

Cost-Effective Surface Modification For Metallic Bipolar Plates

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Overview

Timeline

- Start- Oct 2001 (small exploratory \$ in 1999/2000)
- Finish- Sept 2006
- 90% complete

Budget

- **Total project funding**
 - \$1650K
- **Funding for FY05**
 - \$300K
- **Funding for FY 06**
 - \$300K
 - Addtl. \$150K linked w/NREL

Barriers

- A. Durability
- B. Cost
- Targets (2010)
 - resistivity < 10 mohm-cm²
 - corrosion < 1 x10⁻⁶ A/cm²
 - cost < \$6/kW

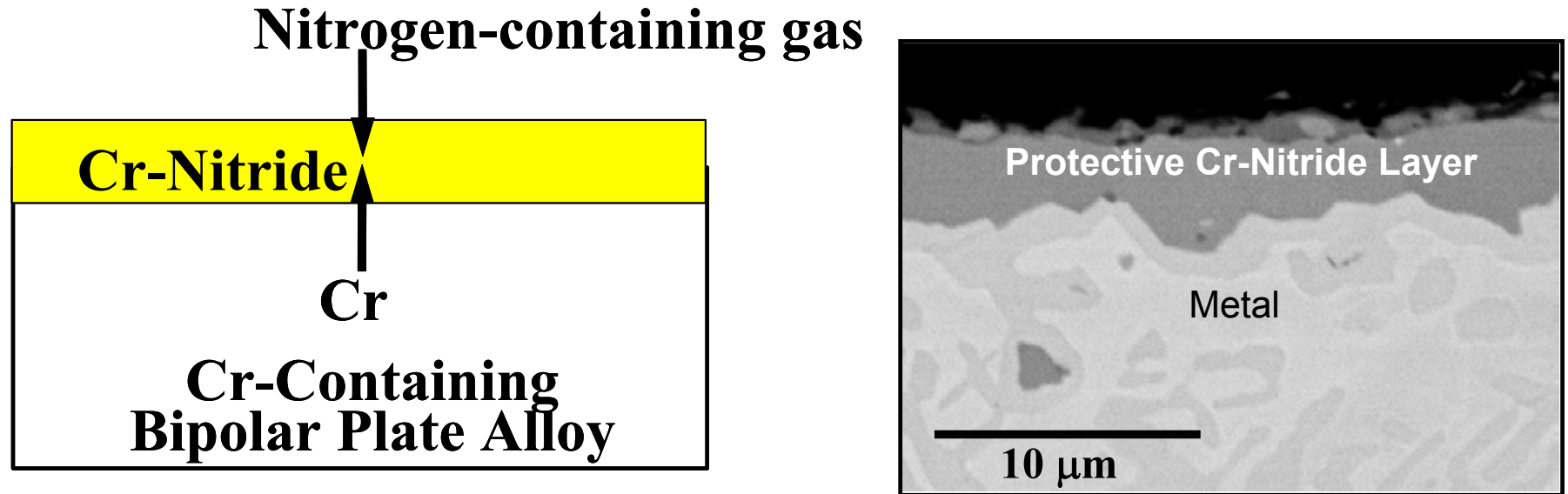
Primary Interactions

- DANA Corp., Fuel Cell Energy, GM, GenCell Corp., Jadoo Power Systems
- Los Alamos National Lab, TN Tech, Ecole des Mines de Paris (nitride characterization)

Objective: Surface Treatment to Protect Metallic Bipolar Plates

- **Overall Goal:** Demonstrate potential for metallic bipolar plates to meet 5000 h durability goals at cost < \$6/kW
- **FY 06 Goals:**
 - Demonstrate cyclic fuel cell test durability for thermally grown Cr-nitride surfaces (nitrided Ni-base alloys)
 - Demonstrate protective Cr-nitride on Fe-base alloys to meet cost goals
 - establish mechanism of nitride formation on Fe-base alloys to provide basis for scale up (cost, repeatability, robustness)
 - deliver plates for single-cell fuel cell testing by collaborators
- **Completion of effort in FY06 to provide basis for Go/No Go decision for scale-up activities (proposal submitted)**

