

V.D.4 Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

John A. Turner (Primary Contact), Heli Wang
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401
Phone: (303) 275-4270; Fax: (303) 275-2905
E-mail: john_turner@nrel.gov

Collaborating Coauthor: Michael P. Brady
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831

DOE Technology Development Manager:
Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811
E-mail: Nancy.Garland@ee.doe.gov

Start Date: 2004
Projected End Date: Project continuation and
direction determined annually by DOE

- Corrosion rate of $<1 \mu\text{A}/\text{cm}^2$
- Resistivity of $<10 \text{ m}\Omega\cdot\text{cm}^2$ by 2010

Accomplishments

- Made significant gains in the understanding of the nitrated surface formed on 446 steel. Thermal nitridation was applied to a simpler alloy, AL29-4C[®], in a mixed N_2 - 4H_2 atmosphere. Short-term corrosion and contact resistance measurements indicate behavior equal to that of the nitrated 446.
- Showed that low-cost alloys (high Mn/N bearing) behaved much better than 316L in simulated aggressive proton exchange membrane fuel cell (PEMFC) environments.
- Modified the deposition of the conducting SnO_2 :F coating and significantly reduced the interfacial contact resistance on stainless steels.
- Identified the influence of the metal ions on the conductivity of membrane. Cr^{3+} is more strongly absorbed in the near surface of the membrane. The membrane's conductivity is relatively unaffected by the Fe^{3+} ion at concentration below 100 ppm in solution.
- Completed testing of selected austenitic stainless steels in $170^\circ\text{C H}_3\text{PO}_4$ for bipolar plate applications.

Objectives

- Explore and understand the relationship between alloy composition and bipolar plate performance in fuel cells.
- Study possible coating materials and surface modification preparations and methods.
- Develop suitable alloys/coatings/surface modification processes that are low-cost, lightweight, corrosion-resistant, gas impermeable, and amenable to mass manufacturing to meet the DOE goals for fuel cell bipolar plates.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

Technical Targets

This project is directed toward the DOE technical targets for bipolar plates:

- \$6/kW
- Weight of 1 kg/kW

Introduction

The bipolar plate is one of the most expensive components in a PEMFC. Present bipolar plates account for about 45% to two-thirds of stack cost and about 78% of total weight. Thin metallic bipolar plates, especially stainless steels, offer the potential for high mechanical strength, gas permeability, reduced weight/volume, amenable pathway towards high-speed high-volume manufacturing, significantly lower cost, and better performance than the machined graphite bipolar plates that are currently used. Stainless steels are naturally protected by passive film in PEMFC environments and although this passive film protects the steel from further corrosion, this leads to high surface electrical resistance that can significantly degrade the performance of the fuel cell stack. If the surface could be made conducting and non-corroding, then it would not only protect the underlying metal plate from corrosion, but also provide a conducting pathway for the flow of current.

Approach

For this work, NREL provided expertise in stainless steel alloys and corrosion testing in collaboration with ORNL to evaluate nitrated samples. This has already led to the filing of a joint patent application for the nitridation of 446. To complete the DOE cost goal, we will continue our survey of commercially available low-cost alloys (specially low-cost Mn/N bearing steels) to determine the best alloy composition and additives that provide acceptable corrosion resistance and low surface interfacial contact resistance (ICR). If the coating develops pinholes, the underlying material will passivate and not significantly affect stack performance. We will then suggest these new alloys for additional coatings/surface modifications. We will also optimize the conducting oxides coating process for low ICR and high corrosion resistance in PEMFC environments. NREL is unique with its extensive experience in conductive oxides and its high-speed application in the photovoltaics field. Since we are not interested in optical transparency, we can focus on optimizing these materials for high conductivity and corrosion resistance. Moreover, we will determine the influence of dissolved metal ions on the conductivity of membrane.

Work on high temperature membranes has led to inquiries from industry concerning the performance of metals in the temperature range of 100-200°C. We have modified our testing system to allow high temperature operation up to 170°C. We will complete the testing of austenitic stainless steels in high temperature poly-phosphoric acid environments.

Results

The following work was performed in FY 2006: 1) improving and adjusting the alloy composition/nitridation parameters on Fe-(20-30)Cr based stainless steels for PEMFC bipolar plates, 2) continuing survey of low-cost stainless steel alloys that would be good candidates as bipolar plates or for further surface modification/coating experiments, 3) optimizing the SnO₂:F coating for lower interfacial contact resistance, 4) determining the influence of dissolved metal ions on the conductivity of membrane, and 5) completing the investigation of the austenitic stainless steels in a high temperature (170°C) H₃PO₄ environment. Items (1) to (4) are intended to meet DOE goals, while (5) addresses inquiries from the stationary industry.

