Cost-Effective Surface Modification For Metallic Bipolar Plates

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May 24, 2005

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Initiated 2001 (small exploratory $ in 1999/2000)
- Goal: Industry Transfer at end of FY 07
- ~ 70% complete

Barriers

- Barriers addressed
  - O. Stack Material and Manufacturing Cost
  - P. Durability

Budget

- Total project funding
  - 1350 k through 2005
- 300 k in FY 04
- 300 k in FY 05
  - Addtl. 150 k linked w/NREL in FY 05

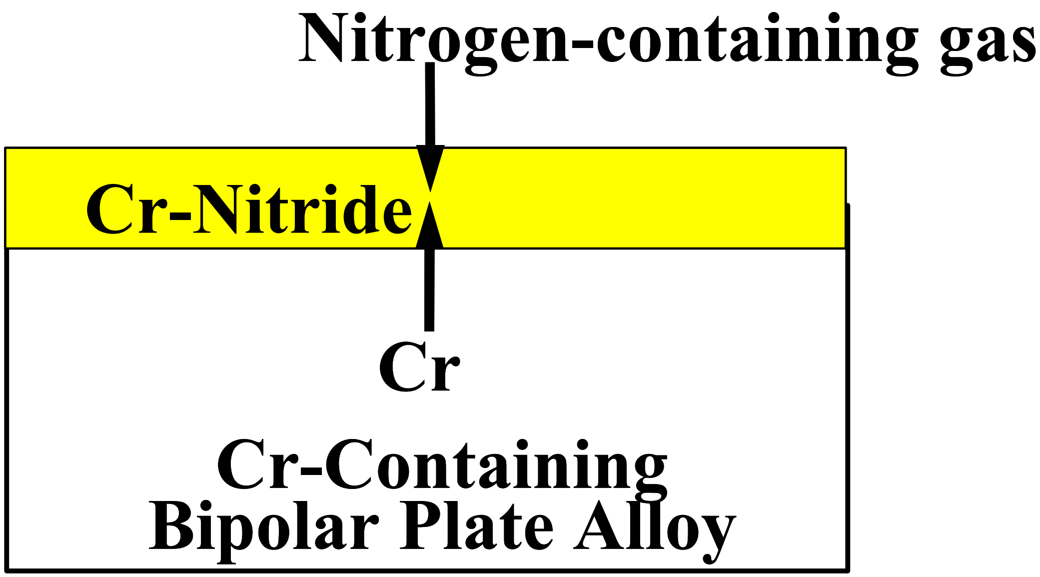
Primary Interactions

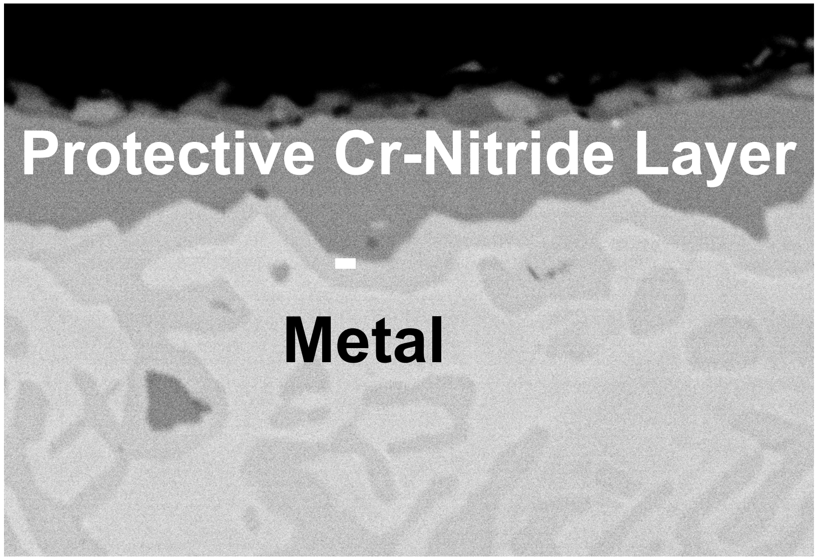
- GM, FuelCell Energy, GenCell Corp., MTI Micro, DANA Corp.
- U. Tenn, TN Tech, LANL

Objective: Develop a Surface Treatment to Protect Metallic Bipolar Plates

- DOE 2010 Technical Targets for Fuel Cell Stacks
  - -Cost $35/kW
  - -Durability 5000 hours
- FY 05 Goals
  - – Post fuel cell test assessment of model nitrided Ni-50Cr test plates (long term, cyclic conditions)
  - – Shift effort to lower Cr, Ni-Cr and Fe-Cr base alloys
  - – Assess amenability of approach to stamped foil

