

V.B.1 Nitrided Metallic Bipolar Plates

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- GenCell Corporation, Southbury, CT

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Objectives

- Develop and optimize stainless steel alloys amenable to formation of a protective Cr-nitride surface by gas nitridation, at a sufficiently low cost to meet DOE targets and with sufficient ductility to permit manufacture by stamping.
- Demonstrate capability of nitridation to yield high-quality stainless steel bipolar plates from thin stamped alloy foils (no significant stamped foil warping or embrittlement).
- Demonstrate single-cell fuel cell performance of stamped and nitrided alloy foils equivalent to that of machined graphite plates of the same flow-field design (~750-1,000 h, cyclic conditions, to include quantification of metal ion contamination of the membrane electrode assembly [MEA] and contact resistance increase attributable to the bipolar plates).
- Demonstrate successful 10-cell, ~250 cm² active area fuel cell stack test utilizing stamped and nitrided metallic bipolar plates (~2,000 h, automotive drive cycle, to include quantification of metal ion contamination of the MEA and contact resistance increases attributable to the bipolar plates).

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:

- (A) Durability
- (B) Cost
- (C) Performance

TABLE 1. Status of Key Technical Targets Relevant for Metallic Bipolar Plates* (Targets obtained from DOE 2007 program plan [where noted] and internal ORNL assessment based on industrial input.)

Material wt% (sheet form unless specified as foil)	¹ Polarization (10 ⁻⁶ A/cm ²)		ICR (mohm-cm ²), both coupon faces, load of 150 N/cm ²		⁴ Estimated alloy cost \$/lb
	Anode	Cathode	As-Received	Polarized	
Targets	² <1	² <1	≤20	≤20	<7
Untreated Stainless Steels					
316L Metal	³ +12	11	300 ⁺	300 ⁺	3-7
446 Metal	-1	1	400	500	3-7
Developmental Nitrided Alloys					
Ni-(30-50)Cr	-3	<1	15-20	20 to 20-40	25-50 ⁺
446	-1	1	10	20-30	3-7
2205 foil (initial results)	-1	1	50-60	60-100	3-7
Fe-27Cr-6V	-6	1-2	10	20	7-15
Fe-20Cr-4V	-1 to -8 range	3-14 range	10	15-20	5-10
Fe-20Cr-4V foil (initial results)	-20	6	10	50-60	5-10

¹ NREL screening protocol. ~7.5 h in 70°C 1M H₂SO₄ + 2 ppm F⁻ at 0.84 V vs SHE (cathode, aerated) and 0.14 V vs SHE (anode, H₂-purged). These conditions represent an accelerated, highly aggressive screening evaluation. Internal ORNL project target current densities are ~ ±5x10⁻⁶ A/cm². Nitrided ORNL alloys have exhibited current densities in the range of 10⁻⁷ A/cm² (and lower) in less-aggressive environments at these potentials (e.g. pH 3 H₂SO₄ at 80°C).

² DOE 2010 targets. The test environment, conditions, and potential are not specified.

³ "+" current under anode conditions suggests metal dissolution which could lead to MEA contamination.

⁴ Estimated alloy cost by ORNL and GenCell to meet DOE bipolar plate cost target of \$5/kW.

* Corrosion and ICR measurements by Wang and Turner, NREL. ICR – interfacial contact resistance; SHE – standard hydrogen electrode

Accomplishments

- Ferritic and duplex stainless steel compositions amenable to 0.1 mm foil manufacture, stamping, and nitriding, that can also potentially meet the

internal ORNL \$5/kW bipolar plate target, have been identified and successfully manufactured into foil form for testing.

- Alloy/nitriding envelope capable of imparting ICR less than the internal ORNL 20 mohm-cm² target and high corrosion resistance (see Table 1) identified. Thermal nitriding cycles that can potentially meet DOE bipolar plate cost goals have also been identified.
- Ability to nitride stamped ~18 cm² active area alloy foils without embrittlement and with little warping demonstrated.



Introduction

Thin stamped 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 and amenability to high volume manufacture than developmental polymer/carbon fiber and graphite composite bipolar plates. However, most metals exhibit inadequate corrosion resistance in proton exchange membrane fuel cell (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 fuel cell 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 scale-up and demonstrate the technological and economic viability of thin (≤ 0.1 mm) stamped metallic bipolar plates protected by a thermal (gas) nitridation surface treatment. Proper selection of bipolar plate alloy composition and nitridation conditions can yield a pinhole free, electrically conductive and corrosion resistant Cr-nitride based protective surface layer. Proof-of-principle evaluation of nitrided model Ni-Cr base alloys (see Table 1) indicated that thermally grown Cr-nitride base surfaces exhibit excellent corrosion resistance and maintain low ICR in PEMFC environments, and based on single-cell fuel cell studies [1-3] have the potential to meet the DOE 5,000 h durability goals for automotive applications. Unfortunately, nickel-base alloys are too expensive for automotive PEMFC bipolar plate applications. Iron-base stainless steel alloys can

potentially meet the DOE cost targets. However, they exhibit high permeabilities to nitrogen, which results in internal Cr-nitride precipitation on nitridation instead of the desired continuous, protective Cr-nitride surface layer.

