Cost Effective Surface Modification For Metallic Bipolar Plates

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Why Metallic Bipolar Plates?

- Better mechanical properties: Permits thinner plates for higher power densities- metals have potential for 0.1-1 mm thick, while composites typically 2-5mm

- Amenable to low cost/high volume manufacturing techniques (e.g. stamping or corrugation)

- Gas impermeable

- Higher electrical and thermal conductivities

Relates to DOE R&D Plan Component Technical Barriers Task 14 "Alternative bipolar plate materials/coatings that are low-cost, lightweight, corrosion-resistant, and impermeable"

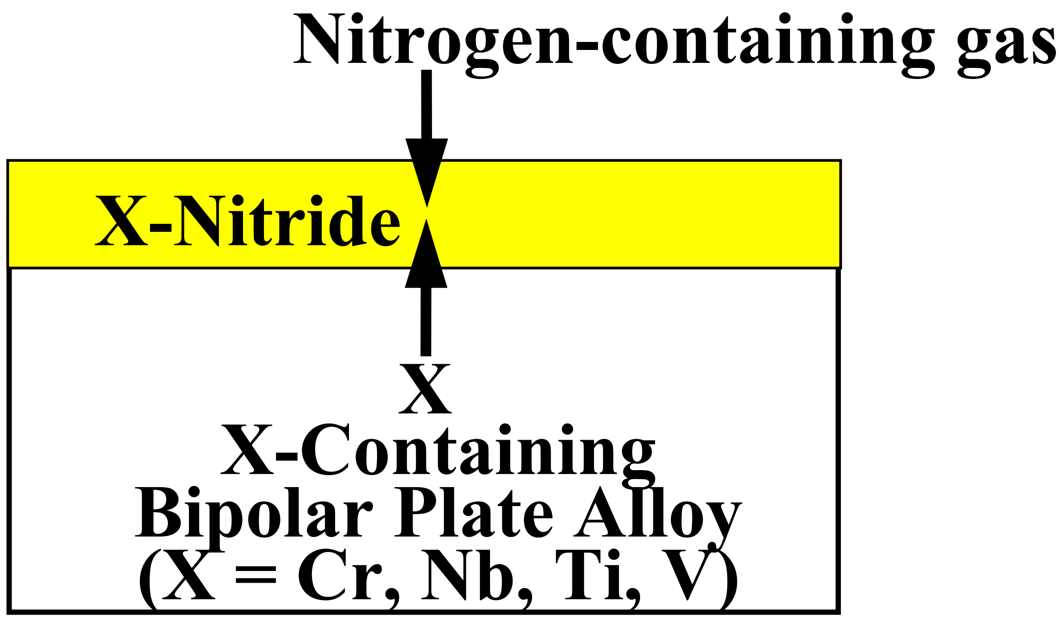
Most Metals Have Inadequate Corrosion Behavior in PEM Fuel Cell Environments

- Contamination of Polymer Membrane by Metal Ions

- High Contact Resistance from Surface Oxide Formation

- Transition Metal Nitrides are Promising Coatings
  - Corrosion Resistant
  - Electrically Conductive
  - Need inexpensive, defect-free coating method

Approach: Thermally Grown Nitride for Corrosion Protection



- Surface Conversion: High temperature favors complete surface metal reaction (amenable to complex geometries)
- Issues relate to achieving nitride continuity, adherence, and desired composition
- Stamp to final form then nitride: Industrially established and cheap

Objective

Develop an alloy which will form an electrical-conductive and corrosion-resistant nitride surface layer during thermal (gas) nitriding

- **Existing commercial alloys designed to form oxide scales, nitridation typically degrades corrosion resistance (primarily currently used for surface hardening)**

- **Must control gas-metal reactions by environmental and compositional manipulation to achieve desired surface**

Timeline and History of Project

- **2000: Showed thermally grown nitride on Nb-Ti base alloy can exhibit corrosion resistance in PEMFC Environment**

- **2001: Demonstrated external, continuous TiN base nitride formation on developmental Ni-Ti and Fe-Ti base alloys**

