Durable Membrane Electrode Assemblies for Proton Exchange Membrane Electrolyzer Systems Operating at High Current Densities

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Outline

• Cost reduction of the PEM electrolyzer stack

• MEA tests in a 20 kW_{el} PEM electrolyzer system

• Protocol of measurements

• Benchmark MEA with Ir-black catalyst

• Electromechanical analysis of degradation mechanisms

• *Post mortem* analysis of the MEAs and water resin

• Summary
How to reduce the stack cost?

- Substitute titanium based components (bipolar plates, current collectors, PTLs, GDLs) by coated stainless steel, steel, copper or aluminium.
- Use thin hydrocarbon based membranes and highly conductive non precious metal coatings. Reduce ohmic losses.
- Develop more efficient anode and cathode catalysts with low loading and improved stability. Use ceramic supports or increase activity surface area ratio.
- **Operate at high current densities.** Extend operation range from 2 (nominal) to 4 A cm$^{-2}$. 

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*Study on development of water electrolysis in the EU. Final Report. E4tech Fuel Cells and Hydrogen Joint Undertaking; 2014*
Project on degradation phenomena in PEM electrolyzer systems operating at high current densities

<table>
<thead>
<tr>
<th>Partner</th>
<th>Tasks in the project</th>
</tr>
</thead>
</table>
| DLR Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft | - Testing of MEAs with different catalysts in a 12 kW_{el} PEM electrolyzer system  
- Assessment of results and post-mortem analysis |
| HYDROGENICS | - Construction a 12 kW_{el} PEM electrolyzer system  
- Stack assembly and evaluation of the degradation tests |

Rainbow stack with different MEA configuration

8 Cell - 120 cm² – 20 kW_{el} PEM electrolyzer stack

12 kW_{el} PEM electrolyzer

Goal of the project: Gain knowledge about degradation mechanism of PEM electrolyzer MEAs
Protocol of measurements

Stack 1: Different catalyst loadings

Stack 2: MEAs from different providers

- There is an urgent need for accelerated stress test (AST) protocols for PEM electrolyzers
- Degradation caused by operation time, current densities, voltage, temperature, water quality, etc. is not well understood
Benchmark PEM electrolyzer anode

- Half cell measurements: OER activity of Ir-black (Umicore) is 3x higher than thermally treated IrO₂ (at 1.48V, 25 °C)
- MEAs with IrO₂ (thermally treated) show lower performance compared to those with Ir-black
- Half cell and single cell measurements correlates well with the PEM electrolyzer results
- Ir-black can be considered as benchmark anode in PEM electrolyzers

<table>
<thead>
<tr>
<th>Company</th>
<th>Anode (mg cm⁻²)</th>
<th>Membrane</th>
<th>Cathode (mg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wuhan WUT</td>
<td>2</td>
<td>N115</td>
<td>0.8</td>
</tr>
<tr>
<td>IRD</td>
<td>2.3</td>
<td>N115</td>
<td>0.5</td>
</tr>
<tr>
<td>FuelCellsEtc</td>
<td>3</td>
<td>N115</td>
<td>3</td>
</tr>
<tr>
<td>E500 (Ir-black)</td>
<td>1</td>
<td>N115</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Electrochemical impedance spectroscopy (EIS)

- EIS was performed before and after 500 h (T1) at 2 A cm², and before and after 250 h (T2) at 4 A cm²
- MEA with Ir-black (1 mg cm⁻²) showed the lowest activation and ohmic resistances
- EIS results correlate well with $E_{\text{cell}} - j$ characteristics
- At high current densities the ohmic resistance has the largest impact
- No mass transport was observed

Electrochimica Acta, 2016, in press
Evolution of $E_{\text{cell}}$ through the time and current density

- Difficult analysis of degradation rate because of temperature fluctuation.
  At $j = 2 \text{ A cm}^{-2}$, $\Delta T = \pm 1.5 \degree \text{C}$ caused by the addition of fresh water into the stack.
  At $j = 4 \text{ A cm}^{-2}$ $\Delta T = \pm 4 \degree \text{C}$ caused by the periodic turn on-off of the fan that cools down the entire system enclosure.
- No increase in $E_{\text{cell}}$ after $4 \text{ A cm}^{-2}$ test for all cells
- No increase of $E_{\text{cell}}$ over time for all cells

_Dr. [Authors Name], Electrochimica Acta, 2016, in press_
Determination of ohmic losses from EIS

- Temperature of the stack was strictly controlled at $29 \pm 0.5 \, ^\circ C$ by shutting off completely the H$_2$-generator. An external pump with low flow rates was used.
- The EIS were simulated using an equivalent circuit.
- The EIS spectra at a given current density changed over time and when the current was increased.
- The cell resistance ($\eta_{Ohm}$) and kinetics ($R_{act}$) were analysed.

