Properties and Stability of Radiation Grafted Membranes for Water Electrolysis Cells

Pacific Polymer Conference 14, 9-13 December 2015, Kauai, Hawaii
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 n° 303484.
Nafion N-115 (127 µm) / N-117 (178 µm):
- Low hydrogen crossover
- Stable
- High area resistance
- High cost

Alternative membrane?
Radiation Grafted Membranes

Radiation grafted membranes:

- Potentially low cost*

*L. Gubler and L. Bonorand, ECS Trans., 2013, 58, 149.

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Radiation grafted membrane

Ethylene tetrafluoroethylene (ETFE) 50 μm

St/AN

St (Styrene) AMS (α-Methylstyrene) AN (Acrylonitrile) DiPB (1,3-Diisopropenylbenzene)
Outline

- Introduction
- Properties
  - Hydrogen crossover
  - Area resistance
  - Mechanical properties
- Stability
- Preliminary test
- Summary
Properties - Experimental

H₂ Crossover & Area Resistance

Single Cell
H₂/N₂(O₂)
80 °C
2.5/2.5 bar
Humidity 100%

Mechanical Properties

Materials Testing Machine
ASTM D 882
Room temperature
Fully hydrated condition
Radiation grafted membranes:

- Lower hydrogen crossover
- Lower area resistance

Radiation grafted membranes:

- Better Mechanical Properties

Introduction

Properties

Stability

Preliminary test

Summary

Outline

Thermal Stress Test

Water

Membrane

UV-Vis

IC

IEC

FTIR

EDX

OCV Hold Test

H₂ crossover & Area resistance

Degradation Mechanisms
Thermal Stress Test (TST)

Membrane 30 cm²
100 ml deionized water
Air/Argon
90 °C
Under stirring
5 days
Degraded species are in the form of polymer fragments.

Crosslinked membranes are more stable.
Less scission of polymer chains, but not completely

O₂ is somehow promoting
### Water - Ion Chromatography (IC)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SO(_4^{2-})</th>
<th>F(^-)</th>
<th>Cl(^-)</th>
<th>NO(_3^-)</th>
<th>PO(_4^{2-})</th>
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</thead>
<tbody>
<tr>
<td>Blank test</td>
<td>0.02</td>
<td>-</td>
<td>0.01</td>
<td>0.60</td>
<td>0.05</td>
</tr>
<tr>
<td>St/AN (Argon)</td>
<td>1.02</td>
<td>0.06</td>
<td>0.26</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>0.03</td>
<td>0.06</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(0.17)</td>
<td>(0.03)</td>
<td>(0.08)</td>
<td></td>
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<td>St/AN/DiPB</td>
<td>3.64</td>
<td>0.14</td>
<td>0.53</td>
<td>0.85</td>
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<tr>
<td>(Argon)</td>
<td>2.02</td>
<td>0.05</td>
<td>0.47</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.64)</td>
<td>(0.05)</td>
<td>(0.48)</td>
<td>(0.05)</td>
<td></td>
</tr>
<tr>
<td>AMS/AN (Argon)</td>
<td>0.64</td>
<td>0.09</td>
<td>0.21</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.07</td>
<td>0.19</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.16)</td>
<td>(0.04)</td>
<td>(0.17)</td>
<td>(0.05)</td>
<td></td>
</tr>
<tr>
<td>AMS/AN/DiPB</td>
<td>1.20</td>
<td>0.02</td>
<td>0.24</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.62</td>
<td>0.05</td>
<td>0.24</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>N115</td>
<td>0.11</td>
<td>0.03</td>
<td>0.04</td>
<td>0.62</td>
<td>-</td>
</tr>
<tr>
<td>N117</td>
<td>0.14</td>
<td>0.04</td>
<td>0.10</td>
<td>0.71</td>
<td>-</td>
</tr>
</tbody>
</table>

*All in ppm ≈ mg/L (1 ppm ≈ 0.05 wt.% of the membrane)

- Very small extent of desulfonation
### Ion Exchange Capacity (mmol/g)

