

V.L.1 Nitrided Metallic Bipolar Plates

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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 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost
- Performance

Objectives

- Develop and optimize stainless steel alloys amenable to formation of a protective Cr-nitride

TABLE 1. Status of key technical targets relevant for metallic bipolar plates (DOE tentative revised targets). Data shown for archival nitrided Fe-20Cr-4V foil coupons from the successful 1,000 h cyclic single-cell fuel cell stamped foil test set [1-3]. Results for a benchmark untreated stainless steel, 904L, are also shown as measured corrosion current density values are sensitive to test cell setup in the pH3 sulfuric acid solutions specified by the DOE targets.

Parameter	2010/2015 Targets	904L Foil (ORNL Benchmark)	Nitrided Foil Fe-20Cr-4V
Plate Cost (\$/kW) ^a	5/3	Estimated 6-10	Estimated 6-7 (1-2 h nitriding cycle)
Current Density Anode ($\mu\text{A}/\text{cm}^2$) ^b	<1 ^e	~8-9 at -0.15 V ~5 at 0 V <1 at +0.25 to +0.6 V, no active peak	<3 at -0.15 to +0.3V (SHE) active peak at +0.4V
Current Density Cathode ($\mu\text{A}/\text{cm}^2$) ^c	<1 ^e	1.5 at 7.5 h hold	~8 to 9 at 7.5 h hold
Areal Specific Resistance ^d ($\text{m}\Omega\text{-cm}^2$) at 150 N/cm ²	<20	As received: 300 Polarized: 700	As received: 12 Polarized: 29
Forming Elongation (%) ^e	40	Estimated \geq ~40	Estimated 20-25

^a Based on 2002 dollars and costs projected to high volume production (500,000 stacks per year).

^b pH 3, 0.1 ppm hydrofluorhydric acid (HF), 80°C, peak active current $< 1 \times 10^{-6}$ A/cm² (potentiodynamic test at 0.1 mV/s, ~ -0.15 V to +0.84 V (standard hydrogen electrode, SHE) de-aerated with Ar purge.

^c pH 3, 0.1 ppm HF, 80°C, passive current $< 5 \times 10^{-8}$ A/cm² (potentiostatic test at +0.84 V (SHE) for at least 24 hours, aerated solution.

^d Includes contact resistance (on as-received and after potentiostatic cathode experiment) measured per Wang, et al, J Power Sources 115 (2003) 243-251. Value shown includes top and bottom face contributions.

^e May have to be as low as 1 nA/cm² if all corrosion product ions remain in ionomer.

Accomplishments

- Promising preliminary results with quartz lamp technology to reduce nitriding cycle time from 1-2 hours to <10 minutes to reduce processing costs.
- Promising preliminary automotive flow field stamping assessment of ORNL Fe-20Cr-4V alloy.



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 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 nitride-based protective surface layer. Proof-of-principle was established via nitridation of model Ni-Cr base alloys to form thermally grown Cr-nitride base surfaces that exhibited excellent corrosion resistance and maintained low interfacial contact resistance (ICR) in PEMFC environments [4]. Unfortunately, Ni-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 and poor corrosion resistance on nitriding instead of the desired continuous, protective Cr-nitride surface layer.

Efforts led by ORNL and NREL [4-6] have identified an approach to bypass the high nitrogen permeability of

Fe-Cr base stainless steels to permit protective nitride surface layer formation. It is based on pre-oxidation to form a Cr-V-rich oxide surface, followed by nitridation of the oxide layer to form a mixed nitride/oxide surface structure [1-4]. The developed alloys contain small additions of V, up to 4 wt%, to aid in conversion of the initially formed surface oxide to nitride. For the low-cost Fe-20Cr-4V wt% alloy developed by ORNL, using short nitriding cycle times (1-2 h) to reduce nitriding cost, a mixed nitride/oxide surface consisting of “through oxide-thickness” V-rich nitride particles dispersed in Cr-rich oxide, is formed [1-3]. The Cr-base oxide and the V-nitride surface provide for corrosion resistance and the V-nitride particles provide low ICR with electrical connectivity from the surface through the oxide to the underlying metal.