It has been shown that after being nitrated 2 h at 1100°C in pure N₂, a complex layer of oxygen-nitrogen mixture with Cr and Fe was generated on the surface of 446. This kind of layer showed excellent corrosion resistance in PEMFC environments and low ICR. This led to a joint ORNL/NREL record of invention. To identify the influence of the alloying elements, AL29-4C[®] steel, a superferritic steel with a simpler composition of Fe-29Cr-4Mo base, was selected for thermal nitridation at 800-900°C in mixed N₂-4H₂. After nitridation, the ICRs for nitrated AL29-4C[®] are very close to those of nitrated 446, matching the DOE 2010 goal. Nitrated AL29-4C[®] steel also showed excellent corrosion resistance in 1 M H₂SO₄ + 2 ppm F⁻ at 70°C, purged either with hydrogen gas or air. Its behavior is summarized in Table 1. Figure 1 shows the depth profile

TABLE 1. DOE Targets for Bipolar Plates and the Status for the Materials Investigated.

Goal/Alloy	ICR@140 N/cm ² mΩ·cm ²	Current @ -0.1 V _{SCE} (H ₂ purge), μA/cm ²	Current at 0.6 V _{SCE} (Air purge), μA/cm ²	Cost* \$/kW
<i>DOE 2010 Goal</i>	<i>10</i>	<i><1</i>	<i><1</i>	<i>6</i>
316L	154	+2.5 ~ +12	0.7 ~ 11	3.41
349 [™]	110	-4.5 ~ -2.0	0.5 ~ 0.8	3.61
AISI446	190	-2.0 ~ -1.0	0.3 ~ 1.0	4.08
2205	130	-0.5 ~ +0.5	0.3 ~ 1.2	3.53
201	158	-0.5 ~ +8.5	0.8 ~ 2.0	2.18
AL219	730	-3.3 ~ -1.5	1.0 ~ 3.0	2.65
Nitrated 446	6.0	-1.7 ~ -0.2	0.7 ~ 1.5	N/A
Modified 446	4.8	-9.0 ~ -0.2	1.5 ~ 4.5	N/A
Nitrated AL29-4C [™]	6.0	-6.5 ~ -3.0	0.3 ~ 0.5	N/A

Note*: Cost data were based on the average 2005 trading price of cold rolled coil 316 steel at London Metals Exchange and the market prices of the metals. The assumed stack was 6 cells/kW for a PEMFC and the dimensions of a bipolar plate are 24 cm × 24 cm × 0.0254 cm (which gives a 400 cm² utilization surface area in a 0.01 inch thick sheet).

of the surface nitride layer on AL29-4C[®] alloy. The outer layer is composed of chromium nitride, followed by an inner layer of chromium oxide and Mn-oxide. It is interesting that Mn is enriched in this oxide layer. Due to the low surface resistivity, a high conductivity of this mixed oxide layer is expected.

Compared to expensive Ni, high Mn/N stainless steels are low cost. The goal is to look for other possible low-cost alloys that would be good candidates as bipolar plates or for further surface modification/coatings experiments. Commercially available alloys of 201 and AL219 were tested for PEMFC bipolar plate applications. Both behaved better than 316L in the same conditions. Figure 2 gives their performance

