

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

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### Objectives

- Develop surface nitriding technology to protect metallic bipolar plates in proton exchange membrane fuel cell (PEMFC) environments.
- Demonstrate target low corrosion current densities and interfacial contact resistance (ICR) values.
- Deliver nitrided bipolar plates to collaborators for fuel cell testing.

### 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

Characteristic	2010 Goal	Status
Corrosion current density	$< 1 \mu\text{A}/\text{cm}^2$	Met in pH3 $\text{H}_2\text{SO}_4$ , 80°C, $\sim 0.9\text{V}$ vs standard hydrogen electrode (SHE)
Contact resistance	$< 10 \text{m}\Omega\text{cm}^2$	Met at $\sim 100\text{-}150 \text{N}/\text{cm}^2$
Durability	$> 5,000$ h stack lifetime under drive cycle conditions	Successful 1,160 h single-cell test under drive-cycle conditions (model nitrided Ni-Cr base alloy)
Cost	\$6/kW: Translates to metal plate $\sim$ \$5-7/lb alloy, 0.1mm thick, 500 $\text{cm}^2$ total plate area and 0.05mm cooling foil	Corrosion and contact resistance screening goals met for nitrided Fe-Cr-V alloys with potential to meet \$6/kW cost goal.

### Accomplishments

- 1,160 h single-cell fuel cell drive cycle test of model nitrided Ni-50Cr alloy plates at LANL with no loss of cell performance (no resistance increase, only 2 ppm Ni detected in MEA, Cr not detected).
- 900 h single-cell fuel cell wet/dry cycling test of nitrided G35™ (Ni-30Cr base) plates at General Motors (no resistance increase, no metal ions detected in the membrane electrode assembly).
- Dense, protective Cr-nitride surface formation demonstrated for Fe-27Cr-(2-6)V alloys that have the potential to meet DOE cost goals. Mechanism of nitridation reaction and basis for optimization established.

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### 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 due to the formation of surface oxides and/or contamination of the MEA 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 pinhole 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 Cr-nitride surface layer during thermal (gas) nitriding. There are three advantages to this approach. First, because the nitriding is performed at elevated temperatures, pinhole defects are not expected because 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 vs. continuous surface layers), which can potentially be controlled through proper selection of alloy composition and nitridation conditions. Second, the alloy can be formed into the final shape by inexpensive metal forming techniques, such as stamping, prior to thermal nitridation. Third, thermal nitridation is an inexpensive, well-established industrial technique (conventionally used for surface hardening).

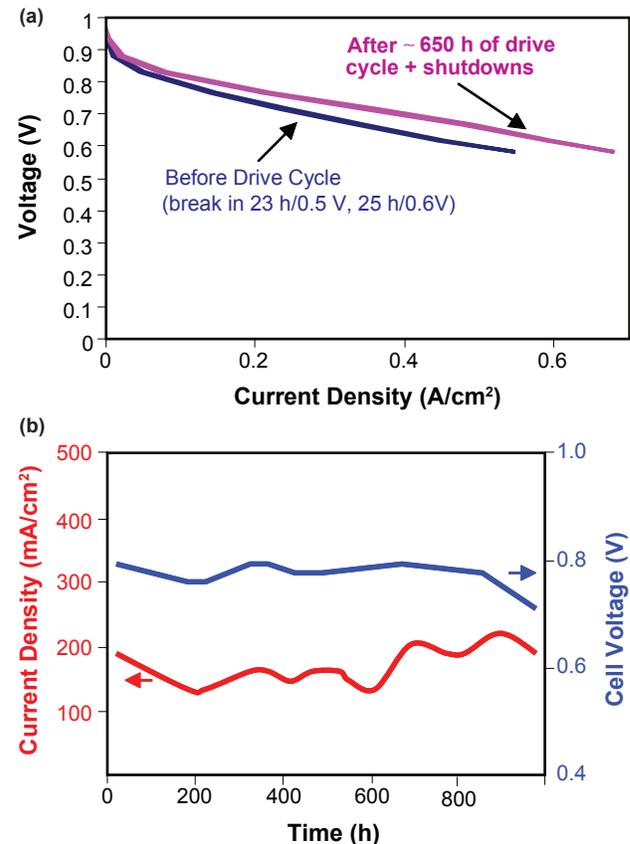
## Results

Work in FY 2006 involved two areas:

