

IV.D.2 Cost-Effective Surface Modification for Metallic Bipolar Plates

Michael P. Brady (Primary Contact), Peter F. Tortorelli, Karren L. More, Harry M. Meyer III, and Larry R. Walker

Oak Ridge National Laboratory

P.O. Box 2008, Oak Ridge, TN 37831-6115

Phone: (865) 574-5153; Fax: (865) 241-0215; E-mail: bradymp@ornl.gov

Collaborating Coauthors: Heli Wang and John A. Turner, National Renewable Energy Laboratory; Bing Yang and Raymond A. Buchanan, University of Tennessee, Knoxville

DOE Technology Development Manager: Nancy Garland

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

Objective

- Develop a low-cost metallic bipolar plate alloy that will form an electrically conductive and corrosion-resistant nitride surface layer during thermal nitriding to enable use in a proton exchange membrane fuel cell (PEMFC) environment.

Technical Barriers

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

- O. Stack Material and Manufacturing Cost
- P. Durability

Approach

- Prepare thermally nitrided Cr-bearing bipolar plate alloys to form a pin-hole-free, protective Cr-nitride surface layer.
- Establish potential to meet durability goals by testing a model thermally nitrided Ni-50Cr alloy in a fuel cell.
- Determine the key issues controlling the mechanism of nitridation to form Cr-nitride surface layers on lower-cost Fe, Fe(Ni), and Ni-Cr base alloys, optimize nitride formation, and evaluate the level of protection achieved by corrosion and fuel cell testing.

Accomplishments

- Bipolar plates of nitrided Ni-50Cr were manufactured and delivered to Los Alamos National Lab (LANL), General Motors (GM), and FuelCell Energy, Inc for single-cell fuel cell testing.
- External Cr-nitride formation was achieved for several commercially available Ni-Cr base alloys (30Cr wt.% range). Polarization testing in aerated pH 3 sulfuric acid solutions indicates corrosion resistance in the range of nitrided Ni-50Cr.
- Nitridation of 446 stainless steel and related alloys was shown to reduce interfacial contact resistance (ICR) to below $20 \text{ m}\Omega\text{-cm}^2$ at loads of 100-150 N/cm². The low ICR was maintained after polarization under simulated cathodic conditions. Polarization under simulated anodic conditions indicated an order of magnitude reduction in Fe dissolution compared to 316L (untreated). These effects resulted from a new type of nitrogen-modified surface film, rather than a dense, continuous Cr-nitride surface layer. A U.S. provisional patent disclosure was filed (joint finding with the National Renewable Energy Laboratory).

- Preliminary efforts suggested that external, dense Cr-nitride formation is possible on Fe-Cr base alloys.

Future Directions

- Post-test analysis of nitrated Ni-50Cr bipolar plates will be carried out to assess the potential of Cr-nitrides to meet DOE durability targets and to provide a basis to determine the optimal Cr-nitride composition and structure.
- Fuel cell testing of nitrated commercially available Ni-Cr alloy, nitrogen-modified 446 stainless steel, and nitrated model Fe-Cr base alloy bipolar plates will be pursued in collaboration with LANL and various industrial partners.
- Demonstrate viability of nitridation approach for thin metal sheets (planned collaboration with GenCell Corp).

Introduction

The bipolar plate is one of the most expensive components in PEMFCs. Thin metallic bipolar plates offer the potential for (1) significantly lower cost than currently-used machined graphite bipolar plates, (2) reduced weight/volume, and (3) better performance than developmental polymer/carbon fiber and graphite composite bipolar plates. However, most metals exhibit inadequate corrosion resistance in PEMFC environments. This leads to high electrical resistance by the formation of surface oxides and/or contamination of the polymer membrane by metallic ions, both of which can significantly degrade performance. Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion-resistant. Unfortunately, most conventional deposited coating methods (for metal nitrides) are too expensive for PEMFC stack commercialization or tend to leave pin-hole defects, which result in accelerated local corrosion and unacceptable performance.

