

# Development of Low-Cost, Clad Metal Bipolar Plates for PEM Fuel Cells

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### Timeline

- Project start date: 10/1/05
- Project end date: 9/31/06
- Percent complete: 50%

### Budget

- Total project funding: \$120K
- Funding received in FY05: \$120K
- Funding received in FY06: \$120K

### Barriers

- This project addresses the following key technical barriers identified in the HFCIT Program Multi-Year Program Plan :
  - ▶ Fuel cell stack (bipolar plate) durability - e.g. corrosion/MEA poisoning effects
  - ▶ Fuel cell stack (bipolar plate) cost

### Partners

- Engineered Materials Solutions Inc. (EMS, Inc.), Attleboro, MA

To assist the DOE in lowering the cost and improving the durability of automotive PEM fuel cell stacks by reducing the material and manufacturing costs of bipolar plates, while substantially increasing their resistance to corrosion and mitigating the release of poisoning metallic ions into the MEA

- **Feasibility study to determine the potential efficacy of a clad metal approach in developing a low-cost/low-mass/low-volume PEM bipolar plate**
  - ▶ Corrosion, polarization, and contact resistance testing of Nb, Ti, NbN, TiN, Ni, and Ni-B cladding layers
  - ▶ Fabrication of Nb clad and Ni clad metals
  - ▶ Boronization of Ni clad metal
  - ▶ Testing of Nb-clad and Ni-B clad metals
- **Formability testing of Nb and Ni clad metals, followed by ex-situ validation testing of formed pieces**
- **Fabrication of small-scale plates for short-stack testing**

- **Development of a clad metal material (a sandwich metal composite) that as formed or post-treated incorporates a passivation layer which is both electrically conductive and corrosion resistant. Roll cladding is a low-cost process that affords great flexibility in fabricating metal materials that are difficult to manufacture by other traditional metallurgical processes.**
  - ▶ **The core metal offers:**
    - ◆ Low base cost (i.e. an inexpensive material)
    - ◆ Mechanical stiffness/robustness
    - ◆ Moderate to low density (i.e. can consider Al alloys)
    - ◆ High thermal conductivity (for better thermal management)
    - ◆ Low hydrogen permeability
  - ▶ **The thin cladding layer offers:**
    - ◆ A low-cost outer surface that forms a conductive passivation layer on the electrolyte exposed surface
    - ◆ A thin brazing layer in the cooling water side that would be useful in forming internal water channels when mated with a second plate
  - ▶ **The overall clad material combination provides:**
    - ◆ Reduced bipolar plate thicknesses (to 100 –150 $\mu$ m) and therefore reduced stack volume, stack weight, lower thermal mass, and lower raw material costs
    - ◆ Excellent geometrical tolerance, material stiffness, and strength; providing mechanical durability and robustness
    - ◆ Excellent ductility and flexural strength for high reliability during stack fabrication and in-vehicle use

## Key Accomplishments to Date

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- **FY06 Project Milestones:**

- ▶ **Report on the initial results to optimize the clad bipolar plate material (complete) . . . . . March '06**
- ▶ **Complete initial investigation of clad material formability . . . August '06**

- **Results to date:**

- ▶ **Initial results from ex-situ testing of Nb clad bipolar plate materials are very promising: (1) excellent corrosion resistance (no weight loss) out to 2000+hrs, (2) inert, Pt-like polarization behavior in anode/cathode half-cell environments, and (3) low contact resistance after simulated stack exposure.**
- ▶ **Results from second candidate clad metal system, Ni clad steel, also are promising. The static corrosion resistance of the nickel cladding layer is dramatically improved by diffusing boron into the surface via boronization. In addition, the contact resistance of these materials are very low. Polarization studies under simulated half-cell conditions are currently underway.**

# Functional Requirements for Bipolar Plates

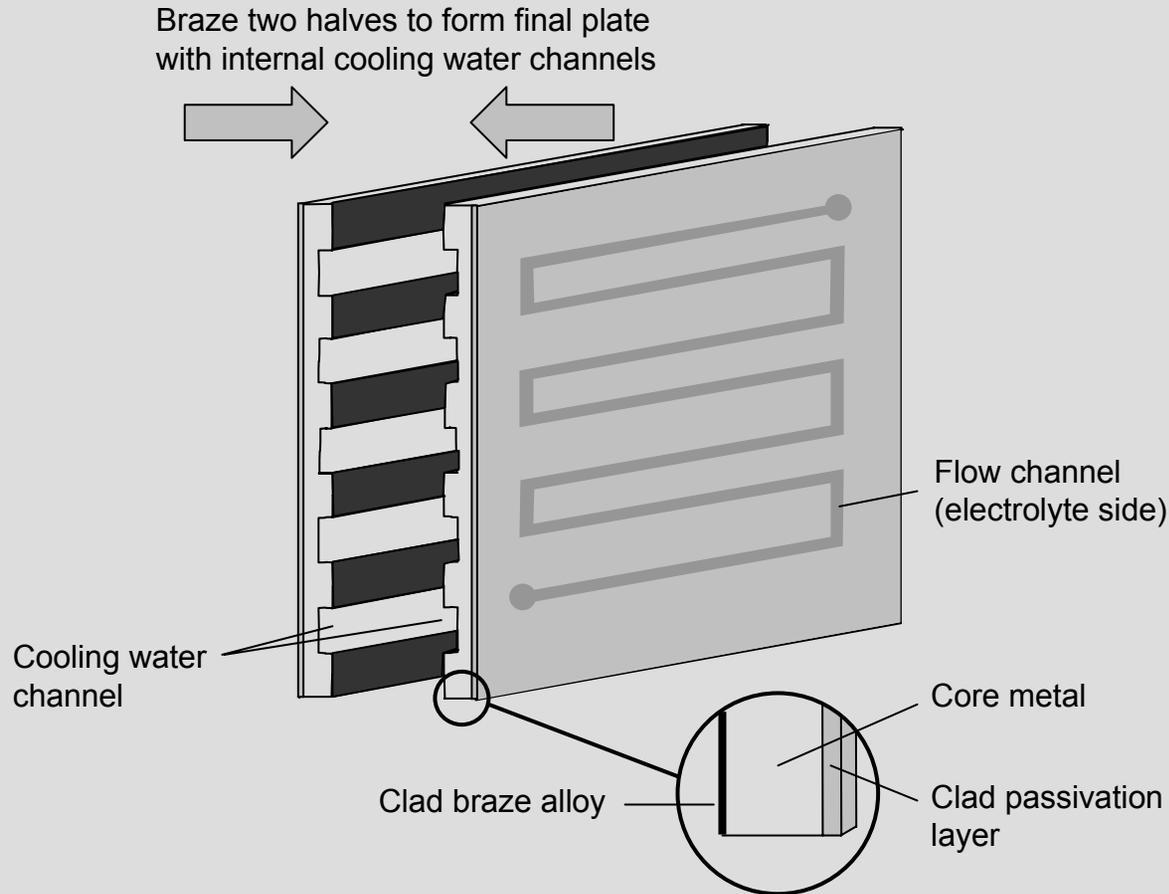
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- **Low Cost**
- **High Corrosion Resistance**
- **High Electrical Conductance**
- **Acceptable Mechanical Strength/Toughness**
- **Lightweight**
- **Low Volume/Thickness**
- **Minimal Interaction(s) with the Electrolyte and/or Membrane Materials – either via direct contact or dissolution**
- **High Thermal Conductivity**
- **Low H<sub>2</sub> Permeability**
- **High Degree of Processability/Manufacturability**