Approach: Thermally Grown Cr-Nitride for Protection





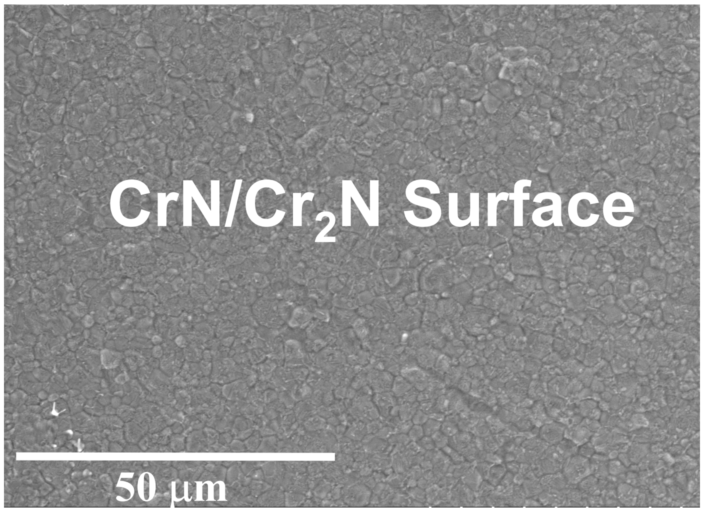
- **Surface conversion <u>not a deposited coating</u>: High temperature favors reaction of all exposed metal surfaces**
  - -No pin-hole defects (other issues to overcome)
  - -Amenable to complex geometries (flow field grooves)
- **Stamp then nitride: Industrially established and cheap**

Good Fuel Cell Behavior for Nitrided Ni-50Cr Plates

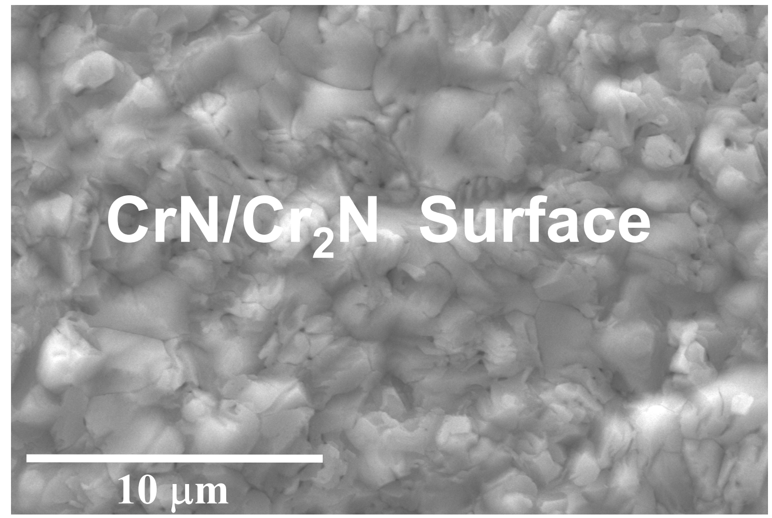
- 2000 h of anode testing at FuelCell Energy (60°C/400 mA/cm^2)
  - -Limited degradation observed: 5.9 mV/1000 h
  - -A few isolated corroded sites, remainder unchanged
- 545 h of anode testing at GM (80°C/Cycled 0.2 A/cm^2 for 23 h, 1A/cm^2 for 1 h)
  - -Trace Ni detected: ~3 μg/cm^2, Cr < 1 μg/cm^2
  - -Plate appeared unchanged
- Anode/Cathode plate tests in progress at LANL
  - -Completed 500 h/0.7V, no degradation evident, now moving to cyclic conditions/higher voltages

