Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

DOE Hydrogen Program 2006 Annual Merit Review

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Washington, DC, May 16-19, 2006

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Project ID #
FCP25

Overview

Timeline

- Project start date: 2004
- Project end date: tbd
- Percent complete: tbd

Barriers

Barriers addressed

- A. Durability, e.g. corrosion.
- B. Cost, stack material and manufacturing costs.

Budget

- Total project funding
  - DOE share: $346k
- Funding received in FY05: $156k
- Funding for FY06: $150k

Partners

Interactions & collaborations

- ORNL
- Plug Power
- Jadoo Power Systems

NREL Research Objectives

- Understanding the relationship between alloy composition and bipolar plate performance
- Study possible coating materials and surface modification preparations and methods.
- Develop suitable alloys/coatings/surface modification processes to meet the DOE goals.
  - DOE 2010 cost goal: $6/kW
  - Resistivity: 0.01 Ohm/cm^2
  - Corrosion rate: < 1 $\mu A/cm^2$

NREL Program Approach

- Collaborate with ORNL to evaluate nitrided surfaces and to develop new alloy composition for PEMFC
- Corrosion testing of new alloys (specially the low cost high Mn/N alloys) and coatings.
- Optimizing the deposition procedure of conductive coating deposition for low interfacial contact resistance and high corrosion resistance in PEMFC environments
- Determine the influence of dissolved metal ions on the conductivity of membrane.
- Complete the investigation of austenitic stainless steels in high temperature poly-phosphoric acid environment

Metallic Bipolar Plates

Advantages

- Wide choices of alloys, low cost, high chemical stability, corrosion resistance
- High strength allowing thin plates for high power density
- High bulk electrical and thermal conductivity
- Existing low cost/high-speed high-volume manufacturing pathway (e.g. stamping, embossing, rolling, etching…)

Challenges

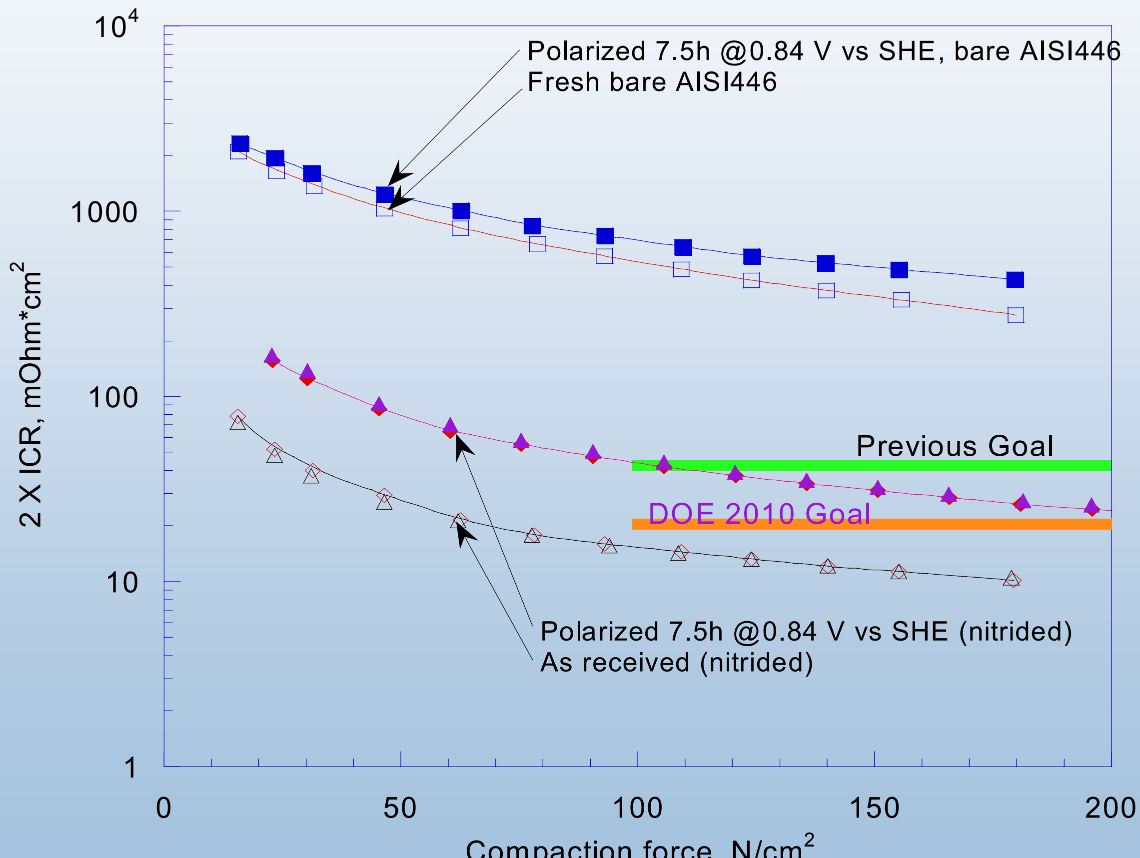
- Surface oxides provide excellent corrosion resistance but lead to higher surface contact resistance
- Possible contamination of the membrane by dissolved metallic ions coming from corrosion byproducts

NREL/ORNL Collaboration

- Improving and adjusting the alloy composition and surface nitridation parameters for PEMFC metallic bipolar plates
  - Influence of added alloying elements on the nitrided layer and effects on contact resistance and corrosion resistance;
  - Influence of nitridation conditions on the contact resistance and corrosion resistance in <u>aggressive</u> PEMFC environments;
- Filed a joint patent application for the nitridation of 446 steel, exploring suitable nitrided alloys for PEMFC bipolar plates.

Initial Nitrogen Modified Oxide Layer on 446-type steel

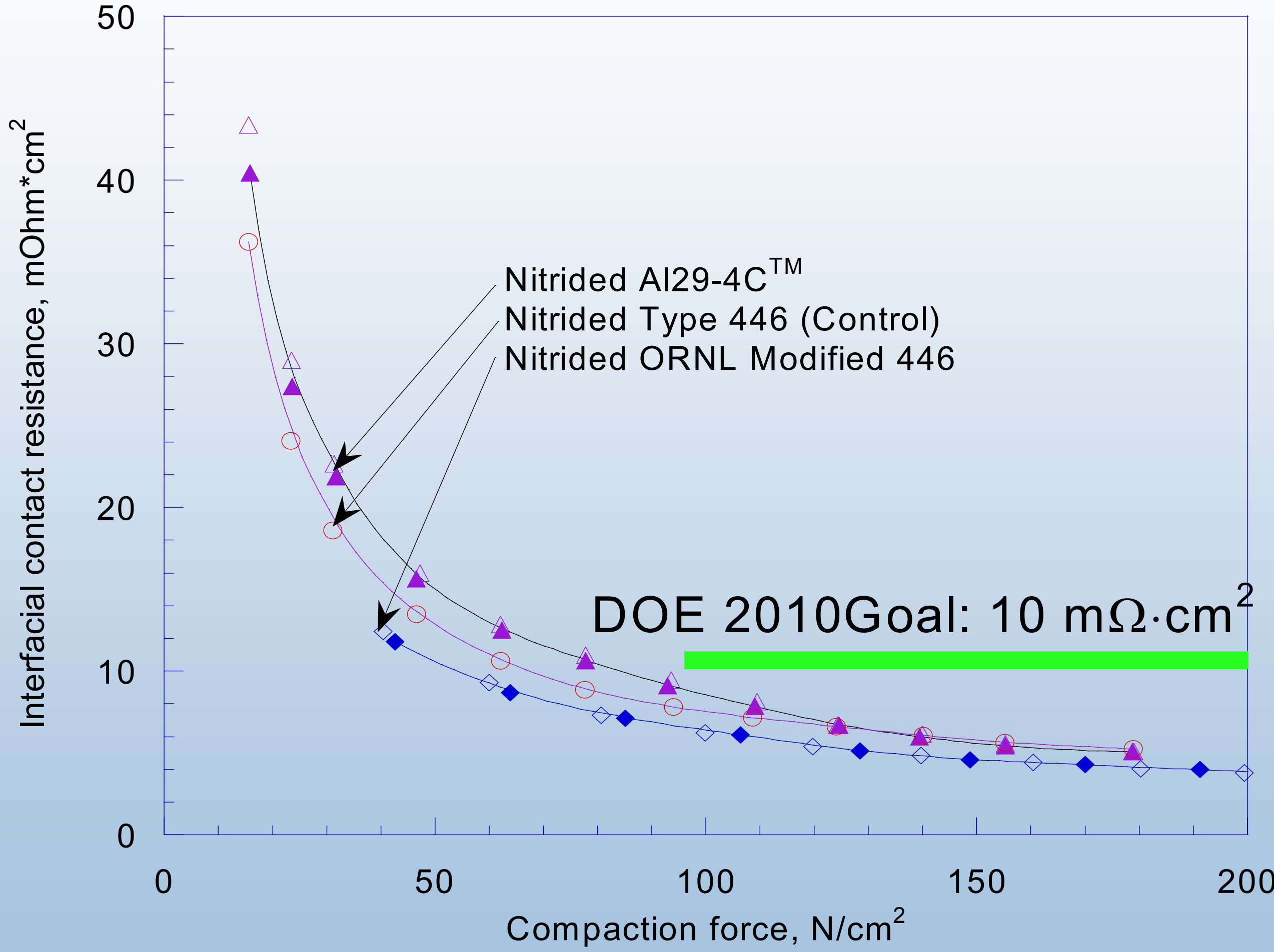
Ferritic Alloy, Fe-based, high Cr, low Ni, low cost