- Primary focus in this feasibility study

# Low-Cost Clad Metal Concept



- **At issue are:**
  - ▶ **The cost of the alloy and/or cost of subsequent stamping/forming processes to manufacture bipolar plates with complex flow field channels**
  - ▶ **The cost of further clad modification, i.e. passivation**
  - ▶ **The reliability of the passivation layer**

## Clad combinations under study

- Nb/430SS/Nb
- Ti/430SS/Ti
- Ni/453SS/Ni

## Set up a series of ex-situ screening tests

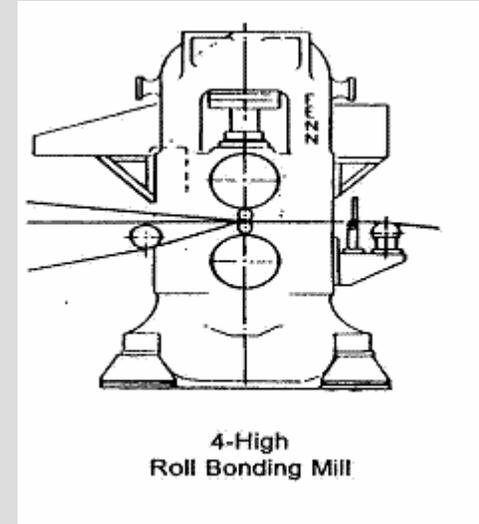
- Corrosion
  - ▶ 1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF
  - ▶ 80°C
  - ▶ Measured weight loss and examined specimens after 100, 300, 400, 700, 1100, and 2000hrs of exposure
- Contact resistance testing with carbon paper before and after exposure to corrodant
- Polarization testing
  - ▶ 1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF, 80°C
  - ▶ Linear sweep voltammetry in H<sub>2</sub> and in air
  - ▶ Potentiostatic testing as a function of time in H<sub>2</sub> and in air



**Nb/430SS/Nb**

# Roll Bonding (Nb)

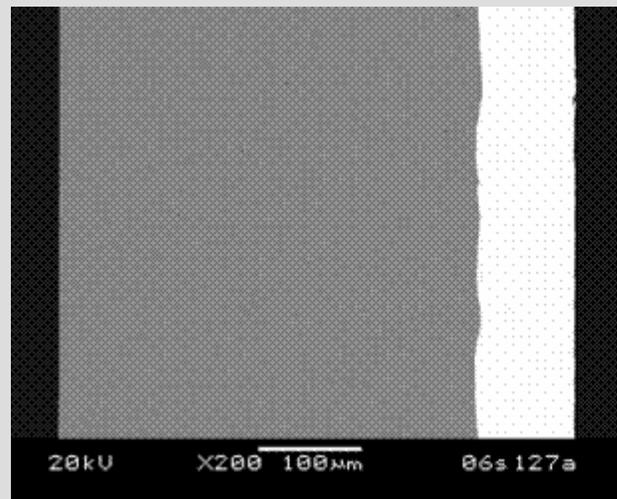
## Rolling cladding at EMS, Inc.



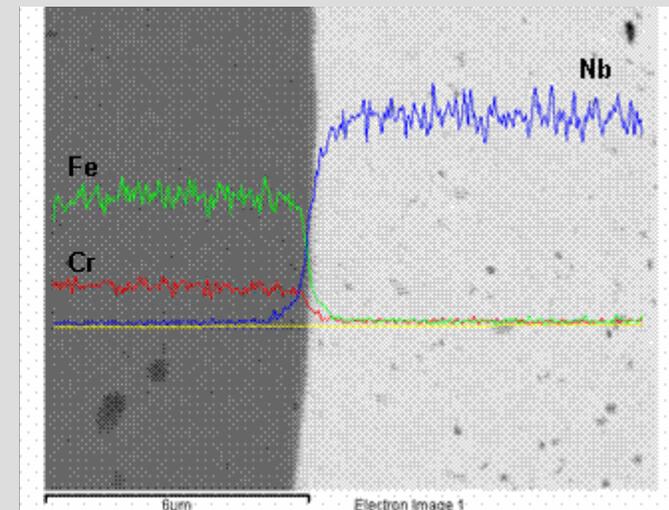
### As-clad Nb/430SS

#### Cladding conditions

- ~450 $\mu\text{m}$  thick 430SS core, ~50 $\mu\text{m}$  Nb clad
- Single pass, ~60% cold reduction
- ~750ksi roll pressure



### Elemental mapping:

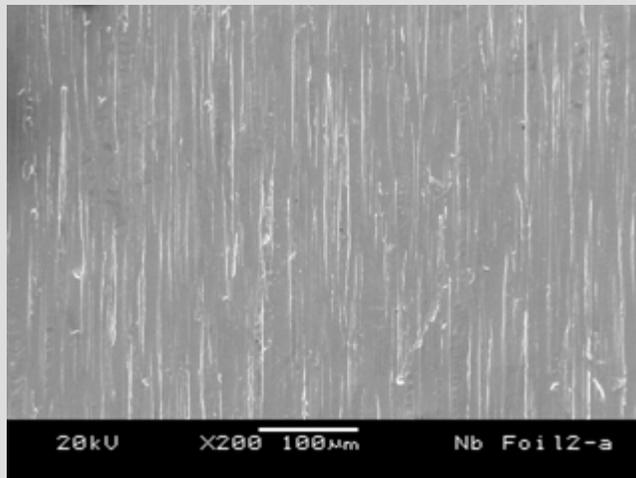


## Corrosion Testing (Nb)

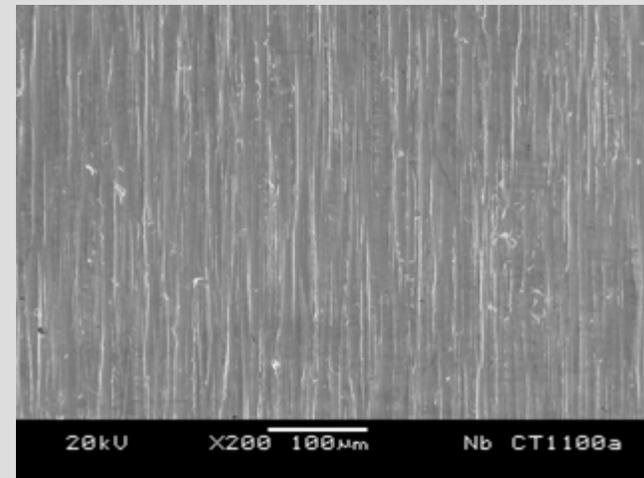
Results from aging tests conducted at 80°C in 1M $\text{H}_2\text{SO}_4$  with 2ppm HF

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%
1126	0%	3.40 ppm	0.015%
2000	0%	4.11 ppm	0.018%

