V.G.1 Nitrided Metallic Bipolar Plates

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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 potential for adoption in automotive fuel cell stacks.

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

Accomplishments

- Designed and manufactured stamped serpentine 16 cm^2 active area anode and cathode plates using 0.1 mm stainless steel foil and modified associated fuel cell test stand hardware to permit durability testing under cyclic single-cell fuel cell test conditions.
- Completed single-cell fuel cell evaluation of stamped, untreated 904L, 2205, and Fe-20Cr-4V stainless steel foils, stamped and pre-oxidized/nitrided 2205 and Fe-20Cr-4V stainless steel foils, and machined graphite plates of similar flow field design.
- Stamped and pre-oxidized/nitrided Fe-20Cr-4V stainless steel foil exhibited comparable voltage-current (V-I) performance curves to benchmark graphite plates over 1,000 h of cyclic single-cell fuel cell testing. Post-test analysis of the MEA by X-ray fluorescence indicated levels of metal ion contamination of only 0.1-0.3 x 10^{-6} g/cm^2 for both pre-oxidized/nitrided Fe-20Cr-4V and graphite plates. This level of contamination is in the range of the fresh MEA starting levels and indicates excellent resistance to metal ion dissolution by the stamped and pre-oxidized/nitrided Fe-20Cr-4V foil.

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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 behavior leads to high electrical resistance due to the formation of surface oxides and/or contamination of the

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%	[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	[1]Polarized	
Targets	[2]<1	[2]<1	≤20	≤20	<7
Untreated Benchmark Stainless Steel Sheet Material					
316L Metal	[3]+12	11	300+	300+	3-7
446 Metal	-1	1	400	500	3-7
Nitrided Sheet Material					
Ni-(30-50)Cr	-3	<1	15-20	20 to 20-40	> 15
446	-1	1	10	20-30	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
Untreated Stainless Steel Foils					
2205	-8	50	670	not checked	3-7
Fe-20Cr-4V	-20	500	370	not checked	5-10
Nitrided Stainless Steel Foils					
2205	-4	1	20-50	50-100	3-7
Fe-20Cr-4V	-3	6	15-20	40-50	5-10

1. NREL screening protocol. ~7.5 h in 70°C 1M H_2SO_4 + 2 ppm F^- at 0.84 V vs SHE (cathode, aerated) and 0.14 V vs SHE (anode, H_2-purged). These conditions represent an accelerated, highly aggressive screening evaluation. Internal ORNL project target current densities are ≤ ~ ±5x10^{-6} A/cm^2.
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

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 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) nitrided surface. Proper selection of bipolar plate alloy composition and nitridation conditions can yield a pin-hole 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 interfacial contact resistance (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 nitriding 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 pre-oxidation to form a Cr-rich oxide surface, followed by conversion of the surface Cr-oxide to Cr-nitride on nitriding. Small additions of vanadium to the alloy improve the behavior by modifying the Cr-oxide to make it more amenable to nitriding. Model pre-oxidized 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, that are 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, which result from the high level of Cr, and the potential for sigma phase formation and embrittlement during thermal 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 formation of a protective Cr-nitride base surface.

Results

A preliminary analysis of nitriding costs was performed by Brian James of Directed Technologies, Inc. in Fiscal Year 2008. Initial feedback was 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. Efforts in FY 2009 were therefore focused on nitriding dwell time cycles of <3 h at 900-1,000°C. Foil form of 2205 stainless steel (Fe-22Cr-5Ni wt% base) and developmental Fe-20Cr-4V alloys were down selected for pre-oxidation/nitridation evaluation and single-cell fuel cell testing. Unlike earlier model sheet form alloys, which formed continuous Cr-nitride surfaces, the surfaces formed on the alloy foils using the short nitriding dwell times consisted of a mixed nitride/oxide structure (Figure 1). The Fe-20Cr-4V formed a Cr_2O_3 surface layer containing through-thickness V-nitride particles (Figure 1a). In contrast, regions of continuous Cr_2O_3 were observed on nitrided 2205 foil (Figure 1b), which resulted in locally unacceptable regions of high electrical resistivity. ICR and corrosion evaluation (Table 1) indicated significant improvement of the pre-oxidation/nitridation properties relative to as-received stainless steel foils (no surface modification treatment); however, the values were not as good as those previously achieved with the model materials that formed continuous Cr-nitride surfaces. In particular, ICR was moderately higher both pre- and post- corrosion testing. There was also some run-to-run ICR scatter, especially for the pre-oxidized/nitrided 2205 foil