- As-nitrided surface is a complex oxygen-nitrogen mixture with Cr, Fe
- ICR shows order of magnitude reduction from bare alloy both as-nitrided and after polarization;
- Excellent substrate corrosion resistance retained.

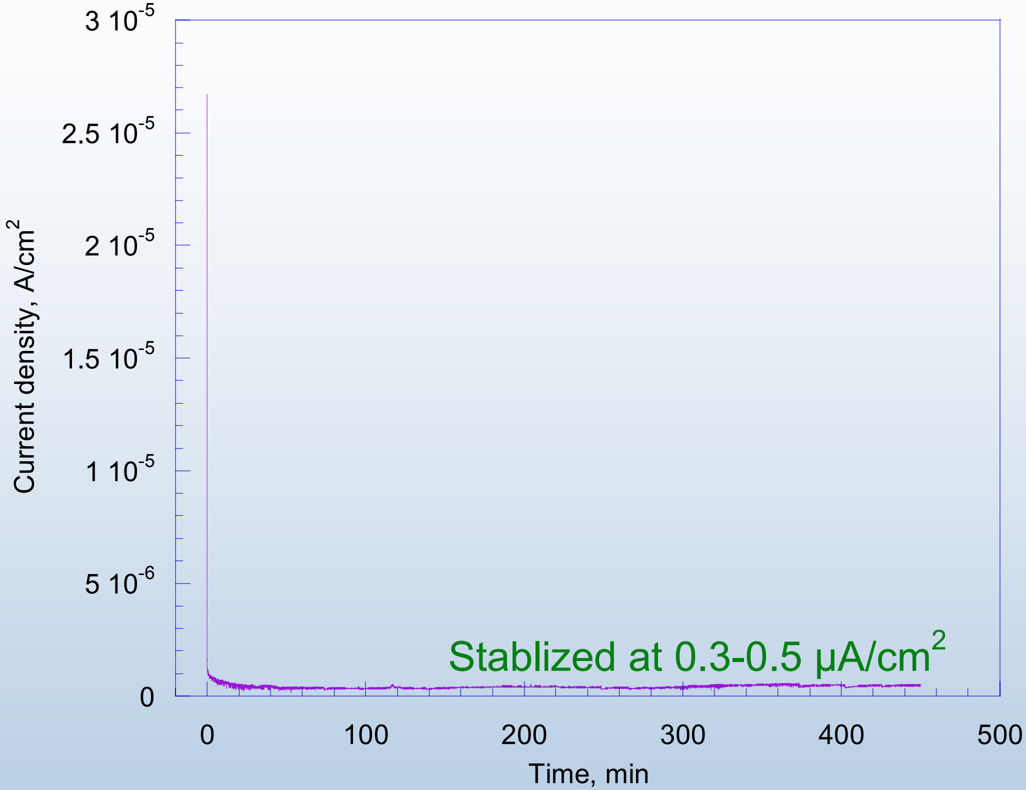
Note: Simulated aggressive PEM environment: 1M H_2SO_4, 2ppm F^-, 70°C

Exploring nitriding of commercially available alloys and developing new alloys with low ICR



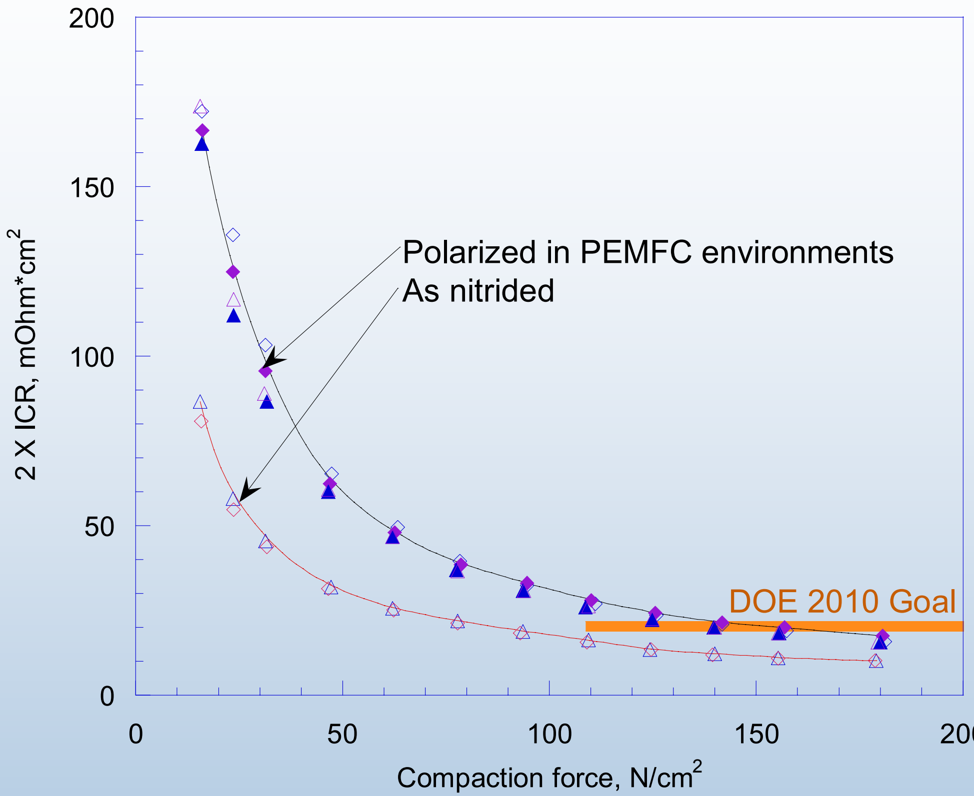
<u>Note:</u> These nitrogen modified surfaces are not a dense Cr nitride layer, but rather Cr-nitride particles interdispersed in the oxide, such that the ICR is low and the passive layer is maintained. The oxygen helps keep the N from forming extensive internal nitridation precipitates which can initiate corrosion.