Approach

The goal of this effort is to develop a bipolar plate alloy that will form an electrically conductive and corrosion-resistant nitride surface layer during thermal (gas) nitriding. There are three advantages to this approach. First, because the nitriding is performed at elevated temperatures, pin-hole defects are not expected. Thermodynamic and kinetic factors favor complete conversion of the metal surface to nitride. Rather, the key issues are nitride layer cracking, adherence, and morphology (discrete internal subsurface precipitates versus continuous surface layers), which can potentially be controlled

through proper selection of alloy composition and nitridation conditions. Second, the alloy can be formed into final shape by inexpensive metal forming techniques such as stamping prior to thermal nitridation. Third, thermal nitridation is an inexpensive, well-established industrial technique.

Results

In FY 2003, nitridation of a model Ni-50Cr alloy resulted in the formation of a Cr-nitride base surface layer that performed well in a 1000-hour, 0.7 V single-cell fuel cell test and a 4000-hour corrosion test at LANL [4]. Efforts in FY 2004 have been divided into two main areas: 1) manufacture and delivery of nitrated Ni-50Cr bipolar plates for fuel cell testing under more aggressive conditions than the 0.7 V test carried out in FY 2003 in order to establish the potential of Cr-nitrides to meet DOE durability goals, and 2) the formation of protective Cr-nitride layers on Ni- and Fe-base alloys with lower levels of Cr to meet DOE cost goals. Nitrated Ni-50Cr plates were delivered to LANL and General Motors for fuel cell testing. Blank plates of Ni-50Cr were also delivered to FuelCell Energy for machining of flow fields, to be followed by nitridation and fuel cell testing.

The Ni-50Cr alloy is ideal for proof-of-principle study of PEMFC behavior due to its amenability to forming external Cr-nitride phases on thermal nitridation. However, it is not commercially viable for most PEMFC applications due to cost (the high level of Ni; Fe is significantly less expensive) and manufacturability issues (the high level of Cr results in limited tensile elongation and rapid work hardening). Steady progress has been made in understanding protective Cr-nitride

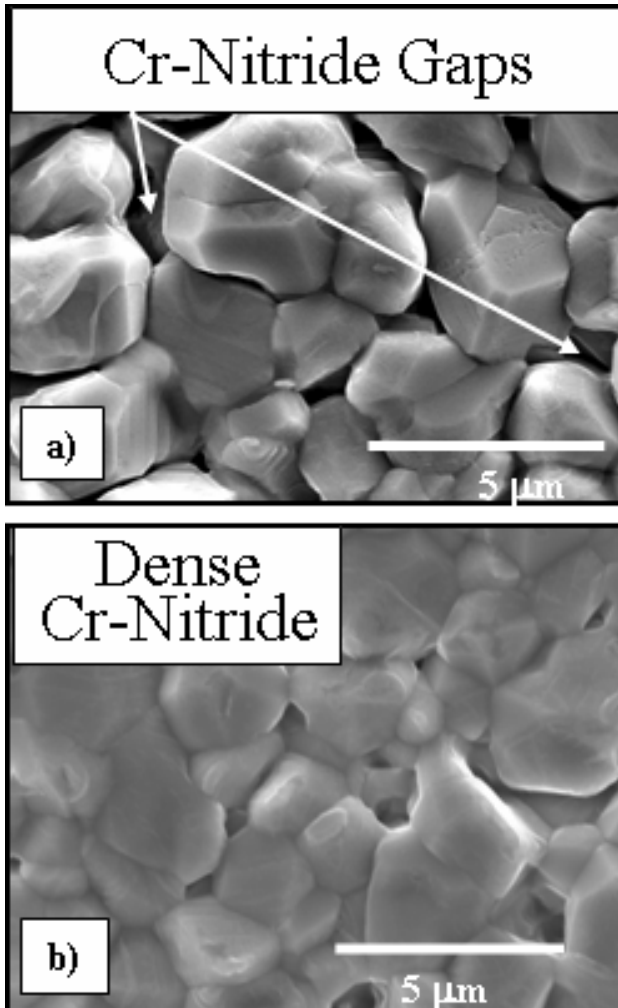


Figure 1. Scanning Electron Micrograph (SEM) Surfaces of Ni-35Cr-20Fe wt.% under Different Nitridation Conditions [3]; a) 1100°C/2 h/N₂, b) Proprietary