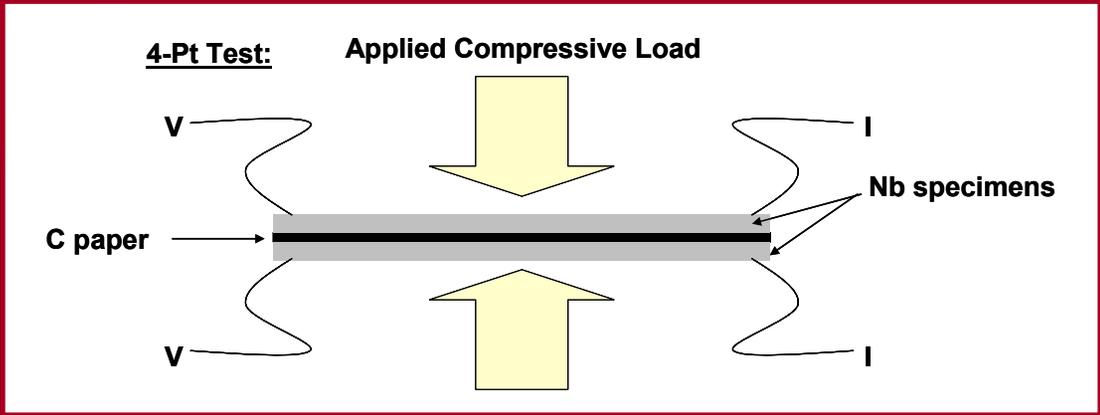
Nb surface: as-received



Nb surface: 1126hrs of exposure



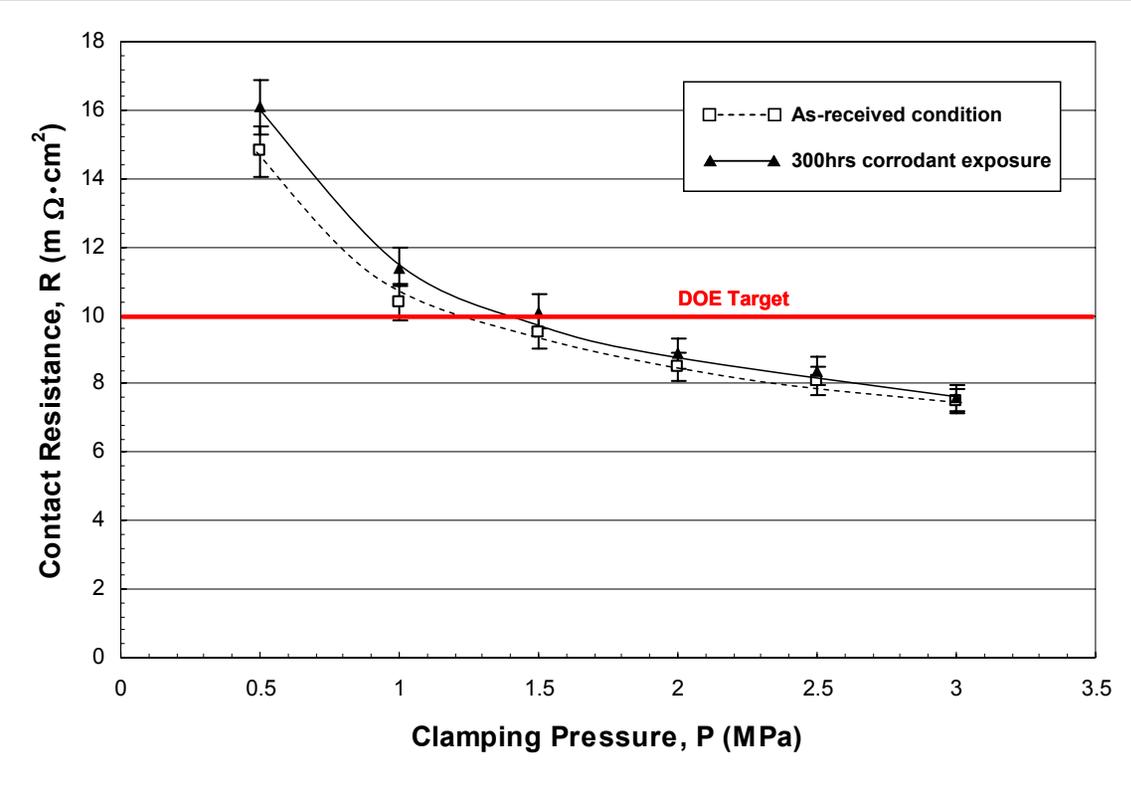
# Contact Resistance (Nb)



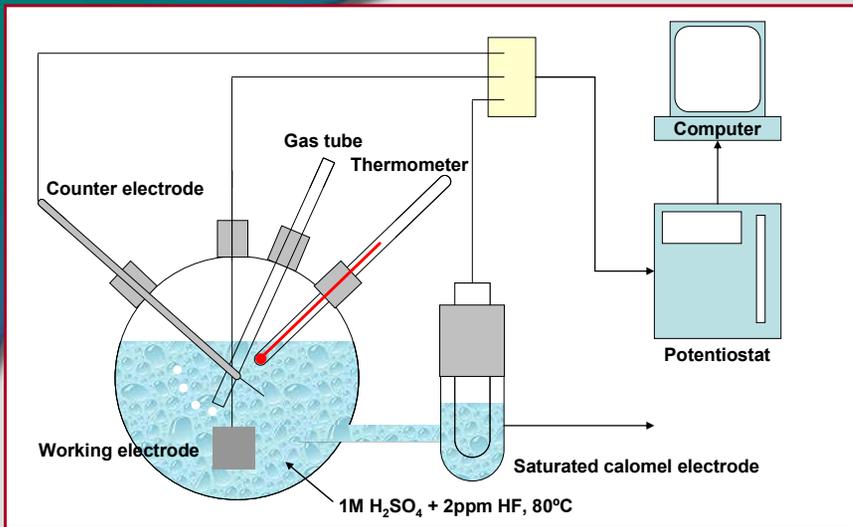
$$R_{\text{contact}} = \frac{V \cdot A_s}{2I} \tag{1}$$