No Degradation of Cr-Nitride on Ni-50Cr After Fuel Cell Tests

545 h GM Tested



2000 h Fuel Cell Energy Tested

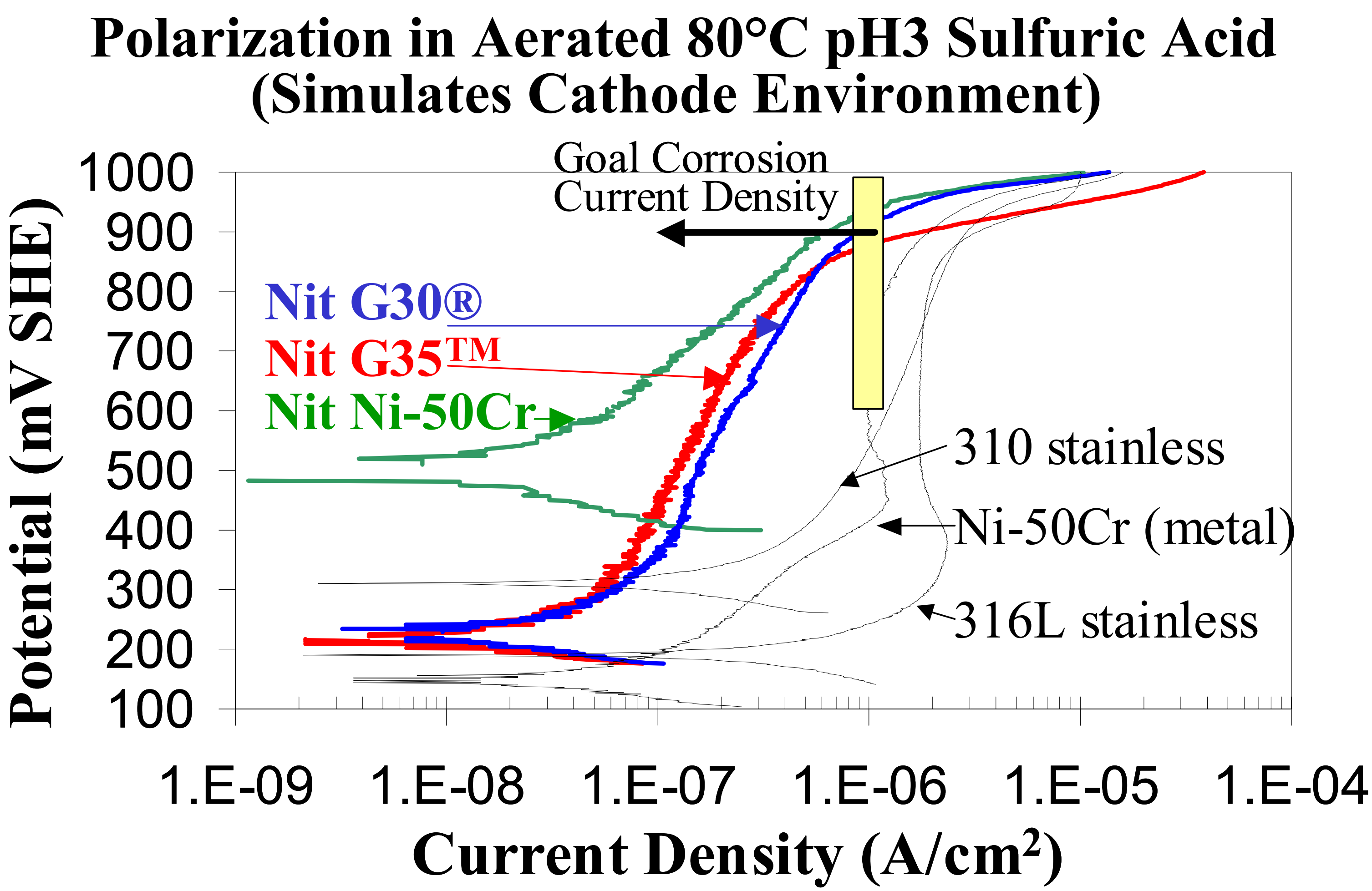


- Growing evidence for durability of CrN/Cr_2N surface
- A few attack spots linked to casting defects in plate
  - Less-resistant NiCrN locally formed instead of CrN/Cr_2N
  - Model Ni-50Cr alloy complex/difficult to manufacture
  - Similar problems not expected with lower Cr alloys

Nitridation of Commercially Available Ni-30Cr Base Alloys

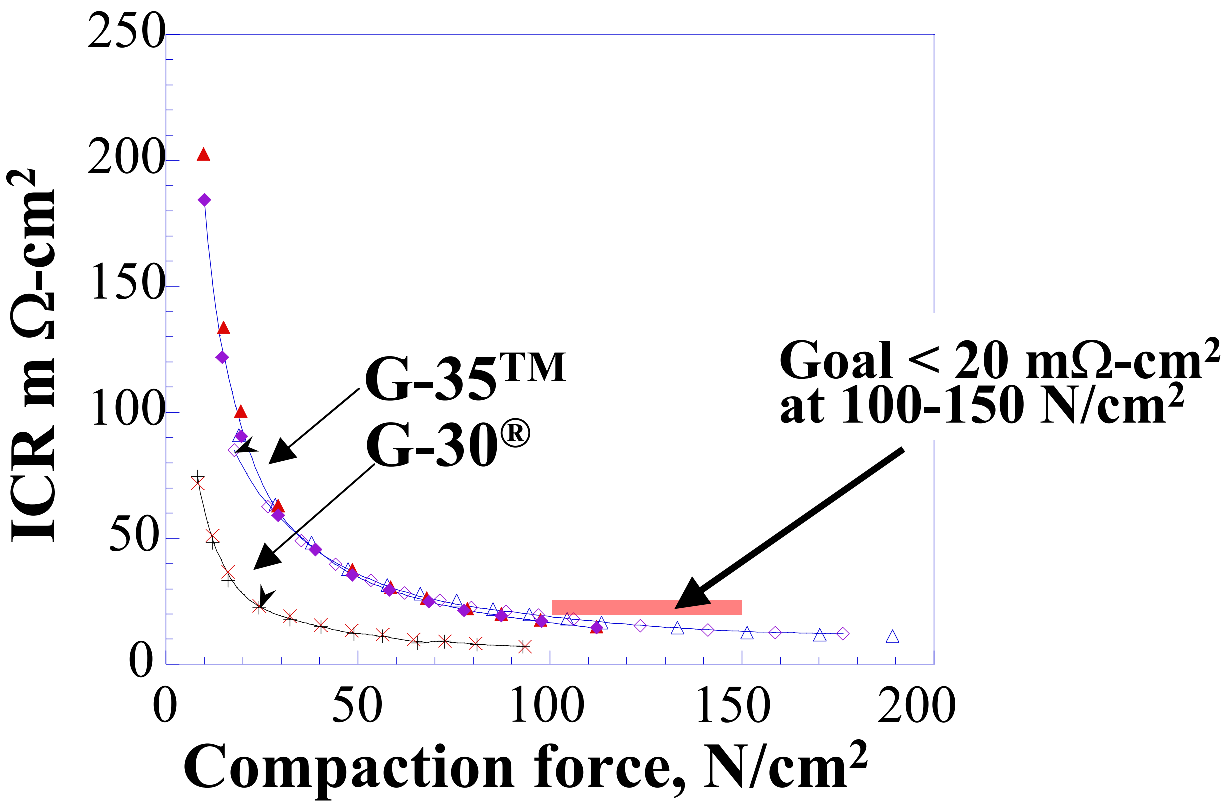
- Cost High: Intermediate step toward DOE goals
  - -Commercially available
  - -Can be stamped (GenCell Corp collaboration)
  - -Understanding gained applied to stainless steels
- Successful coupon corrosion/contact resistance tests at GM, MTI Micro Fuel Cells
- Fuel cell test plates machined for GM, FuelCell Energy
  - -Nitriding planned for May/June
  - -Tests in progress with MTI Micro Fuel Cells

