First International Workshop
Durability and Degradation Issues in PEM Electrolysis Cells and its Components

Degradation issues in NEXPEL and NOVEL

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Outline

• Background
  • Why are we here?
• NEXPEL and NOVEL
  • A brief introduction to PEM degradation activities
• Degradation mechanisms in PEM electrolysers
  • Membranes
  • Catalysts
• First steps in developing AST protocols for PEM electrolysers
• Summary
Progress in efficiency and durability (PEM)


Challenges

- Increased efficiency
  - Higher temperature
- Lower capital costs
  - Reduction of PGM loadings
  - Thinner membranes
  - Simpler systems (water purification, etc.)
- Intermittent operation
  - Temperature and pressure cycling
- High (differential) pressures

Risk of degradation increases significantly
15 years earlier:

Minimal loss in performance after over 3000 h of stack operation

![Graph showing cell potential over operation time.](image)

Fig. 17. The individual performance of the four cells in a Nafion 117 membrane based stack containing low platinum loading Type A cathodes (0.5 mg Pt/cm², 40 w/o Pt/XC72R) and Type B anodes (0.3 mg Pt/cm², 20 w/o Pt/10 w/o Ru/ XC72R). The stack is operating at 538 mA/cm² on simulated reformate/air (with short interruptions to test the performance on H₂) at 5.4/5.4 atm and 1.3/1.8 stoichiometry with a 2% air bleed into the reformate.

Number of hits in Web of Knowledge on the topics "PEM fuel cell degradation" or "degradation of PEM fuel cells" vs "PEM electrolysis degradation" or "degradation of PEM electrolyzer"
NEXPEL main objectives:

Develop and demonstrate a PEM water electrolyser integrated with Renewable Energy Sources (RES):

75% Efficiency (LHV), $\text{H}_2$ production cost $\sim 5,000 / \text{Nm}^3\text{h}^{-1}$, target lifetime of 40,000 h

www.nexpel.eu
Goals of the Novel project:

1. Reduce capital costs of main stack components
2. Increased electrolyser performance with;
   - No impact on lifetime (> 40,000h operation)
3. Design of cost efficient systems with reduced impact on electrolyser lifetime
4. Improved understanding of degradation mechanisms in PEM electrolysers
Todays topic

Degradation mechanisms and AST protocols for
Membranes
Catalysts
Membrane - Mechanical degradation

• Perforations, pinholes, cracks or tears

• Causes
  – In plane tension/compression due local drying/swelling
  – Inadequate heat or gas removal
  – Non-uniform compression / current density
  – Membrane defects from manufacturing or improper MEA assembly

• Often leads to early life failure (catastrophic?)

Fukuoka electrolyser accident
Membrane - Chemical Degradation

- Peroxide formation "fingerprint" for chemical degradation of ionomer

\[
\begin{align*}
\text{H}_2 & \rightarrow \text{H}_2\text{O}_2 \\
\text{O}_2 & \rightarrow \text{H}_2\text{O}_2,_{ads} \rightarrow \text{H}_2\text{O}_2
\end{align*}
\]

Gas crossover & chemical reaction

\[
\text{H}_2\text{O}_2
\]

• \( \cdot \text{OH} \)
• \( \cdot \text{OOH} \)

Oxygen evolution

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad \text{E}^{\text{rev}}=1.776 \text{ V}
\end{align*}
\]
Membrane chemical degradation- Earlier observations

AST protocol for membrane chemical stability

- PEM Fuel cells: OCV hold
- PEM Electrolysers: ?

