Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

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Project ID #: FCP12

Overview

Timeline

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

Budget

- Total project funding
  - DOE share: $196k
- Funding received in FY04: $40k
- Funding for FY05: $156k

Barriers

- Barriers addressed
  - ✓ **Stack Material and Manufacturing costs.**
  - ✓ **Materials Durability**

Partners

- Interactions/ collaborations
  - Oak Ridge National Lab.
  - Plug Power

Approach and Objectives

- Our approach is two fold
  - Understanding the relationship between alloy composition and bipolar plate performance.
  - Study possible coating materials and methods.
- Objectives - FY 05 Goals
  - Corrosion testing of new alloys and coatings
  - Collaborate with ORNL to evaluate nitrided alloys and to determine best alloy composition for PEMFC.
  - Characterize conducting coatings on alloys and their performance in PEMFC environments.
  - Assemble test system for operation in the 100-200 °C range and study materials in this temperature range.
  - Development of corrosion tests for polyphosphoric acid environment at >150C

Why Metallic Bipolar Plates

- Wide choices, high chemical stability, including choices for corrosion resistance
- High strength allowing thinner plates for high power density
- Existing low cost/high volume manufacturing techniques (e.g. stamping);
- High bulk electrical and thermal conductivities;
- Potential for low cost.

- DOE 2010 Technical Targets for Fuel Cell Stacks
  - -Cost $35/kW
  - -Durability 5000 hours

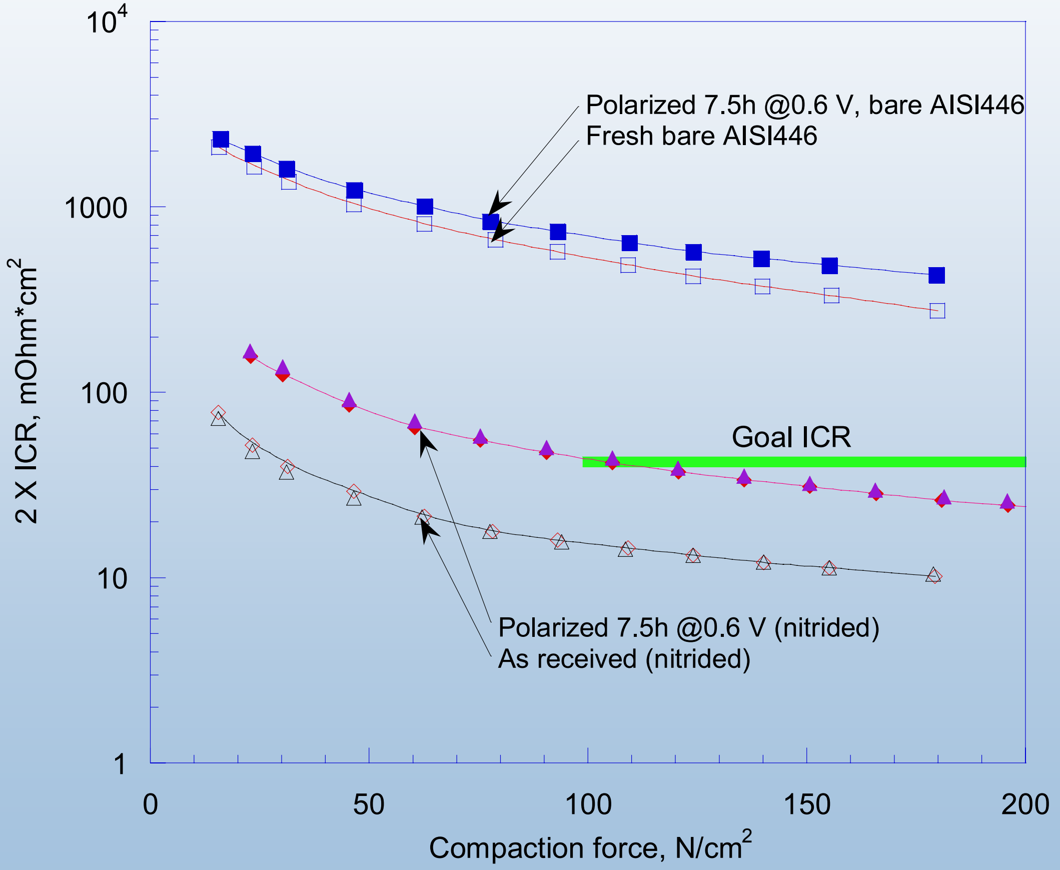
Challenges with Metallic Bipolar Plates in PEMFC

- Possible contamination of polymer membrane by dissolved metal ions
- Higher surface contact resistance due to surface oxides (such oxides provide excellent corrosion resistance however)