Nitrided Ni-30Cr Alloys Show Good Corrosion Resistance



- Nitrided G35™ and G30® in range of nitrided Ni-50Cr
- Similar good corrosion resistance under anodic conditions

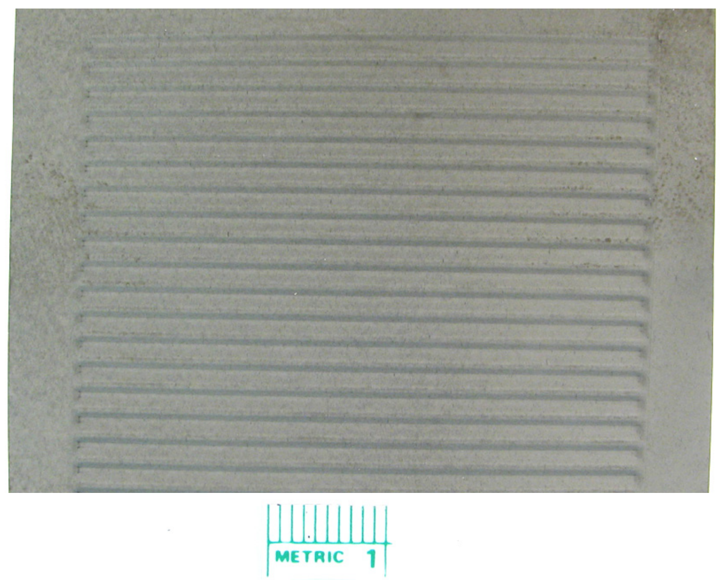
Nitrided Ni-30Cr Alloys Meet ICR Goals



- Corrosion tests at NREL and GM show no increase in ICR in PEMFC environments
- Cr-nitrides polarize as complex "oxy-nitride", stay conductive

0.1 mm G-35^{TM} Stamped Foil Successfully Nitrided

Collaboration with GenCell Corp: Macrograph of Nitrided Stamped G-35^{TM} Foil



- Proof of Principle for Nitriding Stamped Foil
  - -No Significant Warping (2004 review concern)
  - -Did find internal nitridation accompanying treatment can embrittle foil/thin sections if not controlled

Need Fe-Cr Base Alloys to Meet DOE Cost Goals

- **Ni-30Cr Base Alloys in Range of ~$20-30/lb**
- **Fe-(15-30)Cr Base Alloys in Range of ~$2-10/lb**
- **Meeting Cost Goals Will Depend on Use of Thin Stamped Foil (less material/lower cost)**

  -Assume 2 alloy sheets to make bipolar plate w/cooling channels: 0.1 mm thick each, 500cm^2 total area

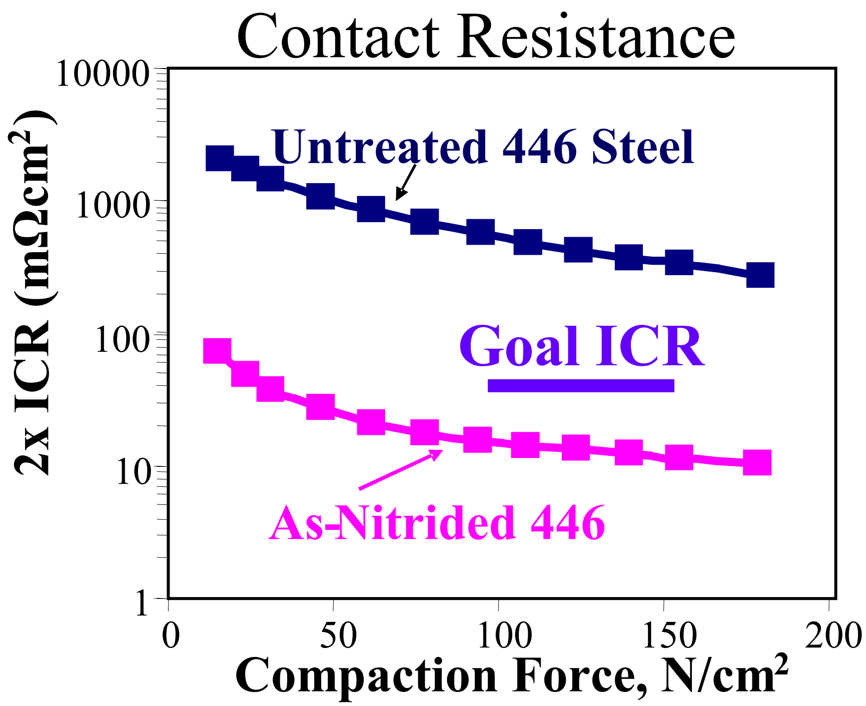
  -$10/lb alloy yields $1.80/ plate assembly