formation on Ni-Cr base alloys in commercially available composition ranges (lower levels of Cr). Figure 1a shows the surface microstructure of a model Ni-35Cr-20Fe alloy after the 1100°C, 2-hour pure nitrogen treatment typically used for Ni-50Cr. An external Cr-nitride layer was formed; however, the Cr-nitride grains were highly faceted, and gaps exposing substrate metal and less corrosion-resistant mixed nitride phases were present at the interfaces between grains. Modification of the nitridation conditions alone (Figure 1b, details proprietary) resulted in a dense Cr-nitride surface layer. Polarization evaluation in aerated pH 3 sulfuric acid at 80°C, which was used to screen for

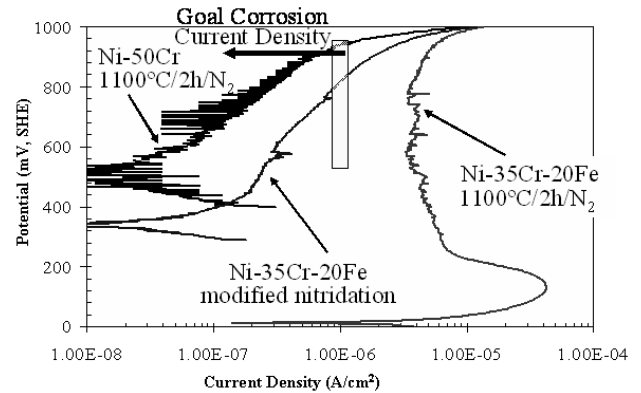


Figure 2. Anodic Polarization Curves in Aerated pH 3 Sulfuric Acid at 80°C (0.1 mV/s) (Ni-35Cr-20Fe nitrided as shown in Figure 1 [3])

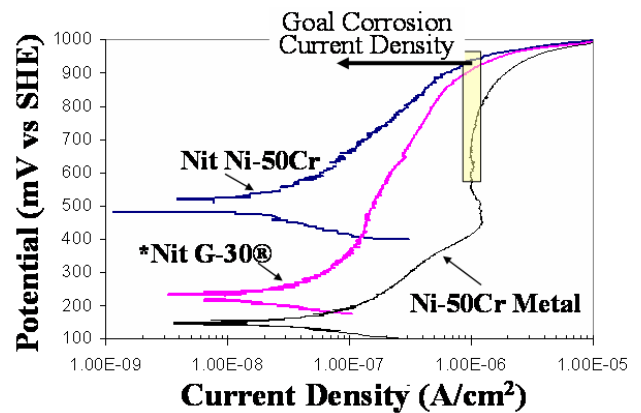


Figure 3. Anodic Polarization Curves in Aerated pH 3 Sulfuric Acid at 80°C (0.1 mV/s) (Nit = nitrided)

behavior under simulated PEMFC cathode conditions, showed that the change in surface morphology significantly improved corrosion resistance, approaching the range exhibited by nitrided Ni-50Cr (Figure 2). Figure 3 shows similar polarization data for a commercially available Ni-30Cr base alloy, HASTELLOY® G-30®, after nitridation (details proprietary). The preliminary results indicate behavior in the range of the nitrided Ni-50Cr. Fuel cell testing of a nitrided commercial Ni-Cr alloy (such as HASTELLOY® G-30®) is planned for a future date.