- **2002: Corrosion resistance demonstrated for nitrided Ni/Fe-Ti but problems at edges/corners, lack of robustness**
  - **New family of <u>Cr-nitride/Ni-Cr alloys</u> identified**
  - **Promise shown for edge/corner coverage**

Comments From 2002 Review (paraphrased)

- Good Approach and Promising Results

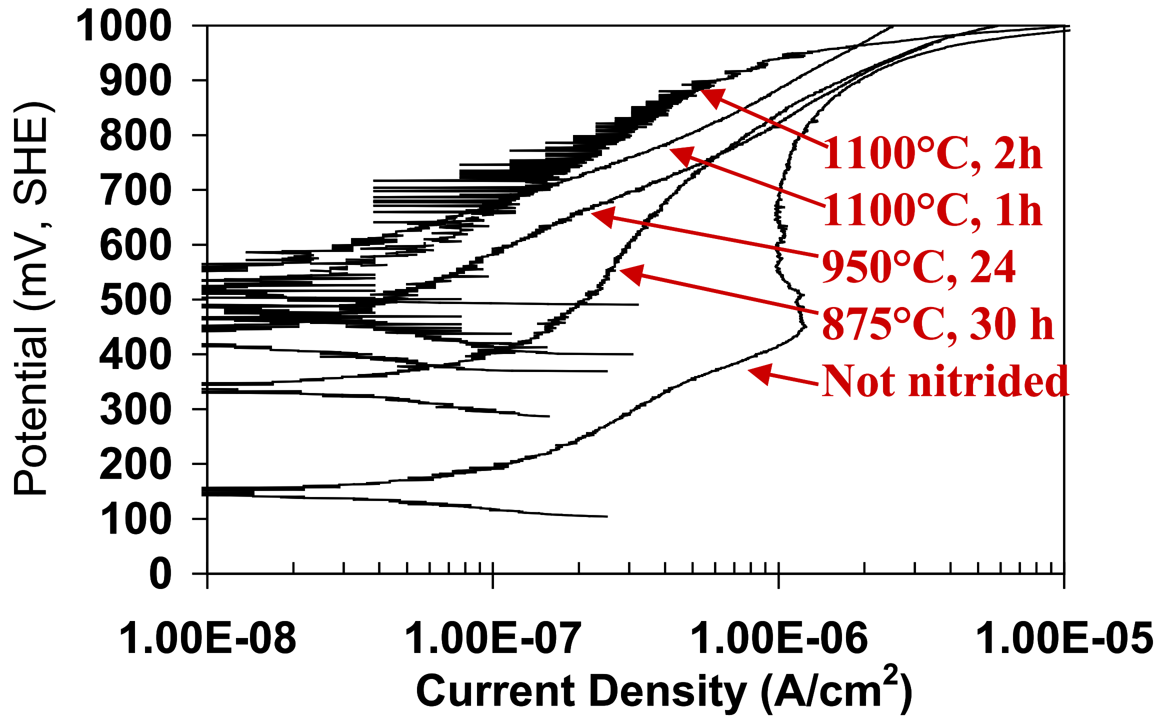
- Need to Demonstrate
  - Ability to protect flow field features
  - Long-term corrosion resistance
  - Successful in-cell test

↓

These Issues Formed the Basis of Our 2003 Milestone and Have Been Achieved

Nitrided Ni-50Cr Used as Model to Study Nitridation/Microstructure/Composition and Corrosion Resistance Relationships

Anodic Polarization curves for Ni-50Cr Nitrided in Pure N_2
Aerated pH3 Sulfuric Acid (0.1 mV/s)



