

VII.D.3 Development of Low-Cost, Clad Metal Bipolar Plates for PEM Fuel Cells

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Assist the DOE in lowering the cost and improving the durability of proton exchange membrane (PEM) fuel cell stacks by reducing the material and manufacturing costs of metal bipolar plates for potential use in transportation applications.
- Substantially increase the resistance of metal bipolar plate materials to corrosion and mitigate the release of poisoning metallic ions into the membrane electrode assembly (MEA).

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

Technical Targets

This project is focused on developing low-cost strategies for fabricating high-performance metallic bipolar plates for PEM fuel cells (PEMFCs). Materials developed in this project will be employed in designing low-cost PEMFC stacks that meet the following DOE 2010 targets for transportation fuel cell stacks:

- Durability with cycling: 5000 hrs
- Cost: \$30/kW_e
- Stack power density: 2000 W/L
- Stack specific power: 2000 W/kg

Approach

In FY 2005, Phase 1 of the project was initiated as a feasibility study to determine the potential efficacy of a clad metal approach in fabricating low-cost/low-mass PEM bipolar plates. This study includes the following development steps:

- Design and analysis of potential clad material options.
- Fabrication of demonstration pieces for testing.
- Development of an appropriate passivation layer.

- Short-term electrical and corrosion testing of the passified clad bipolar plate material.
- Definition of the issues which are key in controlling the cost/properties of clad bipolar plates and identification of the steps required to optimize these characteristics.

Accomplishments

- Material combinations were identified that can be cost-effectively manufactured via roll cladding and thermally treated to potentially form a corrosion-resistant/electrically conductive passivation layer.
- Four of these combinations have been initially fabricated in the following demonstration thicknesses: Ti/430 stainless steel (SS)/Ti ($t_{\text{foil}} \sim 430 \mu\text{m}$), Ni/304 SS/Ni ($t_{\text{foil}} \sim 150 \mu\text{m}$), Ni/453 SS/Ni ($t_{\text{foil}} \sim 280 \mu\text{m}$), and Inconel 625/304 SS/Inconel 625 ($t_{\text{foil}} \sim 520 \mu\text{m}$). The various roll cladding parameters required to fabricate each material combination and the resulting material thicknesses are being optimized.
- A set of 34 experiments has been conducted to develop two different passivation layers, one which is nitride-based and the second which is nickel-based. Processing variables that were examined in this initial test matrix include coating temperature, coating time, process gas/media type and pressure, clad material type, and material surface condition/treatment.
- Corrosion testing for 300 h in 1M H₂SO₄ (with 2 ppm hydrogen fluoride added) at 80°C and polarization testing under similar operating conditions are currently being initiated on the first series of passified clad materials.

Future Directions

- Refine the design of the clad material by investigating the effects of the roll bonding process parameters, laminate geometry, and materials properties on the formability, microstructure, and ease of thermally nitrating the outer surfaces of the final rolled and stamped product.
- Investigate the conditions under which the passivation layer is grown on the laminate. Specific focus will be placed on mapping and understanding the conditions that lead to defects such as pin-holes, thin regions, and delaminations so that the passivation layer can be optimized for later full-size bipolar plates.
- Conduct an initial stamping/formability study.
- Initiate long-term corrosion/electrical testing of the optimized material.

Introduction

The bipolar plate is the most bulky component in the PEMFC stack (in both weight and volume) and one of the most expensive to manufacture. It not only serves as the electrical junction between serially connected cells, but also performs several other key functions in the device:

- Distributes the fuel and oxidant uniformly over the active areas of the cells.
- Facilitates water management of the membrane to keep it humidified, yet mitigate flooding.
- Acts as an impermeable barrier between the fuel and oxidant streams (particularly H₂) to maintain the hydrogen gradient across the membrane necessary for high power output.
- Provides some measure of structural support for the stack.

- Removes heat from the active areas of the cells.

