Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

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This presentation does not contain any proprietary or confidential information
### Overview

#### Timeline
- Project start date: 2004
- Project end date: tbd
- Percent complete: tbd

#### Barriers
- Barriers addressed
  - Stack Material and Manufacturing costs.
  - Materials Durability

#### Budget
- Total project funding
  - DOE share: $196k
- Funding received in FY04: $40k
- Funding for FY05: $156k

#### Partners
- Interactions/ collaborations
  - Oak Ridge National Lab.
  - Plug Power
Approach and Objectives

• Our approach is two fold
  – Understanding the relationship between alloy composition and bipolar plate performance.
  – Study possible coating materials and methods.

• Objectives - FY 05 Goals
  – Corrosion testing of new alloys and coatings
  – Collaborate with ORNL to evaluate nitrided alloys and to determine best alloy composition for PEMFC.
  – Characterize conducting coatings on alloys and their performance in PEMFC environments.
  – Assemble test system for operation in the 100-200 °C range and study materials in this temperature range.
  – Development of corrosion tests for polyphosphoric acid environment at >150°C
Why Metallic Bipolar Plates

- Wide choices, high chemical stability, including choices for corrosion resistance
- High strength allowing thinner plates for high power density
- Existing low cost/high volume manufacturing techniques (e.g. stamping);
- High bulk electrical and thermal conductivities;
- Potential for low cost.

- DOE 2010 Technical Targets for Fuel Cell Stacks
  - Cost $35/kW
  - Durability 5000 hours
Challenges with Metallic Bipolar Plates in PEMFC

- Possible contamination of polymer membrane by dissolved metal ions
- Higher surface contact resistance due to surface oxides (such oxides provide excellent corrosion resistance however)
NREL/ORNL Collaboration

• Evaluated over 10 alloy compositions, both commercially available and synthesized;
• Evaluated the influence of nitridation parameters on the contact resistance and corrosion resistance in PEMFC environments, used for improving and adjusting the alloy composition and nitridation parameters;
• Filled a joint patent application for the nitridation of AISI446 alloy, finding 2 alloys suitable for PEMFC bipolar plates after nitridation.
Initial Success for Fe-Cr alloy via Nitrogen Modified Oxide Layer

- AISI446 and Modified AISI446: Ferritic, Fe-base;
- ICR significantly decreased, both as-nitrided and tested;
- Surface complex of oxygen-nitrogen mixture with Cr, Fe.
Nitrided AISI446 has excellent corrosion resistance in 1M H₂SO₄+2ppm F⁻ at 70 °C with air purge.
Time-dependent data for Nitrided AISI446 in simulated PEMFC environments

- Anodic behavior for nitrided AISI446 in PEMFC environments
  - cathode (a)
  - anode (b) (note the cathodic current).
- DOE target: 16 $\mu$A/cm$^2$
Nitrided G-35™ and G-30® meet the ICR Goal

- Cr-nitrides formed on commercial Ni-base alloys;
- Corrosion test at GM and NREL show no increase in ICR;
- Complex conductive “oxy-nitride” after polarization (master’s thesis).
Developing lower cost alloys with low ICR

![Graph showing interfacial contact resistance vs. compaction force for different alloys.](image)

- Nitrided Al29-4CTM
- Nitrided AISI446 (Control)
- Nitrided ORNL Modified 446

Goal: <20 mΩ⋅cm²
And keep excellent corrosion resistance after modification

**PEMFC anode**

**PEMFC cathode**
ICR for the modified 446 after polarization in PEMFC environments?

**ICR Goal**

- Polarized 7.5h @0.6 V, Air purge
- Polarized 7.5h @-0.1V, H₂ purge

As received

2 X ICR, mOhm*cm²

Compaction force, N/cm²
## Cost - DOE Targets

<table>
<thead>
<tr>
<th>Alloy</th>
<th>ICR@140 N/cm², mΩ·cm²</th>
<th>Current at –0.1 V (H₂ purge), µA/cm²</th>
<th>Current at 0.6 V (air purge), µA/cm²</th>
<th>Cost*, $/kW</th>
</tr>
</thead>
<tbody>
<tr>
<td>349&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>110</td>
<td>-4.5~2.0</td>
<td>0.5~0.8</td>
<td>4.22</td>
</tr>
<tr>
<td>AISI446</td>
<td>190</td>
<td>-2.0~1.0</td>
<td>0.3~1.0</td>
<td>4.76</td>
</tr>
<tr>
<td>2205</td>
<td>130</td>
<td>-0.5~+0.5</td>
<td>0.3~1.2</td>
<td>3.14</td>
</tr>
<tr>
<td>Nitrided AISI446</td>
<td>6.0</td>
<td>-1.7~0.2</td>
<td>0.7~1.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Modified AISI446</td>
<td>4.8</td>
<td>-9.0~0.2</td>
<td>1.5~4.5</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>DOE Target</strong></td>
<td>20 mΩ·cm²</td>
<td>&lt;16 µA/cm²</td>
<td>&lt;16 µA/cm²</td>
<td>$10/kW</td>
</tr>
</tbody>
</table>