NREL/ORNL Collaboration

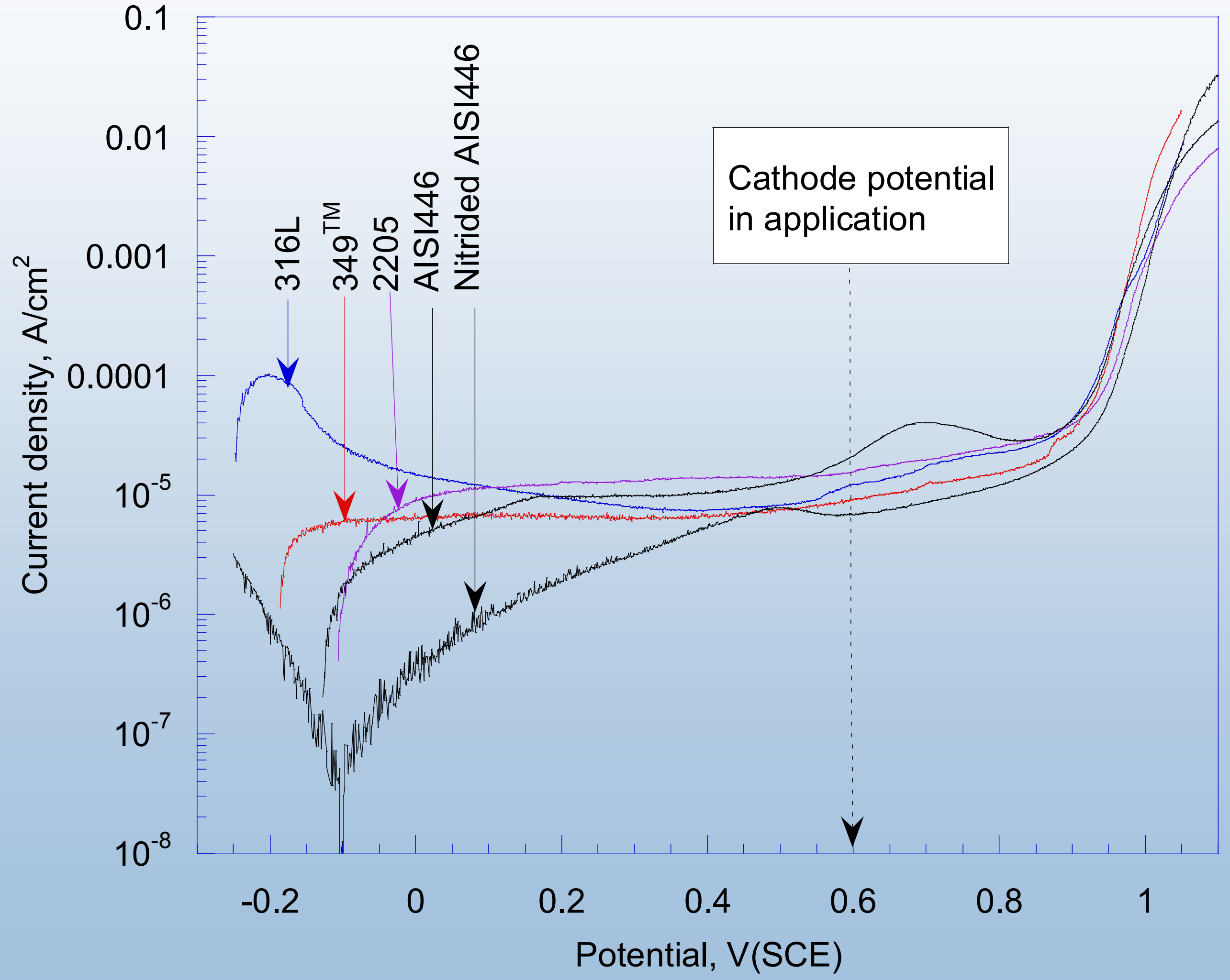
- Evaluated over 10 alloy compositions, both commercially available and synthesized;
- Evaluated the influence of nitridation parameters on the contact resistance and corrosion resistance in PEMFC environments, used for improving and adjusting the alloy composition and nitridation parameters;
- Filled a joint patent application for the nitridation of AISI446 alloy, finding 2 alloys suitable for PEMFC bipolar plates after nitridation.

Initial Success for Fe-Cr alloy via Nitrogen Modified Oxide Layer

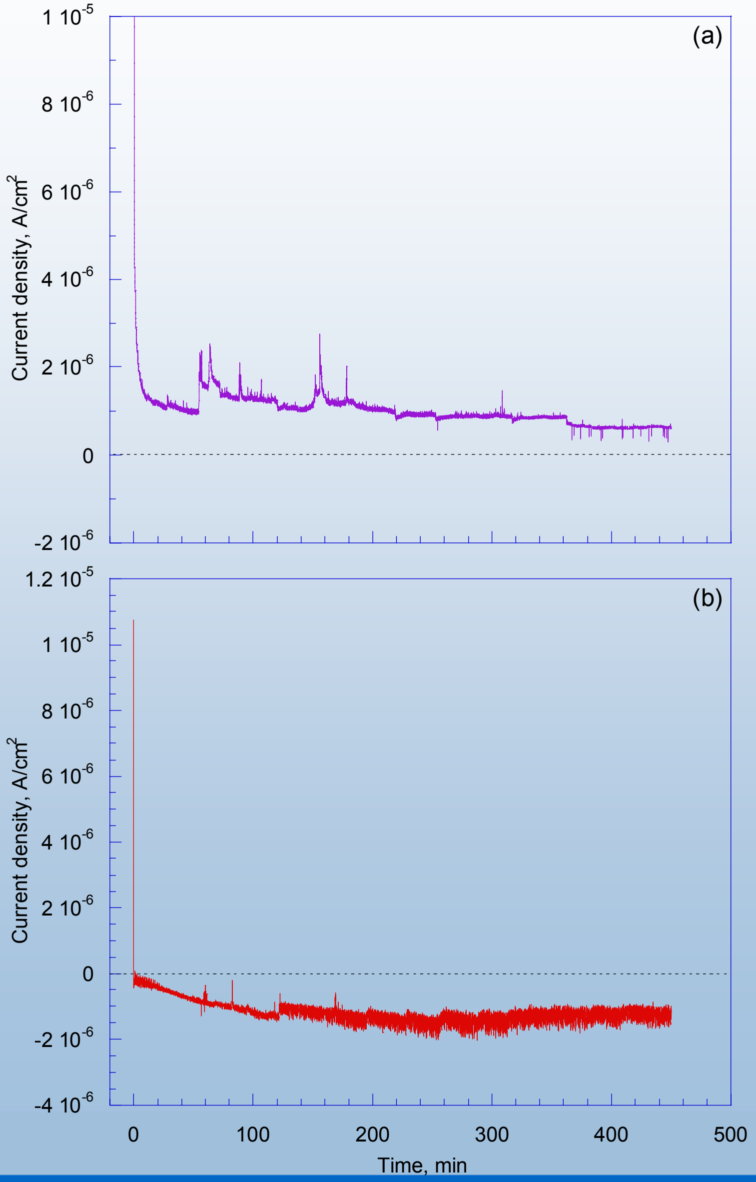


- AISI446 and Modified AISI446: Ferritic, Fe-base;
- ICR significantly decreased, both as-nitrided and tested;
- Surface complex of oxygen-nitrogen mixture with Cr, Fe.

Nitrided AISI446 has excellent corrosion resistance in 1M H_2SO_4+2ppm F^- at 70 °C with air purge