The use of metal-based bipolar plates in PEMFC stacks potentially offers a number of advantages, particularly for transportation applications, including low-cost mass-production via stamping or embossing of sheet product; fabrication in very thin form (<200 μm) to reduce weight and volume in the overall stack; impermeability to fuel, oxidant and water vapor; and in general, excellent thermal conduction properties and good mechanical robustness, even as a thin stamped foil. The primary challenge with metal interconnects is surface corrosion, and the current drive to increase the operating temperature of the stack will only exacerbate this problem. Corrosion of the bipolar plate leads to a release of metal ions that can contaminate the electrolyte membrane and poison the electrode catalysts. In addition, the formation of a passivating oxide or oxyhydroxide

layer on the surface of the metal will increase the contact resistance between the bipolar plate and the adjacent graphite electrode backing layer by many orders of magnitude. Both conditions can significantly degrade stack performance. A number of researchers have investigated various schemes for protecting metallic bipolar plates, most of which rely on a thin, inert yet electrically conductive coating [1]. The greatest level of success that has been openly reported has been achieved with noble metal coatings such as gold and palladium. Unfortunately, commercial use of these materials, even as thin coatings, is cost-prohibitive.

Approach

Transition metal nitrides and carbides both offer a combination of high electrical conductivity and good corrosion resistance that makes them attractive for potential use as a protective surface layer in this application [2,3]. These compounds exhibit room-temperature electrical conductivities approximately one order of magnitude less than those of most metals, but over two orders of magnitude higher than that of graphite. Thus, a thin coating of the nitride or carbide will contribute negligibly to the overall resistance of the metal-based bipolar plate, which is expected to be significantly less than that of the alternative millimeter thick graphite or carbon composite plate during application. The approach in the present project is to fabricate a thin metal laminate sheet consisting of a middle filler layer sandwiched between two transition metal alloy layers that can be thermally nitrided or carbided to form a conductive, yet corrosion-resistant (i.e. passivating) barrier layer. Ideally, the material selected for the filler, which will form the thickest of the three layers, is chosen based primarily on material cost, formability, durability, and thermal conductivity. The cladding material, on the other hand, is selected based on the ease of nitriding or carbiding, the corrosion resistance and electrical transport properties of the resulting nitride or carbide, formability, and cost. In this way, the bipolar plate can be tailored to take advantage of the merits of each material while minimizing material and processing costs. An example of the type of laminate that could be considered for this application is a plain carbon steel alloy clad with a thin layer of titanium. In general, plain carbon steel is very inexpensive,

displays excellent thermal and electrical conductivities, and is quite ductile and readily rolled and stamped. Low-alloyed titanium also displays good formability and is easily nitrided at moderate temperatures, forming an acid-resistant, electrically conductive nitride. The manufacture of clad material products is a well-established, well-understood commercial process, and a number of domestic manufacturers exist that fabricate a wide variety of multilayer clad products in 50 – 300 μm thick sheets.

Results

The clad metal concept under study is shown schematically in Figure 1. The bipolar plate is essentially a composite laminate structure that consists of an inexpensive core material metallurgically bonded to an outer cladding layer via a roll bonding process (i.e., under elevated temperature and pressure). Additional layers can be formed into the laminate as necessary for improved functionality. For example, the structure illustrated in Figure 1 contains a brazing filler metal layer that would afford ready joining of two mated plates after stamping to form a bipolar plate component that contains an internal water cooling channel. With the initiation of this project, the first step was to survey potential candidate alloys for use in either the clad or core layer. For the selection of the core alloy, the following characteristics were desired:

- Low base cost (i.e., an inexpensive material)
- Mechanical robustness
- Moderate to low density

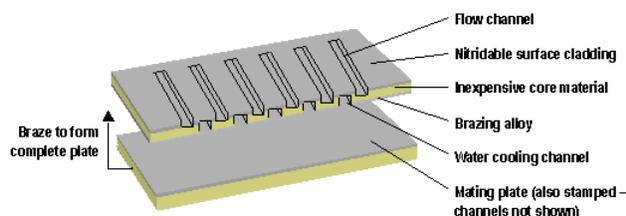


Figure 1. An illustration of the stamped clad metal bipolar plate concept. In this example, the bipolar plate component is formed from two stamped pieces that are joined via a brazing layer to form an internal water channel. Alternatively, the bipolar plate can be formed without the water channel from a single laminated metal piece that is clad on both exposed surfaces with a nitridable layer.