Performance of nitrided AL29-4C alloy in simulated PEMFC environments



Potentiostatic test in PEMFC cathode environment, 0.84V vs SHE, air

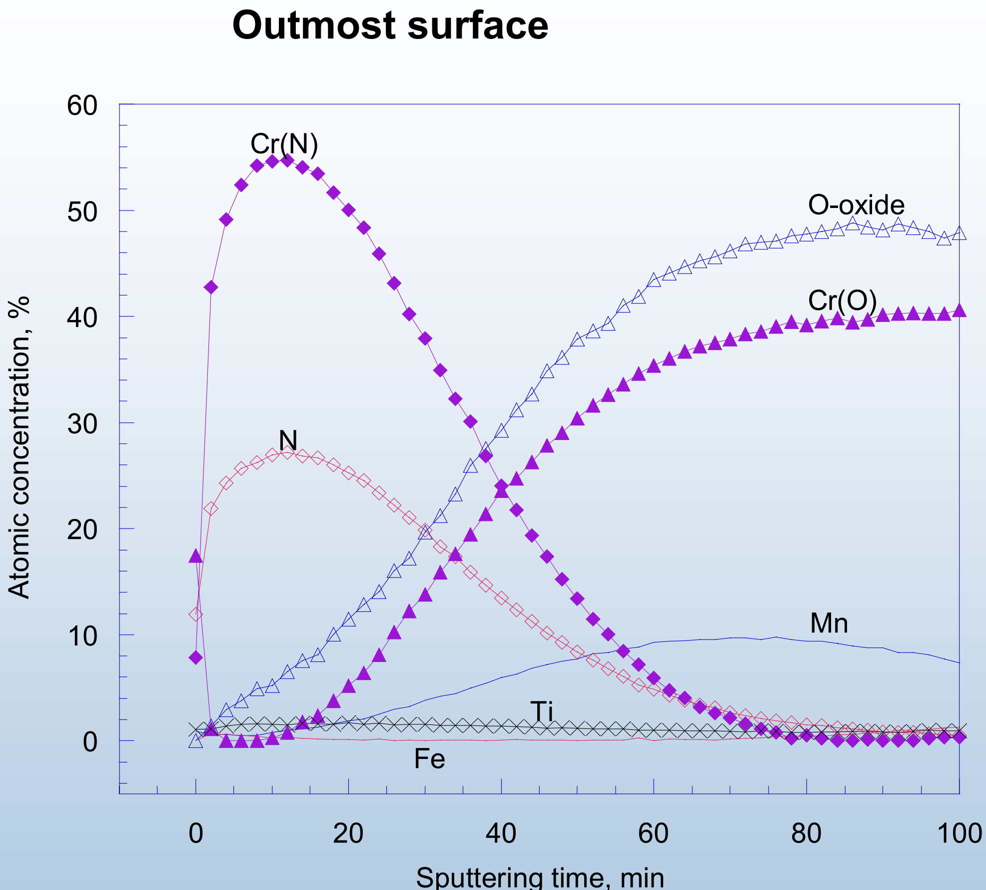
Current in PEMFC anode (-0.1V, H_2) environment stabilizes at -3.0 μA/cm²

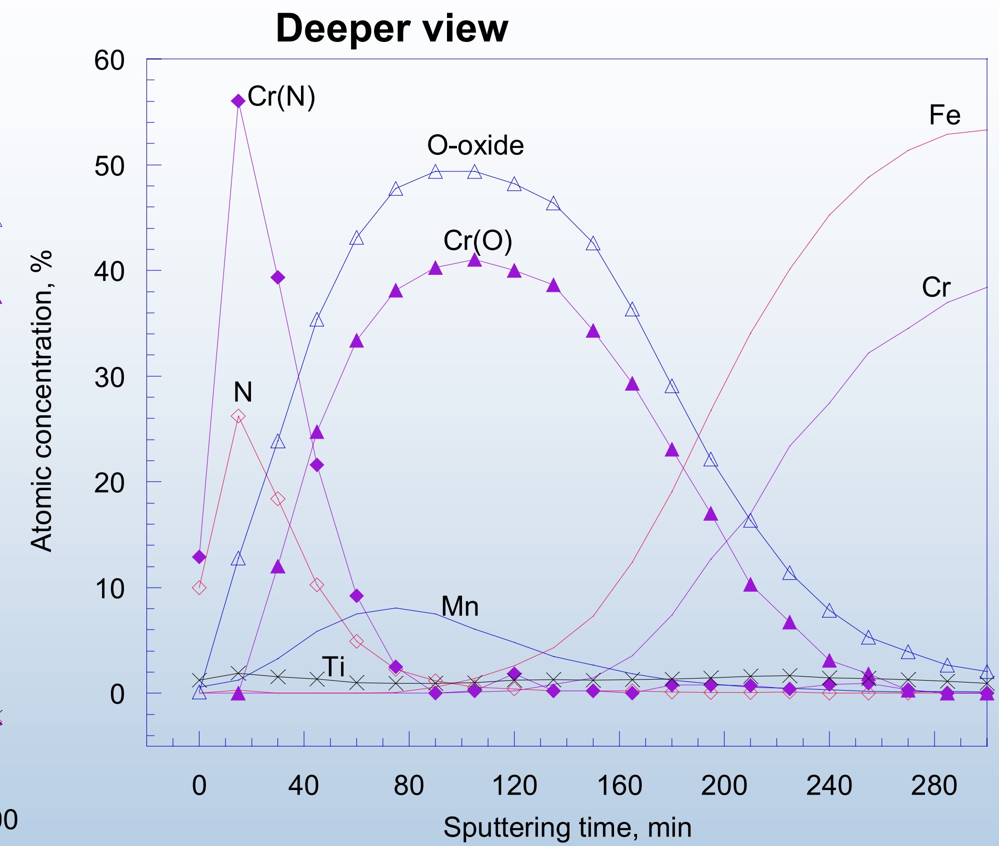


Effect of polarization on the ICR of nitrided AL29-4C™ alloy. Note that 2x ICR is used.