$$R_{\text{contact}} = 2R_{\text{Nb/C}} + R_C \tag{2}$$

~0

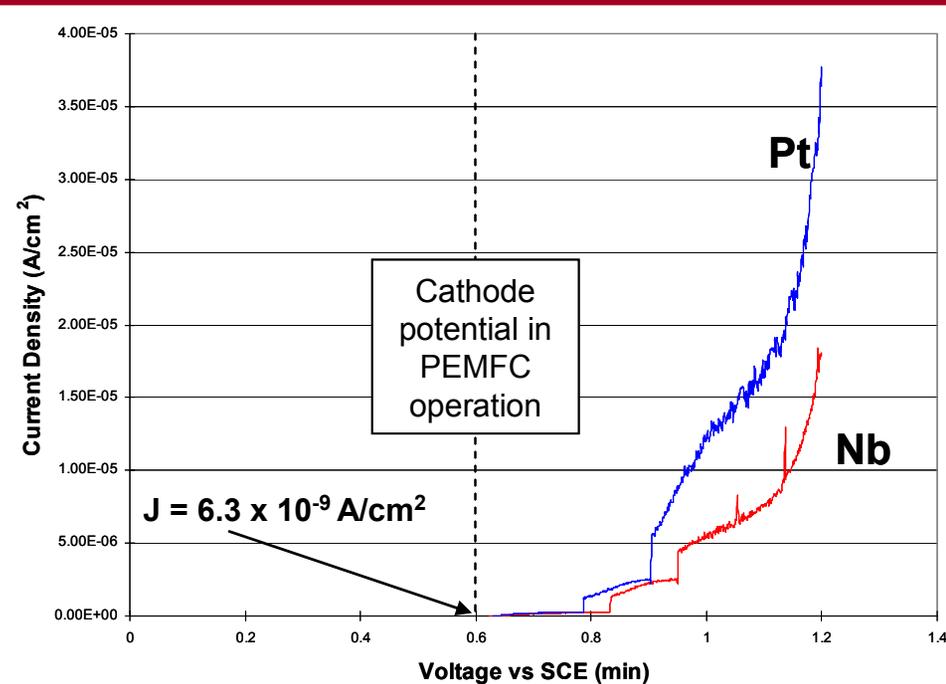
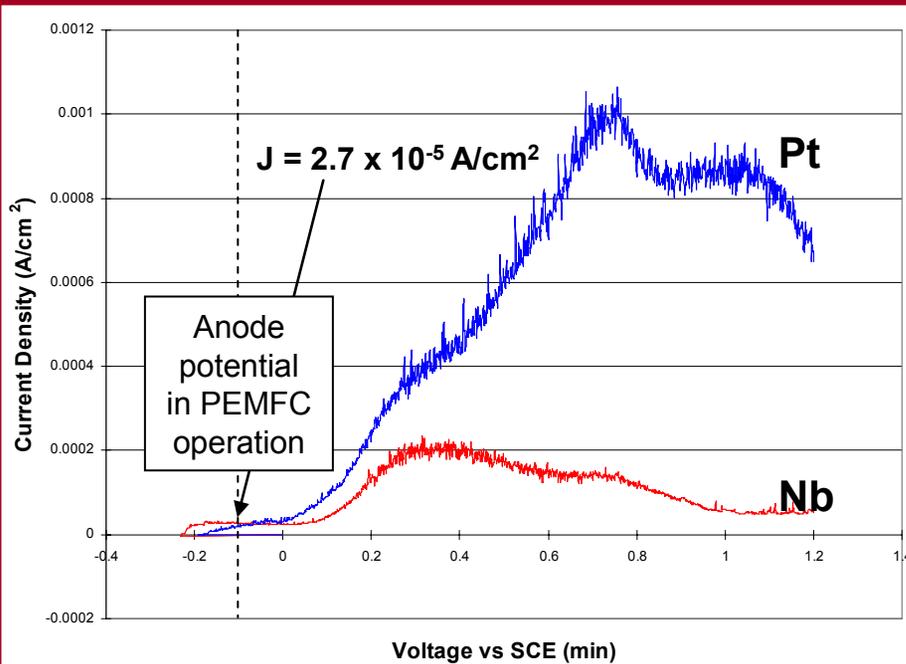


# Linear Voltammetry (Nb)

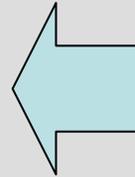
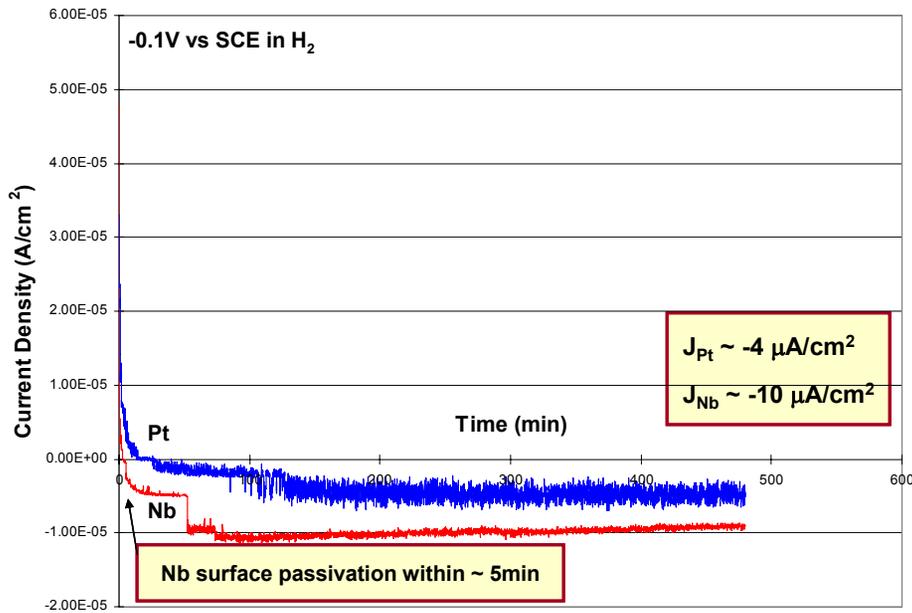


In H<sub>2</sub> (1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF, 80°C):

In Air (1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF, 80°C):

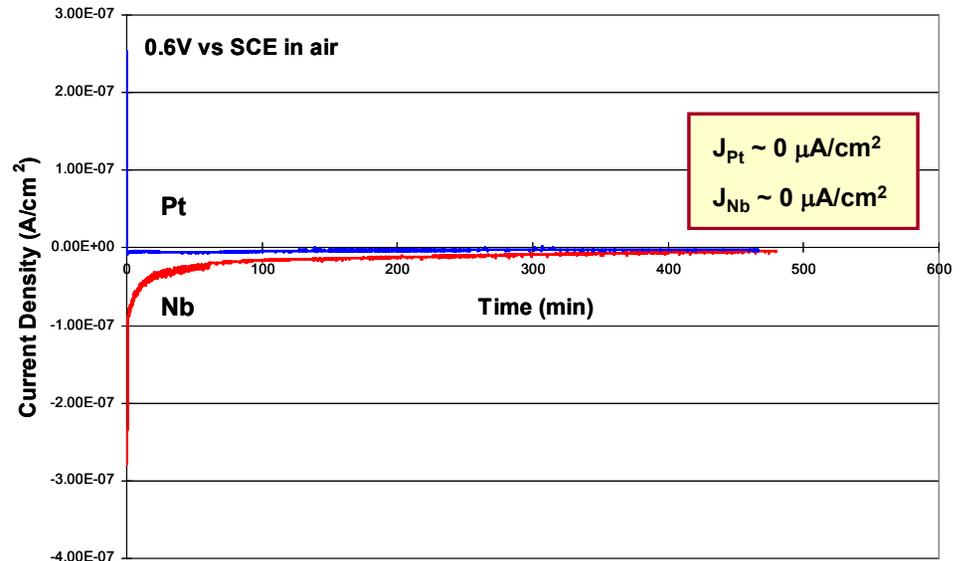
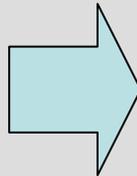


## Potentiostatic testing (Nb)



Comparative behavior of niobium and platinum in 1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF at 80°C under simulated anode operating conditions of -0.1V and sparged hydrogen.

Comparative behavior of niobium and platinum in 1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF at 80°C under simulated cathode operating conditions of 0.6V and sparged air.



- **Niobium displays excellent corrosion resistance**
  - ▶ Tested under accelerated conditions: 80°C, 1M H<sub>2</sub>SO<sub>4</sub> + 2ppm HF
  - ▶ < 0.025% weight loss after 2000hrs of exposure, as measured via ICP-MS analysis of the test effluent
- **Exhibits low contact resistance with carbon paper in both the as-received and passivated conditions**
- **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**
  - ▶ The key is in reducing Nb thickness to below 2mil to meet DOE 2010 cost targets