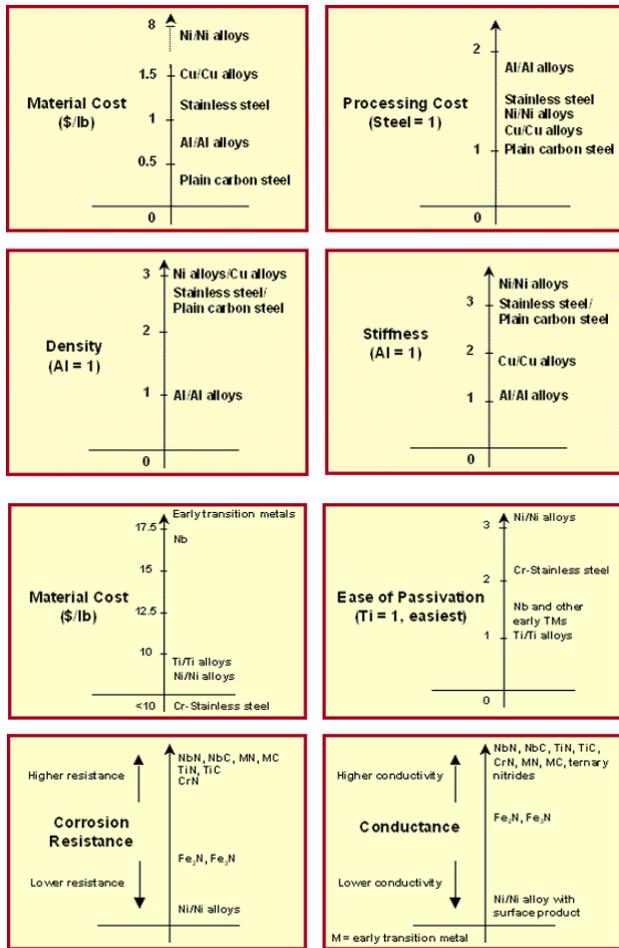


Figure 2. Key Factors Considered in Evaluating (a) Potential Core Material and (b) Potential Clad Material Candidates for the Clad Metal Bipolar Plate Concept

- High thermal conductivity (to facilitate thermal management)
- Low hydrogen permeability

Among these, the key properties were ranked as shown in Figure 2(a). The processing cost factor includes any required pre-treatment processing expenses (e.g., pickling or abrasion to remove surface scale prior to roll cladding). On the basis of this initial analysis, plain carbon steel appears to be the most viable core material candidate. However, given various unknowns, such as the possible need for corrosion resistance in the core layer due to exposure in the gas manifold and/or water feed-through regions of the as-formed bipolar plate, austenitic and ferritic stainless steel alloys were chosen to demonstrate viability in the feasibility

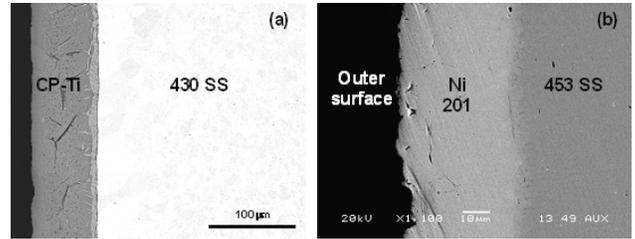


Figure 3. SEM Cross-Section Micrographs of Examples of Symmetric Clad Material Combinations Fabricated to Date: (a) Commercially Pure Titanium (CP-Ti)/430 SS/CP-Ti and (b) Ni 201/453 SS/Ni 201

study. An initial cost analysis indicated that even using the more expensive stainless material, the DOE 2010 bipolar plate cost target of \$2/plate could be achieved. Plain carbon steel alternatives will be re-examined as a means of further reducing component costs once the clad concept is validated.

A similar comparative analysis was conducted for potential clad material candidates. In the clad metal bipolar plate concept, this material is expected to provide a thin, low-cost outer layer that can be thermally treated to form a conductive passivation surface on the side(s) of the bipolar plate exposed to the electrolyte. Initially, thermal nitridation and carburization were considered as the primary methods of passivation. Given in Figure 2(b) are the key characteristics considered in clad material selection. On the basis of this initial analysis, titanium appeared to be the most suitable cladding candidate, with an appropriate chromium-containing alloy to be considered as a back-up option. Elemental chromium is not viable due to its low ductility, and therefore lack of formability, during the roll cladding and subsequent stamping processes. Recently, a novel surface treatment process has been developed that may allow nickel or nickel-based alloys to be considered for use as a cladding material. This process is still proprietary, although patent protection is currently being initiated.