(1) completion of single-cell fuel cell testing of nitrided alloys under aggressive cyclic conditions, studied using nitrided Ni-Cr base alloys, and (2) understanding, evaluation, and optimization of the formation of similar protective Cr-nitride surfaces on Fe-Cr base alloys. Protective Cr-nitride surface formation was initially achieved for Ni-Cr base alloys. Subsequently, these materials have been used to evaluate behavior and performance of thermally grown Cr-nitride surfaces in fuel cell testing. Due to the high cost of Ni, Fe-Cr base alloys are needed to meet transportation cost goals. Protective Cr-nitride formation has proven more difficult to consistently achieve on Fe-Cr base alloys, and has resulted in the need to extensively study their reaction mechanism under nitriding conditions. The majority of effort (~90%) in FY 2006 was devoted to this issue.

Single-cell fuel cell testing of thermally grown Cr-nitride surfaces was conducted using nitrided Ni-50Cr (all compositions reported in wt.%) plates under drive-cycle conditions at LANL and under wet/dry cycling conditions using nitrided HASTELLOY® G-35™ (commercial ~Ni-30Cr base alloy) plates at General Motors (Figure 1). In the LANL drive-cycle test, the plates were initially run for 500 h under constant 0.7 V conditions (80°C). There was no plate resistance

increase or loss of performance. Analysis of the membrane electrode assembly (MEA) by x-ray fluorescence (XRF) indicated no metallic ion contamination within the detection limits of the measurement. The nitrided Ni-50Cr plates were then subjected to an additional 1,160 h of drive-cycle testing using a drive cycle of 0.94 V for 1 min, 0.60 V for 30 min, 0.70 V for 20 min, and 0.50 V for 20 min. An additional 24 full shutdowns (cell cooled off, gases removed, opened to air at connections) were superimposed in an attempt to induce even more aggressive conditions. No loss of performance was observed; in fact, performance slightly increased during drive-cycle testing (Figure 1a). A small amount of Ni contamination of the MEA,  $2 \times 10^{-6}$  g/cm<sup>2</sup>, was however detected. This small amount of Ni was likely the result of leaching from occasional, local regions of CrNiN phase that were initially formed during nitridation, instead of the more protective CrN/Cr<sub>2</sub>N surface. (Such local CrNiN phase formation can occur at regions of significant Cr-depletion in cast Ni-50Cr.) No attack of the CrN/Cr<sub>2</sub>N surface was evident.



**FIGURE 1.** Single-Cell Fuel Cell Test Data a) LANL drive-cycle test using nitrided Ni-50Cr anode and cathode plates. b) General Motors 40%/100% RH cycle test using nitrided HASTELLOY® G-35™ anode and cathode plates. (The performance dips correspond to the cycling in the RH.)

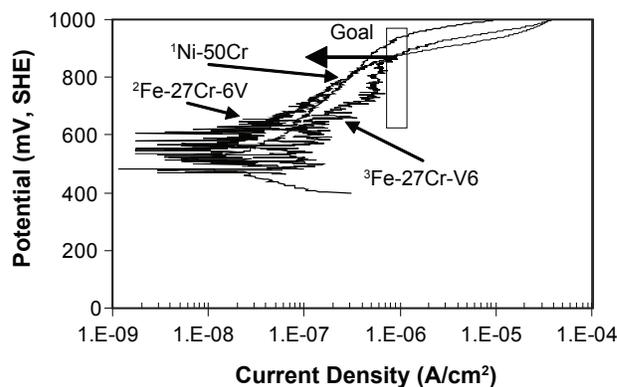
The General Motors test (Figure 1b, courtesy of Mahmoud Abdelhamid) was performed at 80°C and 0.2 A/cm<sup>2</sup>, with relative humidity (RH) cycled from 40% to 100%. Such cycling exacerbates leaching of fluoride ions from the MEA, and results in aggressive corrosion conditions for the bipolar plates. The performance of the nitrated HASTELLOY® G-35™ plates was similar to that of graphite under these test conditions, with no increase in cell resistance due to the plates and no contamination of the MEA with metallic ions detected by XRF after a 900 h test. It should be noted that a single-cell test at Fuel Cell Energy, Inc (courtesy of Ludwig Lipp) showed poor performance of a second set of nitrated HASTELLOY® G-35™ plates under less aggressive stationary fuel cell application conditions of 60°C and 400 mA/cm<sup>2</sup>. Post-test analysis of these plates indicated that they were poorly nitrated, with extensive oxide contamination at the outer surface of the plates and numerous regions where the desired CrN/Cr<sub>2</sub>N layer was not initially formed. Further analysis is in progress to determine whether the poorly nitrated surface in this case was primarily the result of an air leak in the nitrating furnace, or if the nitridation conditions initially selected for this alloy were not sufficiently robust. However, the overall behavior of the thermally grown Cr-nitride surfaces in the LANL and General Motors fuel cell tests showed a promising level of durability under cyclic conditions, and no evidence of attack or degradation of the Cr-nitride itself.