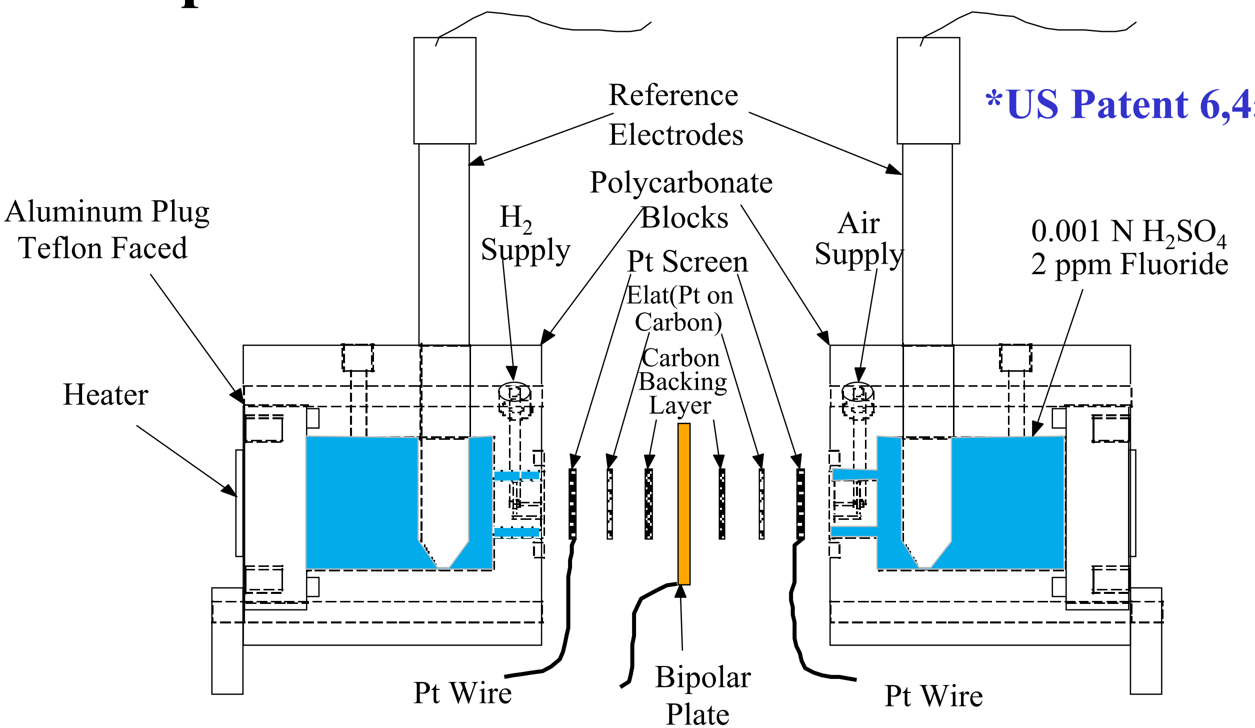
- Corrosion resistance correlated with continuous CrN/Cr_2N surface
- Low temperature nitridation in NH_3or plasma assisted environments possible- Pure N_2 used in demonstration stage for simplicity

1100°C/1 h Nitrided Ni-50Cr Performed Well Over <u>4000 h</u> in *LANL Corrosion Test Cell

Environment 80°C, pH3 H_2SO_4, 2 ppm F^-, open circuit potentials set by contact w/Pt in H_2/Air purged conditions

(anode face experienced ~ -0.31V vs SHE and cathode face ~ +0.87V)

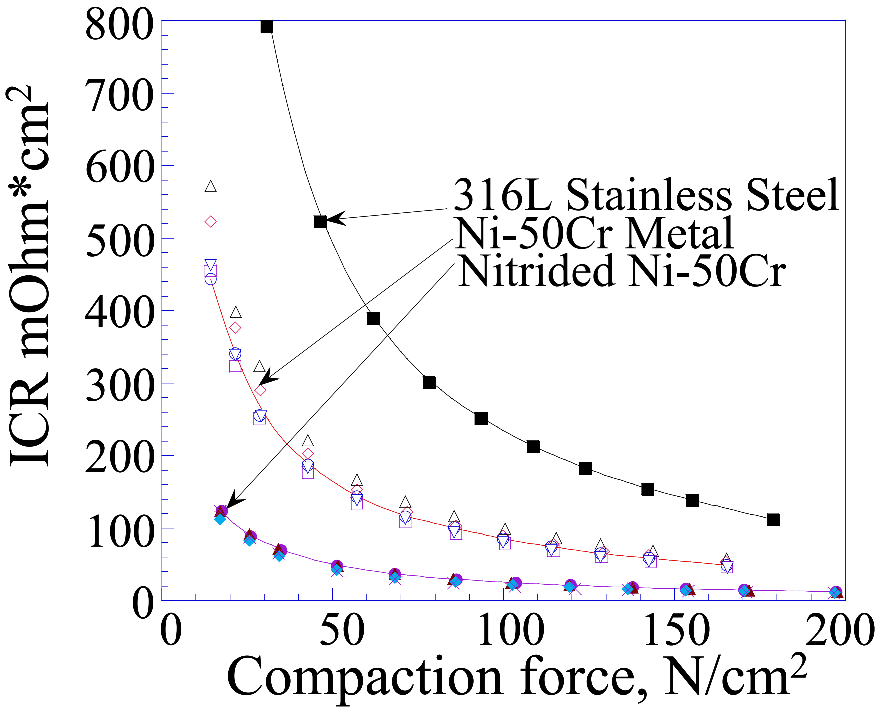
*US Patent 6,454,922 (Weisbrod)