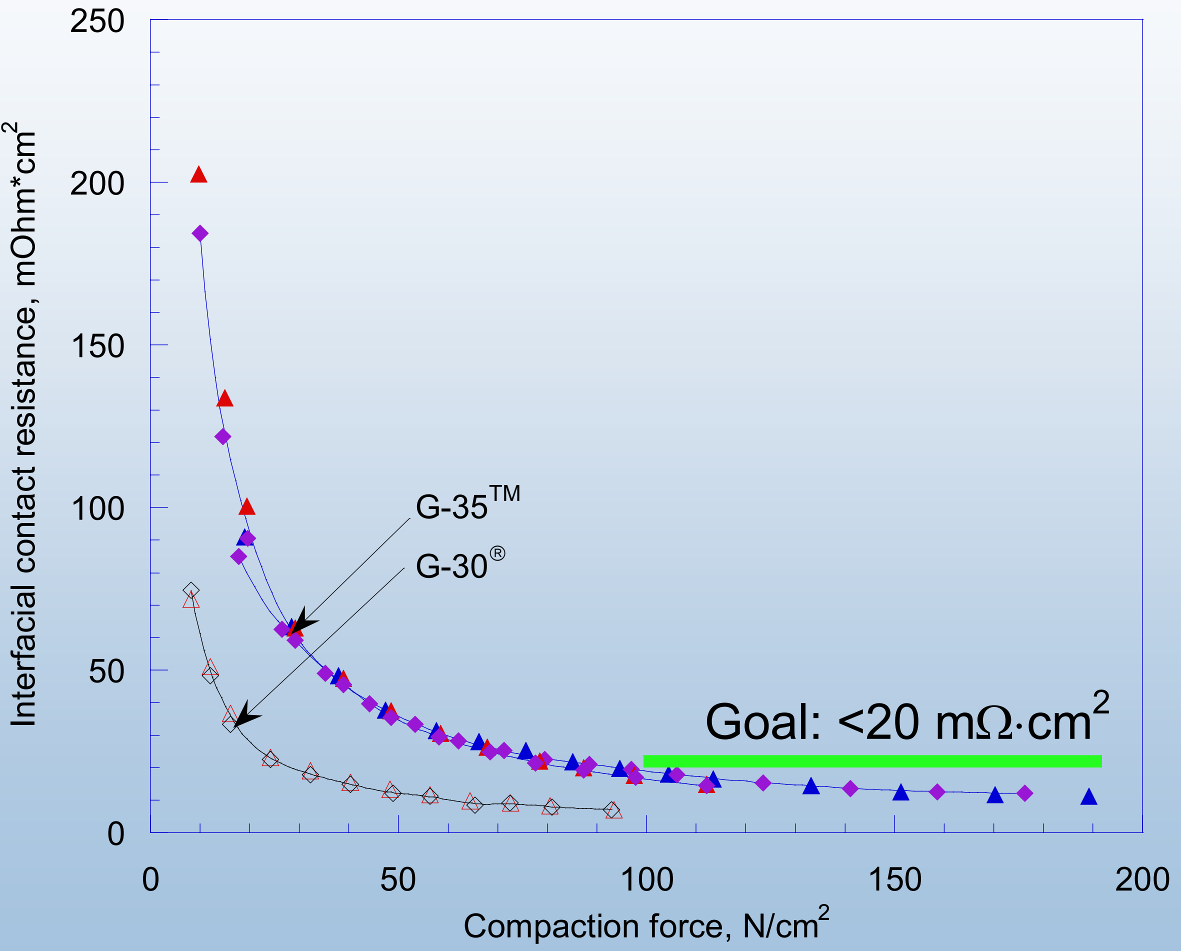


Time-dependent data for Nitrided AISI446 in simulated PEMFC environments



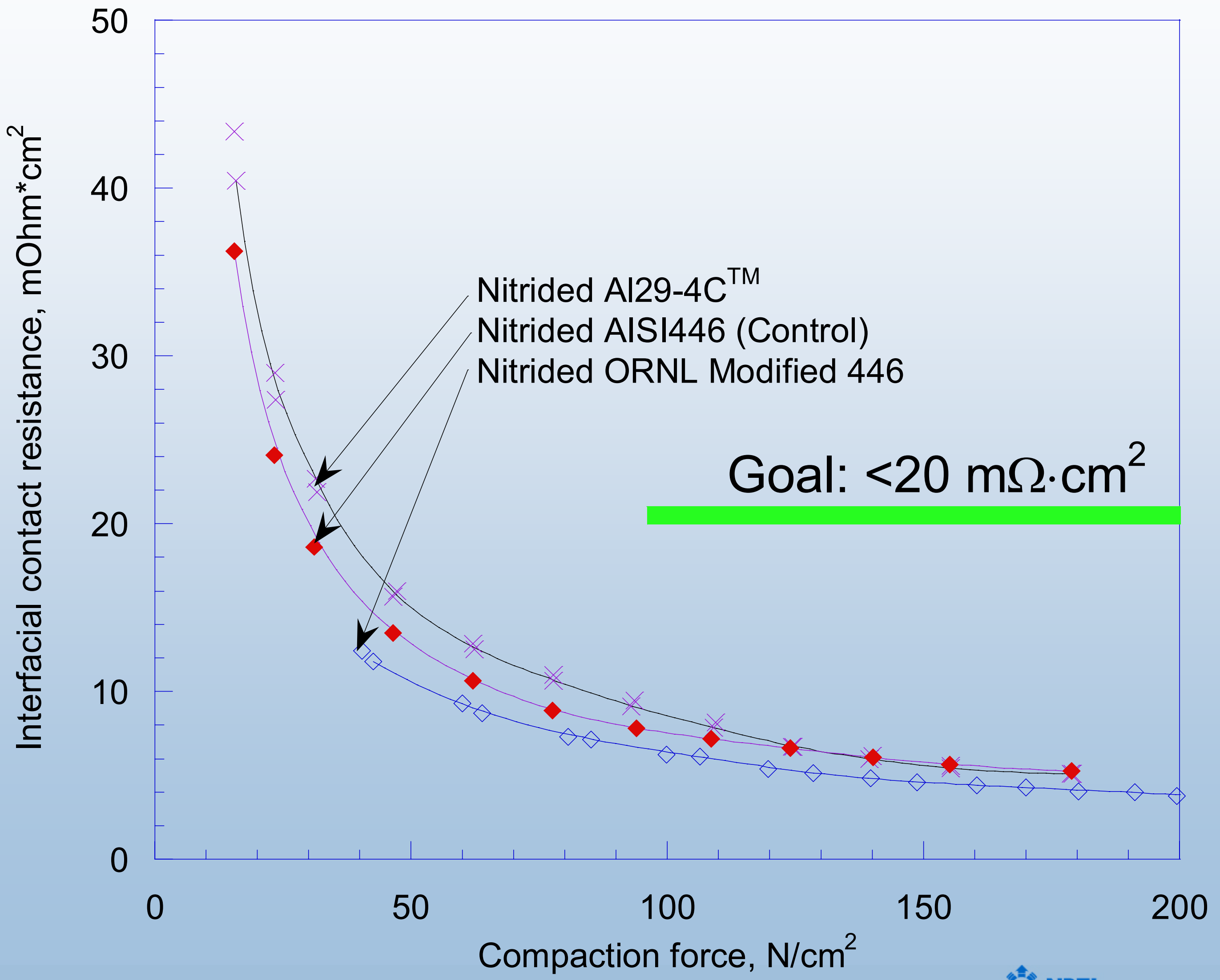
- Anodic behavior for nitrided AISI446 in PEMFC environments
  - cathode (a)
  - anode (b) (note the cathodic current).
- DOE target: 16 μA/cm^2