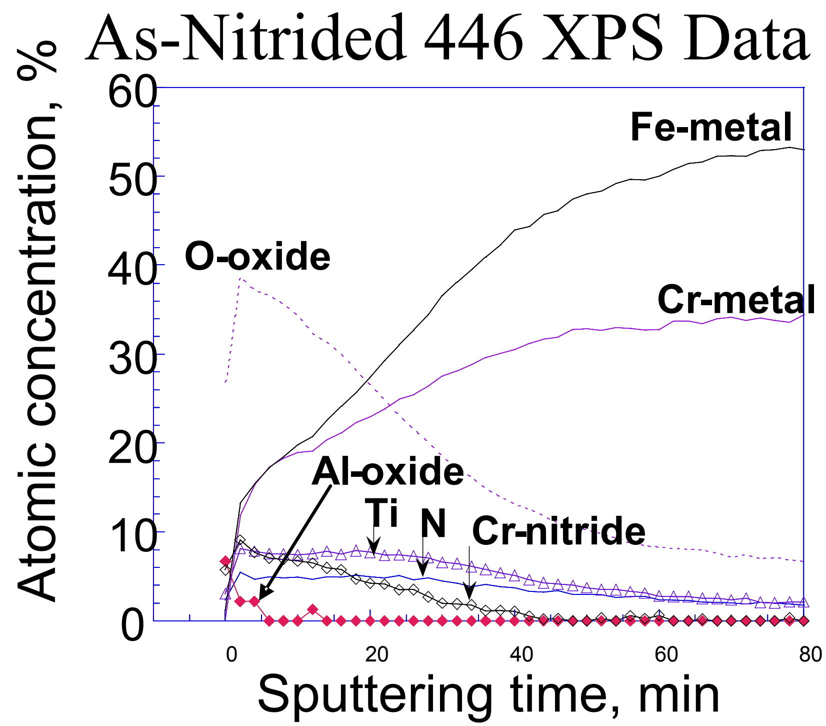
  -nitriding ~10 cents - $1/part, stamping negligible