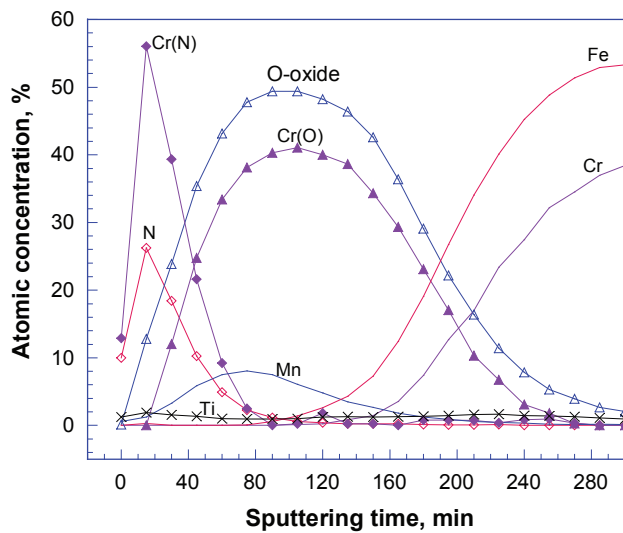


FIGURE 1. XPS Depth Profile for 24 h Nitrided AL29-4C[®] Alloy Sample

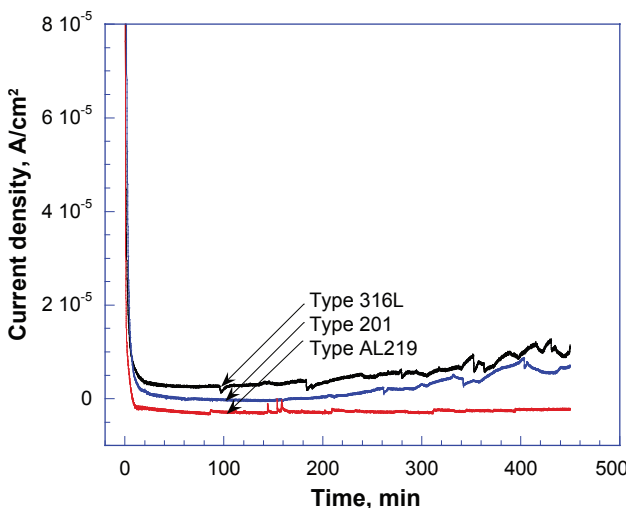


FIGURE 2. Potentiostatic Polarization of Steels at $-0.1 V_{SCE}$ in $1 M H_2SO_4 + 2 ppm F$ at $70^\circ C$ (The solution was purged with hydrogen gas)

in a simulated PEMFC anode environment. Much lower current is obtained with type 201 steel. AL219 even gives very stable cathodic current, which is very promising for the application. In PEMFC cathode environments, both alloys showed much better stability than 316L, although improved corrosion resistance is needed for both alloys. On the other hand, Type 201 alloy gives similar or lower ICR values than 316L, while much higher ICR values are obtained with AL219. This could be related to the surface structure. Thus, surface modification or coatings are needed for these alloys acting as bipolar plates.

$SnO_2:F$ coated steels showed lower corrosion currents than the bare ones in PEMFC environments, indicating the beneficial effect of the coating. Coated 446 seems the best among all the coated steels; it had a very stable cathodic current of -1 to $-3.5 \mu A/cm^2$ in PEMFC anode environments and a stable current of 0 to $1.0 \mu A/cm^2$ in PEMFC cathode environments. Coated 444 steel showed promising lower current. Thus, low-cost alloys could be utilized as a substrate. However, with the previous original $SnO_2:F$ coating, ICR values increase compared with the bare steels. This is due to the fact that the coating simply added additional resistance to the air-formed film, and thus shifted ICR curves up. With a modified deposition procedure, however, the modified coating reduces ICR significantly, shifting ICR curves down below even the fresh steels (Figure 3).

It would be interesting to know the influence of the dissolved metal ions on the conductivity of the membrane. This was done by soaking the Nafion[®] 112 in $1 M H_2SO_4$ solution containing different amounts of Fe^{3+} and/or Cr^{3+} ions at $80^\circ C$ for 24 hours. Conductivity of the membrane was then carried out at $80^\circ C$ and 100%

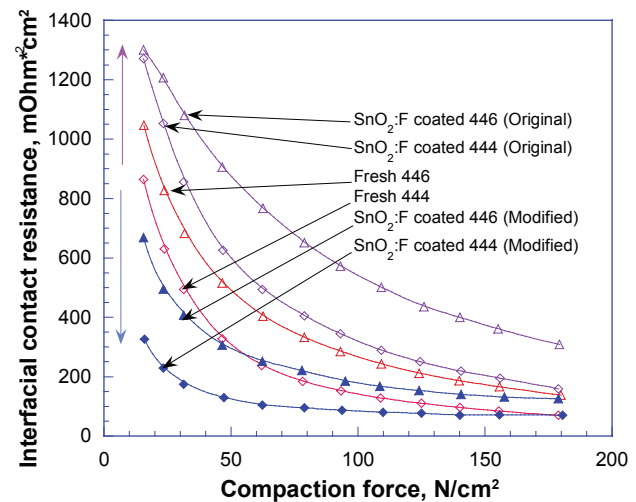


FIGURE 3. ICR of the $SnO_2:F$ Coated Steels with Different Coating Procedures

relative humidity with a back hydrogen gas pressure of 0.103 MPa (15 psi). It is interesting that Cr^{3+} showed much stronger absorption than Fe^{3+} in the near surface of the membrane. Moreover, the conductivity of the membrane material is relatively unaffected by the iron ions at concentrations below 100 ppm (Figure 4). Since the dissolution of our tested candidate samples is typically a few ppm Fe^{3+} , we would not expect that the dissolved metal ions from these candidates would significantly impact the conductivity of the membrane.