Nitrided G-35™ and G-30® meet the ICR Goal

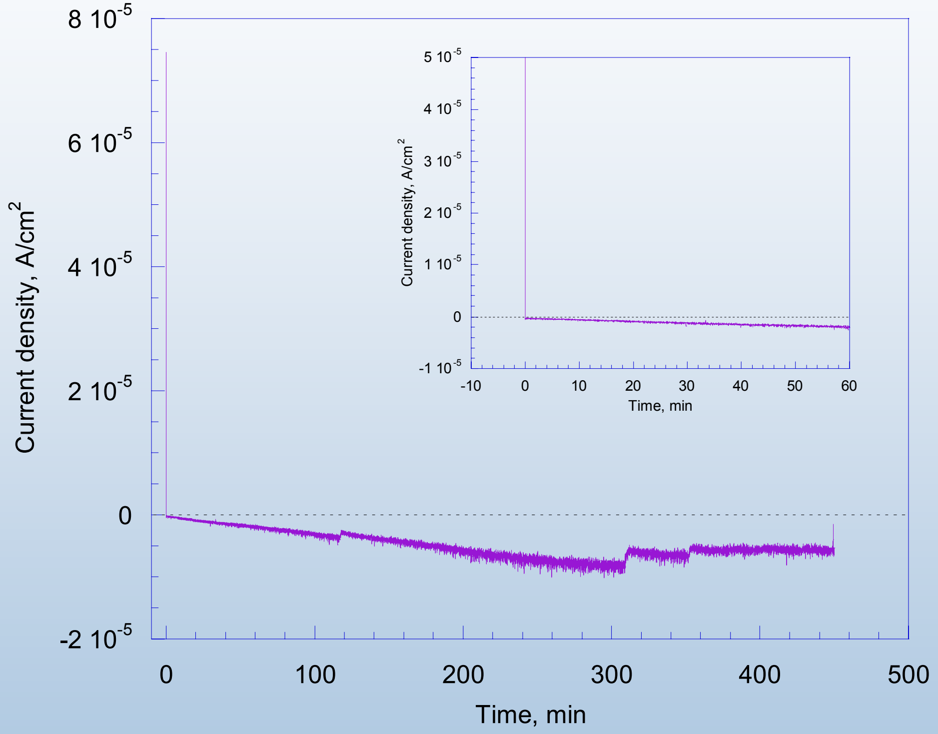


- Cr-nitrides formed on commercial Ni-base alloys;
- Corrosion test at GM and NREL show no increase in ICR;
- Complex conductive "oxy-nitride" after polarization (master's thesis).

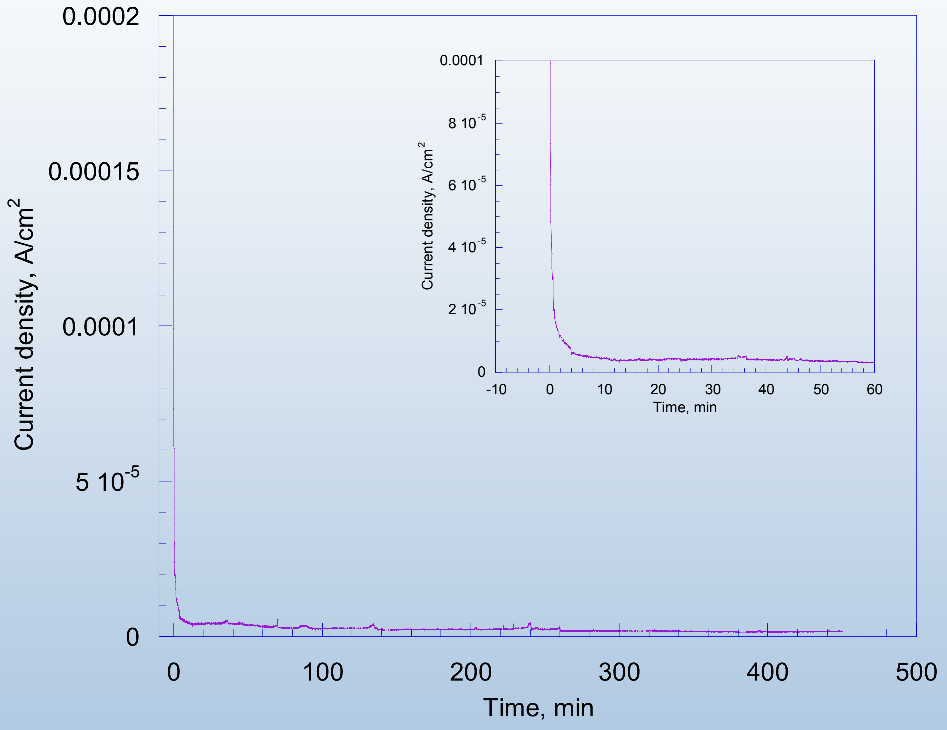
Developing lower cost alloys with low ICR