To meet DOE cost goals for transportation applications, an Fe-base alloy will almost certainly be needed. Formation of external, continuous Cr-nitride

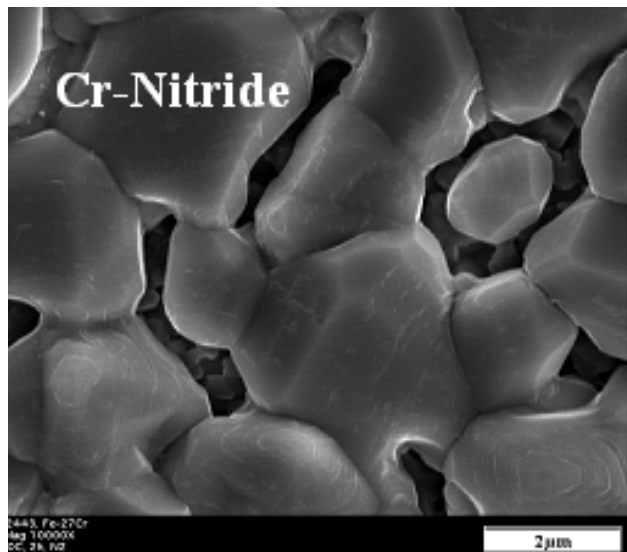


Figure 4. SEM Surface of 1100°C/2 h/N₂ Nitrided Fe-27Cr

surfaces on Fe-Cr base alloys is more complicated because the higher permeability of nitrogen in Fe (relative to Ni) impedes lateral growth to establish continuity and because there is potential for interference in Cr-nitride growth by Fe-base nitride formation. Figure 4 shows the surface of a model Fe-27Cr alloy after nitridation under standard Ni-50Cr conditions (1100°C, 2 hours, N₂). An external Cr-nitride surface was formed; however, it was not fully dense. A dense surface may be achievable via alloying additions and modification of nitridation conditions, similar to that demonstrated for Ni-35Cr-20Fe (Figures 1 and 2). The preliminary results of these efforts are promising and suggest that dense Cr-nitride layers can be formed on Fe-Cr base alloys.

In pursuit of dense Cr-nitride formation on Fe-Cr base alloys, a surface modification other than the formation of a dense continuous Cr-nitride surface layer was observed and imparted significant benefit [1,2]. In this regard, Figure 5 shows ICR data for a nitrided 446 stainless steel. The nitridation treatment decreased the ICR of the alloy by well over an order of magnitude. The effect was particularly evident at the low compaction loads relevant to fuel cell stacks, 100-150 N/cm² range, and was comparable to the levels exhibited by the nitrided Ni-50Cr. As shown in Figure 5, polarization under simulated aggressive

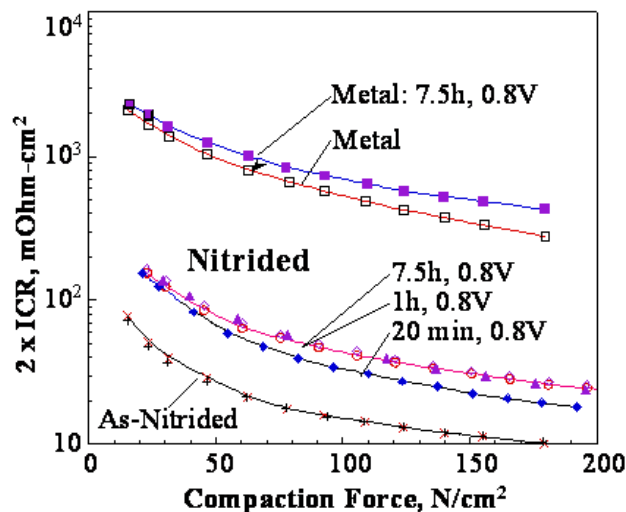


Figure 5. ICR Data for 446 As-Received/Nitrided after Polarization in Aerated pH 0 Sulfuric Acid + 2 ppm F⁻ at 70°C and Held at 0.8 V vs. SHE [1-3] {The plot is for 2x ICR because both coupon faces were measured (only 1 face polarized). Corrosion current densities on polarization hold were on the order of 1x10⁻⁶ A/cm².}