Using the selected core and cladding metals, the following series of experimental symmetric clad material combinations was fabricated for initial feasibility study: Ti/430 SS/Ti ($t_{\text{foil}} \sim 430 \mu\text{m}$), Ni/453 SS/Ni ($t_{\text{foil}} \sim 280 \mu\text{m}$), Ni/304 SS/Ni ($t_{\text{foil}} \sim 150 \mu\text{m}$), and Inconel 625/304 SS/Inconel 625 ($t_{\text{foil}} \sim 520 \mu\text{m}$). Shown in Figures 3(a) and (b) are examples of the first two laminates. In Figure 3(a),

the titanium cladding measures approximately 75 μm in thickness while the 430 SS core is $\sim 280 \mu\text{m}$. These thicknesses can be further reduced with optimization of the roll cladding process.

Additionally, it is anticipated that thinner titanium stock can be employed to reduce the amount of titanium in the final laminate sheet and thereby decrease the overall cost of the clad material. The thicknesses that can be achieved by this method of processing are shown by the second example in Figure 3(b), in which the cladding (Ni 201) measures approximately 40 μm thick and the 453 SS core is $\sim 200 \mu\text{m}$.

From the two micrographs it is noted that each laminate exhibits a distinct diffusion zone between the clad and core layers. In the case of the Ni-based clad, this region is fairly thin and consists of a ductile nickel-iron-chromium alloy. In the Ti-based material, the diffusion zone is composed of two phases: thin needle-shaped iron-titanium precipitates within an iron-titanium-chromium alloy matrix. Further analysis is required, but it is suspected that the Fe-Ti precipitates are intermetallic and therefore brittle in nature and thus may limit the amount of forming that can take place in this particular sheet sample during subsequent stamping operations. Again, it is anticipated that further optimization of the roll bonding process will eliminate the formation of this type of deleterious phase.

In parallel with the development of the clad materials, a series of experiments was conducted to identify appropriate conditions to passivate the candidate titanium, inconel, and nickel clad layers. Nitridation was employed to passivate titanium and inconel. To determine the appropriate nitriding conditions, a 2^4 factorial matrix of experiments was conducted using the factors listed in Table 1. Once nitrided, the samples were tested for electrical conductivity, then cross sectioned and examined via scanning electron microscopy (SEM) to determine the thickness of the nitride layer as well as the microstructure of both the nitride and underlying substrate region. Results from electrical testing indicated that all of the samples nitrided in these experiments displayed high metallic surface and bulk conductivity.

As expected, measurements of titanium nitride thickness (determined to be TiN by glancing angle

Table 1. Factors Employed in the 2^4 Factorial Nitridation Experiments for Titanium and Inconel 625

Parameter	High	Low
Temperature	770°C	550°C
Time at temperature	8 hrs	2 hrs
Nitrogen pressure	30 psi	10 psi
Surface preparation	Pickled	Vacuum-annealed

X-ray diffraction) indicated that temperature was the most sensitive nitridation parameter. In contrast, nitrogen pressure was shown to have essentially no effect under the range considered. The condition of the titanium surface was found to play an important role in the quality and thickness of the as-formed nitride layer. Acid pickling of the titanium to remove any nascent titanium oxide surface scale prior to nitridation consistently gave better results than did the as-received, vacuum-annealed condition. Note that both the pickled and vacuum-annealed surface treatments are commercially accepted methods of pre-treating thin titanium foil prior to subsequent processing steps. Shown in Figures 4(a) and (b) are examples of commercial pure, pickled titanium foil after nitridation under the indicated conditions. Note that at low temperature, i.e., the sample shown in Figure 4(a), little if any TiN forms on the surface of the titanium. However, an extensive alpha titanium zone (α -case) forms over a two-phase core α - β region upon subsequent quenching from the nitridation temperature to room temperature. At higher temperature, a continuous $\sim 0.5 \mu\text{m}$ thick TiN layer develops over the α -case. Corrosion tests are currently being conducted on coupons similar to that shown in Figure 4(b) to determine if this thin nitride layer provides sufficient corrosion resistance for an extended period of time. Testing is being conducted in 1M H_2SO_4 (with 2 ppm hydrogen fluoride) at 80°C for 300 h.

In addition to work conducted on titanium, the same matrix of process variables has been employed in nitriding Inconel 625. Metallographic examination of these samples is currently in process, although initial electrical measurements indicate that the gold layer that forms on the samples during nitridation is conductive, the value of which appears to be dependent on the applied contact pressure

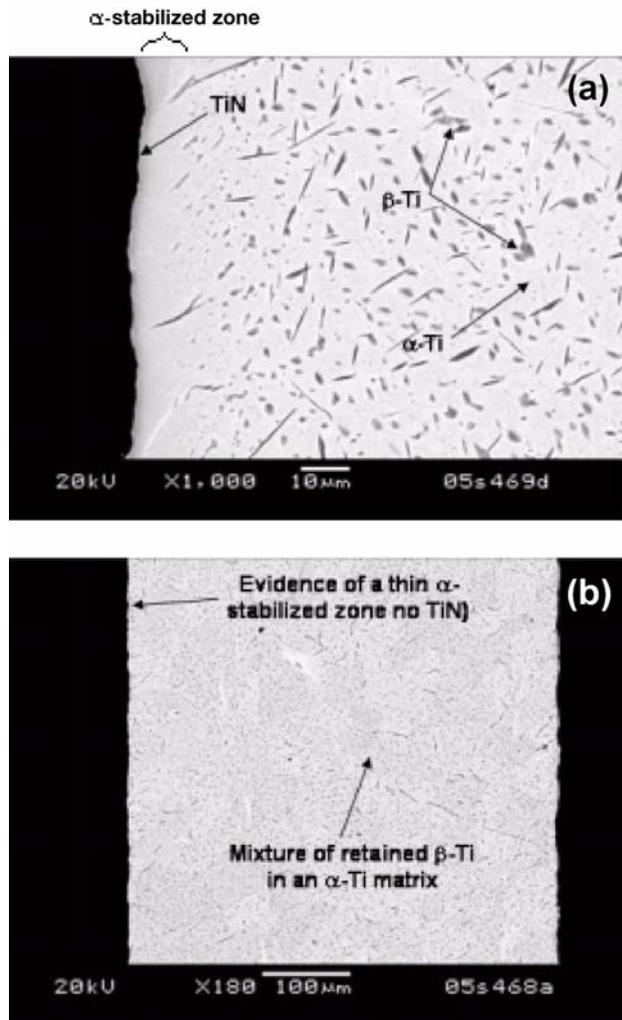


Figure 4. SEM Micrographs of CP-Ti Coupons Nitrided under the Following Conditions: (a) 770°C for 8 h in 10 psi ultra-high purity N₂ and (b) 550°C for 2 h in 10 psi N₂

between the test electrodes and the surfaces of the coupon (a similar dependence was observed with the nitrided titanium coupons). The coating development work conducted on nickel is currently undergoing patent protection. The process appears to yield a surface product that is highly conductive (no contact pressure dependence), although the level of

corrosion resistance in a prototypic PEMFC electrolyte environment still needs to be established. In addition, polarization test equipment has been set up for the testing of the passivated coupons under an applied voltage, again under prototypic PEMFC operating conditions.

Conclusions

- Initial comparative analysis of potential cladding and core alloy candidates is complete.
- Four clad material combinations have been fabricated and will be employed in corrosion and polarization testing.
- Passivation parameters have been investigated for the titanium, inconel, and nickel clad layers, and appropriate conditions are being established via a combination of metallographic examination, corrosion testing, and polarization testing.

Special Recognitions & Awards/Patents Issued

1. K. S. Weil, "An Inexpensive Passivation Surface Coating for PEMFC Bipolar Plates," Pacific Northwest National Laboratory Invention Report, July 2005.

FY 2005 Publications/Presentations

1. K. S. Weil, Z. G. Yang, G. G. Xia, and J. Y. Kim, M. Hardy, and S. Chang, "Development of Low-Cost, Clad Metal Bipolar Plates for PEM Fuel Cells," 2005 DOE Hydrogen Program Review, May 23 - 26, 2005, Washington, D.C.

References

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2. R. Borub and N. E. Vanderborgh, *Mater. Res. Soc. Symp. Proc.*, 393, 151 (1995).
3. L. E. Toth, *Transition Metal Carbides and Nitrides*, p.188, Academic Press, New York (1971).