Results

Single-cell fuel cell testing of pre-oxidized/nitrided Fe-20Cr-4V foil stampings (referred to as “nitrided” in the remainder of the paper for simplicity), 904L (Fe-22Cr-24Ni-4Mo wt% base) stampings (no surface treatment), and machined graphite plates were completed in Fiscal Year (FY) 2009 [1-3]. 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 was used, with 1,000 hours (h) of durability testing evaluated for each material. All three materials showed good durability with no significant degradation in cell power output. Post-test analysis indicated no metal ion contamination of the MEAs occurred with the nitrided Fe-20Cr-4V or graphite plates, and only a minor amount of contamination was detected with the 904L plates ($1.1 \mu\text{g}/\text{cm}^2$ Fe and $0.18 \mu\text{g}/\text{cm}^2$ Cr). The 904L was used as a benchmark material in addition to graphite because its high Cr, Mo, and Ni content result in excellent corrosion resistance in PEMFC environments. However, as shown in Table 1, the ICR value of 904L, similar to other untreated stainless steels, exceeds DOE targets by over an order of magnitude. In FY 2010, untreated stampings of type 321 stainless steel (type 316 Fe-18Cr-12 Ni stainless with 0.3-0.7 wt% Ti) were also evaluated in order to assess the aggressiveness of the aforementioned single-cell test cycle for a lower alloy content, conventional grade austenitic stainless steel. Extensive corrosion of the 321 test plates was observed after only 120 h of operation, indicating that the cyclic test conditions employed were aggressive.

Efforts in FY 2010 were directed to three primary tasks: 1) single-cell fuel cell evaluation of repeat nitrided Fe-20Cr-4V stampings treated over a range of conditions to assess robustness to variable nitridation reaction conditions, 2) assessment of the potential for reduced nitriding cost and improved performance using rapid nitriding cycles with quartz/plasma lamps, and 3) amenability assessment of the developed ferritic Fe-Cr V

alloys for stamping of state-of-the-art automotive bipolar plate flow-fields.

Figure 1 shows initial single-cell fuel cell polarization curves (<150-200 h total cycle testing) for a series of ~15 cm² active area stamped and nitrided Fe-20Cr-4V foils using a Nafion[®] 212 MEA. Nitridation peak temperature hold times were performed at 1, 1.5, and 2 h at 1,000°C to intentionally yield a wide range of nitrogen/oxygen mass uptakes and surface structures to simulate the degree of variability that may be encountered in mass production. For comparative purposes, results obtained with the Nafion[®] 212 MEA for the nitrided (1 h at 1,000°C) Fe-20Cr-4V stampings that previously accumulated ~1,500 h of total fuel cell operation (marked aged 1,500 h in Figure 1) as part of the FY 2009 durability assessment are included in Figure 1 [1-3]. The voltage-current (V-I) curves for these materials were remarkably similar, with the 1- and 1.5-h nitrided plates essentially the same as the 1,500 h aged stampings. The 2-h nitrided stampings, which were intentionally overnitrided, showed slightly higher performance V-I curves, possibly due to a higher volume fraction of conductive nitride phase.

One-thousand h durability evaluation is underway for the 1.5- and 2-h nitrided plates. After ~600 h of evaluation, the V-I curves for the 2-h nitrided material show excellent behavior with no evidence of performance degradation. However, performance degradation was observed after ~600 h for the 1.5-h nitrided material, which, based on N and O mass uptake on nitridation, was expected to exhibit good performance. Visual examination of the 1.5-h nitrided plates confirmed signs of corrosion attack. Surface chemistry and cross-section analysis are planned to identify the reasons for the unexpected susceptibility to corrosion of this material. Although preliminary, the apparent degradation of the 1.5-h nitrided stamping during the durability assessment repeat tests is a concern for scale up of the current Fe-20Cr-4V alloy

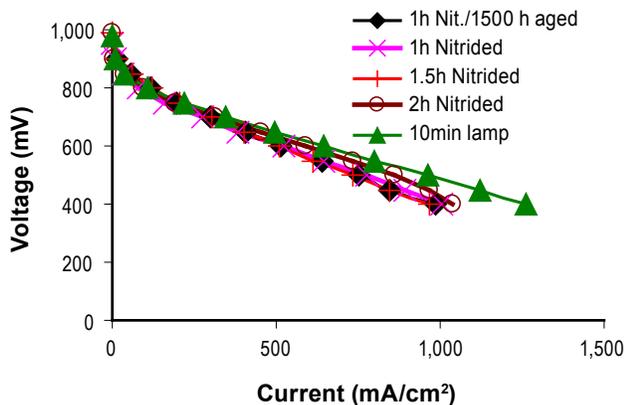


FIGURE 1. Single-Cell Fuel Cell V-I curves for Stamped and Nitrided Fe-20Cr-4V Alloy Foils