Nickel-chromium base alloys cannot meet DOE automotive cost goals due to the high cost of Ni; therefore, efforts were initiated to form a similar protective CrN/Cr<sub>2</sub>N surfaces on Fe-Cr base alloys by thermal nitridation. This is difficult because at commercially viable levels of Cr, < 30 wt.% Cr, permeability of nitrogen in Fe-Cr alloys is sufficiently high that internal nitride precipitates from the desired external protective nitride layer. The presence of an initially-formed Cr<sub>2</sub>O<sub>3</sub> layer was found to be effective in preventing internal nitridation of Fe-Cr base alloys, with subsequent nitridation conversion of the external Cr-oxide surface to external Cr-nitride. This conversion was found to be somewhat sluggish, and resulted in a semi-continuous Cr-nitride overlying the Cr-oxide, and borderline corrosion resistance.

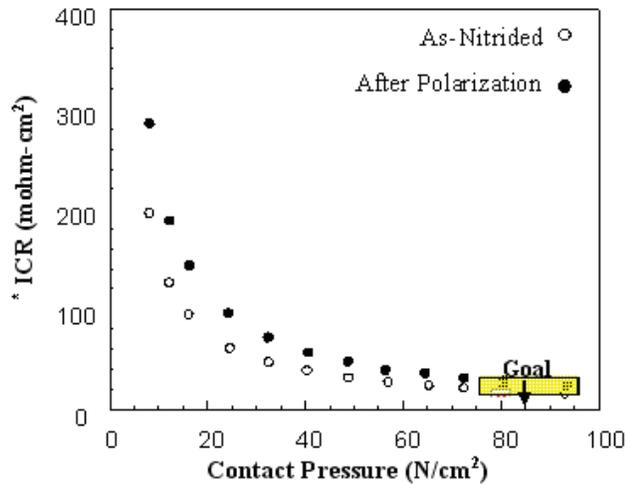
However, the use of initial oxide formation to limit internal nitridation has proven highly effective in Fe-27Cr alloys modified with 2 wt.% and 6 wt.% V. In the Fe-27Cr-2V and 6V alloys, O<sub>2</sub>-impurities in the nitriding environment resulted in the initial formation of a (V,Cr)<sub>2</sub>O<sub>5</sub> surface layer during heat up to the 900°C nitridation temperature, which was subsequently converted to a dense, fully continuous V-doped Cr-nitride surface layer, overlying an intermixed oxide/nitride region. Corrosion resistance and ICR values comparable to the nitrated Ni-50Cr (and thus meeting DOE targets) were achieved. Vanadium was effective

because VN has greater stability relative to V<sub>2</sub>O<sub>5</sub> than does CrN relative to Cr<sub>2</sub>O<sub>3</sub> (approximately 100 ppm O<sub>2</sub> is required to form oxide on V in N<sub>2</sub>-4H<sub>2</sub> at 900°C vs ~10 ppm for Cr), which aided conversion of the initially formed oxide to nitride. Vanadium is also readily soluble in Fe-Cr alloys, and V<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>, CrN-VN, and Cr<sub>2</sub>N-V<sub>2</sub>N are all, respectively, mutually soluble. (Formation of V<sub>2</sub>O<sub>5</sub>, which is toxic, and exhibits a low melting point, was not observed under the conditions studied.)