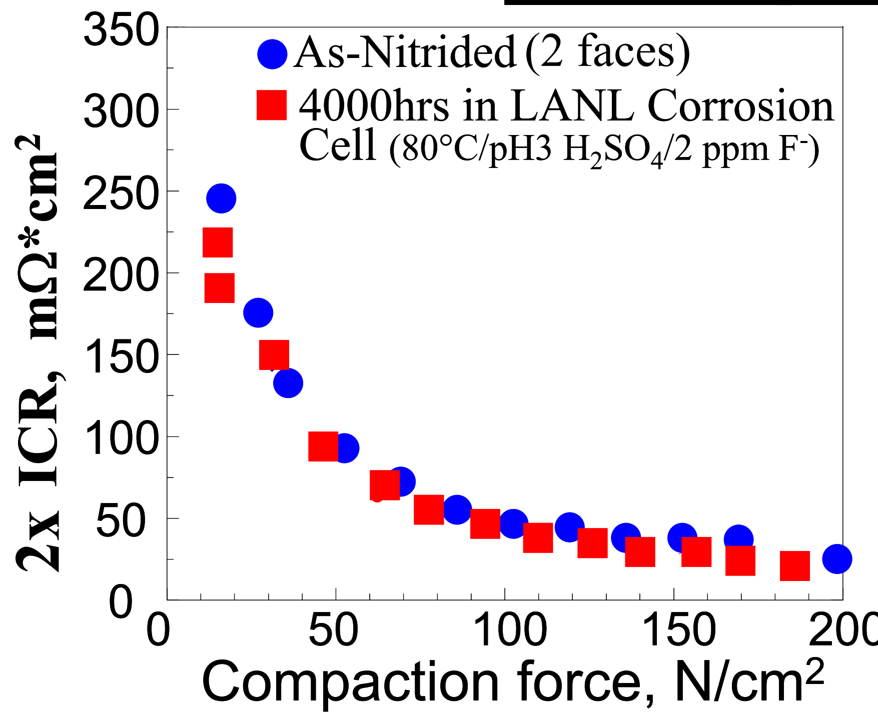
- **Resistance increase of <u>only</u> 2mV/1000 h anode and 2.7 mV/1000 h cathode ($1A/cm^2$)**
- **Little dissolution over 4000 h exposure: only 3.8ppm Ni at anode and 0.08 ppm Ni at cathode (Cr not detected)**

Nitrided Ni-50Cr Exhibits and Maintains Low Contact Resistance
(Measured at NREL)