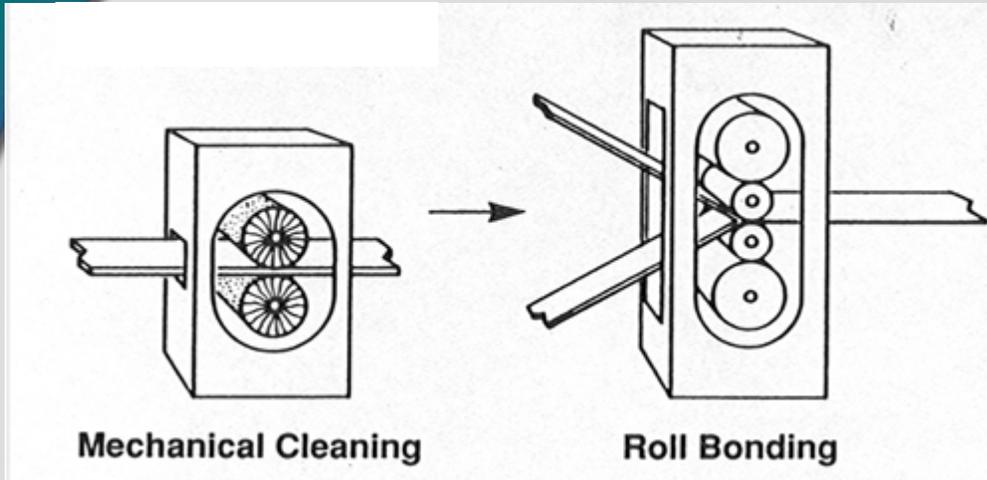


**B-Ni\*/453SS/B-Ni\***

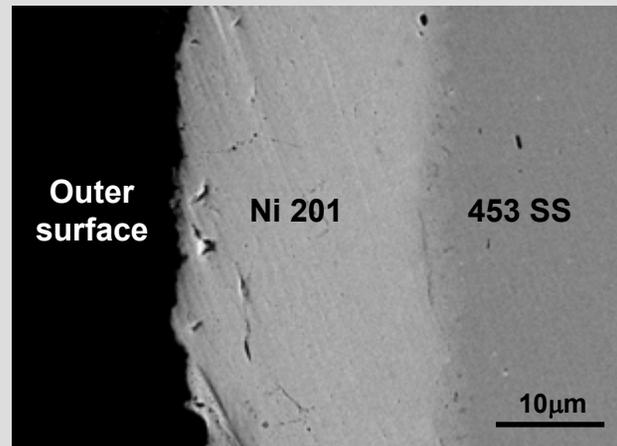
\*where B-Ni = boronized nickel

# Rolling cladding at EMS, Inc.

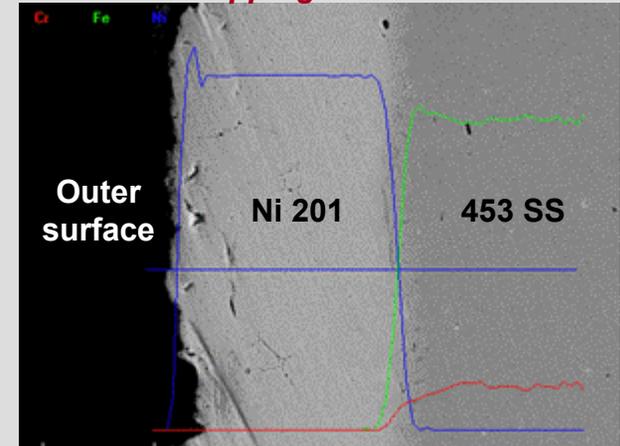
## Roll Bonding (Ni)



*As-clad Ni 201/453 SS/Ni 201:*



*Elemental mapping:*



### Cladding conditions

- ~120 $\mu$ m thick 453 SS core, ~20 $\mu$ m Ni201 clad
- Single pass, ~40% cold reduction
- ~600ksi roll pressure

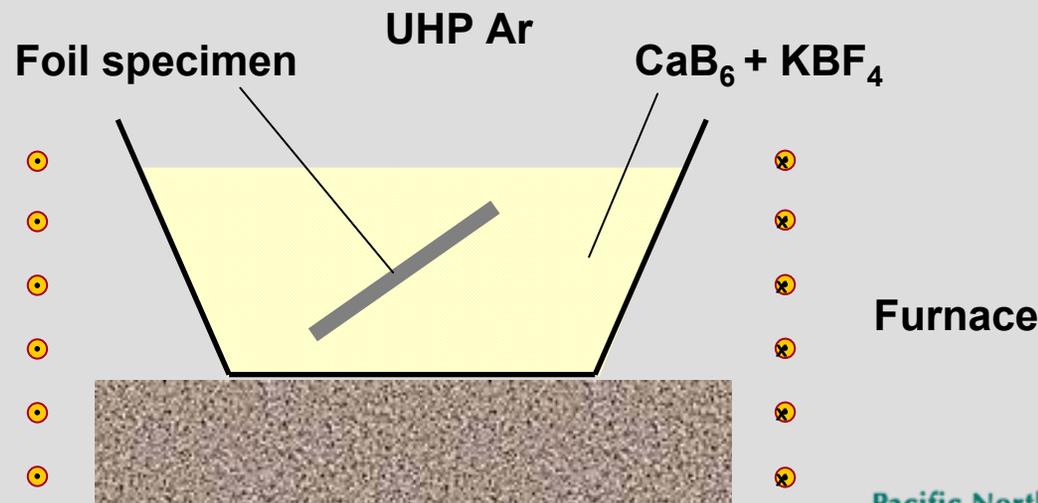
# Boronization Study (Ni Coupons)

## Test matrix:

- Temperature: 500 – 700°C
- Time at temperature: 2 – 8 hrs
- Ratio of  $\text{CaB}_6$  to  $\text{KBF}_4$ : 80:1 to 20:1

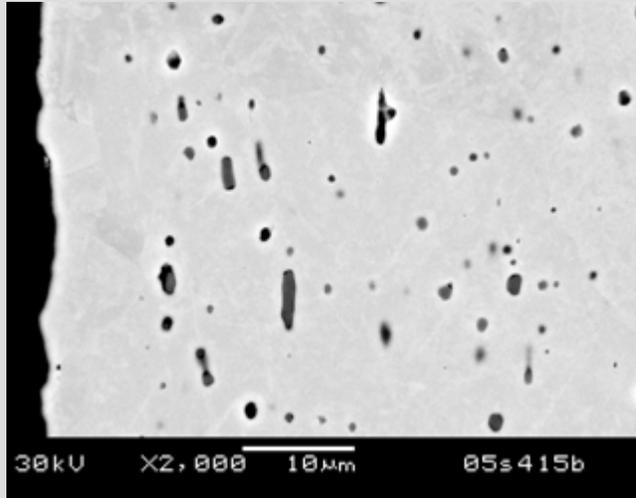
## Measurables:

- Boride composition
- Boride thickness
- Corrosion resistance during initial screening