The promising results obtained with nitrated Fe-27Cr-2V and Fe-27Cr-6V wt.% were accomplished in a sealed nitriding environment, dependent on a narrow range of O<sub>2</sub>-impurity levels, and proved difficult to reproduce consistently. To evaluate the proposed mechanism, and to develop an industrially viable manner of consistently producing protective Cr-nitride surfaces on V-modified Fe-Cr alloys, preoxidation studies were investigated. Figure 2 shows polarization data in aerated pH 3 sulfuric acid at 80°C for Fe-27Cr-6V wt.% nitrated in flowing O<sub>2</sub>-getter N<sub>2</sub>-4H<sub>2</sub> after initial preoxidation in flowing Ar-2O<sub>2</sub> or Ar-10N<sub>2</sub>+O<sub>2</sub> impurities. Corrosion current densities were in the range of the nitrated Ni-50Cr, and met the DOE target of less than 1x10<sup>-6</sup>A/cm<sup>2</sup> up to ~0.9 V vs SHE. ICR values for preoxidized/nitrated Fe-27Cr-6V also met the DOE goal of 10 mohm-cm<sup>2</sup> at a contact pressure of only ~100 N/cm<sup>2</sup> (Figure 3). Corrosion screenings were also conducted under aggressive conditions of aerated pH 0 H<sub>2</sub>SO<sub>4</sub> + 2 ppm F at 70°C held for 7.5 h at 0.84 V vs. SHE. ICR values increased slightly (Figure 3), but still met the DOE goal at contact pressures of only ~100 N/cm<sup>2</sup>. A scanning electron microscope image cross-section of the nitrated Fe-27Cr-6V alloy preoxidized in Ar-10N<sub>2</sub> + O<sub>2</sub> impurities is shown in Figures 4a and 4b. It consisted of external V-doped Cr-nitride with finger-like projections into an inner region of V-Cr oxide,



**FIGURE 2.** Polarization data in aerated pH 3 sulfuric acid at 80°C:  
 (1) Ni-50Cr: nitrated at 1100°C, 2 h, N<sub>2</sub>-4H<sub>2</sub>  
 (2) Fe-27Cr-6V: preoxidized at 900°C for 8 h in flowing Ar-10N<sub>2</sub> + O<sub>2</sub> impurities followed by 900°C for 24 h in flowing, purified N<sub>2</sub>-4H<sub>2</sub>  
 (3) Fe-27Cr-6V: preoxidized at 800°C for 20 minutes in flowing Ar-2O<sub>2</sub> followed by 900°C for 24 h in flowing, purified N<sub>2</sub>-4H<sub>2</sub>.



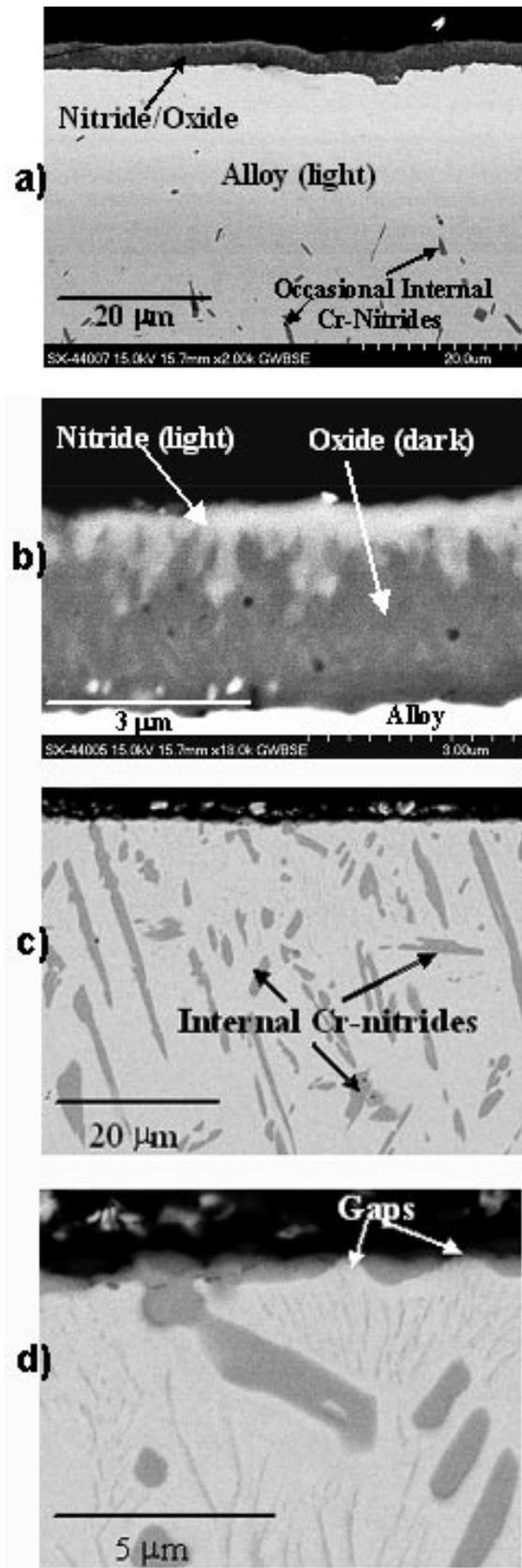
**FIGURE 3.** ICR data for Fe-27Cr-6V preoxidized at 900°C for 8 h in flowing Ar-10N<sub>2</sub> + O<sub>2</sub> impurities followed by 900°C for 24 h in flowing, purified N<sub>2</sub>-4H<sub>2</sub>. As-nitrided and after a 7.5 h hold in aerated pH 0 sulfuric acid + 2 ppm F<sup>-</sup> at 0.84V vs SHE. (Note that the plotted ICR values include resistance contributions from both major coupon faces.)