And keep excellent corrosion resistance after modification

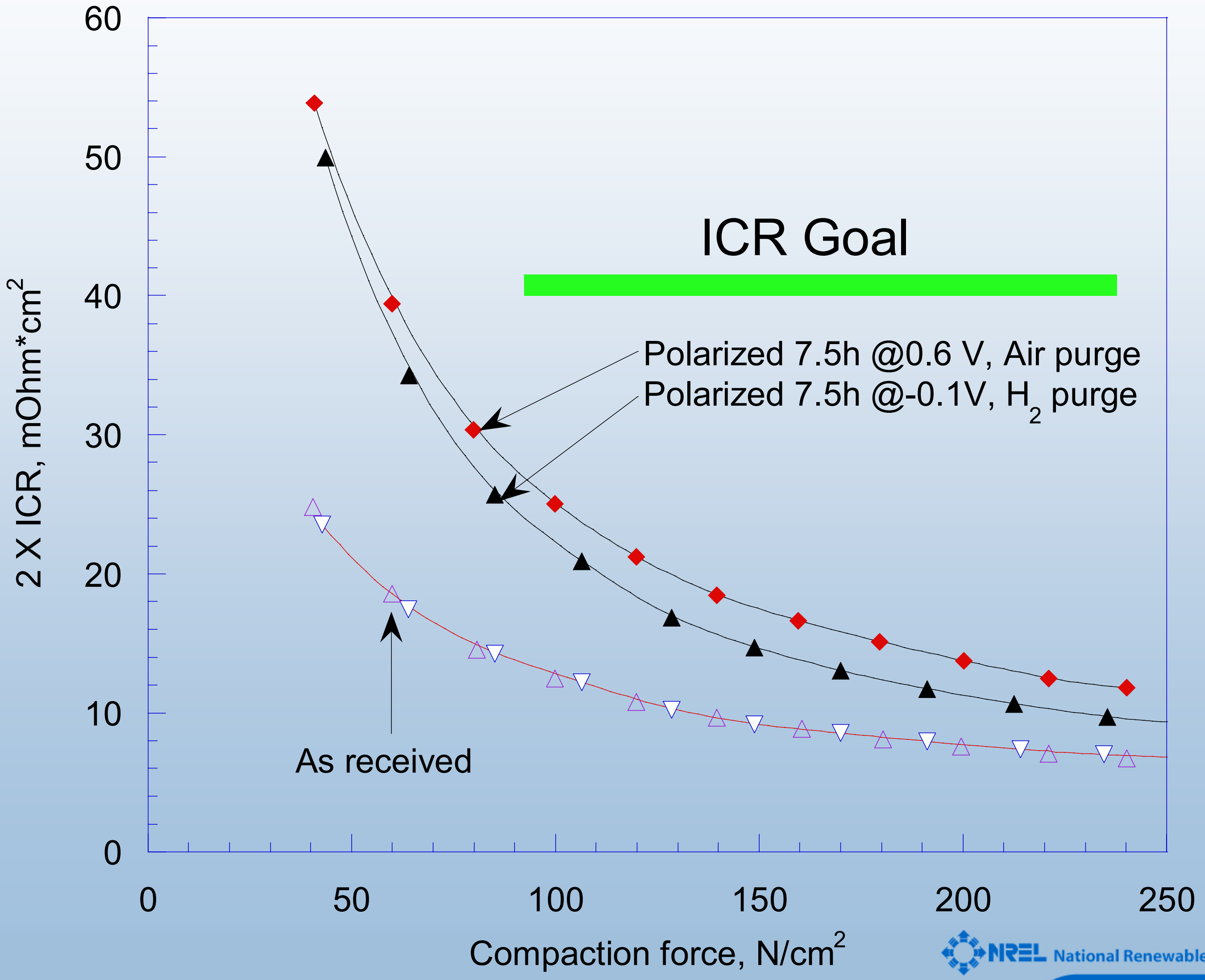


PEMFC anode



PEMFC cathode

ICR for the modified 446 after polarization in PEMFC environments?



Cost - DOE Targets

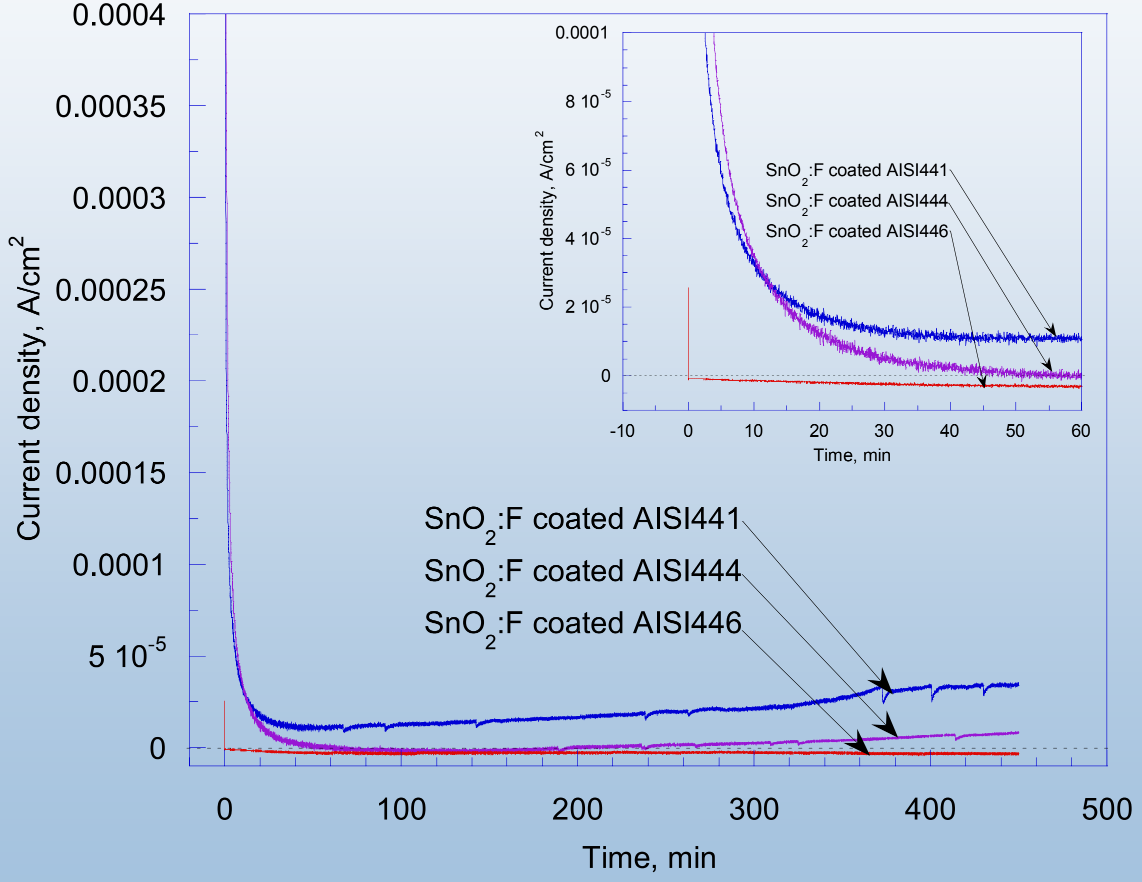
Alloy	ICR@140 N/cm^2, mΩ·cm^2	Current at –0.1 V (H$_2$ purge), μA/cm^2	Current at 0.6 V (air purge), μA/cm^2	Cost*, $/kW
349$^{\text{TM}}$	110	-4.5~-2.0	0.5~0.8	4.22
AISI446	190	-2.0~-1.0	0.3~1.0	4.76
2205	130	-0.5~+0.5	0.3~1.2	3.14
Nitrided AISI446	**6.0**	**-1.7~-0.2**	**0.7~1.5**	**N/A**
Modified AISI446	**4.8**	**-9.0~-0.2**	**1.5~4.5**	**N/A**
DOE Target	***20 mΩ·cm^2***	***<16 μA/cm^2***	***<16 μA/cm^2***	***$10/kW***

Note: Cost data were based on the base price of cold rolled coils from Allegheny Ludlum (see website), and by assuming 6 cells/kW for a PEMFC and the dimensions of a bipolar plate are 24 cm × 24 cm × 0.254 cm (which gives a 400 cm^2 utilization surface area in a 0.01 inch thick sheet).

