>
<td>85</td>
<td>93</td>
<td>1000</td>
</tr>
<tr>
<td>Drive Cycle 1</td>
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<td>85</td>
<td>93</td>
<td>1400*</td>
</tr>
<tr>
<td>Drive Cycle 2</td>
<td>0.85</td>
<td>85</td>
<td>93</td>
<td>1000</td>
</tr>
<tr>
<td>Drive Cycle 3</td>
<td>0.85</td>
<td>75</td>
<td>70</td>
<td>2800</td>
</tr>
</tbody>
</table>

- 4 drive cycles (1 DOE drive cycle and 3 modified drive cycles) were selected and ran on single cell with 50cm² MEA
- Drive cycle 3 was selected based on projections from the Pt-oxide based model
- Drive cycle 1 (0.90V) limit failed after approx. 1400 hours
- Drive cycle 4 continues to run with less than 5% performance loss in High-P Wet conditions
Summary

- Multifactor design of experiments were used to map the impact of operating conditions.
- Operation conditions that can provide reduced ECA Losses were demonstrated.
- Statistical model and Pt-Oxide based damage model were developed to predict ECA and voltage losses.
- Single cell drive cycle tests validate that significant improvements in durability of electrodes can be achieved by optimal selection of operating conditions.
Acknowledgement

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Thank You
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