consistent with (V,Cr)<sub>2</sub>O<sub>3</sub>. Little internal nitridation was evident. The corresponding microstructure for binary Fe-27Cr nitrided in purified N<sub>2</sub>-4H<sub>2</sub> is shown for comparative purposes in Figures 4c and 4d. The alloy suffered from extensive internal nitridation, which partitioned the nitrogen away from the surface and prevented establishment of a dense, protective Cr-nitride surface layer.

A key aspect is that the preoxidation should be conducted so that Fe is not incorporated into the initially formed oxide layer, i.e. only V-Cr oxide is formed. An advantage of using oxidation to initially enrich the surface in Cr and V prior to converting to nitride is that such selective oxidation may be accomplished at relatively low levels of Cr and V, due to the low solubility of oxygen in Fe-base alloys and the high thermodynamic stability of Cr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>. Although ICR and corrosion studies have only been pursued for preoxidized and nitrided Fe-27Cr-6V to date, it is estimated that the composition range amenable to this approach can likely be extended downward to ~15-20 wt.% Cr and 0.5-2 wt.% V, which will lower alloy cost. It is further estimated that preoxidation time on the order of 30 minutes and nitridation time on the order of a few hours should be achievable.

### Conclusions and Future Directions

- Thermally grown Cr-nitride surfaces show good potential for durability under aggressive cyclic fuel cell operating conditions encountered in real-world applications.



**FIGURE 4.** SEM Cross-Sections of Preoxidized/nitrided Fe-27Cr-6V (a,b) and Binary Fe-27Cr (c,d)

- Protective Cr-nitride surface formation is possible on Fe-Cr-V base alloys that can potentially meet DOE cost goals.
- Efforts for the remainder of FY 2006 will focus on optimization of the preoxidation/nitridation treatment for V-modified Fe-Cr alloys, including exploration of lower Cr and V compositions. Test plates of nitrided Fe-27Cr-6V will be delivered to collaborators for fuel cell testing.
- This project ends in FY 2006. A go/no go decision for scale-up of this approach will occur via a proposal submitted for the 2007 DOE fuel cell call.

### Special Recognitions & Awards/Patents Issued

1. M.P. Brady, B. Yang, P.J. Maziasz, "Fe-base alloy and nitridation treatment for PEMFC bipolar plates" internal ORNL invention disclosure, patent disclosure pending.

### FY 2006 Publications/Presentations

1. (Invited) M.P. Brady, B. Yang, H. Wang, J.A. Turner, K.L. More, M. Wilson, F.Garzon, "Growth of Protective Nitride Layers for PEM Fuel Cell Bipolar Plate Applications", to be published in the August 2006 Issue of JOM.

2. B. Yang, M.P. Brady, D.J. Young, K.L. More, P.F. Tortorelli, E.A. Payzant, H. Wang, and J.A. Turner, "Growth of Multi-Functional Protective Nitride Layers on Fe-Cr Base Alloys for PEM Fuel Cell Bipolar Plates", to be submitted to Acta Materialia.

3. M.P. Brady, H. Wang, B. Yang, J.A. Turner, K.L. More, M. Bordignon, R. Molins, "Nitridation of Commercial Ni-Cr and Fe-Cr Base Alloys for PEM Fuel Cell Bipolar Plate Applications", to be submitted to International Journal of Hydrogen Energy.

4. B. Yang, M. P. Brady, P.F. Tororoelli, 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.

5. (Invited) 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.

6. 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", 208th Meeting of the Electrochemical Society, October 22-26, Los Angeles, CA, USA, 2005, paper No. 1007.