Note: *Simulated aggressive PEM environment: 1M H_2SO_4, 2ppm F^-, 70°C*

XPS depth profile for 24h nitrided AL29-4C™ alloy



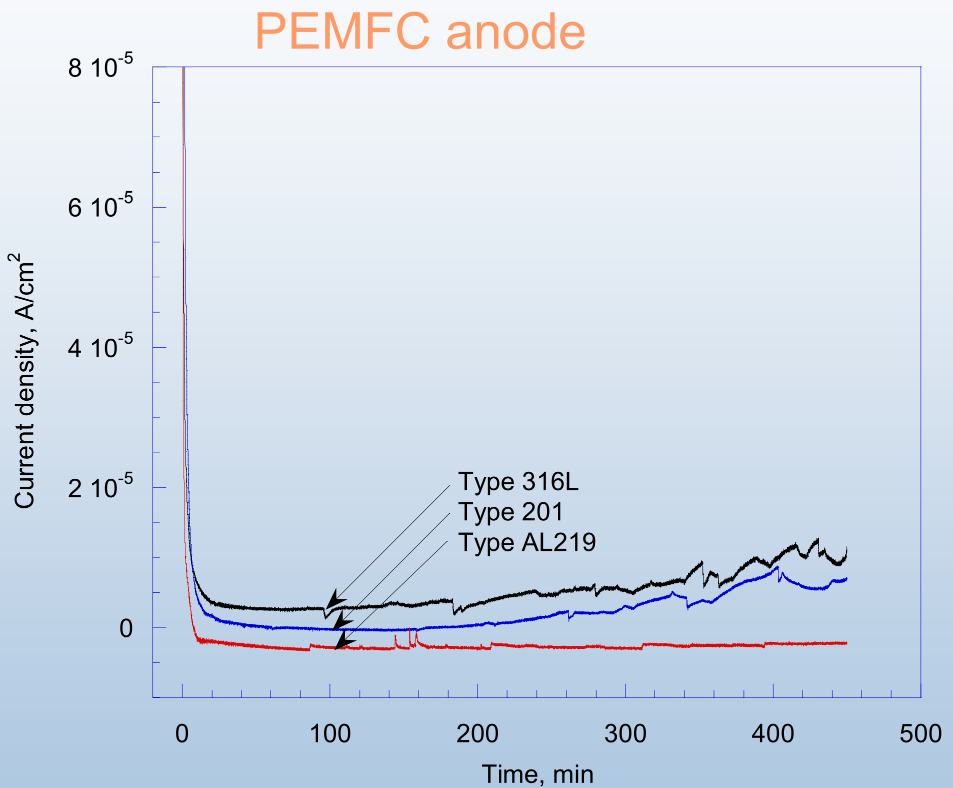


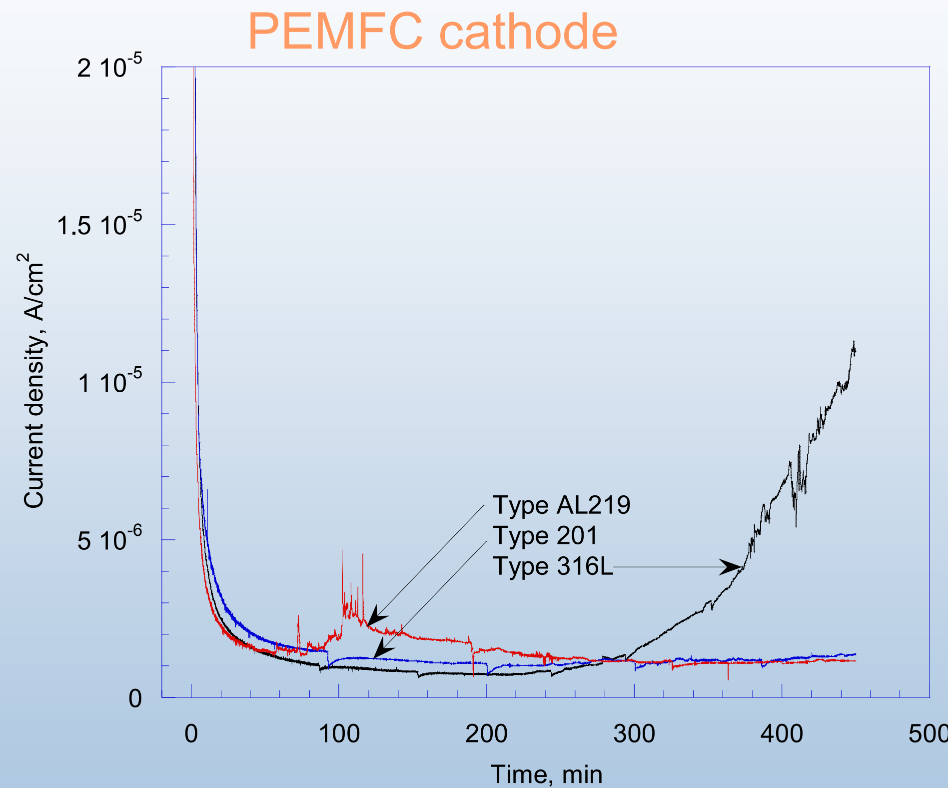
Note: The extent of the nitridation reaction is very low to keep nitride layer thin (0.1 to 1 micron).

Jadoo Power Systems (www.jadoopower.com) will be testing a small stack using nitrided Al29-4C metal bipolar plates.

Continuing survey of low-cost stainless steel alloys

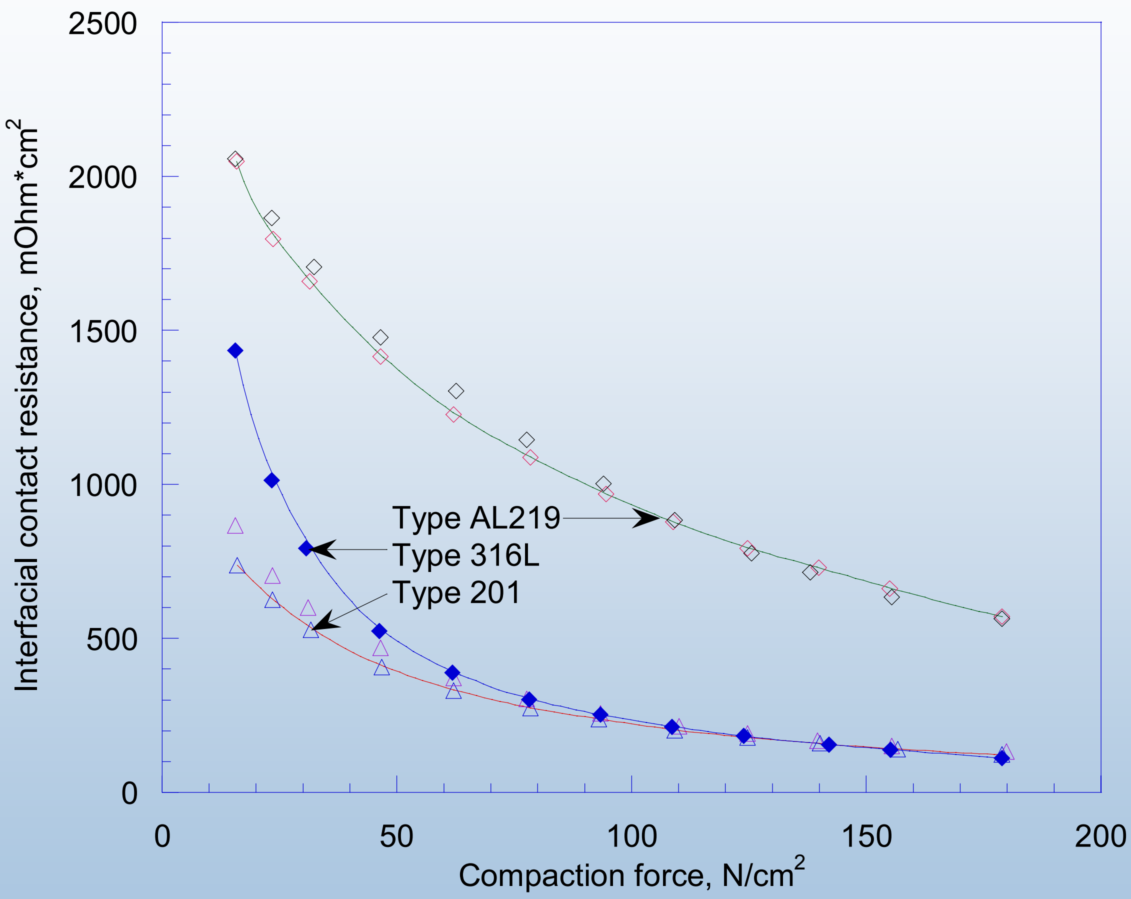
Behavior of 201 and AL219 steels in simulated aggressive PEMFC environments:





The goal of this task is to look for other possible low-cost alloys that would be good candidates as bipolar plates or for surface modification or for coating experiments.