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Before test</th>
<th>After test</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>St/AN (Argon)</strong></td>
<td>1.24 ± 0.01</td>
<td>0.82 ± 0.06</td>
<td>34.1 ± 4.7</td>
</tr>
<tr>
<td></td>
<td>(1.25 ± 0.02)</td>
<td>(0.82 ± 0.01)</td>
<td>(34.4 ± 1.7)</td>
</tr>
<tr>
<td><strong>St/AN/DiPB (Argon)</strong></td>
<td>1.20 ± 0.00</td>
<td>0.67 ± 0.01</td>
<td>44.2 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>(1.11 ± 0.02)</td>
<td>0.57 ± 0.06</td>
<td>(49.1 ± 5.9)</td>
</tr>
<tr>
<td><strong>AMS/AN (Argon)</strong></td>
<td>1.65 ± 0.03</td>
<td>1.48 ± 0.00</td>
<td>10.3 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>(1.65 ± 0.01)</td>
<td>(1.59 ± 0.03)</td>
<td>(3.19 ± 2.0)</td>
</tr>
<tr>
<td><strong>AMS/AN/DiPB</strong></td>
<td>1.58 ± 0.00</td>
<td>1.52 ± 0.01</td>
<td>4.2 ± 0.5</td>
</tr>
</tbody>
</table>

### Stability

- Same IEC % loss of styrene based membranes under argon atmosphere
- Another degradation mechanism without any polymer chain scissions
*Before (in black) and after (in red) 5 days Thermal Stress Test
Membrane - EDX Analysis

<table>
<thead>
<tr>
<th>EDX</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **No localized degradation**

* Energy-dispersive X-ray spectroscopy (EDX)
Outline

- Introduction
- Properties
- Stability
- Preliminary test
- Summary

Thermal Stress Test

Water
  - UV-Vis
  - IC
  - IEC
  - FTIR
  - EDX

Membrane

H₂ crossover & Area resistance

Degradation Mechanisms
Degradation Mechanisms in Hot Water

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Before test</th>
<th>After test</th>
<th>IEC % loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>St/AN</td>
<td>66.6 ± 0.9</td>
<td>54.4 ± 3.0</td>
<td>34.1 ± 4.7</td>
</tr>
<tr>
<td>St/AN/DiPB</td>
<td>35.1 ± 3.2</td>
<td>40.9 ± 3.5</td>
<td>44.2 ± 0.8</td>
</tr>
<tr>
<td>AMS/AN</td>
<td>56.5 ± 0.5</td>
<td>60.0 ± 0.5</td>
<td>10.3 ± 0.0</td>
</tr>
<tr>
<td>AMS/AN/DiPB</td>
<td>31.7 ± 0.6</td>
<td></td>
<td>4.2 ± 0.5</td>
</tr>
</tbody>
</table>

- No correlation between swelling and degradation degree
- Another degradation mechanisms?

Weak-links are formed during polymerization in the presence of O₂

A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, *Article in preparation; Proposed mechanisms.*
Degradation Mechanisms in Hot Water

Oxygen-induced degradation

- O₂ leads to the formation of new weak-links

A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, *Article in preparation; Proposed mechanisms.*
Degradation Mechanisms in Hot Water

Loss of molecules containing sulphonic acid, but no chain scissions

A. Albert, T. Lochner, T. J. Schmidt and L. Gubler, Article in preparation; Proposed mechanisms.
Open Circuit Voltage (OCV) Hold Test

Fuel Cell

H₂/O₂
200 ml/min
80 °C
2.5/2.5 bar
Humidity 100%
5 days

➢ Peroxide rich condition
Stability - H₂ crossover & Area Resistance

**Thermal Stress Test**

- **H₂ crossover (mA/cm²)**
  - 0
  - 1
  - 2
  - 3
  - 4
  - 5
- **Area resistance (mOhm·cm²)**
  - 0
  - 100
  - 200
  - 300
  - 400