Nitridation Significantly Lowers Interfacial Contact Resistance



*Low Resistance of Nitrided Ni-50Cr Maintained After <u>4000 hr Exposure</u>

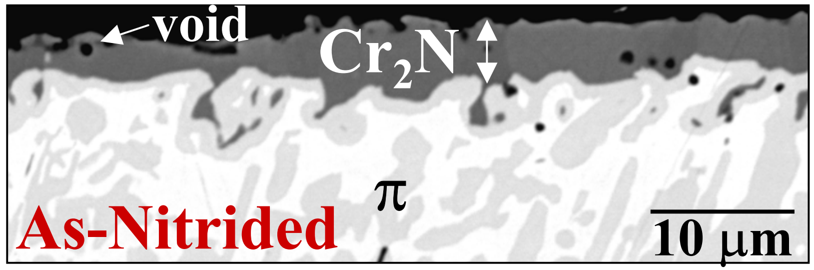


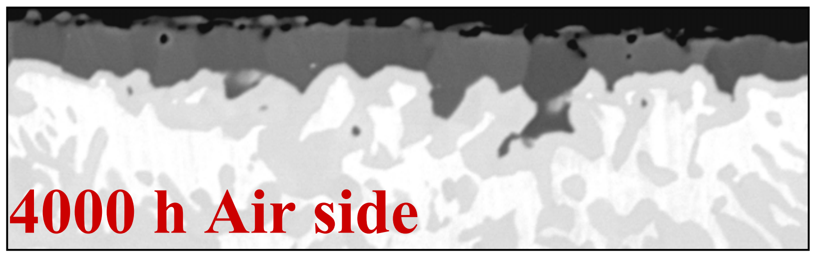
***Measurements for LANL 4000 h coupon include <u>BOTH</u> faces of coupon because 1-face was in anode environment, other in cathode**

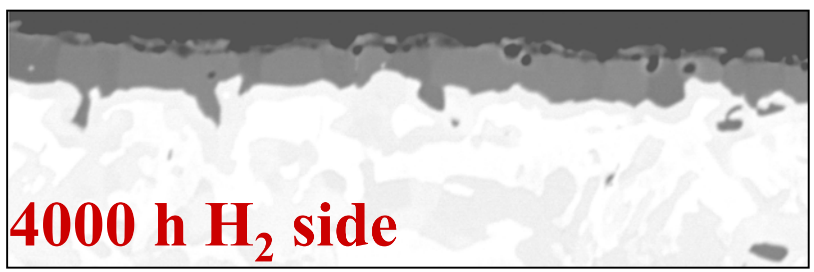
-Control as-nitrided data from chart on left therefore doubled