Interfacial contact resistance of the 200 steels



- Type 201 gives similar or lower ICR values than 316L; while much higher ICR values obtained with AL219---could be related to the surface structure

Composition of the steels, wt%, Fe-balance

Alloy	N	Cr	Ni	Mn	Mo
201	0.067	16-18	3.5-5.5	5.5-7.5	-
AL219	0.315	21.0	6.00	9.00	.05
316L	0.020 - 0.040	16.50 - 16.80	10.10-10.30	1.70-1.95	2.03-2.25

COST! DOE Goals vs. Alloy

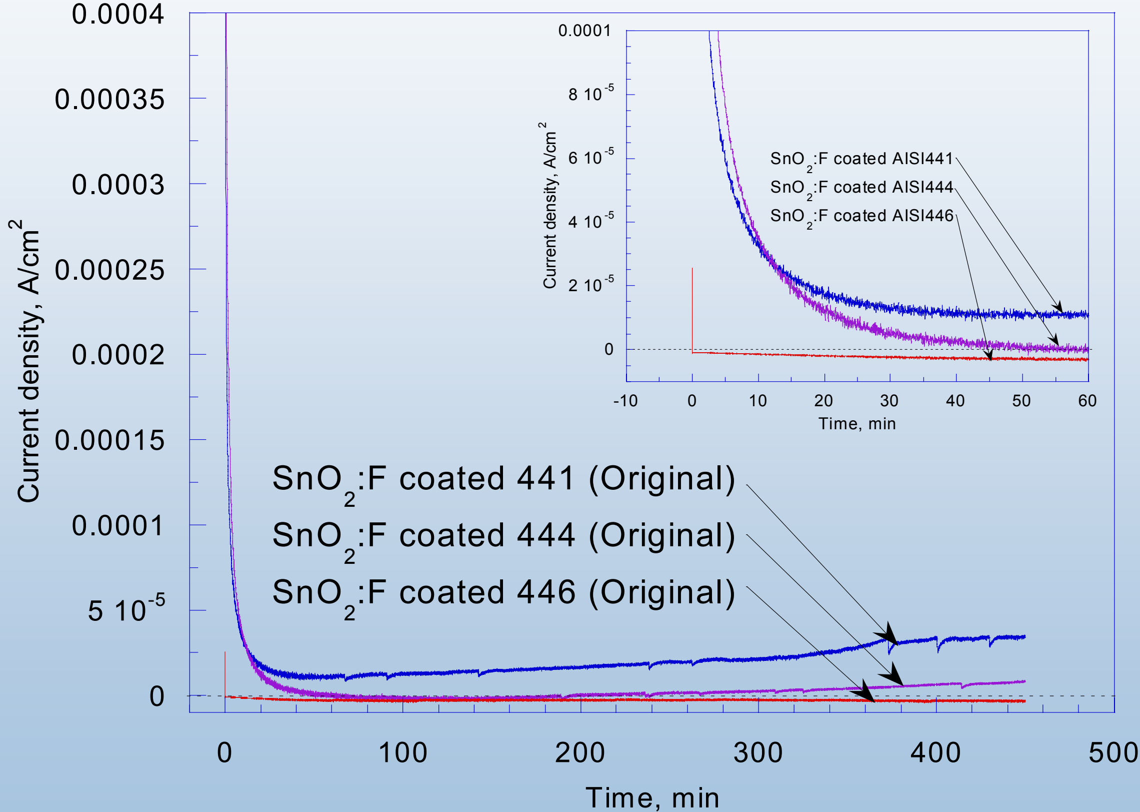
Goal/Alloy	ICR@140 N/cm^2 m$\Omega\cdot$cm^2	Current@ –0.1V (H_2), μA/cm^2	Current at 0.6 V (Air), μA/cm^2	**Cost $/kW**
DOE 2010 Goal	*10*	*< 1*	*< 1*	*6*
316L	**154**	**+2.5 ~ +12**	**0.7 ~ 11**	**3.41**
349^{TM}	110	-4.5 ~ -2.0	0.5 ~ 0.8	**3.61**
AISI446	190	-2.0 ~ -1.0	0.3 ~ 1.0	**4.08**
2205	130	-0.5 ~ +0.5	0.3 ~ 1.2	**3.53**
Nitrided446	6.0	-1.7 ~ -0.2	0.7 ~ 1.5	**N/A**
201	***158***	***-0.5 ~ +8.5***	***0.8 ~ 2.0***	***2.18***
AL219	***730***	***-3.3 ~ -1.5***	***1.0 ~ 3.0***	***2.65***
Nitrided AL29-4C^{TM}	***6.0***	***-6.5 ~ -3.0***	***0.3 ~ 0.5***	***N/A***

Note: Cost data were based on the average 2005 trading price of cold rolled coil 316 steel at London Metals Exchange and the market prices of the metals. The assumed stack was 6 cells/kW for a PEMFC and the dimensions of a bipolar plate are 24 cm × 24 cm × 0.0254 cm (which gives a 400 cm^2 utilization surface area in a 0.01 inch thick sheet)

Conductive SnO_2:F Coating

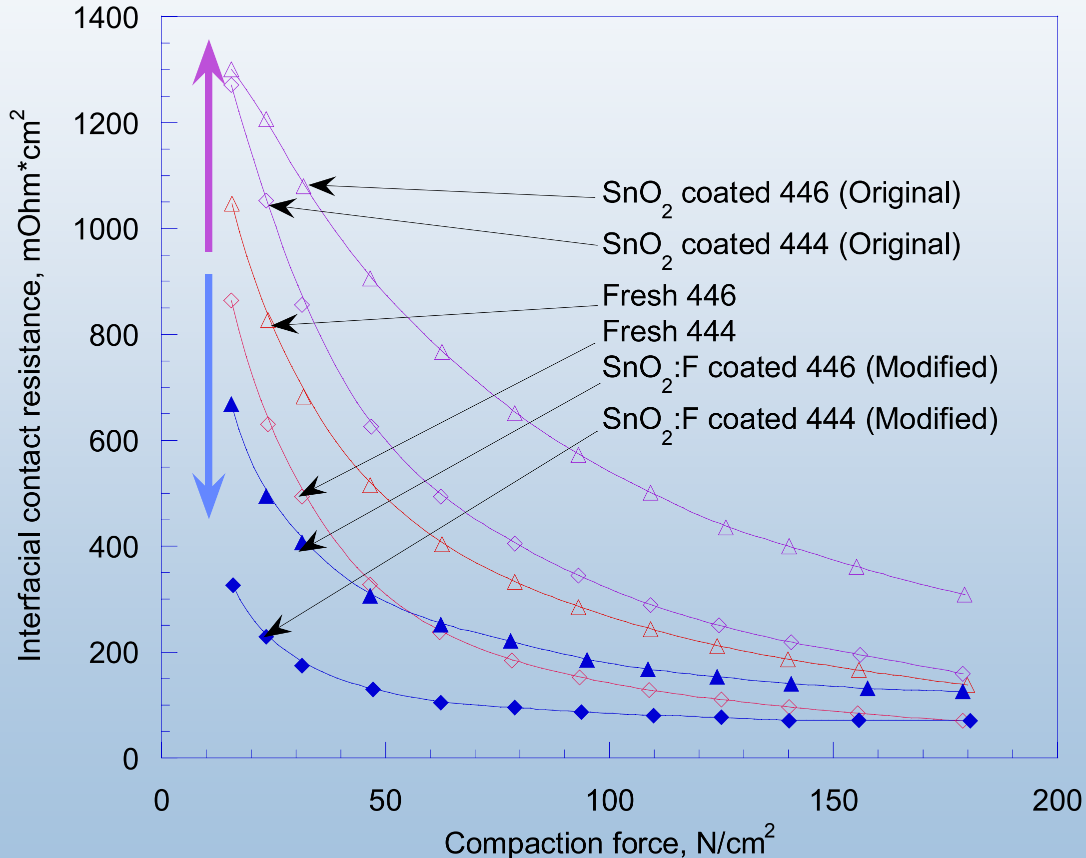
- Known high stability in different electrochemical environments.
- High conductivity; can carry 1 A/cm^2
- Volume production available-PV industry.
  - NREL expertise (National Center for Photovoltaics).;
- Bipolar plate cost reduction possible if used with lower grade lower-cost alloys.