Conductive SnO_2:F Coating

- High conductivity
- High stability in many different environments
- Volume production is available----widely used in PV industry
- May allow reduced cost with lower grade alloys.
- NREL expertise (National Center for Photovoltaics)

Performance of coated steels in PEMFC anode environment



- Excellent behavior of SnO_2:F/AISI446 is expected;
- Good corrosion resistance of SnO_2:F/AISI444 is surprising! But match with ICP analysis (see Table)

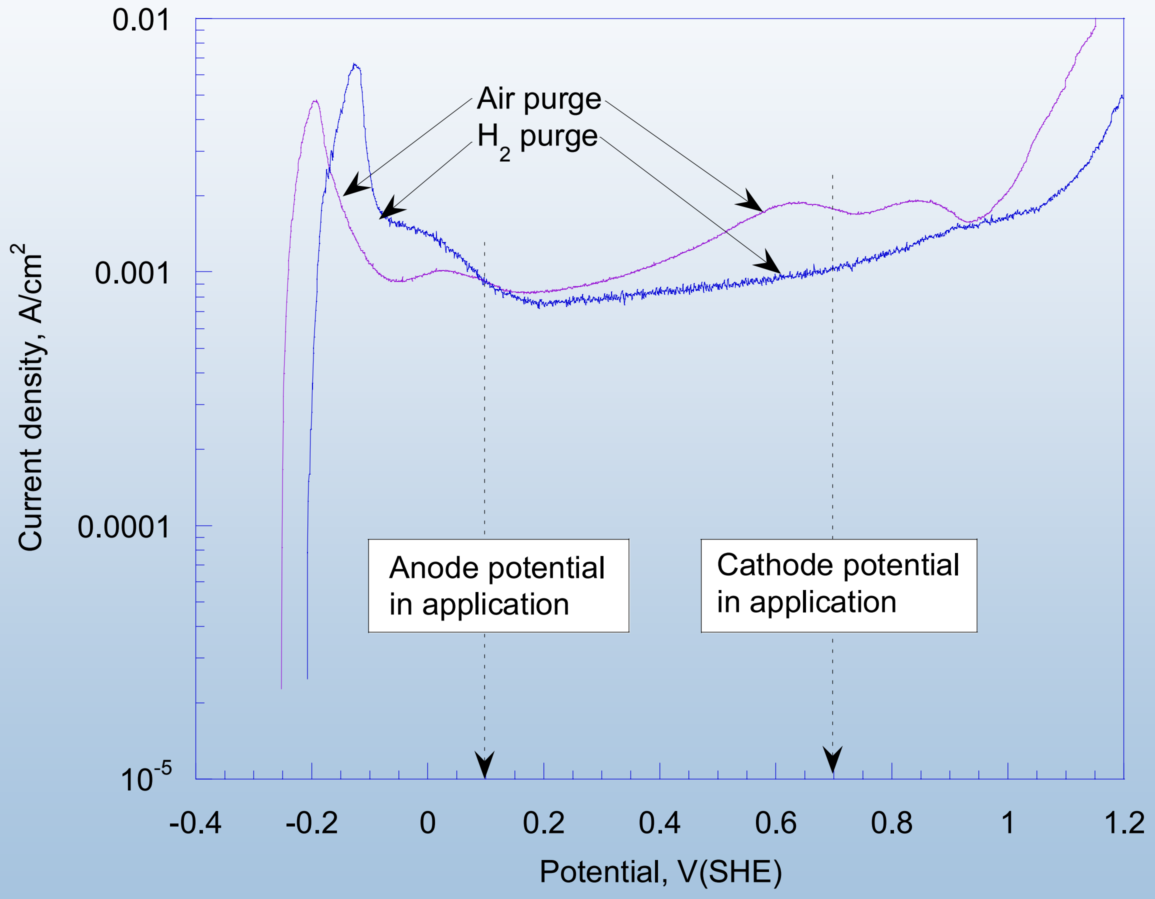
Fe, Cr, Ni ions concentration after polarized in PEMFC environments (average of 3 samples)

Material	Ion concentration in PEMFC anode environment after 7.5h			Ion concentration in PEMFC cathode environment after 7.5h		
	Fe, ppm	Cr, ppm	Ni, ppm	Fe, ppm	Cr, ppm	Ni, ppm
316L	21.18	4.60	2.49	9.02	1.94	1.41
317L	3.98	0.65	0.39	1.29	-	-
349^{TM}	1.70	0.12	-	1.47		
SnO_2/316L	10.83	1.97	1.38	1.12	0.10	0.11
SnO_2/317L	4.03	0.69	0.56	0.87	-	-
$SnO_2/349^{\text{TM}}$	1.27	-	-	1.07	-	-
441	622.9	135.7	1.07	462.8	101.2	0.95
444	141.5	37.86	0.30	328.3	67.97	0.94
446	1.46	-	-	0.99	-	-
SnO_2/441	24.15	4.51	-	330.3	68.72	0.60
SnO_2/444	12.70	2.09	-	64.42	13.73	0.22
SnO_2/446	1.24			0.98	-	-

The Needs and Challenges of High Temperature (HT) bipolar plates ….Starting Point