Efforts at ORNL and NREL [2-4] have identified an approach to bypass the high nitrogen permeability of Fe-Cr base stainless steels to permit protective Cr-nitride surface layer formation. It is based on preoxidation to form a Cr-rich oxide surface, followed by conversion of the surface Cr-oxide to Cr-nitride on nitridation. Small additions of vanadium to the alloy improve the behavior by modifying the Cr-oxide to make it more amenable to nitridation. Model preoxidized and nitrided Fe-27Cr-6V wt% alloy coupons have exhibited target ICR values and low corrosion current densities under simulated aggressive PEMFC anode and cathode conditions, comparable to that of the nitrided Ni-(30-50)Cr wt% base alloys (see Table 1) [3-4]. The model Fe-27Cr-6V wt% alloy is not viable for stamped bipolar plates due to limited ductility resulting from the high level of Cr and the potential for sigma phase formation and embrittlement during the thermal envelope used for nitriding. The relatively high level of expensive V additions also increases the alloy cost. Therefore, work is underway to develop lower Cr and V containing Fe-base alloys that exhibit sufficient ductility to permit stamping and are low cost, yet still amenable to protective Cr-nitride base surface formation on nitridation.

Results

Efforts in Fiscal Year 2008 were focused on co-optimizing “ductility” for stamping and low-cost alloy compositions with protective Cr-nitride surface formation, sufficient to meet DOE ICR and corrosion goals. Computational thermodynamic modeling of the Fe-Cr-V-Ni-C-Mn-Si system was used to guide alloy design, based primarily on considerations of microstructural stability, ferritic/austenitic phase volume fractions, and identifying the upper Cr and V content threshold to avoid embrittlement by sigma phase formation. Developmental ferritic, austenitic, and duplex stainless steel alloy bases were manufactured by laboratory scale arc-casting for evaluation of nitriding behavior and mechanical properties.

The best combination of low ICR and high corrosion resistance on nitriding under simulated aggressive anodic and cathodic PEMFC conditions was exhibited by a ferritic Fe20Cr-4V wt% composition (see Table 1 and Figures 1 and 2). Inductively coupled plasma (ICP) analysis of the test solutions after polarization indicated nitrided Fe-20Cr-4V exhibited 5-10 times lower Fe dissolution levels than control 316L (metal, not nitrided) under these aggressive test conditions, comparable to highly resistant stainless steels