Original coated 400 steels in PEMFC anode environment



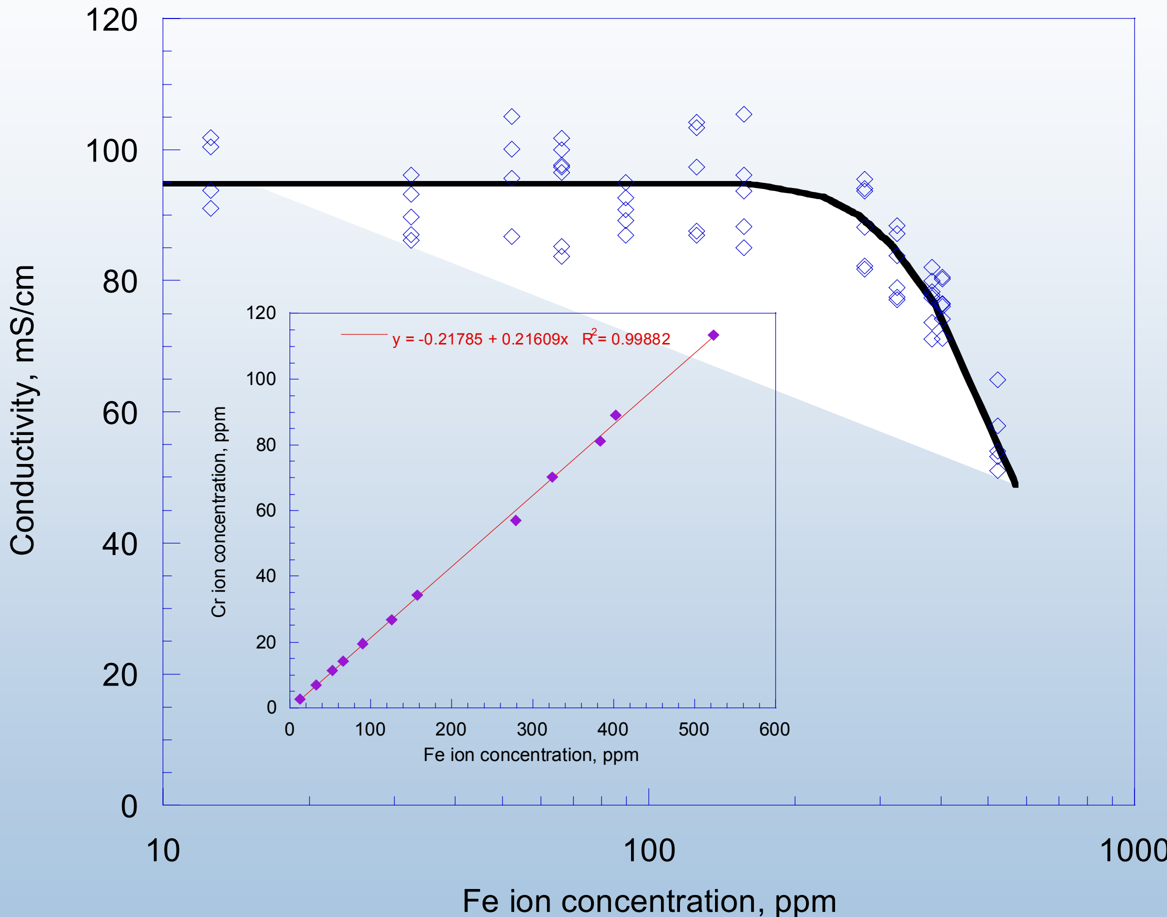
- Corrosion resistance of the coating is strongly related to substrate;
- Excellent behavior of SnO_2:F/446 expected;
- Surprising good corrosion resistance of SnO_2:F/444.

Optimizing the SnO_2:F coating for lower interfacial contact resistance



- Original coating just simply added additional resistance to the air-formed film----thus shifts ICR curves of fresh steels UP;
- Modified coating process reduces ICR significantly---shifts ICR curves of the fresh steels DOWN.

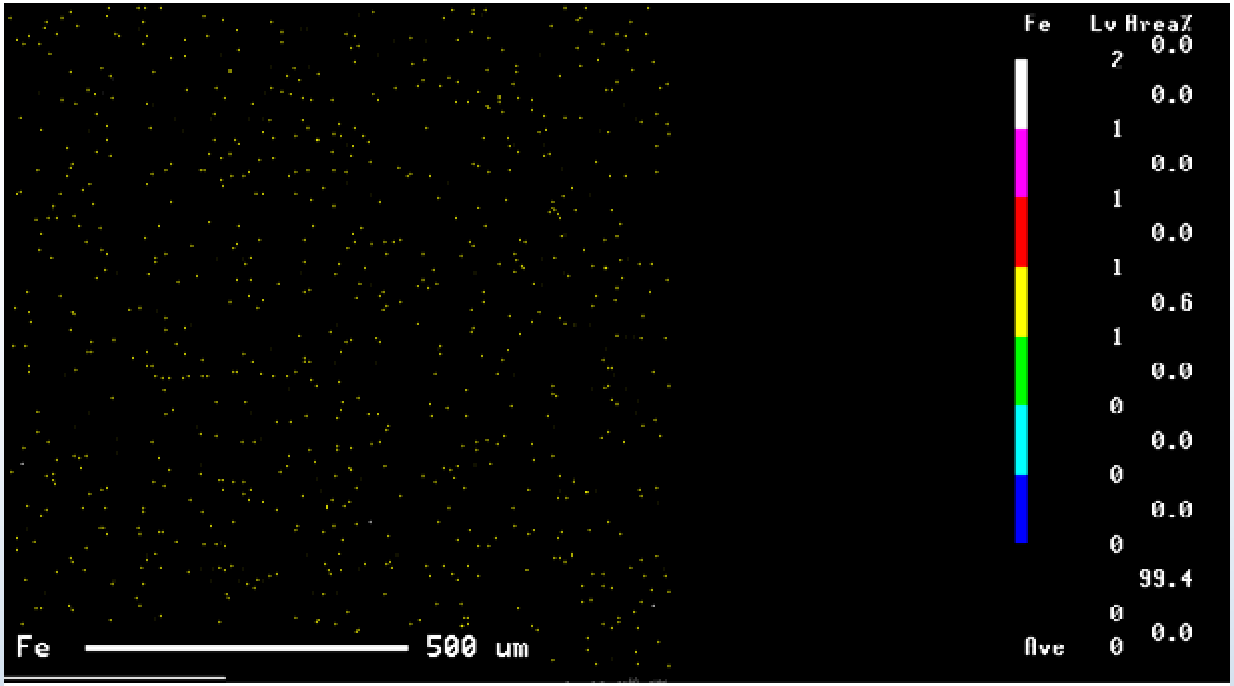
Influence of dissolved metal ions on the conductivity of Nafion 112