Note: Cost data were based on the base price of cold rolled coils from Allegheny Ludlum (see website), and by assuming 6 cells/kW for a PEMFC and the dimensions of a bipolar plate are 24 cm × 24 cm × 0.254 cm (which gives a 400 cm² utilization surface area in a 0.01 inch thick sheet).
Conductive SnO$_2$:F Coating

- High conductivity
- High stability in many different environments
- Volume production is available----widely used in PV industry
- May allow reduced cost with lower grade alloys.
- NREL expertise (National Center for Photovoltaics)
Performance of coated steels in PEMFC anode environment

- Excellent behavior of SnO$_2$:F/AISI446 is expected;
- Good corrosion resistance of SnO$_2$:F/AISI444 is surprising! But match with ICP analysis (see Table)
Fe, Cr, Ni ions concentration after polarized in PEMFC environments (average of 3 samples)

<table>
<thead>
<tr>
<th>Material</th>
<th>Ion concentration in PEMFC anode environment after 7.5h</th>
<th>Ion concentration in PEMFC cathode environment after 7.5h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe, ppm</td>
<td>Cr, ppm</td>
</tr>
<tr>
<td>316L</td>
<td>21.18</td>
<td>4.60</td>
</tr>
<tr>
<td>317L</td>
<td>3.98</td>
<td>0.65</td>
</tr>
<tr>
<td>349TM</td>
<td>1.70</td>
<td>0.12</td>
</tr>
<tr>
<td>SnO₂/316L</td>
<td>10.83</td>
<td>1.97</td>
</tr>
<tr>
<td>SnO₂/317L</td>
<td>4.03</td>
<td>0.69</td>
</tr>
<tr>
<td>SnO₂/349TM</td>
<td>1.27</td>
<td>-</td>
</tr>
<tr>
<td>441</td>
<td>622.9</td>
<td>135.7</td>
</tr>
<tr>
<td>444</td>
<td>141.5</td>
<td>37.86</td>
</tr>
<tr>
<td>446</td>
<td>1.46</td>
<td>-</td>
</tr>
<tr>
<td>SnO₂/441</td>
<td>24.15</td>
<td>4.51</td>
</tr>
<tr>
<td>SnO₂/444</td>
<td>12.70</td>
<td>2.09</td>
</tr>
<tr>
<td>SnO₂/446</td>
<td>1.24</td>
<td>-</td>
</tr>
</tbody>
</table>
The Needs and Challenges of High Temperature (HT) bipolar plates

...Starting Point

• Desire of transportation industry;

• R&D on high temperature membrane, however, exact environments for HT PEMFC not yet defined!

• Accordingly, set HT at 150 - 170 °C, selected H₃PO₄ as electrolyte, evaluated over 12 “HT” epoxies, and chose the best;

• Modified test systems to suite the HT, working with native stainless steel and graphite bipolar plate for PAFC from PlugPower.
Dynamic polarization for 904L steel in H$_3$PO$_4$ at 170 °C

- New condition resulted in significant changes
- Passivation for the steel in both environments;
- High current noted even in the passivation region.
How about potentiostatic polarization for 904L steel in H$_3$PO$_4$ at 170 °C?

- At 0.1 V with H$_2$ purge, current slightly increases from 0.73 to 1.15 mA/cm$^2$ after 15 minutes;
- At 0.7 V with air purge, current peaks at 5 minutes, then stabilized at 1.0-1.25 mA/cm$^2$ after 15 minutes;
- Matches with dynamic polarization.
How about graphite (used in PAFC now)?

- Actual bipolar plate;
- Very low ICR with graphite;
- Tested at room temperature

Goal: <20 mΩ·cm²
Anodic behavior of graphite in H$_3$PO$_4$ at 170 °C with H$_2$ or air purge

- High currents
- 2 Tafel regions.
Dissemination of Results

**Journal Papers**


**Conference Papers/Presentations**


**Patent Application**

Future Work

- Continue NREL/ORNL collaboration with alloy development and nitridation
- Investigate new alloy compositions and coatings
- Bare alloys in HT PAFC environments;
- Nitrided alloys in HT environments;
- Coated steels in HT environments;
- Further NREL/PlugPower collaboration.
Hydrogen Safety

The most significant hydrogen hazard associated with this project is:
- Hydrogen atmosphere used during corrosion tests
Hydrogen Safety

Our approach to deal with this hazard is:

- Limit cell head space to <10ml and use low hydrogen flow rates.
- Perform experiments in a fume hood.
- Project activities are covered by a formal, standard operation procedure and reviewed by ES&H and approved by PI’s and cognizant managers.