Figure 5 shows the potentiostatic polarization of bare stainless steels in 98% H_3PO_4 at 170°C. In both cases, current has a sharp decay as soon as the potential is applied, followed by either a current recovery (Figure 5a) or the secondary current peak (Figure 5b). When polarized at 0.1 V_{RHE} in H_2 purged electrolyte, the current recovery takes *ca.* 5 min for 316L, 6.5 min for 317L, and *ca.* 15 min for 904L (Figure 5a). When polarized at 0.7 V_{RHE} in air purged electrolyte, secondary current peaks are obtained (Figure 5b). They are located at 1 min for 316L, 2 min for 317L, and 5 min for 904L. In both cases, 904L showed the lowest currents among the steels investigated (*ca.* 1.40 mA/cm^2 at 0.1 V_{RHE} and 1.8 mA/cm^2 at 0.7 V_{RHE}), making the advantage of this alloy over the rest. This may be related to the higher alloying content of the 904L alloy. X-ray photoelectron spectroscopy (XPS) profiles revealed that chromium oxide dominates the passive film formed. This is due to the much faster dissolution of iron oxide than chromium oxide. The incorporation of P into the passive film in this environment is found, which is different from that formed in the PEMFC environment.

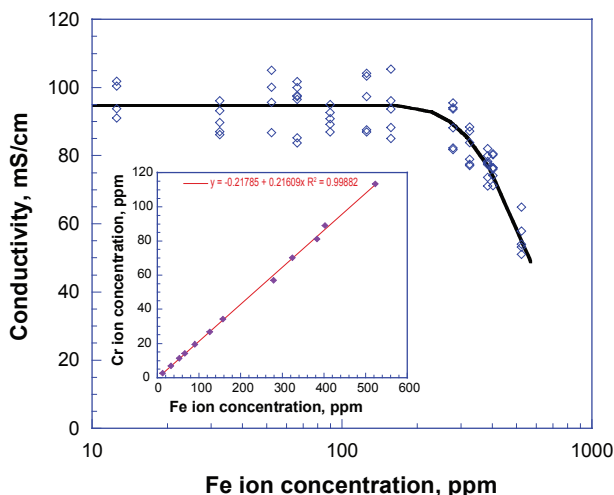


FIGURE 4. Influence of mixed Fe and Cr ions on the conductivity of Nafion® 112 membrane at 80°C cell temperature and 100% relative humidity with back hydrogen pressure of 0.103 MPa (15 psi). Inset shows the relationship of the dissolved Fe and Cr ions in the same tested solution.

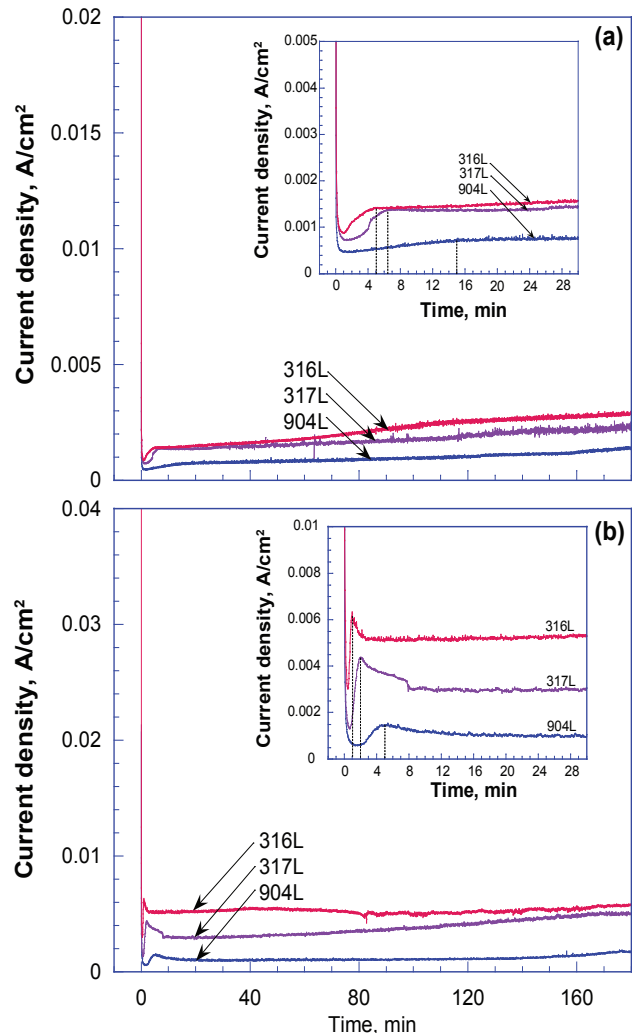


FIGURE 5. (a) Potentiostatic polarization of stainless steels at 0.1 V_{RHE} in H_3PO_4 at 170°C purged with hydrogen gas. Inset shows the current decay during the first 30 min. (b) Potentiostatic polarization of stainless steels at 0.7 V_{RHE} in H_3PO_4 at 170°C purged with air. Inset shows the current decay during the first 30 minutes polarization.