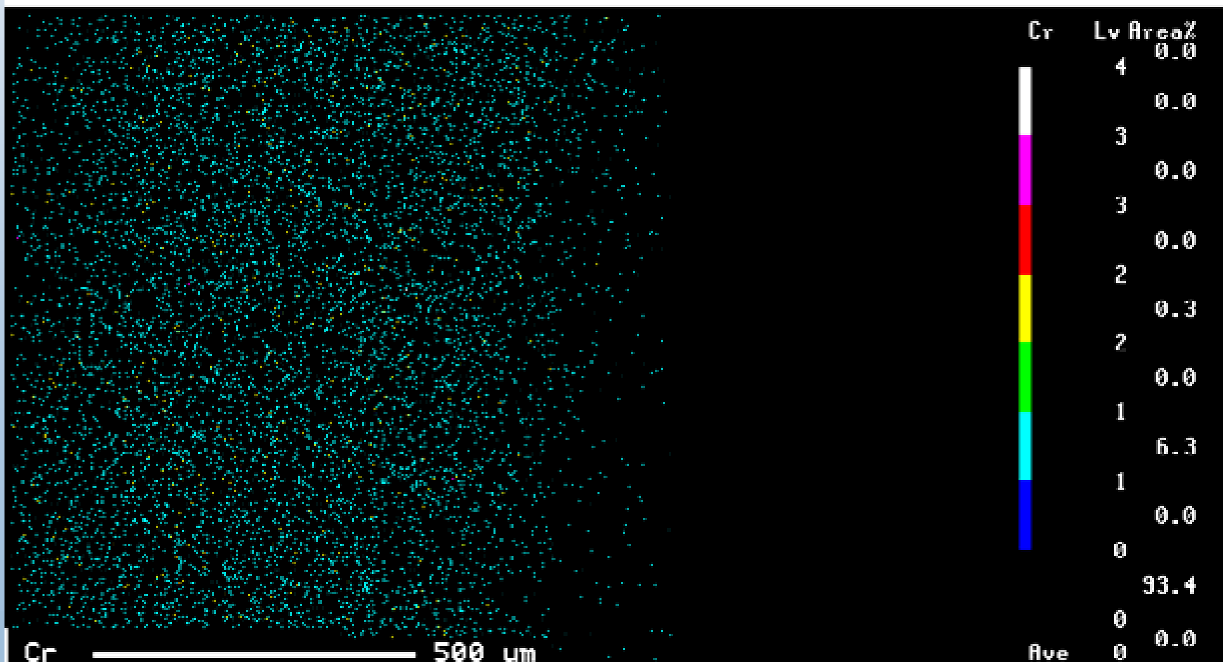


- Influence of mixed Fe and Cr ions on the conductivity of Nafion® 112 membrane.
  - Conductivity measured at 80 ºC and RH 100% with back hydrogen pressure of 0.103 MPa (15 psi).
  - Inset shows the relationship of dissolved Fe and Cr ions coming from the corrosion of a 316-type stainless steel in 1M H_2SO_4 under potentiostatic control.

The conductivity of the membrane material is relatively unaffected by Fe^{+3} metal ion concentration <100ppm (in solution).

Fe and Cr ions absorbed in Nafion 112



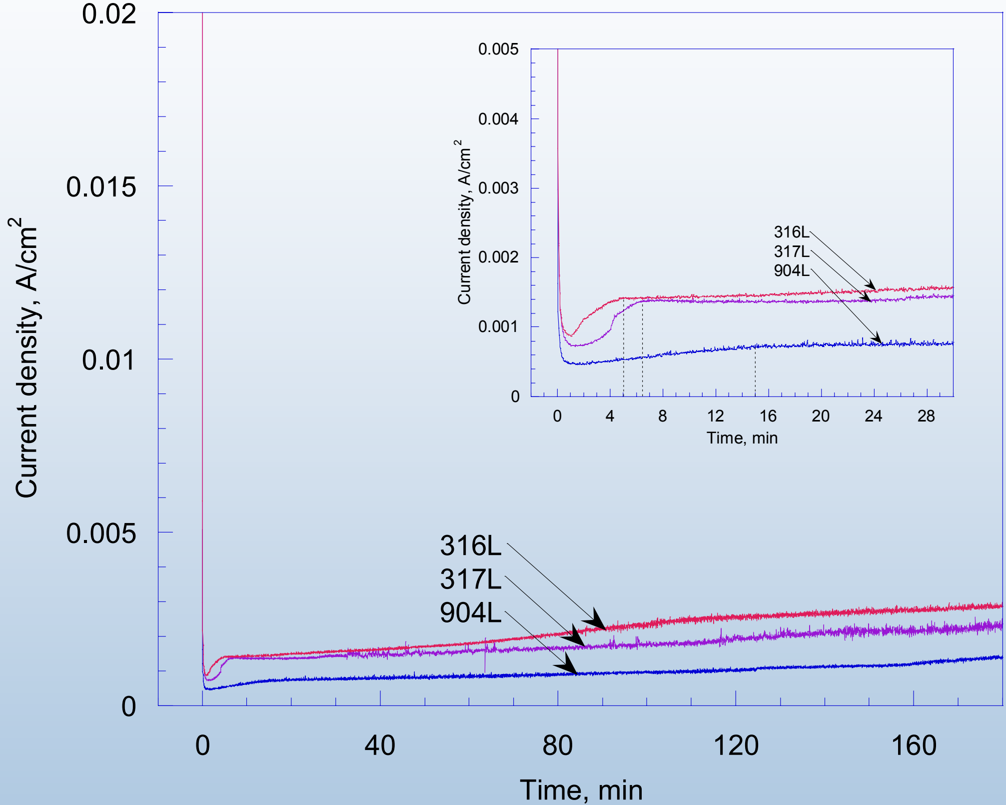


- EPMA images of the Fe^{3+} (above) and Cr^{3+} (bottom) ions across the surface of a Nafion® membrane. Both membranes were soaked in solutions containing 50 ppm metal ions.
- Cr^{+3} is clearly more strongly absorbed in the near surface of the membrane.

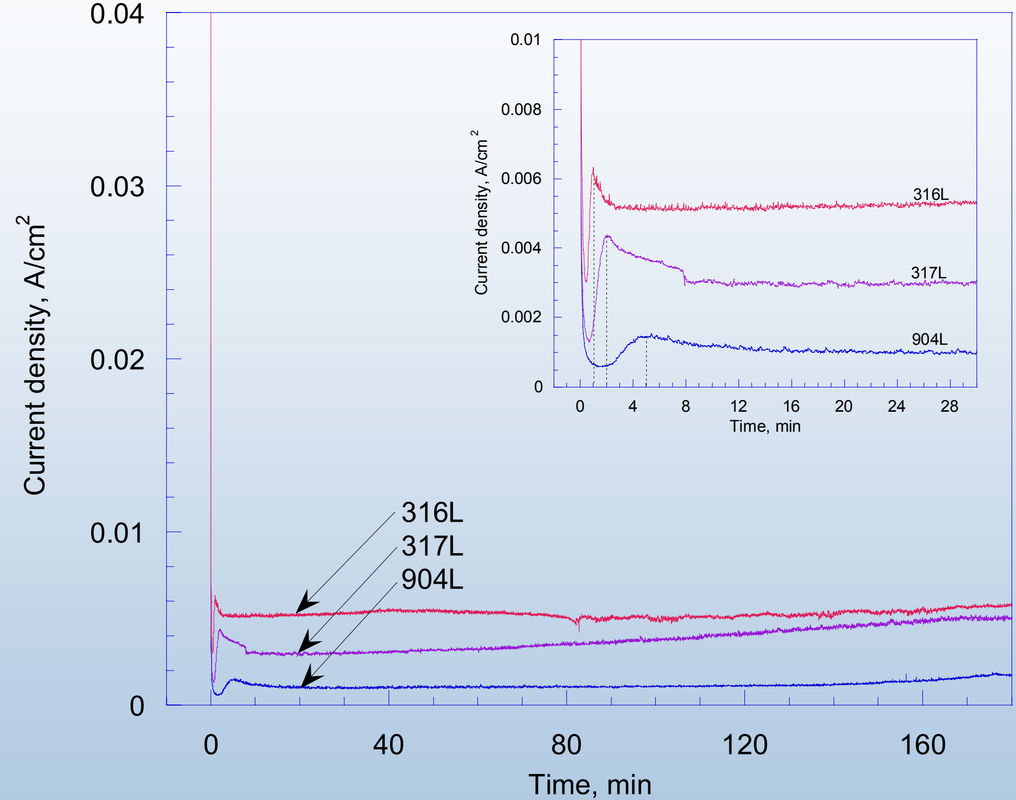
The Needs and Challenges of bipolar plates in a Higher Temperature (HT) PEM environment

- Desire of transportation industry + DOE R&D for high temperature membrane, however, exact environment for a HT PEMFC is not yet defined!
- Characterization of selected stainless steels and graphite-based bipolar plates in 150 - 170 °C, H_3PO_4 may provide some insight into possible issues facing bipolar plates in this future environment

Potentiostatic polarization of stainless steels in H_3PO_4 at 170 °C. Insets show the current decay during the 1st half hour polarization.