  - $10/lb and less moves into range of goal ~ $2/plate

  -metals may permit new designs, better performance

Nitrogen Modified Passive Layer for Fe-Cr Alloys

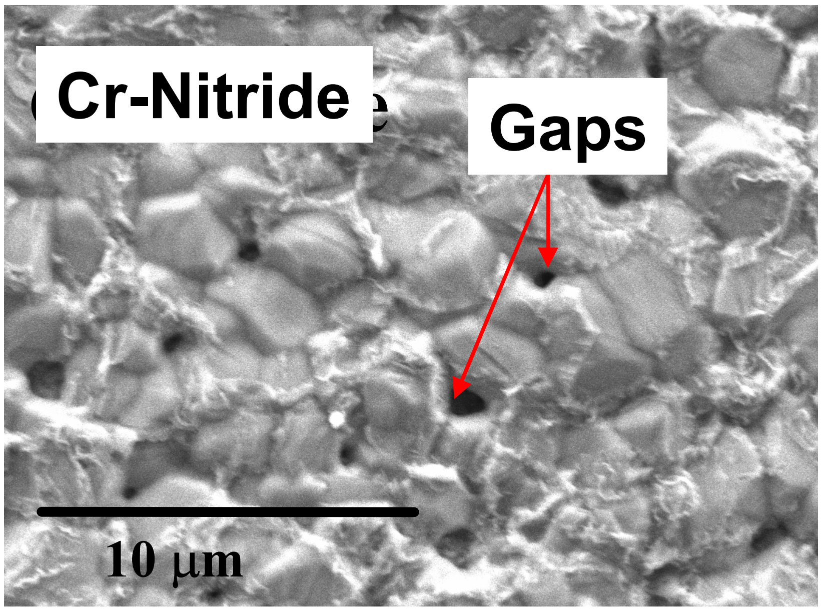




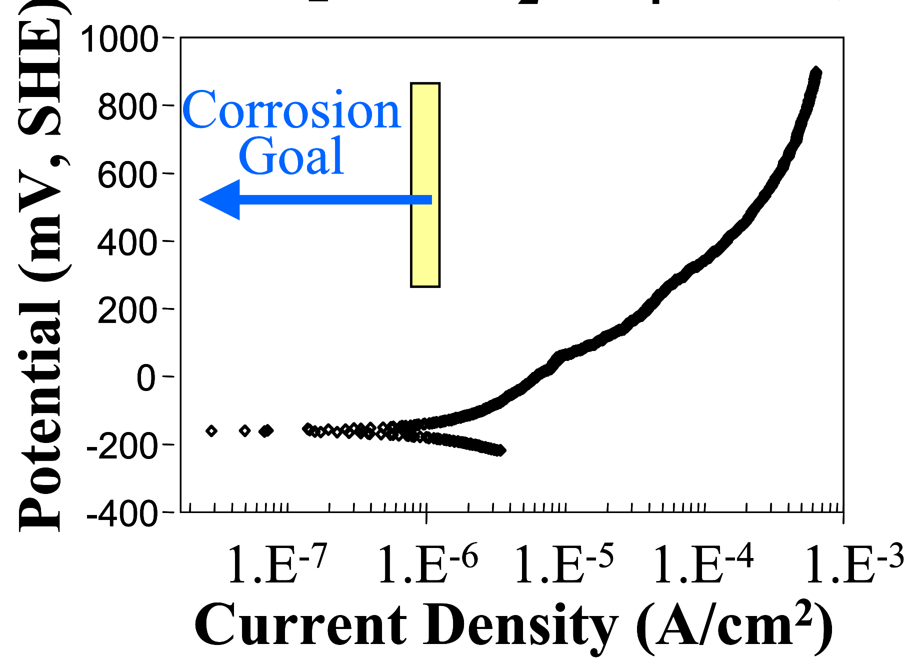
- 446 and AL 29-4C® Steels: Ferritic, Fe-(25-29)Cr base
- Significantly decreased ICR/enhanced corrosion resistance
- Not exclusive Cr-nitride surface, a step forward but issues for robustness/repeatability, borderline corrosion

Baseline Nitriding Does Not Yield Dense Nitride on Fe-27Cr

Typical Nitrided Fe-27Cr Surface



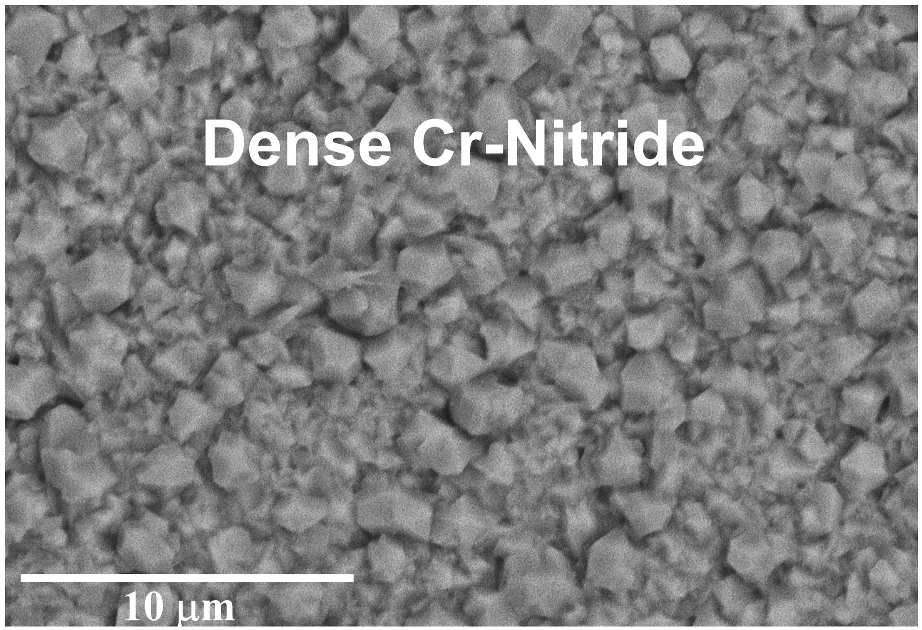
Nitrided Fe-27Cr Polarization (aerated pH3 H_2SO_4 80°C)



- Cr-Nitride triple point gaps lead to poor corrosion resistance
- Need to Change Growth Behavior-detailed study initiated