CrN/Cr_2N Nitride Layer Held Up Well in 4000 h LANL Corrosion Cell Exposure

SEM Cross-Sections of 1100°C, 1h Nitrided Ni-50Cr



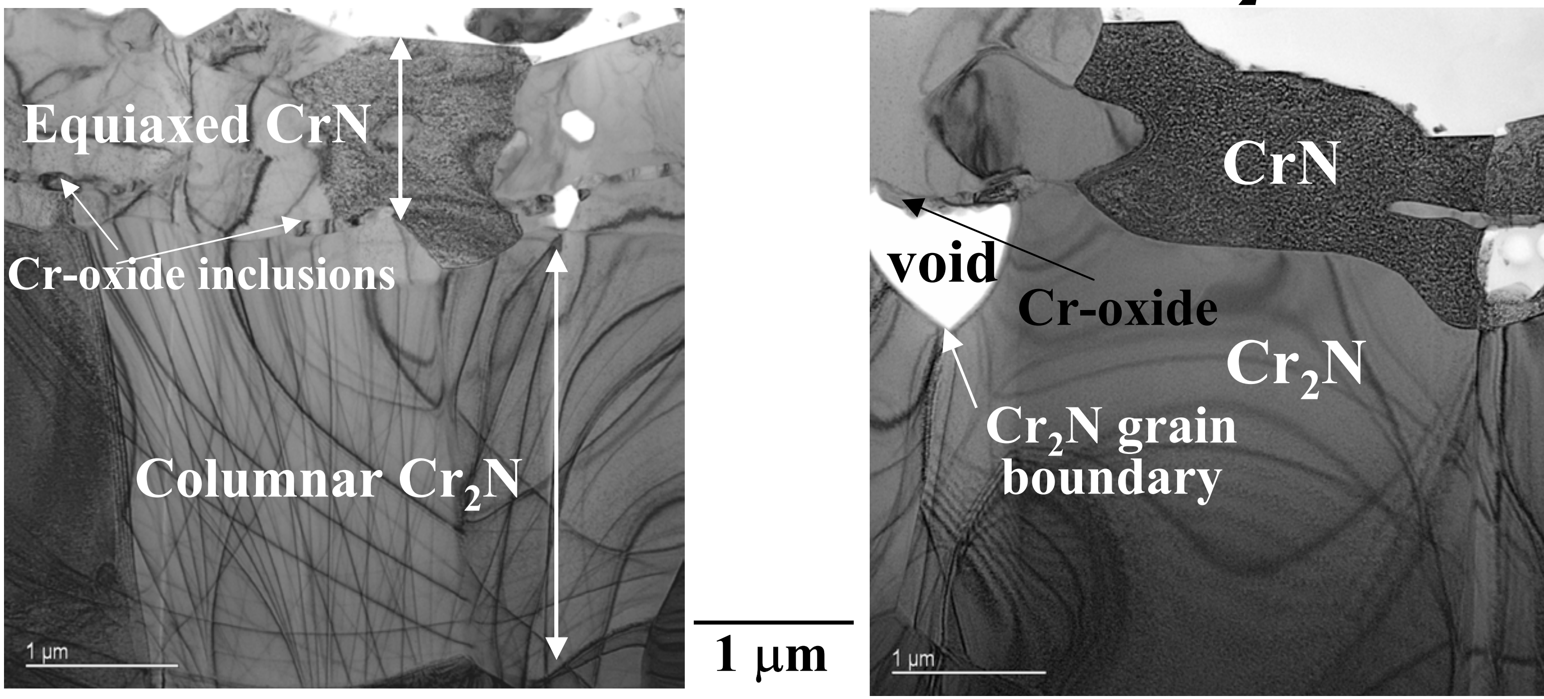




- **Semi-continuous CrN (~ 1 μm) overlying continuous Cr_2N layer**
  - -deep internal nitridation zone of NiCrN π phase in Cr-depleted Ni(Cr)
- **No evidence of significant corrosive attack (may be increase in near surface voids at CrN/Cr_2N interface in H_2 exposed face)**

Cross-Section TEM for Insight into 4000 h Exposed Nitride from LANL Corrosion Cell

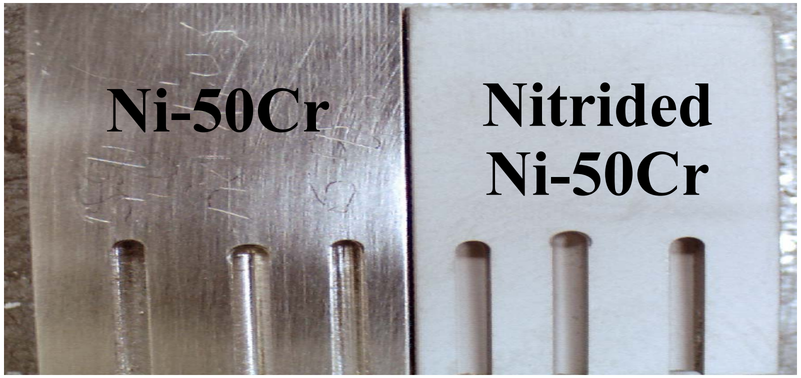
4000 h Air Side | **4000 h H_2 Side**

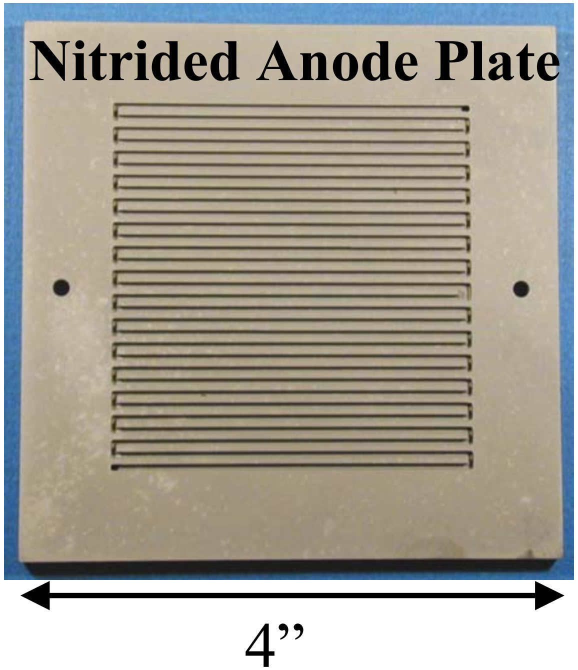


- No evidence of significant surface oxidation or attack
- Voids primarily at Cr_2N grain boundaries near interface w/CrN may have formed during nitridation, not corrosive attack
- Findings used to guide optimization of nitride composition/structure