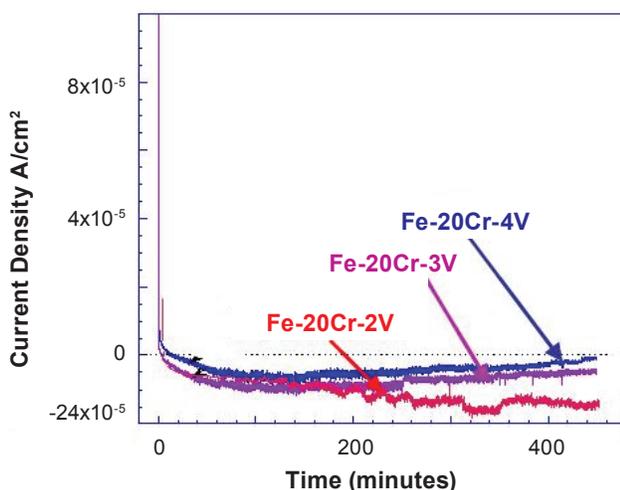


FIGURE 1. Static Polarization in H₂-Purged 1M H₂SO₄ + 2 ppm F/70°C/0.14 V vs SHE

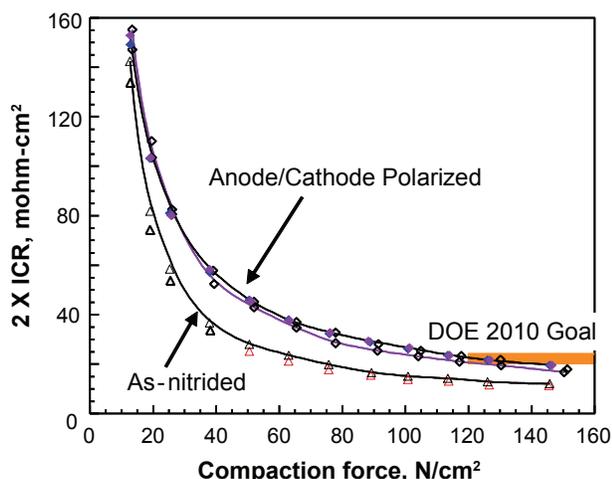


FIGURE 2. ICR data for nitrated Fe-20Cr-4V pre/post polarization of ~7.5 h in 70°C 1M H₂SO₄ + 2 ppm F at 0.84 V vs SHE (cathode, aerated, solid data points) and 0.14 V vs SHE (anode, H₂-purged, hollow data points). Note that this data reflects 2 x ICR, i.e. resistance at both coupon front and back faces included.

such as type 446 [5] (Tables 1 and 2). A drawback of 446 stainless steel (as with other stainless steels) is very high ICR values (Table 1). Nitridation can be used to reduce ICR without loss of corrosion resistance in 446 stainless steel [6], but the nitriding temperature cycle can result in brittle sigma phase formation and susceptibility to cracking of the test plates under loading. Hence, there is the need to develop the lower Cr, Fe-20Cr-4V and related alloys.

Relatively low ICR and high corrosion resistance was also exhibited by nitrated foil of a commercial duplex alloy 2205 (Tables 1 and 2). ICR values of the nitrated Fe-20Cr-4V and 2205 foils were moderately higher than the internal ORNL targets (Table 1),

and reflect the need for further optimization of the nitridation conditions for foil product. (Target ICR values were met in Fe-20Cr-4V and 446 sheet form, for example, see Table 1 and Figure 2.) Additions of Ni to improve ductility/amenability to stamping of Fe-Cr-V alloys were found to complicate protective Cr-nitride surface formation. Promising ICR and corrosion behavior was, however, exhibited by nitrated Fe-20Cr-2V-5Ni wt% (duplex) and Fe-20Cr-4V-10Ni wt% (primarily austenitic) alloys.

TABLE 2. NREL ICP analysis of test solutions from samples exposed for 7.5 h in 70°C 1M H₂SO₄ + 2 ppm F at 0.84 V vs SHE (cathode, aerated) and 0.14 V vs SHE (anode, H₂-purged).

Material	Metals ions in 100 ml solution (rounded to nearest 1 ppm)							
	Anode simulation				Cathode simulation			
	Fe	Ni	Cr	Mn	Fe	Ni	Cr	Mn
316L metal	21	2	5	-	9	1	2	-
Nitrated cast Fe-20Cr-4V	2	-	-	-	not available			
*Nitrated Fe-20Cr-4V foil	4	-	-	2	2	-	-	2
*Nitrated 2205 foil	1	-	-	1	1	-	-	1

* initial nitriding attempt

Exploratory compositions of Fe-20Cr-2V, Fe-20Cr-4V, Fe-15Cr-10Ni-3V, and Fe-20Cr-5Ni-2V wt% were successfully manufactured into 0.1 mm thick foil by ATI Allegheny Ludlum. Studies at GenCell Corp showed both developmental ferritic Fe-Cr-V alloys exhibited good amenability to stamping (Table 3). These findings illustrate that amenability to stamping flow fields does not necessarily correlate directly with uniaxial tensile elongation values, as evidenced by the superior stamping characteristics of the 444 ferritic alloy as compared to 316L and 904L austenitics (Table 3). This is an important consideration, as expensive Ni additions are needed to stabilize austenite, which typically exhibits higher levels of tensile elongation than ferritic and duplex alloys.

Stamped 18 cm² active area parallel flow field plates of Fe-20Cr-4V and commercial 2205 alloy foils were successfully nitrided (Figure 3). Some minor wrinkling of the foil after nitridation was noted, but in general the extent was less than the milestone target for warping (<2 mm) in these size test plates. The stamped foils could also be plastically deformed after nitriding, indicating significant embrittlement did not occur.