### Table 3
**MEA Chemical Stability and Metrics**
Table revised December 10, 2009

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Steady state OCV, single cell 25-50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total time</td>
<td>500 h</td>
</tr>
<tr>
<td>Temperature</td>
<td>90°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Anode/Cathode 30/30%</td>
</tr>
<tr>
<td>Fuel/Oxidant</td>
<td>Hydrogen/Air at stoics of 10/10 at 0.2 A/cm² equivalent flow</td>
</tr>
<tr>
<td>Pressure, Inlet kPa abs (bara)</td>
<td>Anode 150 (1.5), Cathode 150 (1.5)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metric</th>
<th>Frequency</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>F release or equivalent for non-fluorine membranes</td>
<td>At least every 24 h</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Hydrogen Crossover (mA/cm²)*</td>
<td>Every 24 h</td>
<td>≤2 mA/cm²</td>
</tr>
<tr>
<td>OCV</td>
<td>Continuous</td>
<td>≤20% loss in OCV</td>
</tr>
<tr>
<td>High-frequency resistance</td>
<td>Every 24 h at 0.2 A/cm²</td>
<td>No target – for monitoring</td>
</tr>
<tr>
<td>Shorting resistance**</td>
<td>Every 24 h</td>
<td>&gt;1,000 ohm cm²</td>
</tr>
</tbody>
</table>

* Crossover current per USFCC “Single Cell Test Protocol” Section A3-2, electrochemical hydrogen crossover method.
** Measured at 0.5V applied potential, 80°C and 100% RH N₂/N₂. Compression to 20% strain on the GDL.

**USCAR FUEL CELL TECH TEAM**
**CELL COMPONENT ACCELERATED STRESS TEST PROTOCOLS FOR PEM FUEL CELLS, 2010**
PEM Fuel cells vs. PEM electrolysers

PEMFC

- H₂
- O₂
- H⁺
- H₂O
- H₂O₂
- Pt

PEMWE

- H₂
- O₂
- H⁺
- H₂O
- H₂O₂
- Pt?
Peroxide detection using µ-electrodes.

- Electrolyser operated at 25 °C, at current densities between 50 mA and 1.5 Acm⁻²
Peroxide detection using µ-electrodes.
Peroxide detection using μ-electrodes.

- Convective flux seems to outweigh peroxide diffusion above 1.2 Acm²
- Peroxide concentrations will be significant at positions close to the anode, even at high current densities.
Electrodes / Bipolar plates

- Catalyst dissolution and particle growth
- Ti support oxidation

- GDL and MPL degradation (carbon)
- Metal deposition (Fe, Co) on catalysts
Nanostructuring of Ir and Ru

Supported vs. unsupported Ir
Supported vs. unsupported Ru
AST – Potential hold vs. voltage cycling

1.55 V 5h

1.35-1.55 V, 10000 cycles, 1h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta E$ @ 1 mA mg$^{-1}$</th>
<th>$\Delta E$ @ 10 mA mg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Ir$<em>{0.7}$Ru$</em>{0.2}$Ta$_{0.1}$</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>Ir$<em>{0.8}$Ru$</em>{0.2}$</td>
<td>15</td>
<td>19</td>
</tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Ir$<em>{0.7}$Ru$</em>{0.2}$Ta$_{0.1}$</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>Ir$<em>{0.8}$Ru$</em>{0.2}$</td>
<td>15</td>
<td>18</td>
</tr>
</tbody>
</table>
AST – Potential hold vs. voltage cycling

![Graphs showing CVs before and after AST and the difference in CVs before and after degradation.]
In situ degradation protocols

- Current cycling at 80 °C
- Polarisation curve every 10 h
Long term test – TEM cross section analysis
Ir/ATO - Anode

• A significant part of the Ir catalyst particles has diffused into the membrane
• No diffusion of ATO support into the membrane
Pt/C - Cathode

The interface between the membrane and the Pt/C cathode layer is sharp without any diffusion of particles into the membrane.
Summary

• The move towards cost reduction and efficiency improvements of PEM electrolyser will probably lead to increased degradation

• A lot can be learned / transferred from PEM fuel cells
  – Methodology
  – Diagnostic tools

• However, some degradation mechanisms are different

• Common accelerated stress test protocols (AST) for PEM electrolyser components is needed
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