Approach: Thermally Grown Cr-Nitride for Protection

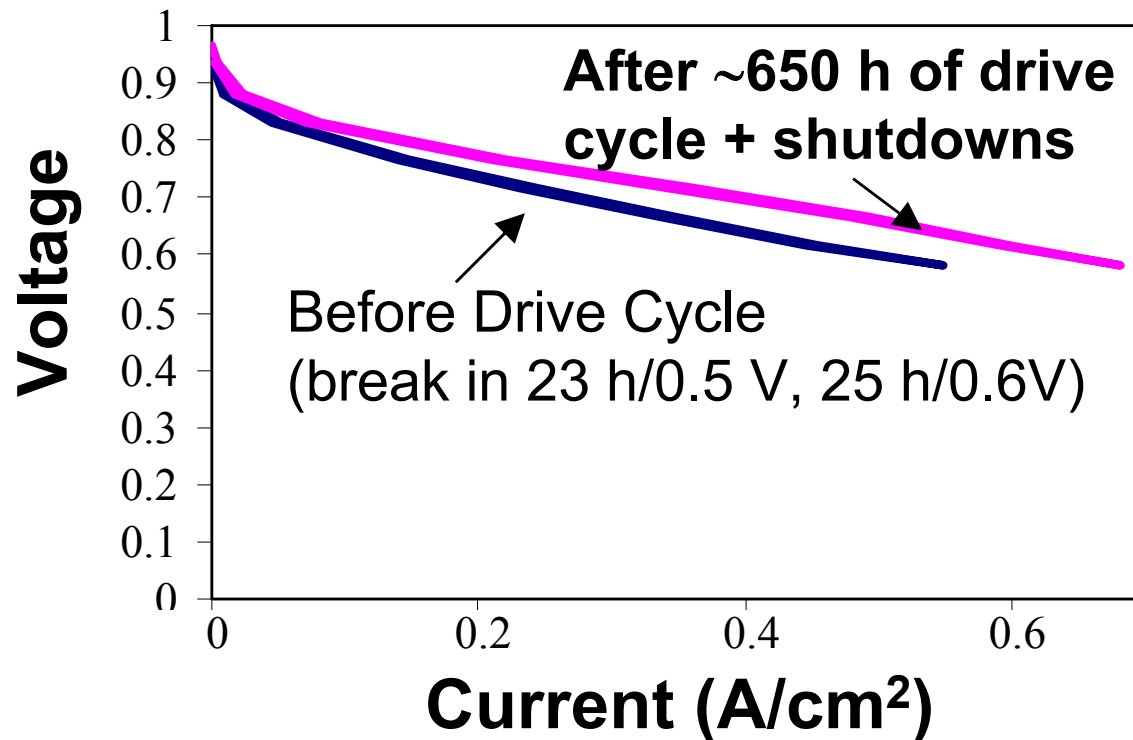


- **Surface conversion, not a deposited coating: High temperature favors reaction of all exposed metal surfaces**
 - No pin-hole defects (other issues to overcome)
 - Amenable to complex geometries (flow field grooves)
- **Stamp then nitride: Industrially established and cheap**

Durability/Performance Studied with CrN/Cr₂N Surfaces Formed on Ni-Cr Alloys

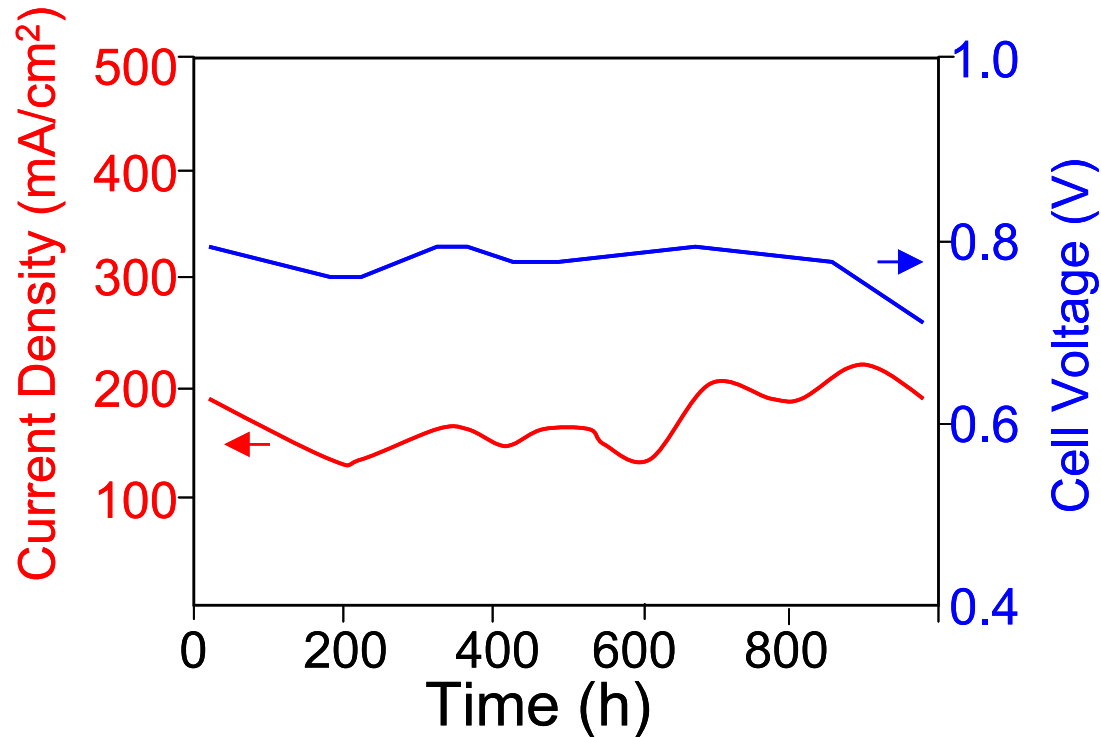
- **Protective Cr-nitride surfaces achieved for model and commercial Ni-(30-50)Cr base alloys**
 - Used to establish whether thermally grown CrN/Cr₂N can meet DOE corrosion, contact resistance, and durability goals
- **Formation of similar Cr-nitride surfaces on Fe-base alloys needed to meet cost goals (Ni-base high \$)**
 - More difficult to do than for Ni-base alloys
 - Lower Cr level alloys, interference from Fe
 - Focus of FY 05 and 06 efforts