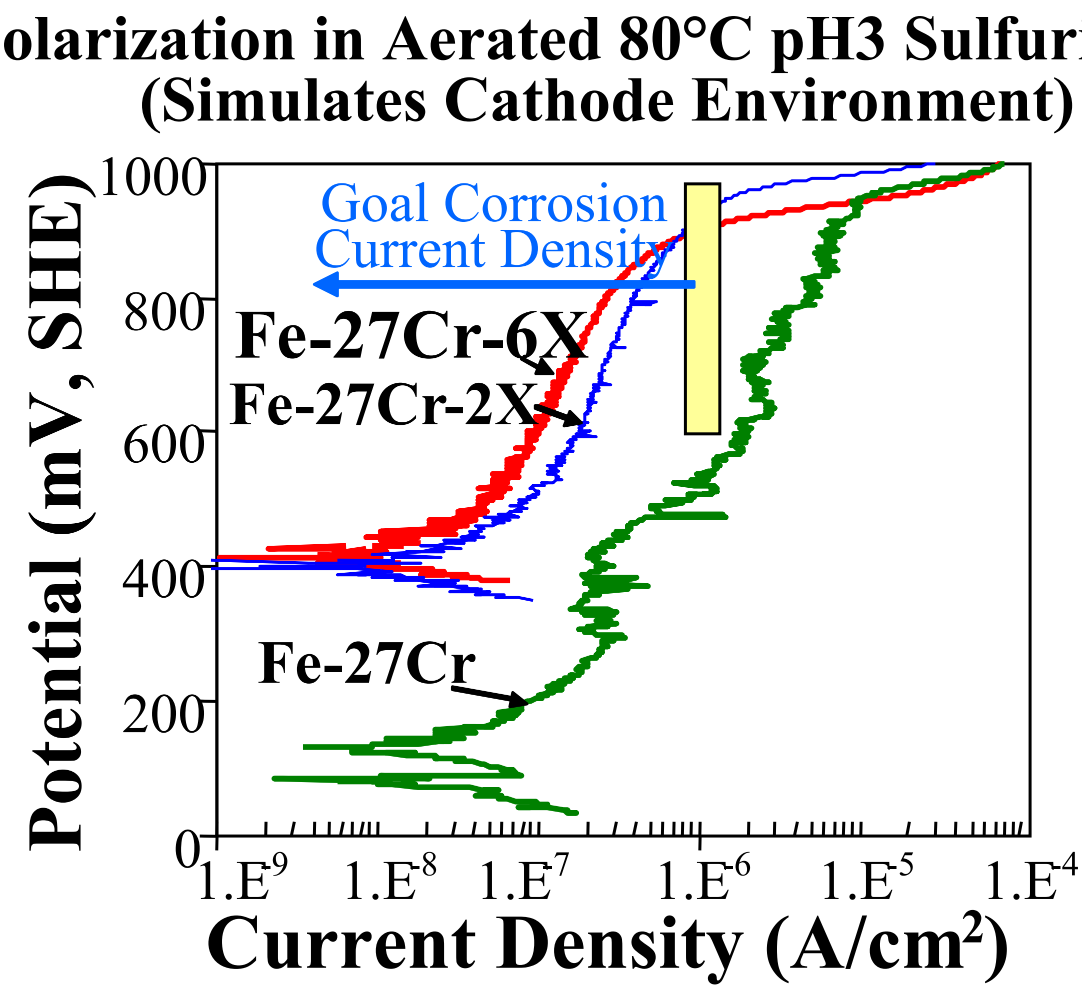
Nitriding Changes + Minor Alloy Addition Yielded Dense Nitride

SEM Surface of Nitrided Modified Fe-27Cr



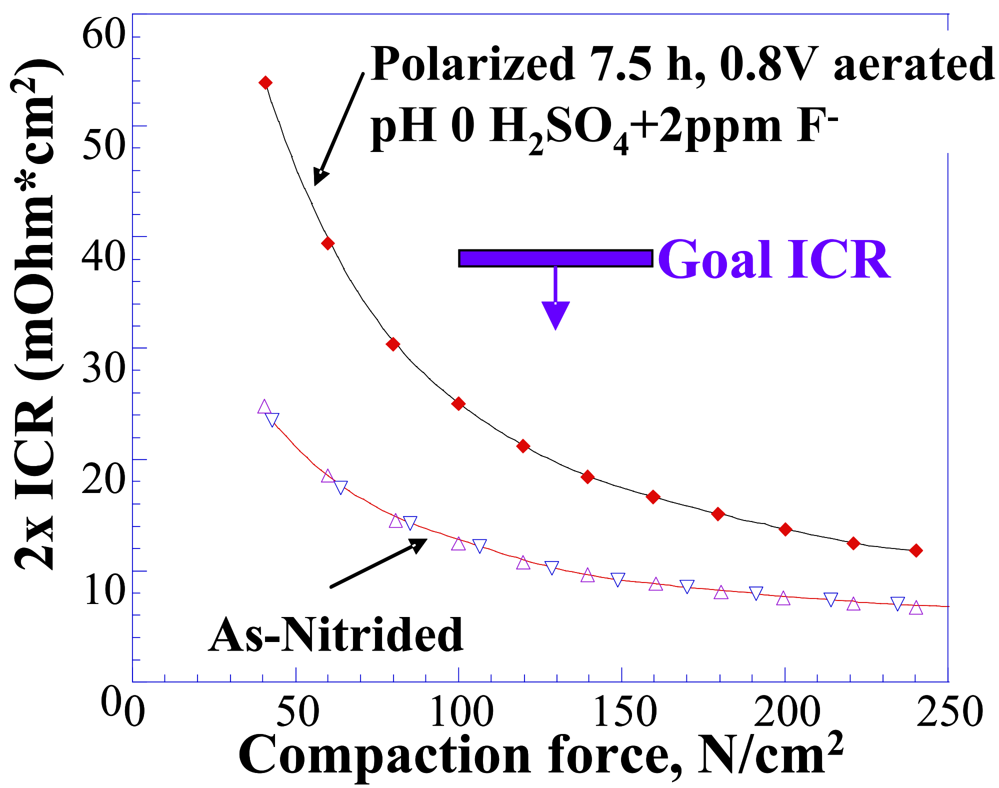
- More robust/repeatable than nitrogen modified passive layer
    - -Thin surface layer, <950°C/<24 h nitriding cycle
    - -Conditions amenable to foil/thin section plates
- Some issues remain for oxygen impurities during nitridation