50cm² Active Area Anode and Cathode Plates Successfully Nitrided for Single-Cell Test

Nitride coverage of flow field grooves





- **Tests run at 0.7V, 80°C, 3 atm. (30 psi) using neat hydrogen at 0.3 sLPM and compressed air at 1.8 sLPM (Tested at LANL)**
  - -1st run: 500 h using Nafion 112 with 0.2/0.2 mg/cm² Pt anode/ cathode (MEA damaged by inadvertent loss of H_2 supply during test)
  - -2nd run: 500 h using Nafion 1135 with 0.23/0.37 mg/cm² Pt
  - -Nitrided Ni-50Cr plates exposed for 1000 h cumulative total

Membranes Clean After Two, 500 h In-Cell Exposures w/Nitrided Ni-50Cr Plates

- **X-ray fluorescence of anode/cathode MEAs show Ni/Cr levels of only 0.01- 0.3 μg/cm^2 - among cleanest membranes tested at LANL!**
  - -Cr-rich liquid found in one alignment pin port of the cathode plate on cell disassembly- may have resulted from poor nitridation due to casting flaw (suspect local Cr-depleted inclusion)

- **No increase in cell resistance over the 2nd 500 h test (resistance data from 1st 500 h test unreliable due to MEA damage from H_2 interruption)**
  - -Baseline interfacial resistance contribution of 5 mΩ-cm^2 cathode and 1 mΩ-cm^2 anode

VERY PROMISING INITIAL RESULTS!

What About Cost?

- **Initial input garnered from commercial alloy producers suggests Ni-(40-50)Cr in range of \$10-15/lb possible (concern for impurity effects/rate of work hardening above ~42Cr)**

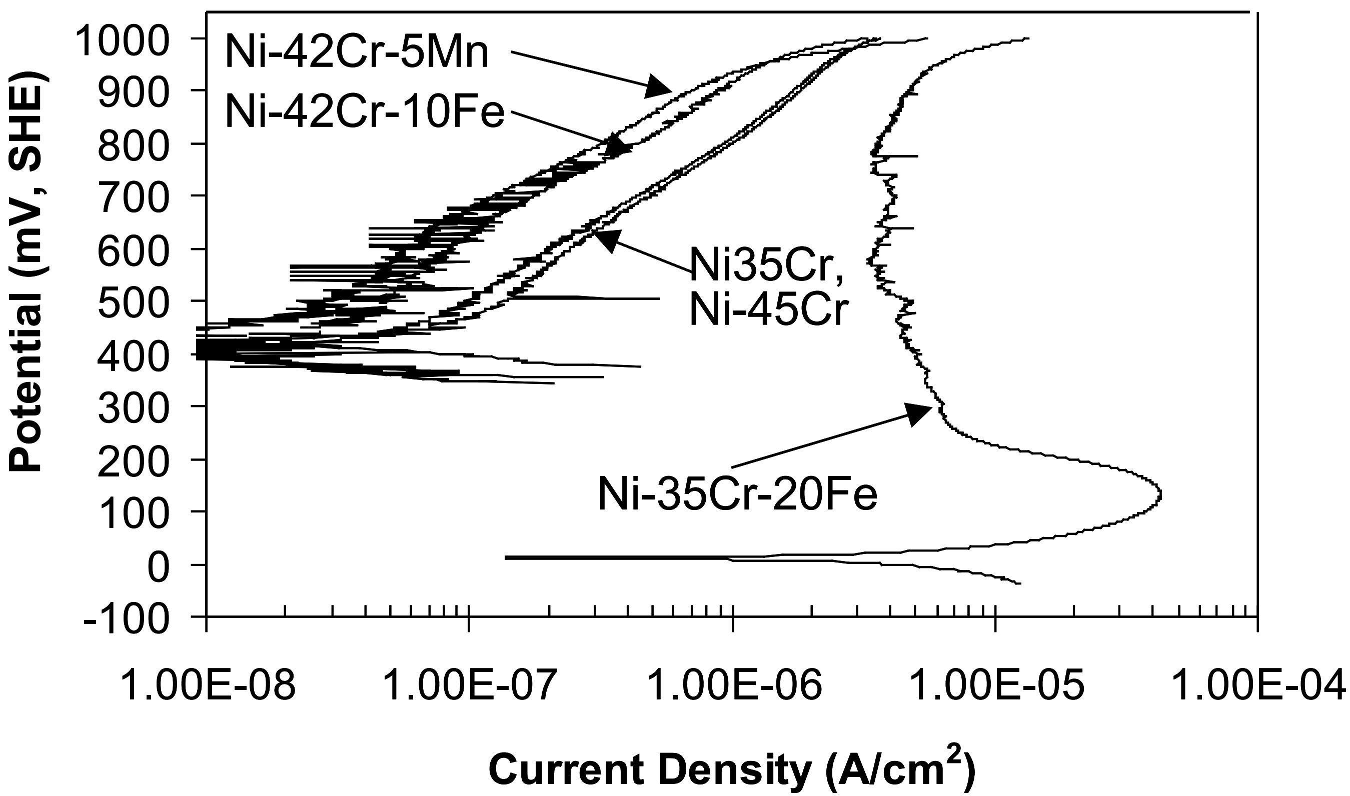
Assuming \$12.50/lb, 500 cm^2 plate (no stamping/nitriding)