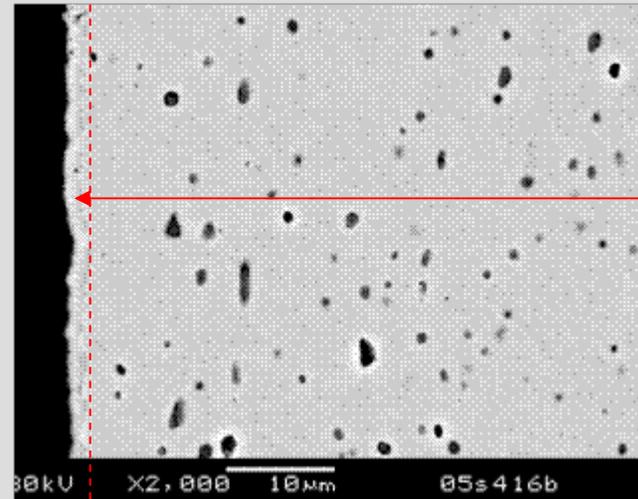


# Microstructure of the Boronized Ni Layer

As-received Ni

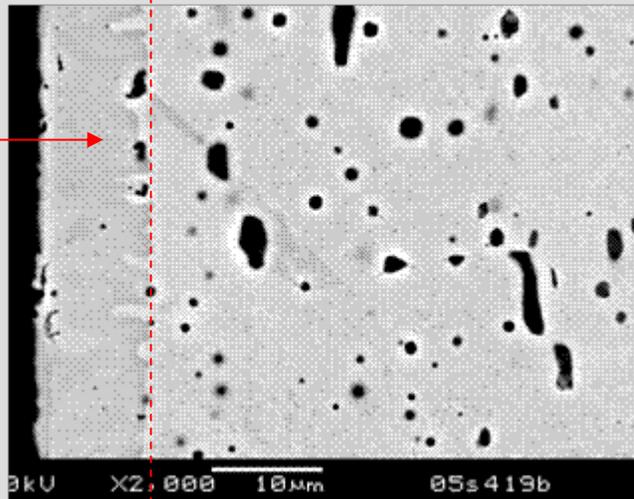


500°C, 8hrs; 80:1



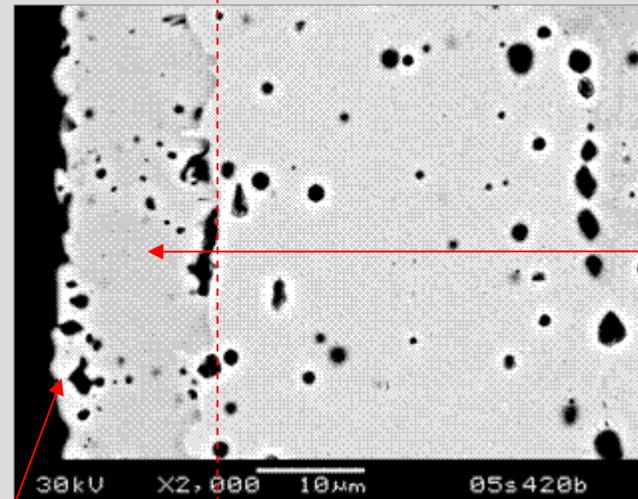
$\text{Ni}_3\text{B}$

800°C, 2hrs; 80:1



$\text{Ni}_3\text{B}$

800°C, 8hrs; 80:1



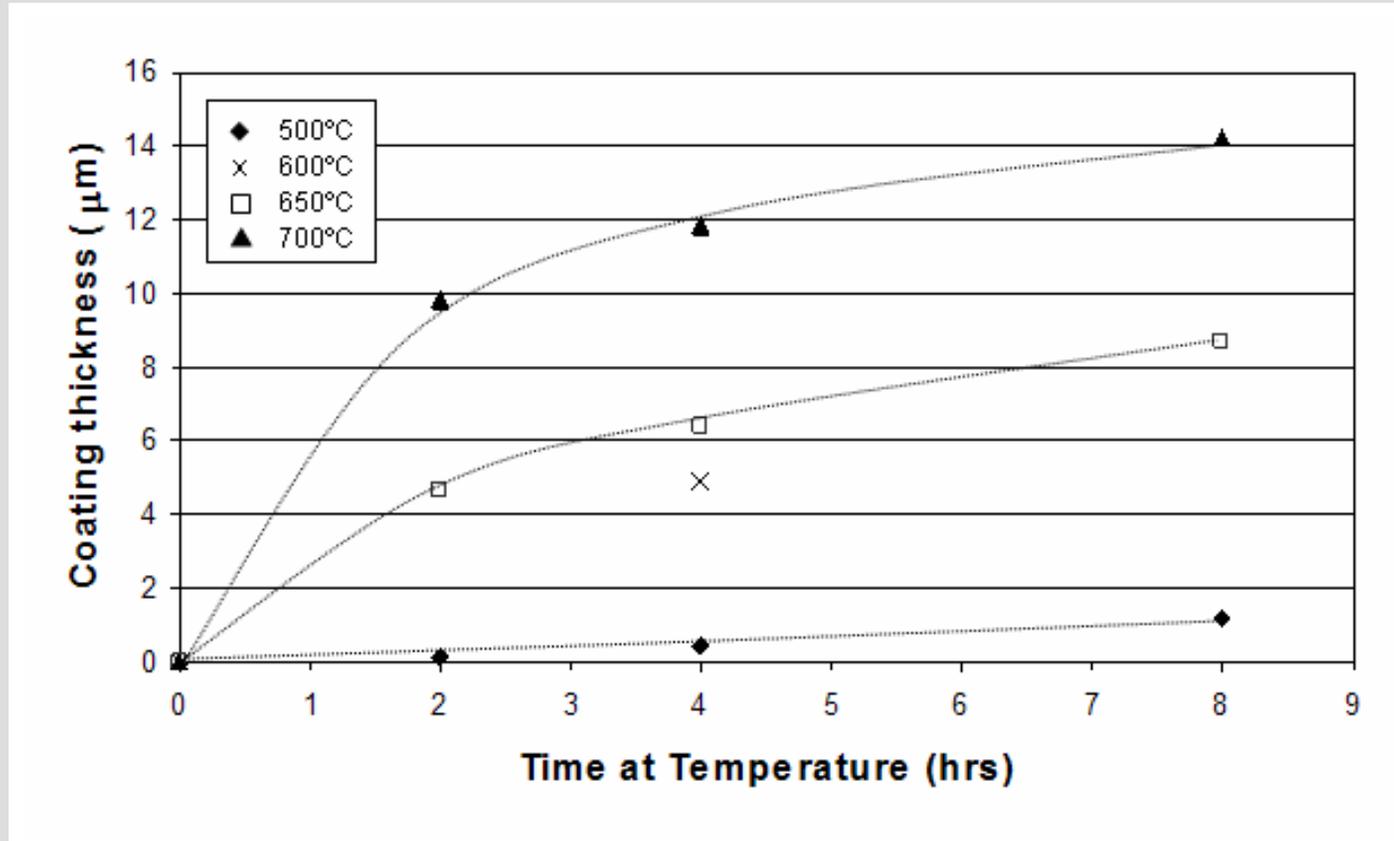
$\text{Ni}_3\text{B}$

$\text{Ni}_2\text{B}$

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CaB<sub>6</sub>:KBF<sub>4</sub> of 80:1

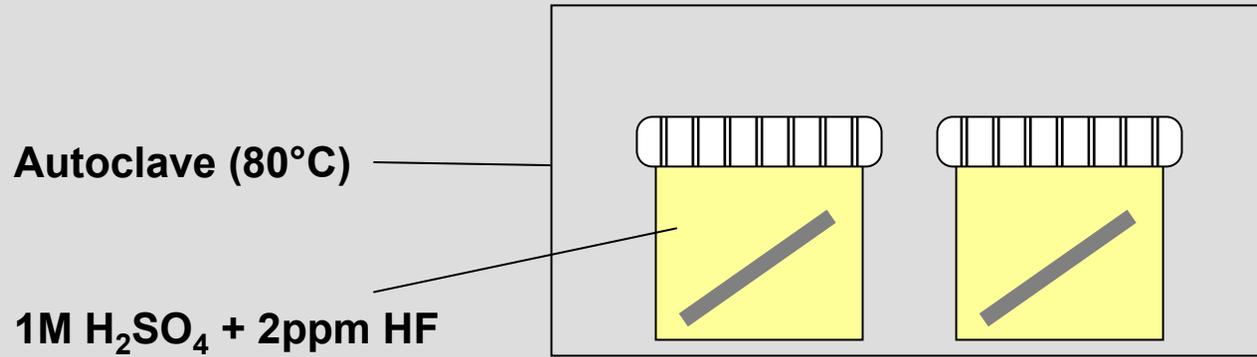


Growth follows a Wagner-type expression:

$$x^2 = k_p t$$

$k_p$ :  $9.99 \times 10^{-3} \text{ mm}^2/\text{s}$  at  $700^\circ\text{C}$ ,  $2.85 \times 10^{-3} \text{ mm}^2/\text{s}$  at  $650^\circ\text{C}$ ,  
 $2.18 \times 10^{-5} \text{ mm}^2/\text{s}$  at  $500^\circ\text{C}$