**Open Circuit Voltage (OCV) Hold Test**

- **H₂ crossover (mA/cm²)**
  - 0
  - 1
  - 2
  - 3
  - 4
  - 5
- **Area resistance (mOhm·cm²)**
  - 0
  - 100
  - 200
  - 300
  - 400

- **St/AN**
- **St/AN/DiPB**
- **AMS/AN**
- **AMS/AN/DiPB**
- **S/AN/DiPB**

**Stability**

- ETFE
- St/AN
- St/AN/DiPB
- AMS/AN
- AMS/AN/DiPB

- Before Test
- After Test
Outline

- Introduction
- Properties
- Stability
- Preliminary test
- Summary
Preliminary in-situ electrolyzer test

Performance is comparable to commercial MEA at low current density (Homogeneity problem of St/AN/DiPB membrane)

In-situ electrolyzer tests of other membranes will be performed

H₂O
500 ml/min
80 °C
25 cm²
IrO₂/Pt
Ti/C
Summary

Properties of radiation grafted membranes:
- Lower hydrogen crossover
- Lower area resistance
- Better mechanical properties
- Potentially low cost*

Stability of radiation grafted membranes:

Degradation mechanisms in hot water:
- Degradation at the weak-link
- Oxygen-induced degradation
- Hydrothermal degradation

Wir schaffen Wissen – heute für morgen

Questions or comments?
Back Up Slides
H2 crossover measurement principle

**Normal Fuel Cell Operation**

(-) \( H_2 \rightarrow 2H^+ + 2e^- \)

(+) \( \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \)

**Crossover Experiment**

\( 2H^+ + 2e^- \rightarrow H_2 \)

\( H_2 \rightarrow 2H^+ + 2e^- \)

Potential is set.

Current density is measured.
Hydrogen Permeation

Cell at 80°C, H2/N2 1.5/1.5 stoich (min. 200/200 ml/min), pressure 2.5/2.5 bara, humidifier temperature 85/85°C

Current density / mA cm⁻²

Cell potential / mV
Mechanical Properties

Tensile Test in Machine Direction
(Ambient condition)

Tensile Test in Machine Direction
(Fully hydrated condition)

Radiation grafted membranes:
> Better Mechanical Properties
Tensile Energy to Break / Toughness

Ambient condition (MD)

Fully hydrated condition (MD)
UV-Vis Spectroscopy - Nafion

Nafion

Blank Test  \( \left\{ (\text{CF}_2\text{CF}_2)_n - (\text{CF}_2\text{CF}) \right\}_x \)  N115  \( \text{OCF}_2\text{CFOCF}_2\text{CF}_2 - \text{SO}_3\text{H} \)  N117  \( \text{CF}_3 \)

Day 5  Day 5  Day 5  Day 1
$$\left\{ (\text{CF}_2\text{CF}_2)_{n} - (\text{CF}_2\text{CF}) \right\}_x$$

$$\text{OCF}_2\text{CFOCF}_2\text{CF}_2 - \text{SO}_3\text{H}$$

N115

N117
## Swelling under Argon Atmosphere

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Before test</th>
<th>After test</th>
<th>IEC % loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>St/AN (Argon)</td>
<td>66.6 ± 0.9</td>
<td>54.4 ± 3.0</td>
<td>34.1 ± 4.7</td>
</tr>
<tr>
<td></td>
<td>(67.8 ± 2.4)</td>
<td>(63.2 ± 1.6)</td>
<td>(34.4 ± 1.7)</td>
</tr>
<tr>
<td>St/AN/DiPB (Argon)</td>
<td>35.1 ± 3.2</td>
<td>40.9 ± 3.5</td>
<td>44.2 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>(34.9 ± 1.5)</td>
<td>(31.7 ± 6.3)</td>
<td>(49.1 ± 5.9)</td>
</tr>
<tr>
<td>AMS/AN (Argon)</td>
<td>56.5 ± 0.5</td>
<td>60.0 ± 0.5</td>
<td>10.3 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>(53.0 ± 1.3)</td>
<td>(58.5 ± 1.3)</td>
<td>(3.19 ± 2.0)</td>
</tr>
<tr>
<td>AMS/AN/DiPB</td>
<td>31.7 ± 0.6</td>
<td>-</td>
<td>4.2 ± 0.5</td>
</tr>
</tbody>
</table>
## Raw Datas