Conclusions and Future Directions

- Evaluation of metal alloys/coating combinations for fuel cell bipolar plates. Related work involves research on corrosion resistance in simulated aggressive PEMFC environments, high temperature H_3PO_4 environments, ICR testing, and surface characterization.
- Nitrided AL29-4C® stainless steel showed low ICR and excellent corrosion resistance in PEMFC environments. A small stack using nitrided AL29-4C® bipolar plates will be tested by an industrial partner. Further research is needed to determine the best alloy composition(s) for PEMFC bipolar plate applications and to optimize nitridation parameters.

- Correlated the results with the composition of the base alloy/coating to develop low-cost alloys with low interfacial contact resistance and excellent corrosion resistance in PEMFC environments. Related future development will require a lot more effort.
- Conductive SnO₂:F coating is beneficial to the application of lower cost stainless steels for PEMFC bipolar plates. With a modified deposition process, lower interfacial contact resistance can be obtained with coated 444 and 446. Areas for future investigation include improving the surface treatments and deposition parameters.
- Completed work on austenitic stainless steels in high temperature H₃PO₄. 904L behaved the best among the steels investigated.

Special Recognitions & Awards/Patents Issued

1. M.P. Brady, H. Wang, and J.A. Turner, "Surface Modified Stainless Steels for PEM Fuel Cell Bipolar Plates," U.S. Patent Disclosure, 2005.

FY 2006 Publications/Presentations

Publications/manuscripts

1. Heli Wang and John A. Turner, Influence of Metallic Ions on the Conductivity of Nafion[®] 112 in Polymer Electrolyte Membrane Fuel Cell (in manuscript).
2. Heli Wang and John A. Turner, The Corrosion of a Stainless Steel in High Temperature Phosphoric Acid (in manuscript).
3. Heli Wang and John A. Turner, Austenitic Stainless Steels in High Temperature Phosphoric Acid (in manuscript).
4. Heli Wang and John A. Turner, SnO₂:F Coated Ferritic Stainless Steels for PEM Fuel Cell Bipolar Plates, submitted to *Journal of Power Sources*.
5. Heli Wang and John Turner, On the Passivation of 349TM Stainless Steel in Simulated PEMFC Cathode Environment, ECS Transactions, Vol.1, No.LA-P1: *Proton Exchange Membrane Fuel Cells V, in Honor of Supramaniam Srinivasan* - Editors: S.R. Narayanan, C. Bock, T. Fuller, S. Mukerjee, C. Lamy, E. Stuve, and J. Weidner (in press).
6. Heli Wang, Glen Teeter, and J.A. Turner, Investigation of a Duplex Stainless Steel as PEMFC Bipolar Plate Material, *Journal of the Electrochemical Society*, 152 (3) B99-B104 (2005).

Presentations

1. B. Yang, M.P. Brady, P.F. Tortorelli, K.L. More, H. Wang, J.A. Turner and D.J. Young, Nitrided Stainless Steels for PEM Fuel Cell Bipolar Plates, TMS Annual Meeting, San Antonio, TX, March 15, 2006.
2. M.P. Brady, B. Yang, K.L. More, P.F. Tortorelli, Tim Armstrong, H. Wang and J.A. Turner, Cost Effective Surface Modification for Metallic Bipolar Plates, Fuel Cell Tech Team Meeting, USCAR, Southfield, MI, July 18, 2006.
3. M.P. Brady, B. Yang, Peter Tortorelli, K.L. More, H. Wang, and J.A. Turner, Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells, Materials Science and Technology 2005, Pittsburgh, PA, September 26, 2005.
4. Heli Wang and John A. Turner, On the Passivation of 349TM Stainless Steel in a Simulated PEMFC Cathode Environment, *Proceedings of the 208th Meeting of the Electrochemical Society*, October 22-26, Los Angeles, CA, USA, 2005, paper No. 976.
5. B. Yang, M.P. Brady, D.J. Young, K.L. More, H. Wang and J.A. Turner, Thermally Nitrided Stainless Steel Bipolar Plates for Proton Exchange Membrane Fuel Cells, *Proceedings of the 208th Meeting of the Electrochemical Society*, October 22-26, 2005, Los Angeles, CA, paper No. 1007.