Single-cell fuel cell testing was conducted with a test cycle of open-circuit voltage for 1 min, 0.60 V for 30 min, 0.70 V for 20 min, and 0.50 V for 20 min using a 50 micron high-performance MEA. The best short term V-I performance curves were exhibited by pre-oxidized/nitrided Fe-20Cr-4V, which was moderately better than untreated 904L stainless steel (highly alloyed stainless steel benchmark based on Fe-25Ni-20Cr-5Mo wt%) and machined graphite (Figure 2a). (It is speculated that the graphite plate V-I performance behavior was moderately lower due to minor differences between the machined graphite and stamped stainless steel flow fields.) The stamped and pre-oxidized/nitrided 2205 foils exhibited

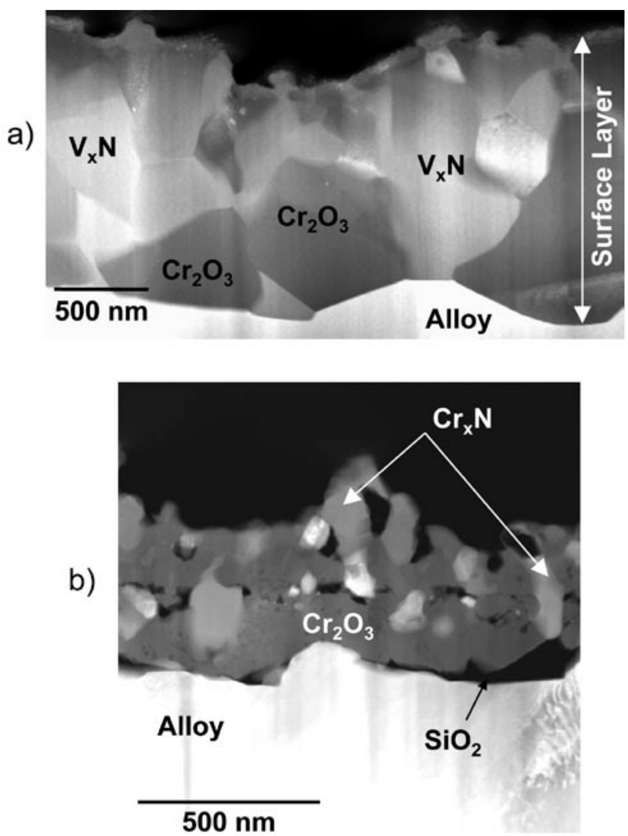

FIGURE 1. High angle annular dark field scanning transmission electron microscopy cross-section of pre-oxidized and nitrided Fe-20Cr-4V (a) and 2205 (b) stainless steel foils.

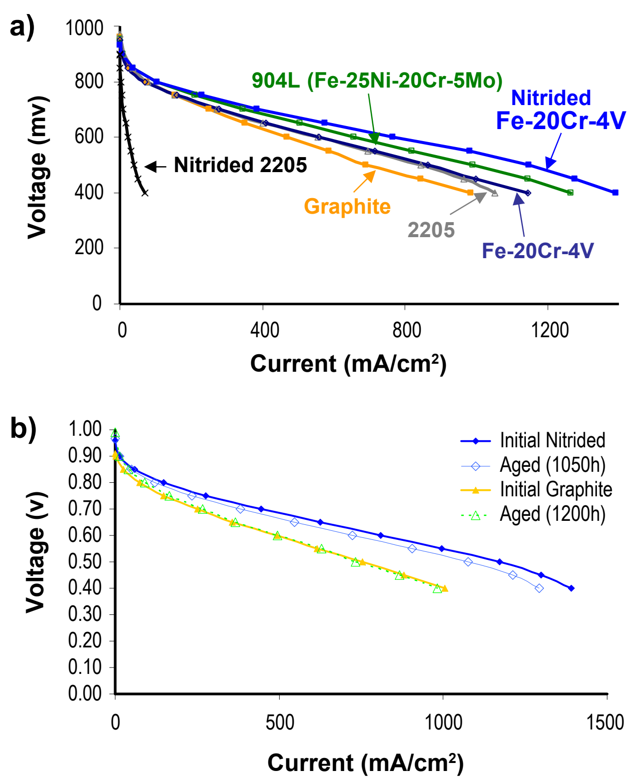

FIGURE 2. Single-Cell fuel cell test V-I curves. a) initial performance; b) performance of 1,000+ h aged plates using a fresh MEA.

poor behavior (Figure 2a), which was attributed to regions of continuous Cr_2O_3 formed in the surface, and were dropped from the test matrix. Stamped plate/MEA integration design issues resulted in MEA failure at gas inlet/outlet regions after only 50-100 h of operation for all materials evaluated (not related to bipolar plate materials effects). This issue was resolved by switching to thicker 175 micron MEAs for durability testing, with a final performance check made with fresh 50 micron MEAs using the aged test plates/foils.