A preliminary analysis of nitriding costs was performed by Brian James of Directed Technologies, Inc. Initial feedback is that DOE cost targets are potentially achievable at large volumes assuming a dwell time at the nitriding temperature on the order of 1-3 h. Use of

TABLE 3. Stamping Assessment of Commercial and Developmental Alloy Foils in the 0.1 mm Thickness Range (18 cm² active area parallel flow fields formed)

Alloy	Description	Flow-Field Stamping (maximum channel depth/foil thickness)
444	Fe-18Cr-2Mo base ferritic	6
316L	Fe-18Cr-12Ni austenitic	5.25
904L	Fe-20Cr-25Ni-5Mo austenitic	5.25
Fe-15Cr-10Ni-3V	near austenitic	5.25
Fe-20Cr-4V	ferritic	4.38
Fe-20Cr-2V-5Ni	duplex	4.25
Fe-20Cr-2V	ferritic	4.13
2205	Fe-22Cr-5Ni-3Mo duplex	3.75
E-BRITE [®]	Fe-26Cr-1Mo ferritic	2.5

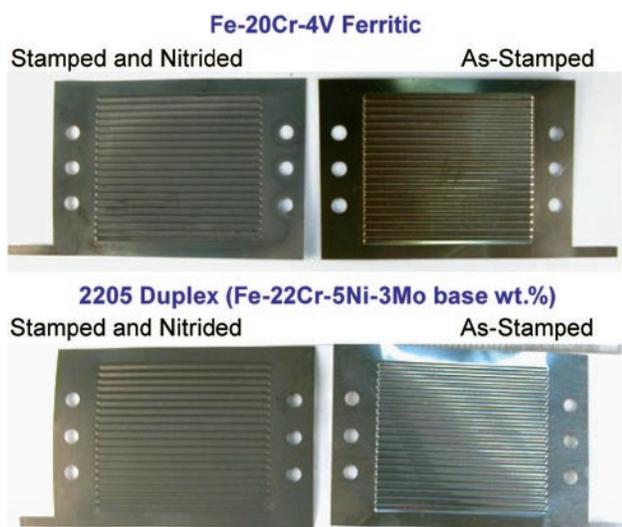


FIGURE 3. Preoxidized and Nitrided (1,000°C/2h) 18 cm² Active Area Parallel Flow Field Stampings of Fe-20Cr-4V and 2205

pulsed-mode, infrared-heating approaches for nitriding also holds the potential to meet DOE cost targets. This input will be used to guide optimization of the nitridation processing envelope.

Conclusions and Future Directions

The findings to date suggest sufficient compositional overlap exists to potentially balance the competing characteristics of stampability, alloy cost, and amenability to protective nitride formation. Near-term efforts will focus on:

- Detailed characterization and optimization of the surface chemistry and structure, corrosion, and electrical properties of nitrided Fe-20Cr-4V and nitrided 2205 foils.
- Finalization of baseline 15-25 cm² active area plate design for single-cell fuel cell testing of stamped and nitrided foils.
- Comparison of the single-cell fuel cell behavior of stamped and nitrided stainless steel foil bipolar plates with performance of graphite bipolar plates of similar flow field design. These results will serve as a go/no-go decision point for further scale-up and assessment of stamped and nitrided stainless steels by a 10-cell stack test using ~250 cm² active area plates.

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 7,247,403 (issued July 24, 2007).
2. M.P. Brady, J. H. Schneibel, B.A. Pint, P.J. Maziasz "Corrosion Resistant Metallic Bipolar Plates" U.S. Patent 7,211,346 (issued May 1, 2007).

FY 2008 Publications/Presentations

1. M.P. Brady et al., "Alloy Effects and Processing of Nitrided Metallic Bipolar Plates for Proton Exchange Membrane Fuel Cells", TMS Annual Meeting, March 9-13, New Orleans, Louisiana.
2. M.P. Brady et al., "Stamped and Nitrided Stainless Steels for PEM Fuel Cell Bipolar Plates", 2007 Fuel Cell Seminar & Exposition San Antonio, Texas, Oct 15-19, 2007.
3. H. Wang, J. A. Turner and M. P. Brady, "Nitridation of a super-ferritic stainless steel for PEMFC bipolar plate", 212th ECS meeting, Washington, D.C., USA, Oct. 7-12, 2007.

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1. 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).
2. M.P. Brady, H. Wang, B. Yang, J.A. Turner, M. Bordignon, R. Molins, M. Abd Elhamid, L. Lipp, L.R. Walker, "Growth of Cr-Nitrides on Commercial Ni-Cr and Fe-Cr Base Alloys to Protect PEMFC Bipolar Plates", *International Journal of Hydrogen Energy*, 32(16), pp. 3778-3788 (2007).
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5. H.L. Wang and J.A. Turner, "Ferritic stainless steels as bipolar plate material for polymer electrolyte membrane fuel cells", Journal of Power Sources, 128 (2), pp. 193-200 (2004).

6. 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 138 (1-2), 75 (2004).