- 0.1mm thick ~ \$1.10 / plate
- 0.25mm thick ~ \$2.75/ plate

- **Decrease Cr level/switch to Ni(Fe)- or Fe- base alloy to lower cost**
  - -Alloying additions to reduce level of Cr needed to form external nitride
  - -Modified nitridation conditions to promote external nitride formation

Preliminary Efforts Suggest Alloying Can Lower Cr Level Needed for Protective Nitride

Anodic Polarization curves for Alloys Nitrided at 1100°C, 2h in Pure N_2, Aerated pH3 Sulfuric Acid (0.1 mV/s)



- Key issues are formation of external Cr-nitride and elimination of less corrosion-resistant mixed Ni/Fe-Cr nitride phases

Future Plans

- **Further in-cell testing of nitrided Ni-50Cr**
  - **Determine optimal Cr-nitride surface structure/composition**
  - **Longer-term/more aggressive conditions and stack tests (tests also planned with DANA Corp and G.M.)**
  - **Coupons/Plates Available for Testing- Please ASK!**

- **Demonstrate corrosion-resistant Cr-nitride formation on Ni(Fe)-or Fe-base alloy that can meet < $2/plate cost goals**
  - **Key issue for next year**

- **Initiate transfer of technology to alloy producer(s)/fuel cell manufacturer(s) to examine scale-up issues**

Collaborations Significant Part of Effort

- **Corrosion Evaluation**
  - -Los Alamos National Lab (K. Weisbrod)
  - -U. Tennessee (R.A. Buchanan, I. Paulauskas)
  - -National Renewable Energy Lab (H. Wang)
  - -General Motors (R. Blunk, M. Abdelhamid)

- **In-Cell Testing**
  - -Los Alamos National Lab (M. Wilson, F. Garzon)
  - -General Motors (anode plate test planned for summer 03)
  - -DANA Corp (E. Steigerwalt): State Energy Demonstration Project for sealing/stack testing (also w/ Tennessee Tech and U. Minnesota)

- **Alloy Scale-Up Issues**
  - -Input/guidance received from several commercial alloy producers

Conclusions

- **Thermal nitridation is capable of protecting metal plates with complex surface geometries such as flow-field features**

- **Thermally grown CrN/Cr_2N shows excellent promise for PEMFC anode and cathode environments**
  - **-Low contact resistance maintained**
  - **-Low metal ion membrane contamination**