Over 1,000 h of single-cell fuel cell testing was accomplished for the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils and benchmark graphite plates. No degradation in V-I performance curves was observed for the thicker 175 micron MEA. Figure 2b shows the final evaluation of the $1{,}000^+$ h aged plates with a fresh 50 micron MEA. The V-I curves for the graphite were essentially identical to the initial curves obtained with fresh graphite plates. A very slight performance decline was noted in the V-I data for the stamped and pre-oxidized/nitrided Fe-20Cr-4V, and this difference may be within the range of run-to-run variation. Post-test visual examination of the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils (Figure 3) showed no evidence of corrosion attack (some slight staining and carbon deposition from the MEA was observed- analysis of the post-test surface is planned). Analysis of the 175 micron MEAs from the 1,000 h durability tests indicated levels of Fe contamination of only 0.1-0.3 x 10^{-6} g/cm^2 for both the stamped and pre-oxidized/nitrided Fe-20Cr-4V and graphite plates. (No Cr or V was detected.) This level of Fe contamination is in the range of the fresh MEA starting levels and indicates excellent resistance to metal ion dissolution by the stamped and nitrided Fe-20Cr-4V foil.

Conclusions and Future Directions

The findings to date indicate good promise for the stamped and pre-oxidized/nitrided Fe-20Cr-4V foils as a bipolar plate material. Efforts in FY 2010 will focus on:

- Reduced nitriding cost and improving performance using rapid nitriding cycles with quartz/plasma lamps.
- Teaming with a fuel cell equipment manufacturer for manufacturability assessment (stamping and welding) and extensive fuel cell testing.

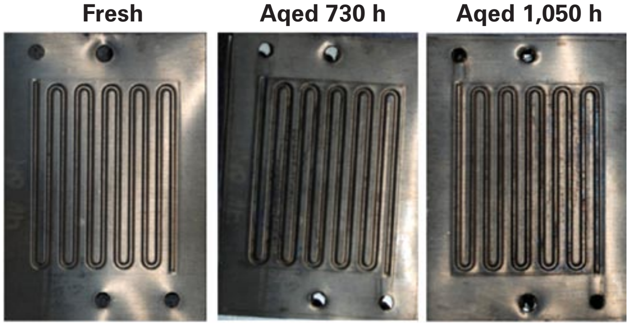

FIGURE 3. Macrographs of cathode-side stamped and pre-oxidized/nitrided Fe-20Cr-4V test foils as-nitrided and after 730 and 1,050 h of single-cell fuel cell testing.

FY 2009 Publications/Presentations

1. M.P. Brady, H. Wang, J.A. Turner, H.M. Meyer, K.L. More, P.F. Tortorelli, and B. McCarthy, "Pre-Oxidized and Nitrided Stainless Steel Foil for Proton Exchange Membrane Fuel Cell Bipolar Plates: Part 1 Corrosion, Interfacial Contact Resistance, and Surface Structure" to be submitted to Journal of Power Sources 2009.

2. T.J. Toops, M.P. Brady, F. Garzon, T. Rockward, J. Pihl, P.F. Tortorelli, D. Gervasio, and F. Estevez, "Pre-Oxidized and Nitrided Stainless Steel Foil for Proton Exchange Membrane Fuel Cell Bipolar Plates: Part 2 Single-Cell Fuel Cell Evaluation" to be submitted to Journal of Power Sources 2009.

References

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, 3778 (2007).

3. M.P. Brady, B.Yang, H. Wang, J.A. Turner, K.L. More, M. Wilson, and F. Garzon, "Formation of Protective Nitride Surfaces for PEM Fuel Cell Metallic Bipolar Plates", JOM-Journal of Metals, Minerals, and Materials Society, 58, 50 August 2006.

4. B. Yang, M.P. Brady, H. Wang, J.A. Turner, K.L. More, D.J. Young, P.F. Tortorelli, E.A. Payzant, and L.R. Walker, "Growth of Cr-Nitride Surfaces to Protect Stainless Steels for Proton Exchange Membrane Fuel Cell Bipolar Plates", Journal of Power Sources, 174, 228 (2007).

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, 193 (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, 75 (2004).