Good Single-Cell Drive-Cycle Durability Test Results for Nitrided Ni-50Cr Plates



- **1160 h of drive-cycle testing** (after initial 500 h/0.7V/80°C test screening)
 - 0.94V/1 min; 0.60V/30 min; 0.70V/20 min; 0.50V/20 min
 - additional 24 full shutdowns superimposed
- No performance degradation/No attack of the Cr-nitride
 - trace level (2×10^{-6} g/cm²) of Ni detected in MEA, suspect local CrNiN spots

Good Single-Cell Performance of Nitrided G35™ (Ni-30Cr base) for Dry/Wet Cycling (40%/100% RH) Test at GM



- Dry/wet cycling accelerates MEA degradation/high fluoride release rate to produce aggressive bipolar plate conditions
- No metal ion contamination and low resistance: comparable behavior to Poco graphite plates (post-test examination of plates underway)

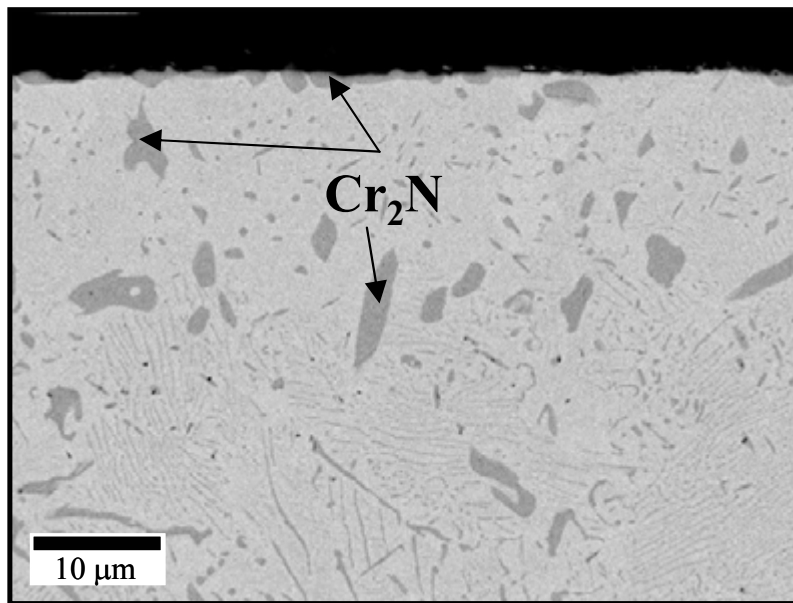
Need Fe-Base Alloys to Meet \$6/kW Bipolar Plate Cost Goals