and nitriding cycle to commercial production. It is possible that the steps taken to reduce bipolar plate cost, relatively low alloy Cr and V content and use of short, 1-2 h conventional furnace peak temperature holds for nitriding may result in excessive variability in corrosion resistance of the nitrided surface. Longer nitriding cycles may solve this issue, but would also result in increased production cost. Two routes to addressing this potential issue without cost increase are being pursued: 1) use of rapid thermal cycle quartz lamp technology for nitriding of Fe-20Cr-4V and 2) evaluation of a more Cr-rich alloy foil (Fe-23Cr-4V), which is expected to exhibit a more robust nitrided surface structure, but must first demonstrate sufficient amenability to stamping. The increase in Cr level from 20 wt% to 23 wt% is not expected to significantly increase alloy cost, but may decrease alloy ductility and amenability to stamping.

Initial single-cell fuel cell polarization curves for stamped Fe-20Cr-4V foil nitrided at 1,000°C for 10 minutes using quartz lamp technology for heating are also shown in Figure 1. Despite the very short nitriding cycle, V-I performance behavior superior to the conventional furnace nitrided Fe-20Cr-4V foils was observed. Figure 2 shows X-ray photoelectron spectroscopy (XPS) of the as-nitrided surface. Strong enrichment of V and N are evident, suggesting a high volume fraction of V_xN phase particles in the (Cr,V)₂O₃ surface, consistent with the excellent single-cell V-I polarization curves obtained with this material (Figure 1). Of particular importance with regards to potential durability performance, no Fe was detected in the surface regions of the quartz lamp nitrided material. Nitridation of Fe-20Cr-4V foil using conventional furnaces typically results in a small amount of Fe retained in the surface (a few atomic percent), which may result in a lower degree of corrosion resistance. The rapid thermal cycle of the quartz lamp, which involves heating to peak temperatures in minutes rather than the hours for the conventional furnace, is speculated to minimize transient formation of Fe-rich oxidation

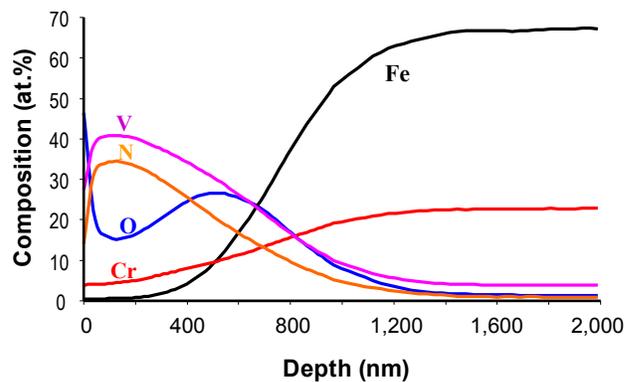


FIGURE 2. XPS Surface Analysis of 1,000°C/10 min. Quartz Lamp Treated Fe-20Cr-4V Alloy Foil

and/or nitridation products compared to conventional heating technology. Further exploration of quartz lamp nitriding is underway, with cyclic single cell fuel cell durability assessment of quartz furnace treated stampings planned.

As a prelude to automotive bipolar plate evaluation of nitrided Fe-20Cr-4V foil, a preliminary stamping assessment of the Fe-20Cr-4V foil for suitability to automotive fuel cell bipolar plate flow field designs was conducted in conjunction with General Motors (GM). Figure 3 shows results of the automotive stamping screening of the Fe-20Cr-4V alloy foil relative to austenitic 316L stainless steel foil. Comparable flow-field structures were obtained, which suggests that the mechanical properties of the Fe-Cr-V alloys may be sufficient for manufacture of stamped automotive flow-field designs.