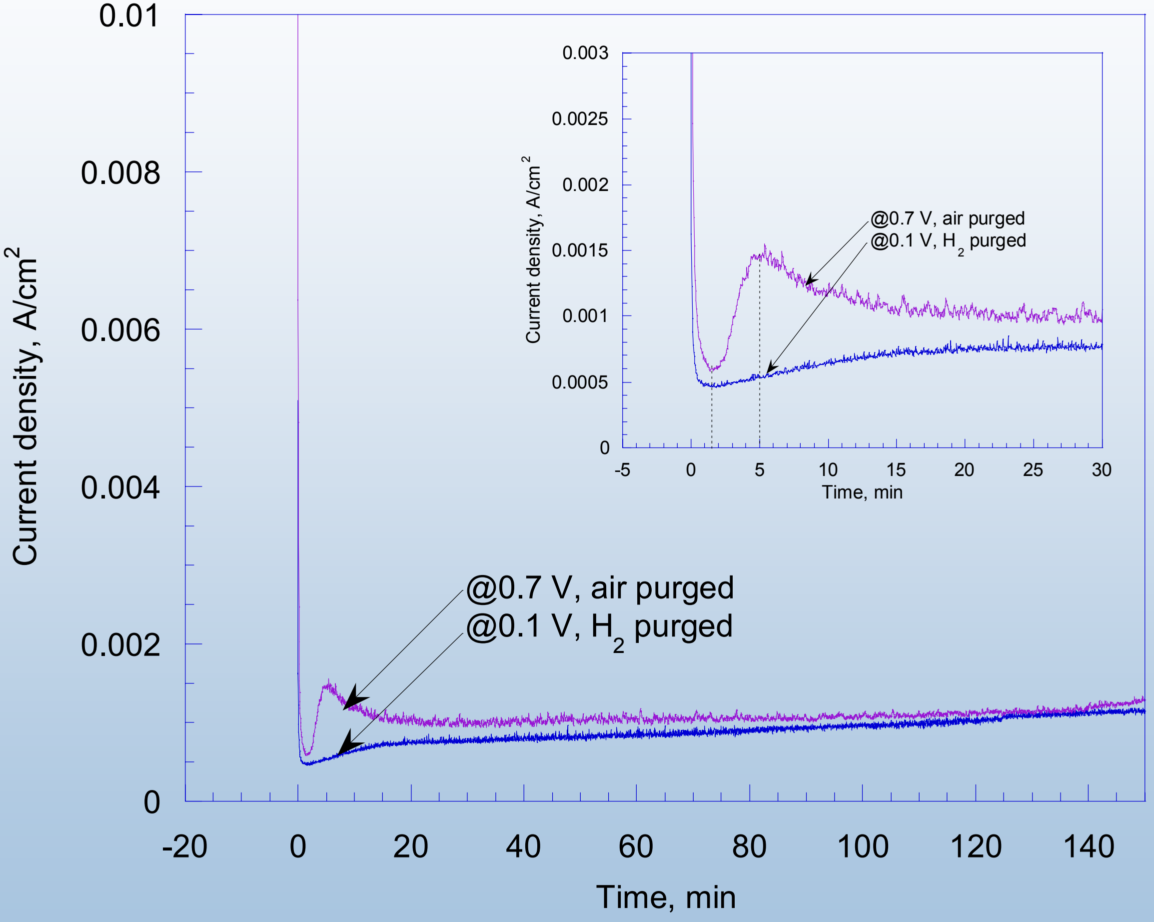
- Desire of transportation industry;
- R&D on high temperature membrane, however, exact environments for HT PEMFC not yet defined!
- Accordingly, set HT at 150 - 170 °C, selected H_3PO_4 as electrolyte, evaluated over 12 "HT" epoxies, and chose the best;
- Modified test systems to suite the HT, working with native stainless steel and graphite bipolar plate for PAFC from PlugPower.

Dynamic polarization for 904L steel in H_3PO_4 at 170 °C



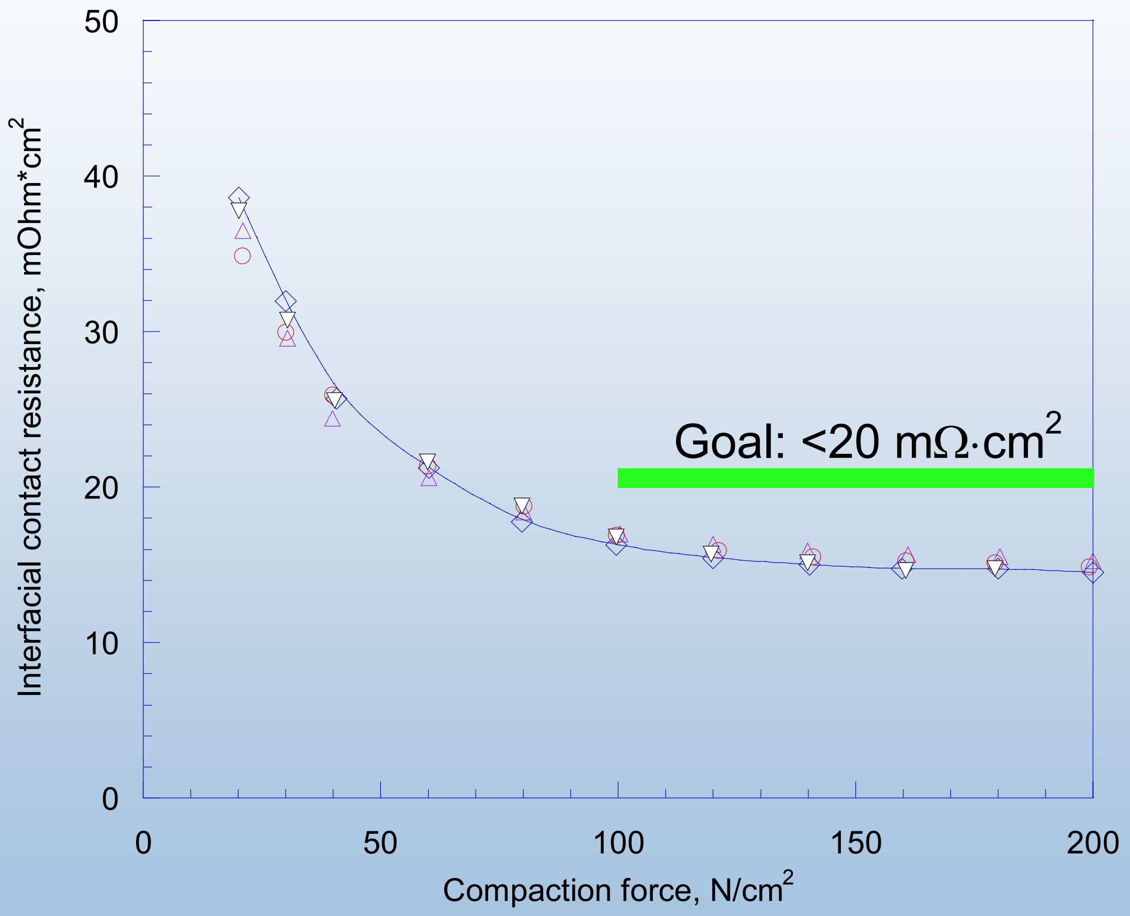
- New condition resulted in significant changes
- Passivation for the steel in both environments;
- High current noted even in the passivation region.

How about potentiostatic polarization for 904L steel in H_3PO_4 at 170 °C?