Excellent Corrosion Resistance for Nitrided Mod Fe-27Cr



- Modified nitridation moderately improved Fe-27Cr
- X addition yields behavior equal to that of nitrided Ni-50Cr

Low ICR for Nitrided Mod Fe-27Cr Pre/Post Polarization



- Similar good corrosion/low ICR under anodic conditions
- Fuel cell test screen: 5 cm^2 test plates with TN Tech

  -Plates machined, to be nitrided May/June 05

Responses to Previous Year Reviewers' Comments

- Wean program from Nitrided Ni-50Cr
  - Proof of principle material/many scientific insights gained
  - Time lag between testing w/outside parties/post-test analysis
  - Most of FY04/FY05 spent on lower Cr, Ni-Cr and Fe-Cr work
- Slow progress with stainless steel results
  - New finding/Issues with repeatability/robustness: inadequate presentation time to go into details: significant effort on this
  - Success this year with X additions-moving to fuel cell testing
- 1 Negative review: "Nitriding will warp thin plates like a "potato chip", complicated/costly process, …"
  - Nitrided stamped foil without significant warpage
  - Nitriding simple coating method, cheap w/short cycles
  - Complexity in alloy design to impart robustness: progress made

Future Work

- **Remainder of FY05**
  - Nitride G-35™ and G-30® plates for GM and FuelCell Energy
  - Nitride X-modified Fe-27Cr for fuel cell test screen at TN Tech
  - Optimize nitriding for X-modified Fe-27Cr, initiate coupon delivery to partners for ICR/Corrosion screening as prelude to fuel cell tests
  - Revisit nitridation of commercial stainless steels based on X-addition insights
- **FY06**
  - Complete optimization of X-effect/expand fuel cell test efforts
  - Assess potential for dense Cr-nitride formation on lower Cr and/or austenitic alloys (or establish stampability of ferritic alloys)
  - Expand interactions with alloy manufacturers/foil producers

Publications and Presentations

A) 2 patent disclosures pending, 1 addition invention disclosure in progress
B) 6 journal papers (several additional to be submitted after invention disclosure)

1) M.P. Brady, P.F. Tortorelli, K.L. More, E.A Payzant, B.L. Armstrong, H.T. Lin, M.J. Lance, F. Huang, and M.L Weaver, "Coating and Surface Modification Design Strategies for Protective and Functional Surfaces", submitted to Materials and Corrosion
2) I. Paulauskas, M.P. Brady, H. M.Meyer III , R.A. Buchanan, L.R. Walker, "Corrosion Behavior of CrN, Cr_2N and π Phase Surfaces Formed on Nitrided Ni-50Cr with Application to Proton Exchange Membrane Fuel Cell Bipolar Plates", submitted to Corrosion Science
3)M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, "Preferential Thermal Nitridation to Form Pin-Hole Free Cr-Nitrides to Protect Proton Exchange Membrane Fuel Cell Metallic Bipolar Plates", Scripta Materialia, 50(7) pp.1017-1022 (2004).
4) H. Wang, M P. Brady, K.L. More, H.M. Meyer, and J. A. Turner, "Thermally 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 (1-2), 75 (2004)
5) H. Wang, M. P. Brady, and J. A. Turner, "Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 1 Model Ni-50Cr and Austenitic 349™ alloys", Journal of Power Sources , 138 (1-2), 86 (2004)
6) M. P. Brady K. Weisbrod, C. Zawodzinski I. Paulauskas,R. A. Buchanan,and L. R. Walker, " Assessment of Thermal Nitridation to Protect Metal Bipolar Plates in Polymer Electrolyte Membrane Fuel Cells", Electrochemical and Solid-State Letters, 5, 11 2002

C) 2 Conference Presentations with Proceedings Papers, 6 total oral presentations not including DOE Hydrogen Program Review, Presentations planned for the Fall 2005 ASM Meeting (invited) and Fall 2005 ECS Meeting, Several additional university/student 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 on Fuel Cell Science, Engineering and Technology, Rochester, NY (June 14-16, 2004).
2) M. P. Brady, I. Paulauskas, R. A. Buchanan, K. Weisbrod, H. Wang, L. R. Walker, L. S. Miller "Evaluation of Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells ", in Proceedings of 2nd European Fuel Cell Forum, Lucerne, Switzerland, June 30-July 4, 2003.
3, 4) two presentations at Spring Electrochemical Society, Orlando, FL (2003).
5) ASM, Pittsburgh, PA (2003)
6) Fall Meeting of The Materials Research Society (2002).
7) Fuel Cell Seminar 2003, 2004 poster presentations

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Fuel cell testing performed by collaborators (no pure H_2 used by us)
- Nitriding in N_2-H_2 mixtures up to 4%H_2
- Acid mixtures used for corrosion testing (reducing conditions with Ar-4%H_2 purge)

Hydrogen Safety

Our approach to deal with this hazard is:

- Limit gas H_2 content to 4% or less
- Project activities are covered by a formal, integrated work control process for each practice/facility
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers