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

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Projected End Date: September 30, 2009

- Cost: \$6/kg
- Weight: <1 kg/kW
- Corrosion: <1 mA/cm<sup>2</sup>
- Conductivity: >100 S/cm
- H<sub>2</sub> permeation rate: <2x10<sup>-6</sup> cm<sup>3</sup>/sec•cm<sup>2</sup> at 80°C and 3 atm
- Resistivity: <0.01 Ω•cm<sup>2</sup>
- Flexural strength: >4 MPa
- Flexibility: 3-5% at mid-span

### Accomplishments

- Screen testing of niobium, to be used in a low-cost clad material, was conducted and yielded the following results: 0.018% weight loss after 2,000 hrs of exposure in 80°C 1M H<sub>2</sub>SO<sub>4</sub> with 2 ppm HF, ≤ 10 mΩ•cm<sup>2</sup> contact resistance after 300 hrs of prototypic PEMFC environmental exposure, and corrosion current densities of 2.7 x 10<sup>-5</sup> A/cm<sup>2</sup> and 6.3 x 10<sup>-9</sup> A/cm<sup>2</sup> at half cell potentials of -0.1 V and 0.6 V, respectively, under prototypic anode and cathode environmental conditions.
- Based on the favorable screening results, a niobium clad stainless material was developed. Initial polarization and contact resistance testing of this material indicates that it behaves in the same manner as pure niobium.
- A nickel clad stainless steel material has also been developed. In addition, a surface boronization process was demonstrated to substantially improve the corrosion resistance of this material under the aggressive screening conditions employed above for niobium.

### Objectives

- To assist the DOE in lowering the cost and improving the durability of proton exchange membrane fuel cell (PEMFC) stacks by reducing the material and manufacturing costs of metal bipolar plates for potential use in transportation applications.
- To substantially increase the resistance of metal bipolar plate materials to corrosion and mitigate the release of poisoning metallic ions into the MEA, while at the same time maintaining low bulk and surface electrical resistances.

### 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

This project is focused on developing low-cost strategies for fabricating high-performance metallic bipolar plates that meet the following DOE 2010 targets for transportation fuel cell stacks:

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### Introduction

While progress continues to be made toward developing commercially viable PEMFC systems, these devices currently find use only in niche applications. The primary reasons for this are the high cost of manufacture and the steady loss in power output during long-term, continuous operation. In addition, their acceptance in transportation markets has been hindered by their current size and weight [1]. One of the most bulky and expensive components in the stack is the bipolar plate, which serves as the electrical junction between serially connected cells in the stack. It also

performs several other key functions including: (1) uniform distribution of fuel and oxidant over the active areas of the cells, (2) facilitation of water management in the electrolyte membrane, (3) impermeable barrier between the fuel and oxidant streams, (4) structural support for the stack, and (5) heat removal from the cells.

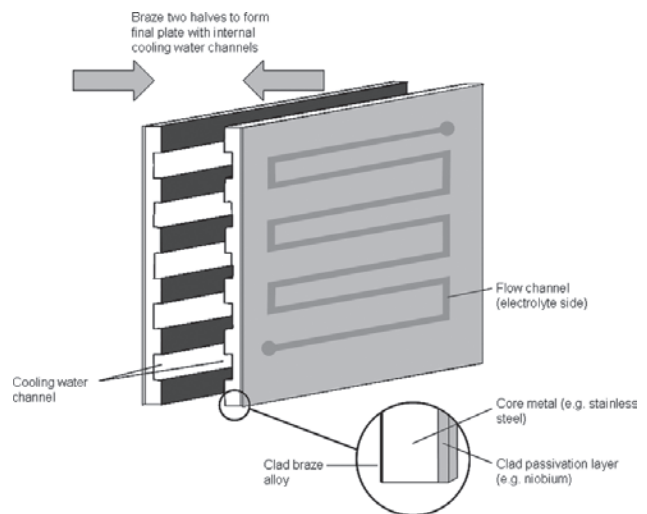
The use of metal-based bipolar plates in PEMFC stacks potentially offers a number of advantages particularly for transportation applications including: low-cost, mass-production via stamping or embossing of sheet product; fabrication in very thin form (<200  $\mu\text{m}$ ) to reduce weight and volume 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 [2]. 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

Early transition metal elements such as Ti, Zr, Mo, V, and Nb are known to form a thin, adherent native oxide layer that passivates the underlying metal against corrosion in low pH, mineral acid environments. Of these, niobium exhibits the best resistance to sulfuric acid, nominally the composition of the liquid environment within the PEMFC stack, with a reported rate of metal loss of <0.2  $\mu\text{m}/\text{yr}$  in boiling 1M  $\text{H}_2\text{SO}_4$  [3]. At issue is the relative cost of niobium compared to alternative, albeit less corrosion resistant, bipolar plate material candidates such as 304SS. The approach presently under development is to fabricate a metal laminate sheet consisting of a metallic core roll bonded to a thin sheet of a transition metal alloy that forms a passivating surface when exposed to the low pH aqueous environment within the stack. The manufacture of this type of clad material product is well-established commercially, with clad metal producers capable of

routinely fabricating various multilayer products in 50–500  $\mu\text{m}$  thick sheets. Ideally, the material selected for the core, which will form the thickest layer, is chosen based primarily on material cost, formability, durability, and thermal conductivity. On the other hand, the material used in the cladding layer is selected based on corrosion resistance, surface contact resistance, 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.

Shown schematically in Figure 1 is one of the clad metal concepts currently under study. The bipolar plate consists of a composite laminate structure formed by roll bonding a thin layer of niobium to one side of an inexpensive steel core and a braze filler metal layer on the other. The latter material facilitates the joining of two mated plates after stamping to form a bipolar plate component that contains an internal water cooling channel. As a first step in developing and evaluating this material, commercial purity niobium (cp-Nb) was clad to 430 stainless steel (430SS). 430SS was chosen because it is an inexpensive stainless steel that displays excellent formability. In the annealed condition cp-Nb also displays very good formability and ductility (up to 80% cold reduction) and is readily roll bonded to 430SS [4]. It is anticipated that once concept viability is validated through ex-situ testing, the stainless core could be eventually replaced with an even lower cost material such as 1008 carbon steel.



**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.

## Results

Shown in Table 1 are the results from screening exposure tests conducted on Nb coupons in an 80°C, 1M H<sub>2</sub>SO<sub>4</sub> + 2 ppm HF solution (an aqueous environment that is comparable to, albeit more aggressive, than that within the PEMFC stack). Weight measurements taken directly on the specimens before and after exposure indicate that niobium undergoes essentially no change in weight and is quite resistant to corrosion under these conditions. These results are validated by inductively coupled plasma mass spectrometry (ICP-MS) measurements of the amount of dissolved niobium in the effluent, provided in column 3 of Table 1 and converted to an equivalent weight loss in column 4. According to this second set of data, the maximum amount of niobium loss observed was 0.022% over 2,000 hrs of exposure and it appears that much of this weight loss is achieved within the first 100 hrs of exposure. Like other early transition metals, niobium derives its corrosion resistance from a readily formed adherent oxide surface film, typically Nb<sub>2</sub>O<sub>5</sub>, on the order of a few nanometers thick [3,5]. SEM examination of the surfaces of the exposed coupons revealed no change in surface morphology between the as-received state and the various as-aged conditions up to 2,000 hrs of exposure [6].

Measurements of the area specific interfacial contact resistance between niobium and a representative GDL carbon paper were recorded as a function of compaction force to determine the magnitude of loading required to establish an acceptably low level of contact resistance between the two materials. Plotted in Figure 2 are the corresponding results for niobium in the as-received condition and after 300 hrs of exposure in 1M H<sub>2</sub>SO<sub>4</sub> + 2 ppm HF at 80°C. For each clamping pressure, three independent samples were tested and the variation of contact resistance is denoted by the vertical error bars. Note that contact resistance decreases dramatically with increasing compaction pressure, a behavior that is typically observed in these types of measurements for metal bipolar plate candidate materials [7-9]. In

**TABLE 1.** Results from Aging Tests Conducted at 80°C in 1M H<sub>2</sub>SO<sub>4</sub> with 2 ppm HF

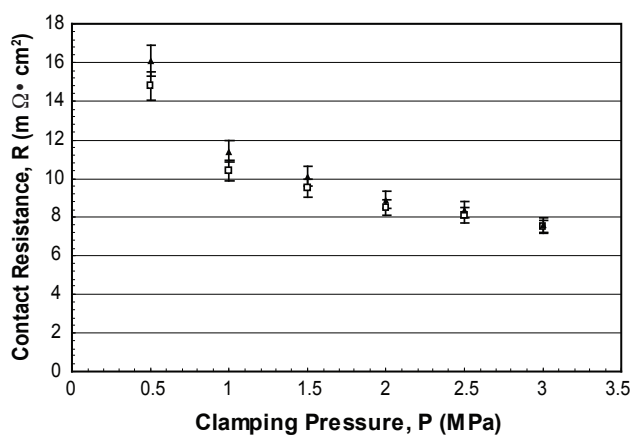
Time of Exposure (hrs)	Measured Wt. Loss	[Nb] in Effluent	Estimated Wt. Loss
100	0%	3.15 ppm	0.014%
300	0%	3.76 ppm	0.016%
400	0%	4.75 ppm	0.021%
700	0%	4.97 ppm	0.022%
1,100	0%	3.40 ppm	0.015%
2,000	0%	4.11 ppm	0.018%

addition, the magnitude of contact resistance compares quite well with previously reported values for nitrided Ni-50Cr, 349 SS, and 446SS [8,9], all of which are only slightly higher than that reported for carbon paper to graphite bipolar plate contact [9].

Shown in Figures 3(a) and (b) are anodic polarization curves for niobium in 1M H<sub>2</sub>SO<sub>4</sub> + 2 ppm HF at 80°C under sparged hydrogen and air respectively. For comparison, similar curves generated for a monolithic platinum electrode are plotted along with those for Nb. In addition, the anode and cathode potentials under typical PEMFC operation are marked. The current densities for Nb at -0.1 V in sparged hydrogen and 0.6 V in sparged air are quite low,  $2.7 \times 10^{-5}$  A/cm<sup>2</sup> and  $6.3 \times 10^{-9}$  A/cm<sup>2</sup>, respectively. Note that these values are nearly equivalent to those of platinum at each potential. In fact, the general behavior of the two metals under linear polarization is very similar, indicating that Nb is quite noble under simulated PEMFC operating conditions.

Further evidence of this is seen in the potentiostatic results shown in Figures 4(a) and (b). Under the hydrogen purged anode half-cell environment, the transient current observed for both metals decays quickly and reaches a stable current of approximately -4 μA/cm<sup>2</sup> in the case of platinum and approximately -10 μA/cm<sup>2</sup> for Nb. The decay in current is related to passive film formation. In the air-sparged simulated PEMFC environment, platinum displays almost no transient current and a subsequent current of essentially zero throughout testing to 550 minutes. The niobium exhibits a transient current that decays to approximately zero after ~300 minutes of testing.

A 75 μm sheet of Nb was roll bonded to a 450 μm sheet of 430SS to form the clad material shown in Figure 5. The bondline between the two materials



**FIGURE 2.** Interfacial contact resistance between niobium and carbon paper as a function of compaction pressure.

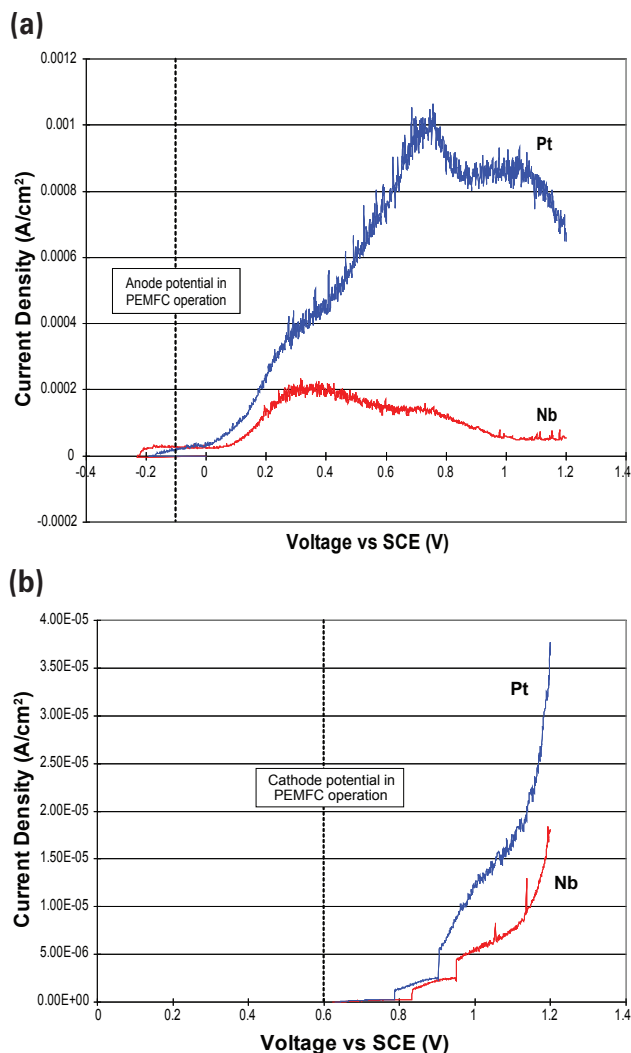


FIGURE 3. Anodic behavior of niobium and platinum in 1M H<sub>2</sub>SO<sub>4</sub> + 2 ppm HF at 80°C under (a) sparged hydrogen and (b) sparged air.

is quite distinct, with no interfacial porosity present. Results from energy dispersive x-ray spectrometer (EDS) characterization demonstrate only a minor amount of iron diffusion into the Nb cladding during the rolling process. Unlike previous results obtained with a titanium clad stainless steel material, the diffusion zone is free of brittle intermetallic phases that could potentially limit the amount of forming that can take place in the clad sheet during subsequent stamping operations. Measurements of area specific interfacial contact resistance between this material and carbon paper are displayed in Figure 6 as a function of compaction pressure. As with monolithic Nb, the amount of compression required to achieve a low level of contact resistance is quite small and the magnitude of resistance is again quite comparable to that observed

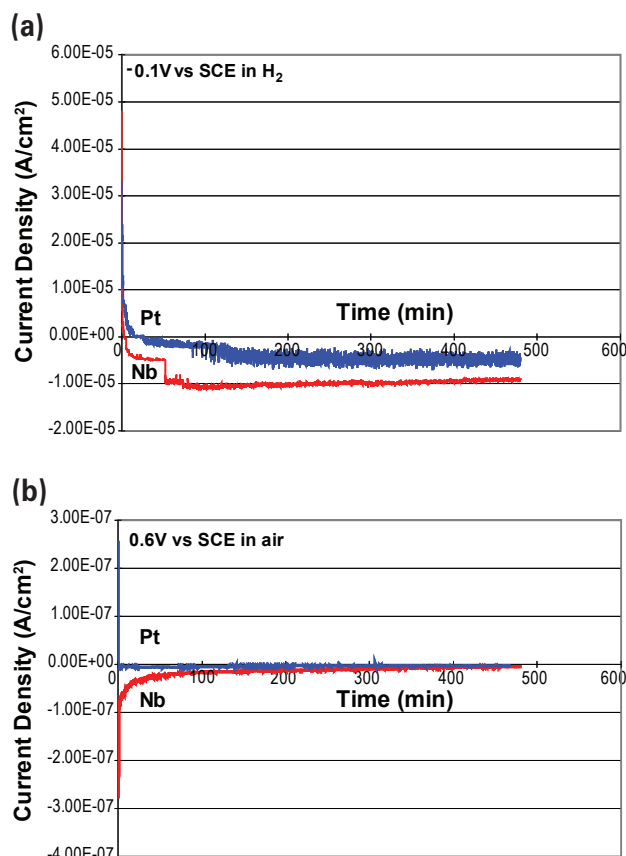


FIGURE 4. Behavior of niobium and platinum in 1M H<sub>2</sub>SO<sub>4</sub> + 2 ppm HF at 80°C under (a) simulated anode operating conditions of -0.1 V and sparged hydrogen, and (b) simulated cathode operating conditions of 0.6 V and sparged air.

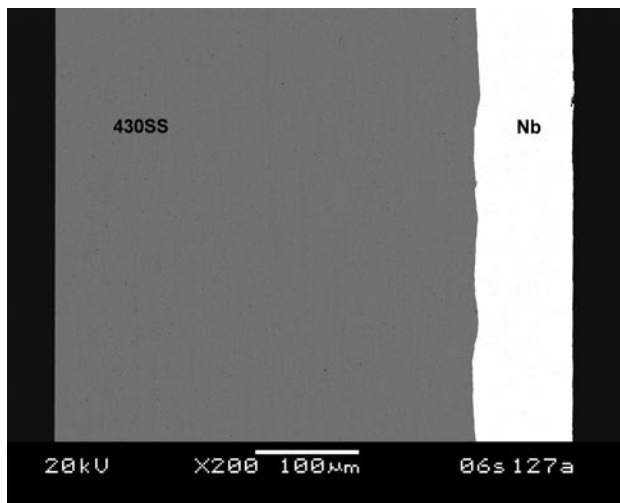
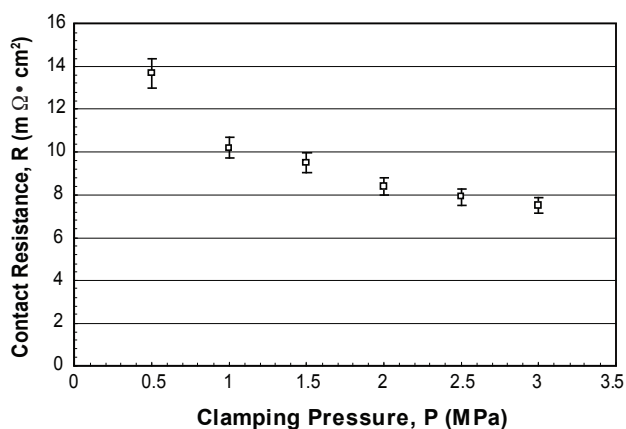


FIGURE 5. Cross-sectional SEM micrograph of the clad Nb/430SS material in the as-received condition.



**FIGURE 6.** Interfacial contact resistance between Nb/430SS and carbon paper as a function of compaction pressure.

in surface treated and graphitic bipolar plate materials. Initial polarization testing of the clad material under both the anode and cathode half-cell conditions described above indicated nearly identical behavior to that of cp-Nb.

A second clad material being developed and tested for potential PEMFC bipolar plate application is Ni-clad steel. While nickel is significantly less expensive than niobium, it requires pre-passivation prior to use because of its comparably poor corrosion resistance under the screen test conditions described above. This was accomplished by a powder-pack boronization process, carried out over a temperature range of 500 to 700°C. It was determined that the extent of boride layer formation follows a parabolic relationship with respect to reaction time and  $\text{Ni}_3\text{B}$  is observed as the surface phase under moderate heat treatment conditions. Boronization in the Ni/304SS/Ni laminate was found to follow the same trend observed in the nickel coupons, although boride layer formation is not nearly as uniform possibly due to the diffusion of iron into the nickel cladding during heat treatment. Initial static corrosion testing in 80°C 1M  $\text{H}_2\text{SO}_4$  + 2 ppm HF demonstrate that boronization dramatically increases the resistance of nickel in this corrodant, although additional development is needed to further improve these effects. Measurements of contact resistance as a function of loading indicate that the material behaves in a manner similar to graphite.

## Conclusions and Future Directions

- Niobium displays excellent corrosion resistance under conditions more aggressive to those anticipated internally within the PEMFC stack. Less than 0.022% weight loss was observed after 2,000 hrs of exposure, as measured via ICP-MS analysis.

- Niobium exhibits low contact resistance with carbon paper in both the as-received and passivated conditions and polarization testing indicates that the properties of Nb are similar to those of Pt under an accelerated PEMFC operating environment. Linear sweep voltammetry displays current densities of  $2.7 \times 10^{-5}$  and  $6.3 \times 10^{-9}$  A/cm<sup>2</sup>, respectively under anodic and cathodic test conditions. Potentiostatic testing indicates stable passivation under both simulated anode and cathode operating conditions.
- The Nb-clad stainless material is readily prepared and initial contact resistance and polarization testing indicates behavior nearly identical to that of cp-Nb.
- Ni-clad steel is readily prepared and when boronized displays excellent corrosion resistance under accelerated test conditions, which is particularly interesting.
- The next steps in this project will include: (1) demonstrating fabrication of a <25 μm Nb cladding layer, followed by electrochemical property characterization via ex-situ testing; (2) investigating the formability of both the Nb- and Ni-clad materials, followed by electrochemical property characterization; and (3) fabricating preliminary small-scale stamped pieces for ex-situ testing.

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