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Graft level (%)</th>
<th>Wet thickness (µm)</th>
<th>IEC (mmol/g)</th>
<th>Swelling (m%)</th>
<th>Hydration (H₂O/SO₃H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/AN (D)</td>
<td>41</td>
<td>86.0 ± 1.0</td>
<td>1.25 ± 0.02</td>
<td>67.8 ± 2.4</td>
<td>30.1 ± 0.9</td>
</tr>
<tr>
<td>S/AN (SG)</td>
<td>40</td>
<td>95.3 ± 1.1</td>
<td>1.29 ± 0.02</td>
<td>68.6 ± 1.7</td>
<td>29.6 ± 0.3</td>
</tr>
<tr>
<td>S/AN/DiPB (D)</td>
<td>41</td>
<td>79.5 ± 0.7</td>
<td>1.20 ± 0.00</td>
<td>33.1 ± 1.0</td>
<td>15.3 ± 0.5</td>
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<tr>
<td>S/AN/DiPB (SG)</td>
<td>39</td>
<td>79.5 ± 0.5</td>
<td>1.15 ± 0.02</td>
<td>34.4 ± 1.9</td>
<td>16.6 ± 1.1</td>
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<tr>
<td>AMS/AN/DiPB (SG)</td>
<td>42</td>
<td>74.5 ± 3.5</td>
<td>1.59 ± 0.01</td>
<td>30.1 ± 0.5</td>
<td>10.5 ± 0.1</td>
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<tr>
<td>NR211</td>
<td>-</td>
<td>30.5 ± 0.0</td>
<td>1.22 ± 0.01</td>
<td>28.1 ± 13.6</td>
<td>12.7 ± 6.1</td>
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<tr>
<td>NXL-100</td>
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<td>37.3 ± 0.3</td>
<td>1.01 ± 0.04</td>
<td>29.3 ± 4.7</td>
<td>16.1 ± 2.1</td>
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<tr>
<td>NR212</td>
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<td>38.6 ± 6.8</td>
<td>18.6 ± 3.3</td>
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<td>N1035</td>
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<td>N1135</td>
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<td>103.8 ± 1.5</td>
<td>1.05 ± 0.02</td>
<td>39.3 ± 2.4</td>
<td>20.8 ± 1.0</td>
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<td>N105</td>
<td>-</td>
<td>152.3 ± 1.5</td>
<td>1.10 ± 0.00</td>
<td>47.9 ± 0.3</td>
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<td>N115</td>
<td>-</td>
<td>153.0 ± 1.0</td>
<td>1.04 ± 0.02</td>
<td>39.9 ± 2.9</td>
<td>21.2 ± 1.2</td>
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<tr>
<td>N117</td>
<td>-</td>
<td>202.7 ± 1.0</td>
<td>1.04 ± 0.00</td>
<td>39.9 ± 0.1</td>
<td>21.4 ± 0.0</td>
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<td>N120</td>
<td>-</td>
<td>293.0 ± 8.2</td>
<td>0.83 ± 0.00</td>
<td>27.2 ± 0.3</td>
<td>18.3 ± 0.2</td>
</tr>
<tr>
<td>Membrane</td>
<td>SEM-EDX</td>
<td>Sulphur</td>
<td>Nitrogen</td>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>---------</td>
<td>-----------</td>
<td>-----------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>S/AN/DiPB (DuPont)</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td></td>
</tr>
<tr>
<td>S/AN/DiPB (Saint-Gobain)</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td></td>
</tr>
</tbody>
</table>
Swelling-Induced Detachment

Estimated cost of radiation grafted membranes

*L. Gubler and L. Bonorand, *ECS Trans.*, 2013, 58, 149.*