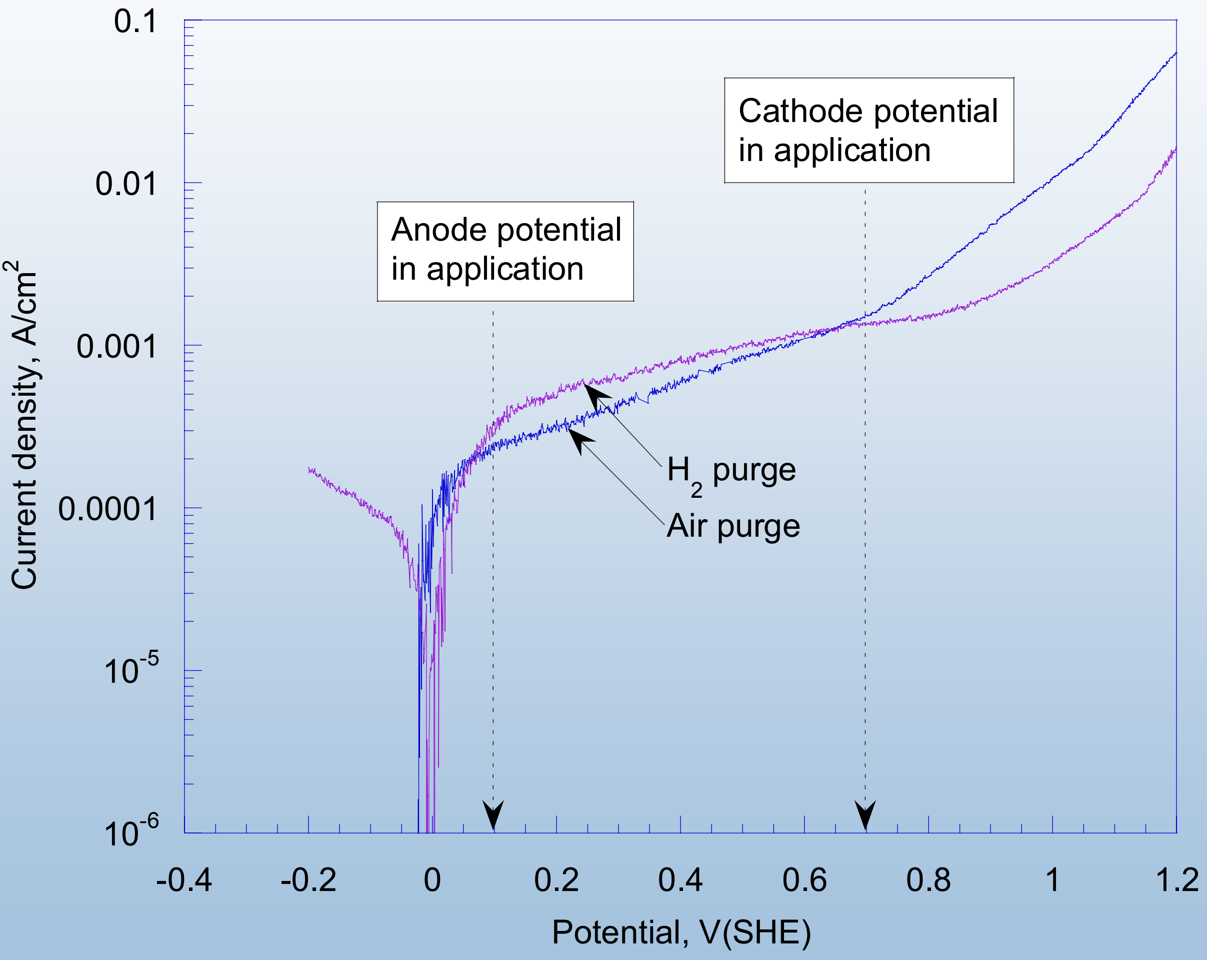
- At 0.1 V with H_2 purge, current slightly increases from 0.73 to 1.15 mA/cm^2 after 15 minutes;
- At 0.7 V with air purge, current peaks at 5 minutes, then stabilized at 1.0-1.25 mA/cm^2 after 15 minutes;
- Matches with dynamic polarization.

How about graphite (used in PAFC now)?



- Actual bipolar plate;
- Very low ICR with graphite;
- Tested at room temperature

Anodic behavior of graphite in H_3PO_4 at 170 °C with H_2 or air purge



- High currents
- 2 Tafel regions.

Dissemination of Results

Journal Papers

1. Heli Wang and John A. Turner:
SnO_2:F Coated Ferritic Stainless Steels for PEM Fuel Cell Bipolar Plates, submitted to *Journal of Power Sources*.

2. Heli Wang, Glen Teeter and John A. Turner:
Investigation of a Duplex Stainless Steel as Polymer Electrolyte Membrane Fuel Cell Bipolar Plate Material, *Journal of the Electrochemical Society*, 152 (3) B99-B104(2005).

3. Heli Wang, Michael P. Brady, Glenn Teeter and John A. Turner:
Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 1: Model Ni-50Cr and Austenitic 349^{TM} alloys, *Journal of Power Sources* 138, 86-93(2004).

4. Heli Wang, Michael P. Brady, K. L. More, H. M. Meyer III and John A. Turner:
Thermal Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates, Part 2: Beneficial Modification of Passive Layer on AISI446, *Journal of Power Sources* 138, 79-85(2004).

5. Heli Wang and John A. Turner:
Ferritic Stainless Steels for Bipolar Plate for Polymer Electrolyte Membrane Fuel Cells, *Journal of Power Sources* 128, 193-200(2004).

6. Heli Wang, Mary Ann Sweikart, John A. Turner:
Stainless Steel as Bipolar Plate Material for Polymer Electrolyte Membrane Fuel Cells, *Journal of Power Sources* 115, 243-251(2003).

Conference Papers/Presentations

1. M. P. Brady, H. Wang, I. Paulauskas, B. Yang, P. Sachenko, P. F. Tortorelli, J. A. Turner, R. A. Buchanan: Nitrided Metallic Bipolar Plates for PEM Fuel Cells, Proceedings of the 2nd International Conference of Fuel Cell Science, Engineering and Technology, Rochester NY, June 14-16, 2004.

2. Heli Wang and John A. Turner: Using Duplex, Austenite and Ferrite Stainless Steels for Bipolar Plate in PEM Fuel Cells, Proceedings of the 204th Meeting of the Electrochemical Society, October 12-16, Orlando, FL, USA, 2003, paper No. 1004.

Paten Application

M. P. Brady, H. Wang and J. A. Turner, Surface Modified Stainless Steels for PEM Fuel Cell Bipolar Plates, US Patent Application, 2005 (pending).

Future Work

- Continue NREL/ORNL collaboration with alloy development and nitridation
- Investigate new alloy compositions and coatings
- Bare alloys in HT PAFC environments;
- Nitrided alloys in HT environments;
- Coated steels in HT environments;
- Further NREL/PlugPower collaboration.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen atmosphere used during corrosion tests

Hydrogen Safety

Our approach to deal with this hazard is:

- Limit cell head space to <10ml and use low hydrogen flow rates.
- Perform experiments in a fume hood.
- Project activities are covered by a formal, standard operation procedure and reviewed by ES&H and approved by PI’s and cognizant managers.