cathodic conditions (aerated 1M sulfuric acid + 2 ppm F⁻ at 70°C and ~0.8 V vs. SHE) for 20 minutes resulted in only a moderate increase in ICR. A slight further increase in ICR occurred between 20 minutes and 1 hour of polarization; the ICR effectively remained unchanged between 1 - 7.5 hours of polarization (the longest polarization hold time studied). After the 7.5-hour polarization, the ICR remained in the goal range of 20 mΩ-cm² at a load of ~150 N/cm² (note that 2x the ICR was plotted in Figure 5). Exposure of nitrided 446 (and untreated 446) under simulated aggressive anodic conditions (H₂-purged 1M sulfuric acid + 2 ppm F⁻ at 70°C and ~0.1 V vs. SHE) indicated an order-of-magnitude reduction in Fe dissolution compared to a 316L control coupon. Surprisingly, analysis of the nitrided 446 surface indicated that a dense, continuous Cr-nitride layer was not formed. Rather, a different mode of surface modification and protection mechanism was enacted—effectively a nitrogen modification of the native passive oxide layer. Detailed surface characterization and studies designed to understand and optimize this new effect are in progress. This finding can have important consequences because stainless steels hold the

potential to meet the cost goal for PEMFC bipolar plates in transportation applications.

Conclusions

Dense, electrically conductive, corrosion-resistant Cr-nitride surfaces can be formed on Ni-Cr and Ni(Fe)-Cr base alloys at Cr levels < 35 weight percent by thermal nitridation. Similar surfaces also appear possible on Fe-Cr base alloys. Further, nitridation of 446 stainless steel (and likely other Fe-Cr base alloys), under certain conditions that modify the native passive oxide layer but do not form a dense Cr-nitride surface, can lower ICR by over an order of magnitude without compromising corrosion resistance. Both of these surface modifications show promise for protecting metallic bipolar plates in PEMFC environments.

FY 2004 Publications/Presentations

1. H. Wang, M.P. Brady, K.L. More, H.M. Meyer, and J.A. Turner, "Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 2: Beneficial Modification of Passive Layer on AISI446", Journal of Power Sources (in press).
2. H. Wang, M.P. Brady, and J.A. Turner, "Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 1 Model Ni-50Cr and Austenitic 349TM Alloys", Journal of Power Sources (in press).
3. M.P. Brady, H. Wang, I. Paulauskas, B. Yang, P. Sachenko, P.F. Tortorelli, J.A. Turner, R.A. Buchanan, "Nitrided Metallic Bipolar Plates for PEM Fuel Cells", Proceedings of The 2nd International Conference on Fuel Cell Science, Engineering and Technology, Rochester, NY (June 14-16, 2004). [paper and presentation].

4. M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, "Preferential Thermal Nitridation to Form Pin-Hole Free Cr-Nitrides to Protect Proton Exchange Membrane Fuel Cell Metallic Bipolar Plates", Scripta Materialia, 50(7) pp.1017-1022 (2004). [submitted FY 2003, Accepted FY 2004].
5. M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, "Thermally Grown Cr-Nitrides to Protect PEM Fuel Cell Metallic Bipolar Plates", presented at the 204th Meeting of the Electrochemical Society, Orlando, FL (October 16, 2003).
6. M.P. Brady, K.L. More, P.F. Tortorelli, I. Paulauskas, R.A. Buchanan, L.R. Walker, "Alloy and Process Development of Thermally Nitrided Metallic Bipolar Plates for Proton Exchange Membrane Fuel Cells", presented at ASM Fuel Cells: Materials, Processing, and Manufacturing Technologies Symposia, Pittsburgh, PA (October, 2003).

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", ORNL Invention Disclosure, February 1, 2004 (ID 1371,S-101, 971 provisional application April 2004).