Electrochimica Acta, 2016, in press
Degradation mechanism from EIS analysis

- The degradation was analyzed through changes in ohmic loses and potential over time.
- The kinetic resistance ($R_{\text{act}}$) increased over time.
- The ohmic resistance ($\eta_{\text{Ohm}}$) decreased at high current densities.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Change at 0.33 A cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{cell}}$</td>
<td>↑ +10μV/h</td>
</tr>
<tr>
<td>$\eta_{\text{Ohm}}$</td>
<td>↓ -2μV/h</td>
</tr>
<tr>
<td>$\eta_{\text{Ox}}$</td>
<td>→</td>
</tr>
<tr>
<td>$\eta_{\text{Act}}$</td>
<td>↑ +13μV/h</td>
</tr>
</tbody>
</table>

Electrochimica Acta, 2016, in press
Degradation analysis and XPS on DI water resin

- Nafion degradation:
  - Presence of F in the DI water resin

- Degradation of intrinsic properties:
  - Significant decrease of exchange current density during time of measurement.
  - Deactivation of the anode
  - Presence of Ir in the DI water resin

### Table: \( T / ^\circ C \) | \( \beta / mV \text{dec}^{-1} \) | \( j_o / 10^{-9} A \text{mg}_{\text{Ir}}^{-1} \)
---|---|---
Ir-Black (Umicore) | 25 | 43.1 | 2.5
(Half Cell, kinetic analysis) | 30 | 43.1 | 3
| 40 | 43.2 | 5.8
| 50 | 43.6 | 12.0
| 60 | 43.9 | 22.8
| 70 | 44.6 | 46.2
Before 2A/cm\(^2\) | 30 | 44.3 | 18.1
After 2A/cm\(^2\) | 30 | 41.1 | 3.5
After 4A/cm\(^2\) | 30 | 41.1 | 2.8

### Table: Elemental Analysis

<table>
<thead>
<tr>
<th>Elem.</th>
<th>Fresh [wt%]</th>
<th>Used [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.0</td>
<td>2.6</td>
</tr>
<tr>
<td>F</td>
<td>0.0</td>
<td>2.9</td>
</tr>
<tr>
<td>O</td>
<td>10.9</td>
<td>21.4</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0</td>
<td>2.7</td>
</tr>
<tr>
<td>N</td>
<td>2.4</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>79.6</td>
<td>52.9</td>
</tr>
<tr>
<td>S</td>
<td>7.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Si</td>
<td>0.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Ir</td>
<td>0.0</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Post mortem analysis of the MEAs

- No decrease of membrane thickness was observed from cross-section SEM images.
- Release and diffusion of Ir catalyst into the membrane.
- After operation, the conductive area of the anode increased by approximately 50% while the conductive area of the cathode remained the same.
- Surface conductivity of the catalyst layer changed due to ionomer loss.

**SEM**

**AFM**

<table>
<thead>
<tr>
<th>Conductive area (%)</th>
<th>Average Thickness / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>unused</td>
<td>Cell 8 (used)</td>
</tr>
<tr>
<td>unused</td>
<td>Cell 8 (used)</td>
</tr>
<tr>
<td>Anode</td>
<td>30 ± 4</td>
</tr>
<tr>
<td>Cathode</td>
<td>37 ± 2</td>
</tr>
<tr>
<td>Membrane</td>
<td>121.5 ± 1.5</td>
</tr>
</tbody>
</table>
Summary

• Investment cost can be reduced by operating the PEM electrolyzer at high current densities

• The lowest Ir catalyst loading (1 mg cm$^{-2}$) showed the lowest $E_{cell}$ at any current density.

• Aging of the PEM electrolyzer MEAs depends on current density and operation time, but the associated degradation mechanisms are different in each case.

• EIS shows a progressive decrease in the specific exchange current, while the ohmic resistance decreases when doubling the nominal current density.

• *Post mortem* analysis of the MEAs (SEM and AFM) and water resin (XPS) revealed a current dependent loss of ionomer and catalyst material in the anode, which resulted in an unexpected enhancement of cell performance at high current densities.

• A first step towards developing an accelerated stress test protocol (AST) for PEM electrolyzers has been given
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DLR
Grand Challenges in Energy Conversion and Storage 2
Tuesday, 31 May 2016: 11:30 a.m.
Aqua Salon F (Hilton San Diego Bayfront)

Novel Components for PEM Electrolysis: Status and Challenges
A. S. Gago, P. Lettenmeier, L. Wang, S. Kolb, F. Burggraf, and K. A. Friedrich

Thank you for your attention
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