# Initial Corrosion Results

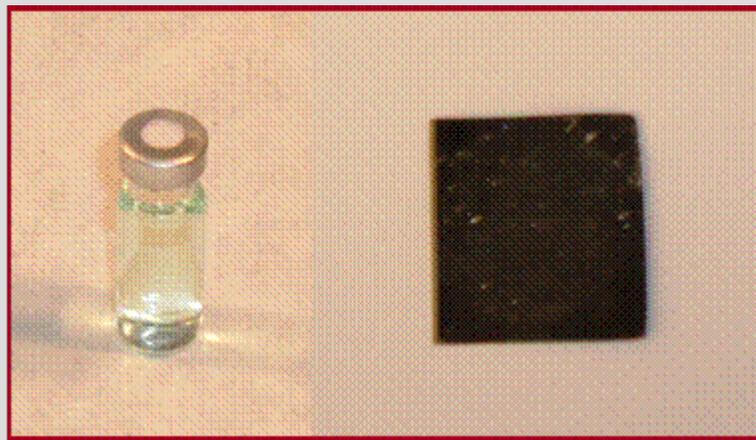


As -received Ni



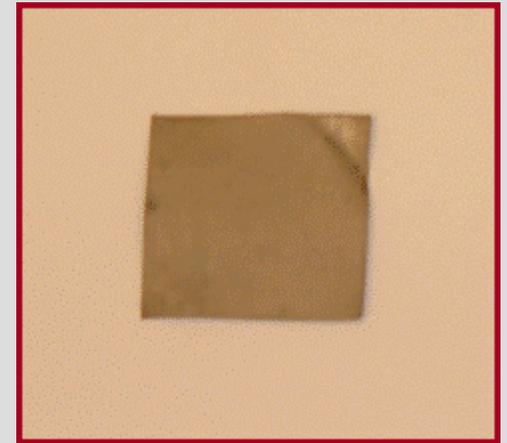
100% weight loss  
in 100hrs!

Ni treated at 700°C, 8hrs



3.3% weight loss in 300hrs

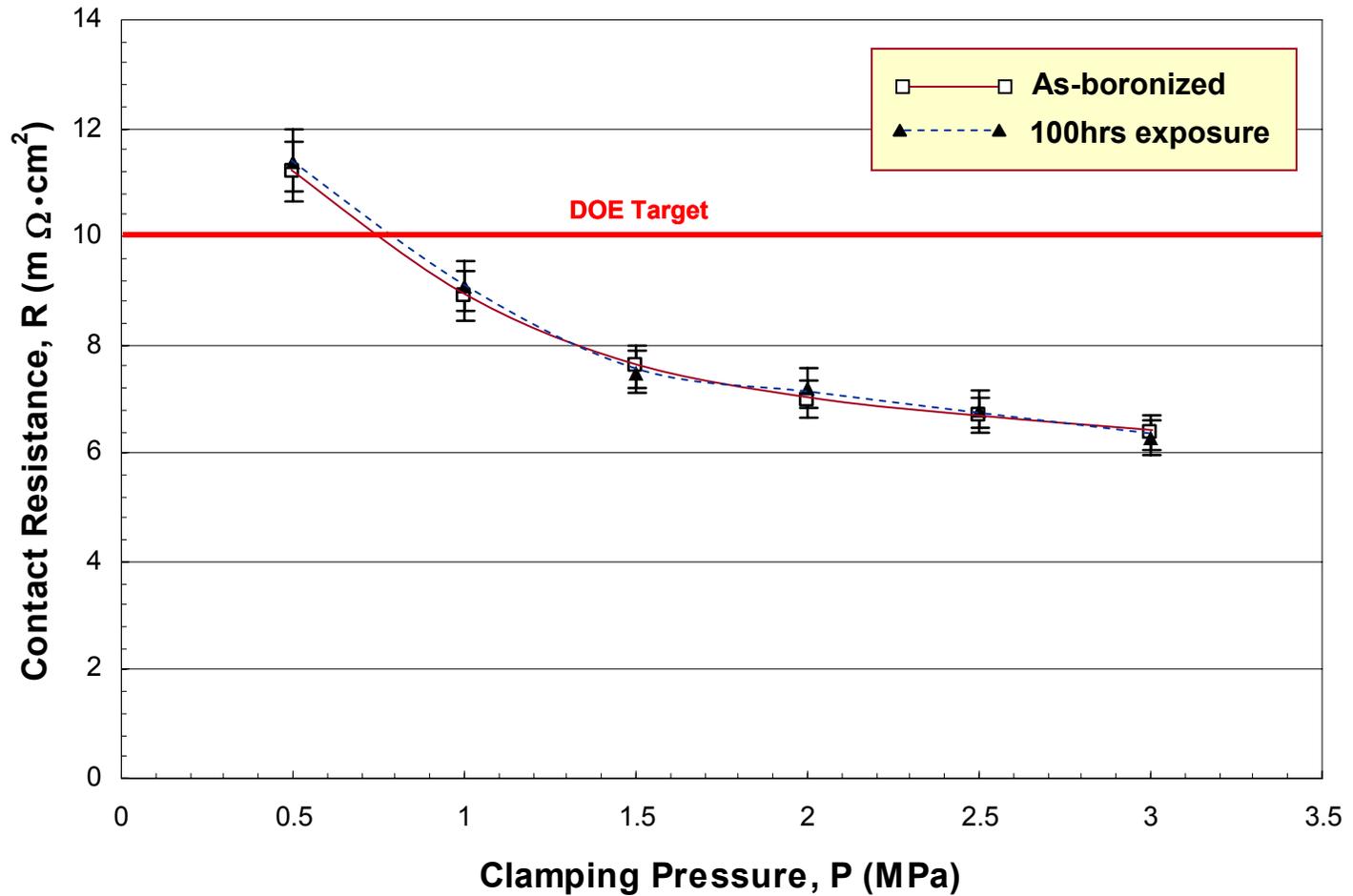
Ni treated 600°C, 8hrs



>1.0% weight loss  
in 500hrs

# Initial Contact Resistance Results

Boronized at 700°C for 8hrs; tested in 1M H<sub>2</sub>SO<sub>4</sub> (2ppm HF) at 80°C



# Clad Metal Boronization

As-received Ni/453SS/Ni

20kV X750 20µm 05s680a

Boridized at 700°C, 8hrs

$\text{Ni}_2\text{B}$

$\text{Ni}_3\text{B}$

Ni

453 SS

20kV X750 20µm 05s681a

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- **Nickel is particularly interesting**
  - ▶ Low cost relative to other transition metal passivation layers
  - ▶ Corrosion properties can be greatly improved via boronization
- **Have developed boronization curves over 500 – 700°C**
  - ▶ High temperature, longer times →  $\text{Ni}_2\text{B}$ , less aggressive conditions →  $\text{Ni}_3\text{B}$
  - ▶ Coating grows uniformly and the kinetics follow a typical diffusional trend:  $x^2 \propto t$
  - ▶ No measurable effects of the  $\text{CaB}_6:\text{KBF}_4$  ratio in the boronization media
- **Boronization leads to improved corrosion resistance and higher surface conductance**
  - ▶ Key is likely the thickness/composition of the boronized layer – although additional work is required to verify this
- **The clad material is readily boronized**