Conclusions and Future Directions

Although some concerns still exist regarding repeatability and robustness of the nitrided surface formed on stamped Fe-Cr-V alloy foils using short, low-cost cycle times, results obtained to date have indicated sufficient promise to warrant evaluation for scale up by industrial end users. A cost-shared subcontract was placed with GM in summer 2010 to perform an in-depth manufacturing evaluation of Fe-Cr-V alloys, including stamping and laser joining of bipolar plate cooling channels. GM will also pursue single-cell fuel cell evaluation of bipolar plates made by GM from Fe-Cr-V alloy foils after nitridation at ORNL. Both conventional furnace nitriding and quartz lamp nitriding will be

evaluated. The project will conclude with completion of the GM evaluation effort.

Special Recognitions & Awards/Patents Issued

1. Claims for the patent disclosure “Iron-Based Alloy and Nitridation Treatment for PEM Fuel Cell Bipolar Plates” were allowed by the United State Patent Office in July 2010 (patent number not yet issued at the time of this report). Two previous patents were issued for the nitrided bipolar plate technology, #7,247,403 “Surface modified stainless steels for PEM fuel cell bipolar plates” and # 7,211,346 “Corrosion resistant metallic bipolar plate”

FY 2010 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”, *Journal of Power Sources*, 195 (17), pp 5610-5618 (2010).
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”, *Journal of Power Sources*, 195 (17), pp 5619-5627 (2010).
3. H. Wang et al., “Surface Modified Stainless Steels for PEM Fuel Cell Bipolar Plates” presented at the 216th Meeting of the Electrochemical Society, Oct 4–9, 2009, Vienna, Austria.

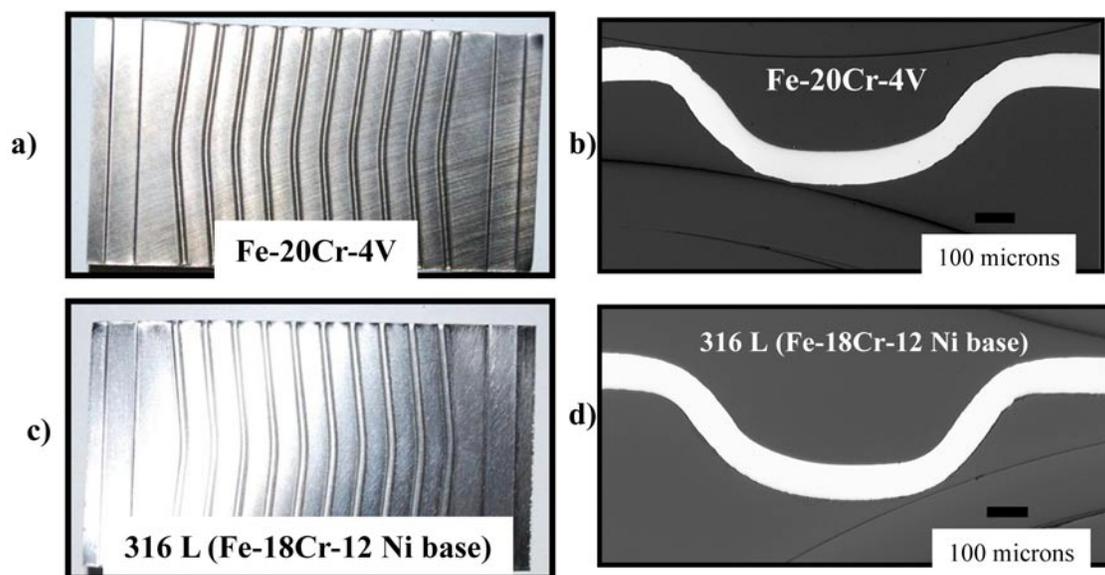


FIGURE 3. Macrographs (a,c) of a small stamped segment and light microscopy cross-sections (b,d) of Fe-20Cr-4V and 316L foils after stamping to an automotive bipolar plate flow-field configuration.

4. T.J. Toops et al, “Nitrided Metallic Bipolar Foils in PEM Fuel Cells”, presented at the 2009 Fuel Cell Seminar and Exhibition, Nov 16–19, 2009, Palm Springs CA USA.
5. P.F. Tortorelli et al, “Pre-Oxidized and Nitrided Stainless Steel Foil for Proton Exchange Membrane Fuel Cell Bipolar Plates”, presented at the 2010 TMS Annual Meeting, Feb 14–18, 2010, Seattle, WA USA.

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5. H. Wang et al, Journal of Power Sources, 138 (1-2), 75 (2004).
6. M.P. Brady et al., International Journal of Hydrogen Energy, 32(16), pp. 3778-3788 (2007).