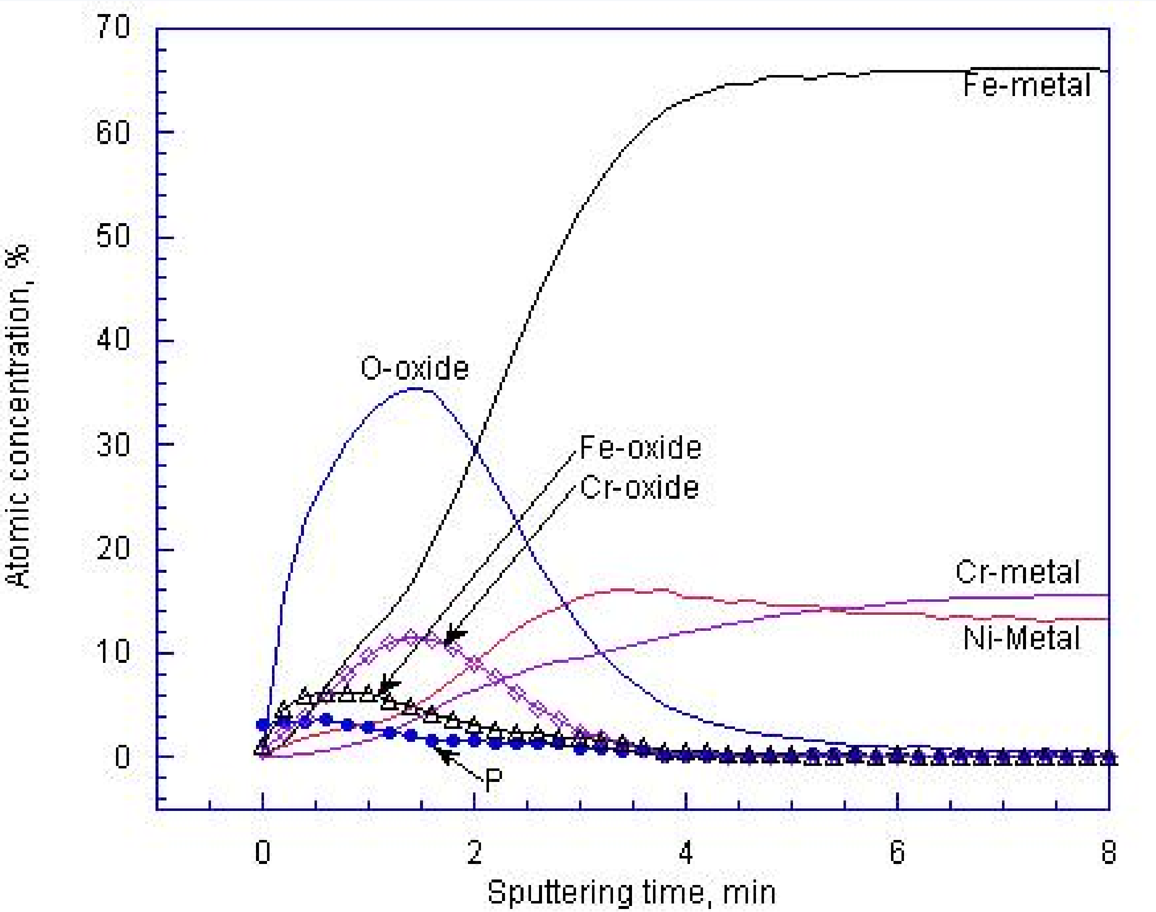
0.1V (RHE) with H_2 purge



0.7 V (RHE) with air purge

All of these alloys show significant (> 1mA/cm^2) corrosion rates!

Passive film formed on 316L steel in H_3PO_4 at 170 °C



- Polarized 3h at 0.1 V with H2 purge;
- Film ~4 nm thick;
- Fe-oxide selectively dissolved;
- P incorporation;
- <u>Different chemical composition here as compared to the passive film formed in PEMFC environments.</u>

Future Work

- Continuing NREL/ORNL collaboration with alloy development and nitridation;
- Identify low-cost alloys for future development.
- Optimizing surface treatments and coating deposition processes.
- Determine formability characteristics for alloy/coating combinations from above.

Project Summary

- ✓ Evaluation of metal alloys/coating combinations for fuel cell bipolar plates. Work involves research on corrosion resistance in simulated PEMFC environments, interfacial contact resistance testing, and surface characterization;
- ✓ Correlated the results with the composition of the base metal/coating to develop low cost metallic alloys with low interfacial contact resistance and excellent corrosion resistance in PEMFC environments.
- ✓ Determined the effect of metallic ions on the conductivity of membrane;
- ✓ Portion of the work is in collaboration with ORNL.

Responses to Previous Year Reviewers' Comments

1. Why not compare ionic conductivity of membrane before and after exposure to metal ions in solution?
   - *Completed*
2. Should conduct cycling tests be more representative of automotive cycles?
   - *Under development*
3. Should have a more structured approach for determining potential alloy candidates.
   - *This area lacks sufficient background information about the influence of alloy composition on the bipolar plate performance. Our approach is very structured in that we are systematically surveying alloy groups and determining the alloy/performance relationships to gather the necessary background.*

Publications and Presentations

Publications/manuscripts

1. Heli Wang and John A. Turner: Influence of Metallic Ions on the Conductivity of Nafion® 112 in Polymer Electrolyte Membrane Fuel Cell, in manuscript
2. Heli Wang and John A. Turner, The Corrosion of a Stainless Steel in High Temperature Phosphoric Acid, in manuscript.
3. Heli Wang and John A. Turner:, Austenitic Stainless Steels in High Temperature Phosphoric Acid, in manuscript
4. Heli Wang and John A. Turner:, SnO2:F Coated Ferritic Stainless Steels for PEM Fuel Cell Bipolar Plates, submitted to *Journal of Power Sources*.
5. Heli Wang and John Turner, On the Passivation of 349TM Stainless Steel in Simulated PEMFC Cathode Environment, ECS Transactions, Vol.1, No.LA-P1: *Proton Exchange Membrane Fuel Cells V, in Honor of Supramaniam Srinivasan* - Editors: S. R. Narayanan, C. Bock, T. Fuller, S. Mukerjee , C. Lamy, E. Stuve, and J. Weidner, in press.
6. Heli Wang, Glen Teeter and J. A. Turner, Investigation of a Duplex Stainless Steel as PEMFC Bipolar Plate Material, *Journal of the Electrochemical Society*, 152 (3) B99-B104 (2005).

Presentations

1. B. Yang, M. P. Brady, P.F. Tororoelli, K. L. More, H. Wang, J. A. Turner and D.J. Young, Nitrided Stainless Steels for PEM Fuel Cell Bipolar Plates, *TMS Annual Meeting* San Antonia, TX, March 15, 2006
2. M. P. Brady, B. Yang, K. L. More, P. F. Tortorelli, Tim Armstrong, H. Wang and J. A. Turner, Cost Effective Surface Modification for Metallic Bipolar Plates, Fuel Cell Tech Team Meeting, USCAR Facility, Southfield, MI, January 18, 2006.
3. M.P. Brady, B. Yang, Peter Tortorelli, K. L. More, H. Wang and J. A. Turner, Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells, Materials Science and Technology 2005, Pittsburgh, PA, September 26, 2005.
4. Heli Wang and John A. Turner, On the Passivation of 349TM Stainless Steel in a Simulated PEMFC Cathode Environment, *Proceedings of the 208th Meeting of the Electrochemical Society*, October 22-26, Los Angles, CA, USA, 2005, paper No. 976.
5. B. Yang, M. P. Brady, D. J. Young, K. L. More, H. Wang and J. A. Turner, Thermally Nitrided Stainless Steel Bipolar Plates for Proton Exchange Membrane Fuel Cells, *Proceedings of the 208th Meeting of the Electrochemical Society*, October 22-26, Los Angles, CA, USA, 2005, paper No. 1007.