- **Remainder of FY 2006:**
  - ▶ **Demonstrate a Nb cladding layer of  $<25\mu\text{m}$  (1mil) thick and validate the properties via ex-situ testing**
  - ▶ **Investigate the formability of the candidate clad metals in preparation for stamping tests (will meet the second FY06 milestone)**
    - **Primary focus: demonstrate that the clad material can be stamped without dramatically thinning or forming defects in the cladding layer**
    - **Secondary focus: demonstrate the protection/passivation of through-holes (i.e. gas manifold holes) in the clad material via coining**
  - ▶ **Fabricate preliminary small-scale stamped pieces for ex-situ testing**

- **In FY 2007:**
  - ▶ **Conduct ex-situ testing of preliminary small-scale stamped pieces**
  - ▶ **Investigate the corrosion/polarization properties of boronized Ni clad material as a function of boronization temperature and time**
  - ▶ **Fabricate large scale boronized Ni-clad bipolar plates for off-site stack testing**
  - ▶ **Investigate a third, lower-cost clad metal system (anticipated to readily meet the DOE's 2015 cost targets)**

## Summary: Comparison with DOE 2010 Targets

### Comparison of DOE bipolar plate technical targets and calculated/measured clad metal characteristics

Characteristic	2010 target	Nb-clad steel	Ni-clad steel <sup>a</sup>
Cost (\$/kg)	6	5.0 <sup>c</sup>	4.5 <sup>d</sup>
Weight (kg/kW)	<1	0.7 <sup>c</sup>	0.72 <sup>d</sup>
H <sub>2</sub> permeation rate <sup>b</sup>	<2x10 <sup>-6</sup>	0.35 x 10 <sup>-7 c</sup>	0.37 x 10 <sup>-7 d</sup>
Corrosion (mA/cm <sup>2</sup> )	<1	<1 <sup>e</sup>	TBD <sup>f</sup>
Conductivity (S/cm)	>100	0.6x10 <sup>5</sup>	0.8x10 <sup>5</sup>
Resistivity (Ω•cm <sup>2</sup> )	0.01	<0.01 <sup>g</sup>	<0.01
Flexural strength (MPa)	>4	Expected to meet <sup>f</sup>	Expected to meet <sup>f</sup>
Flexibility (% at mid-span)	3-5	Expected to meet <sup>f</sup>	Expected to meet <sup>f</sup>

<sup>a</sup> Boronized.

<sup>b</sup> In cm<sup>3</sup>/sec•cm<sup>2</sup> at 80°C and 3atm.

<sup>c</sup> Assumes a <20μm thick Nb cladding layer over a 130μm steel core. Cost information is based on discussions with ATI Wah Chang, a leading world-wide producer of Nb sheet product.

<sup>d</sup> Assumes a 40μm thick cladding layer over a 110μm steel core.

<sup>e</sup> Anticipated based on preliminary screening tests.

<sup>f</sup> Yet to be determined.

<sup>g</sup> At clamping pressures > 1.5MPa.

## Response to Previous Reviewer's Comments

- **None were offered (the project had just started a month prior to last year's review meeting and there was no data to review)**

## Publications/Presentations

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- K. S. Weil, J. Y. Kim, J. E. Coleman, G. G. Xia, and Z. G. Yang, “Development of a boronized passivation layer for use in low-cost PEM fuel cell bipolar plates,” *Ceramic Engineering and Science Proceedings*, in press.
- K. S. Weil, G. G. Xia, Z. G. Yang, and J. Y. Kim, “Development of a niobium clad PEM fuel cell bipolar plate material,” *International Journal of Hydrogen Energy*, in review.
- K. S. Weil, J. Y. Kim, G. G. Xia, J. E. Coleman, and Z. G. Yang, “Boronization of nickel and nickel clad materials for potential use in polymer electrolyte membrane fuel cells,” *Surfaces and Coatings Technology*, in review.
- K. S. Weil, J. Y. Kim, J. E. Coleman, G. G. Xia, and Z. G. Yang, “Development of a boronized passivation layer for use in low-cost PEM fuel cell bipolar plates,” presented at the 30<sup>th</sup> International Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, 2006.
- K. S. Weil, G. G. Xia, Z. G. Yang, and J. Y. Kim, “Investigation of clad materials for use in PEMFC bipolar plates,” presented at the 135<sup>th</sup> TMS Annual Meeting, San Antonio, TX, 2006.
- K. S. Weil, J. Y. Kim, J. E. Coleman, G. G. Xia, and Z. G. Yang, “Development of low-cost, clad metal for use in PEM fuel cell bipolar plates,” presented at the International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, 2006.
- K. S. Weil, G. G. Xia, Z. G. Yang, and J. Y. Kim, “Consideration of a niobium clad material as potential PEMFC bipolar plate material,” presented at the 209<sup>th</sup> Annual Electrochemical Society Meeting, Denver, CO, 2006.

## Critical Assumptions/Issues

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- **Issue:** Performance of the clad material after stamping/coining – in particular, potential issues regarding thinning or cracking of the protective cladding layer.
- **Address:** This will be one of the issues we focus on later this year regarding the formability of the clad material. The goal will be to stamp small-scale pieces that incorporate the same size gas channel widths, depths, and bend radii anticipated in the full-scale component and examine the cross-sections of the resulting parts before and after corrosion testing.
  
- **Issue:** Corrosion at surfaces where the core material may be potentially exposed (i.e. manifold holes)
- **Address:** This will be the second key metal forming issue we address this year. There are coining approaches that have been employed to swag a cladding layer over a core layer in potential exposure areas. Our goal will be in understanding the process/material design limits in using this technique.
  
- **Issue:** Long-term (5,000 – 10,000hr) corrosion performance of both Nb and B-Ni in a prototypic stack environment
- **Address:** Our testing program will eventually need to move to in-situ stack testing and prototypic lifetime testing. Although the results of our work are promising, the project is still in the feasibility stage. We anticipate being able to begin considering this issue with respect to the Ni-B material in FY07.

- The most significant hydrogen hazard associated with this project is:
  - ▶ *Is the use of bubbled hydrogen in our linear voltammetry and potentiostatic testing to simulate the anode half-cell environment. The primary hazard associated with this work is changing the high pressure hydrogen gas bottles used to provide the low flow of hydrogen in the experiments.*

- Our approach to deal with this hazard is:
  - ▶ *The flow rate of H<sub>2</sub> in the polarization experiments is quite low and the amount of H<sub>2</sub> employed is small. The electrochemical testing studies are conducted in a well-ventilated hood to mitigate the potential build-up of hydrogen and to avoid exposure of the test researcher to the acid electrolyte environment.*
  - ▶ *In our laboratory, hydrogen gas bottles are kept in a safety cabinet (designed specifically for flammable/explosive gases) during the entire use. The hydrogen line is hard plumbed from the gas cabinet to the point of use.*
  - ▶ *Only trained personnel are allowed to change out hydrogen gas bottles. They employ non-sparking tools and use appropriate electrical grounding during the operation.*
  - ▶ *All of the experimental researchers working on this program have taken and passed a hydrogen safety class.*
  - ▶ *Prior to conducting these experiments, the personnel in charge of testing reviewed the test procedures with the safety staff at PNNL.*