30,000 hours of PEMFC system operation at a chlor-alkali plant

Stayers: effect of feed contaminants

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Stationary PEM fuel cells with lifetimes beyond 5 years

**Goal:**
> 40,000 hours stationary operation lifetime of PEM fuel cell

**Motivation:**
lower replacement frequency PEMFC stacks over economic lifetime Power Plant → lower cost of ownership PEMFC Power Plant

Development & Commercialization:

- Membrane
- MEA
- Stack
- System integrators
- End users

Testing + modeling:
Research topics STAYERS project

<table>
<thead>
<tr>
<th>A</th>
<th>Components Investigated / Developed (I/D):</th>
<th>STAYERS</th>
<th>Presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>membrane</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>MEA</td>
<td>D</td>
<td>X</td>
</tr>
<tr>
<td>3</td>
<td>catalyst/electrode</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>GDL</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>cell plates</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>seals</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>BOP</td>
<td>I</td>
<td>X</td>
</tr>
</tbody>
</table>
Set up & conditions stack duration test at a chlor-alkali plant

- Tower of 2x6 stacks
- 75 cell/stack, 900 cells
- Avg output: 100 A / 600V: 60 kW
- Start: April 2007
- March 2013: Total hours to grid >33,000

Operation conditions favorable for durability:

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Power plant Delfzijl</td>
<td>0.5</td>
<td>3.3</td>
<td>2.4</td>
<td>65</td>
<td>85</td>
<td>85</td>
</tr>
</tbody>
</table>
System layout

Air Compression → Air Humidification → Fuel Cells → Air Exhaust → Hydrogen Vent

Coolant Recirculation

Hydrogen Humidification

Hydrogen Recirculation

DC/AC → Grid
System uptime over period September 2010 – January 2013

System uptime

Compare recent data: uptime 2013 = 97%
BOP very reliable!
Stack characteristics

T stack = 65 °; RH anode and cathode = 80%; P = 1 bara; Stoichiometry H₂/air = 1.25/2
MEA with low vs. high reversible decay
### Widespread lifetimes of various MEAs tested in Pem Power Plant

<table>
<thead>
<tr>
<th>MEA</th>
<th>Number of stacks tested</th>
<th>Typical lifetime (hrs before stack voltage has reached low voltage limit)</th>
<th>Linear cell voltage decay rate (μV/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>under 5k MEAs</td>
<td>63</td>
<td>&lt; 5,000</td>
<td>15 to 60</td>
</tr>
<tr>
<td>6k MEAs</td>
<td>2</td>
<td>6,000</td>
<td>11 ± 0.3</td>
</tr>
<tr>
<td>8k MEAs</td>
<td>9</td>
<td>8,000</td>
<td>6.2 ± 1.3</td>
</tr>
<tr>
<td>16k+ MEAs*</td>
<td>8</td>
<td>&gt; 16,000</td>
<td>2.5 ± 0.5</td>
</tr>
</tbody>
</table>
Cell voltage versus time for 8k MEAs
Nedstack’s XXL stacks using 16 k+ MEAs can operate for more than 20,000 hours.

Average cell voltage
mV at 120 A

March 2013: 20,000 hrs

Decay rate
3 μV/h
Conclusions – good news

1. System is in operation for > 33,000 hours without replacement of Balance of Plant Components

2. Fuel cell related downtime < 10% readily achievable

3. MEA and stack technology is capable of lasting > 20,000 hours
Conclusions - degradation

1. In the PEM Power Plant, conditions are relatively mild:
   - Stationary operation, no load cycles, no air/air starts
   - Gases are wet (80% RH at inlet)
   - Temperature is low (65 °C)

2. Still, many MEAs do not exceed 5,000 hours of operation

3. Reversible decay mainly linked to contaminants
   - Accumulation in recycle and long runtimes make even ppb levels of contaminants relevant

4. Irreversible decay linked to multiple causes:
   - Loss of cathode ECSA
   - Loss of water removal capability
   - Irreversible adsorption of contaminants
Contamination determined in air

<table>
<thead>
<tr>
<th></th>
<th>Air (Outside)</th>
<th>Air (Filter)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NOx</strong></td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>SO2</strong></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Ammonia</strong></td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td><strong>Hydrocarbons</strong></td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

Remarks:
- NOx difficult to remove
- SO2 also (partially) removed in humidifier/scrubber
SO2 determined in Rainbow-2

Cyclic voltamograms of two cells with different MEA’s in same stack
Cathode ECSA reduction seems to correspond with Anode ECSA reduction
Contamination determined in H2 feed

<table>
<thead>
<tr>
<th>All in ppb (V)</th>
<th>H2 Feed A</th>
<th>H2 recirculation A</th>
<th>H2 Recirculation B</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>100</td>
<td>70-140</td>
<td>320</td>
</tr>
<tr>
<td>CH4</td>
<td>100</td>
<td>170</td>
<td>X</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>X</td>
<td>X</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Chlorine</td>
<td>X</td>
<td>X</td>
<td>&lt;20</td>
</tr>
<tr>
<td>S</td>
<td>X</td>
<td>&lt; 1</td>
<td>X</td>
</tr>
</tbody>
</table>

A, B different analytical labs and different sample moments
X: not checked

Conclusions:
- Presence of CO may result in substantial reversible decay
- No accumulation of CO in recirculation loop?
  - \( \text{CO}_{(g)} + \text{H}_2\text{O} (v) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \)?
- Origin of CH4?
  - Stable component inside recirculation loop?
Cell voltage loss with 1 ppm CO @ 200 A
Cell voltage loss at various CO concentrations @120A
Conclusions

Ranking suspected degradation mechanisms:

1. Cathode loss of active surface area; irreversible
2. Anode loss of active surface area by poisoning; reversible
3. Cathode loss of active surface area by poisoning; reversible
4. Cathode increase of proton resistance; irreversible

Order and extent largely depend on MEA / catalyst formulation
Acknowledgements

The research leading to these results has received funding from the European Union’s Seventh Framework Programme FP7/2007-2013 for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement no. 256721 (STAYERS)

See also:
Adriaan J.L. Verhage, Jorg F. Coolegem, Martijn J.J Mulder, M. Hakan Yildirim, Frank A. de Bruijn, 30,000 h operation of a 70 kW stationary PEM fuel cell system using hydrogen from a chlorine factory, Int. Journal of hydrogen energy 38 (2013), 4714-4724