Status at FY05 Review

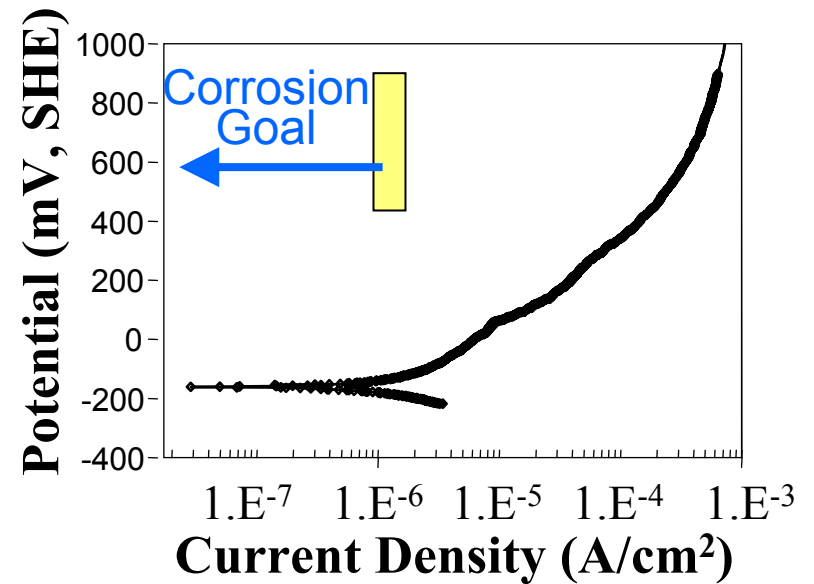
- Dense Cr-nitride formation demonstrated on Fe-Cr base alloy
 - low corrosion current densities in 1st polarization screenings
 - low interfacial contact resistance
- At that time:
 - repeatability issues encountered
 - surface layer microstructure not well characterized
 - mechanism of formation not well understood
(needed to improve repeatability and optimize)

Problem: Internal Nitridation Partitions Nitrogen Away from Surface Layer Growth in Fe-Cr Base Alloys

Typical Nitrided Cross-Section for a Fe-27Cr wt.% Base Alloy



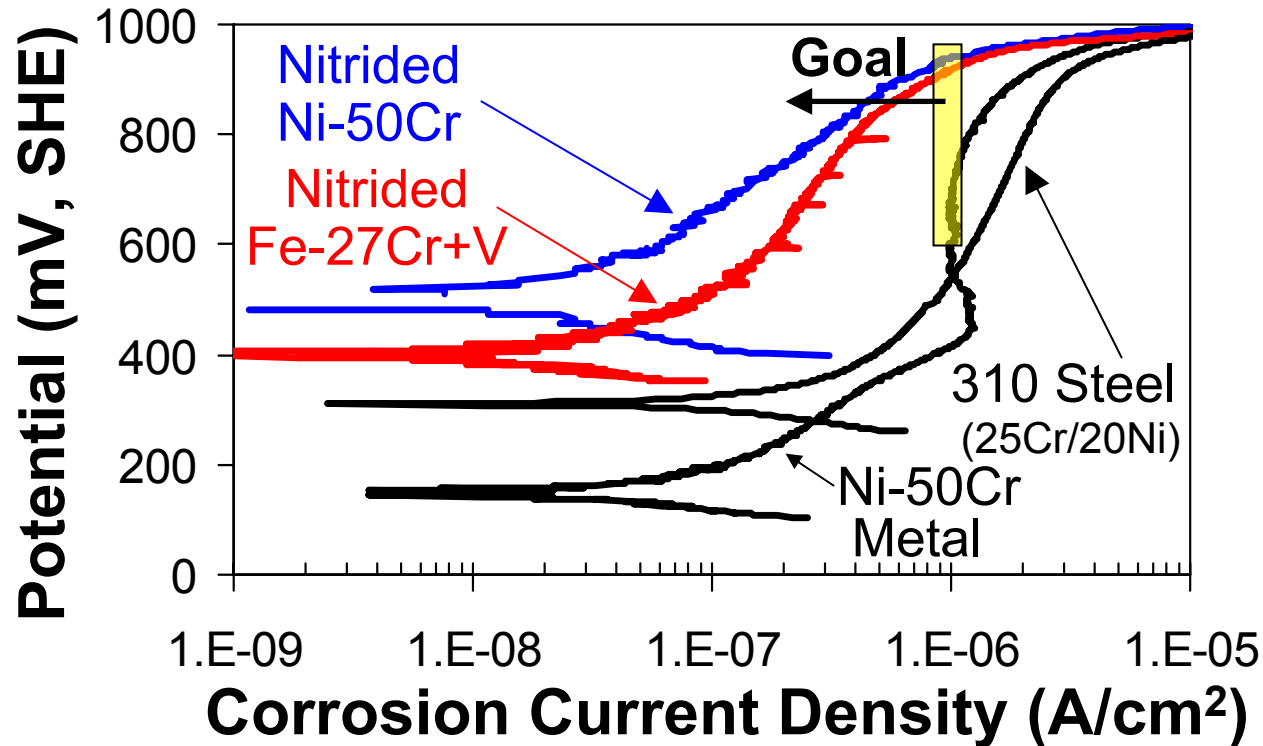
Typical Nitrided Fe-27Cr Polarization (aerated pH3 H₂SO₄ 80°C)



- Mechanical property, cost, and phase stability issues limit viable range of Fe-Cr base alloys to < 30 wt.% Cr
- High alloy N₂ permeability prevents dense Cr-nitride surface

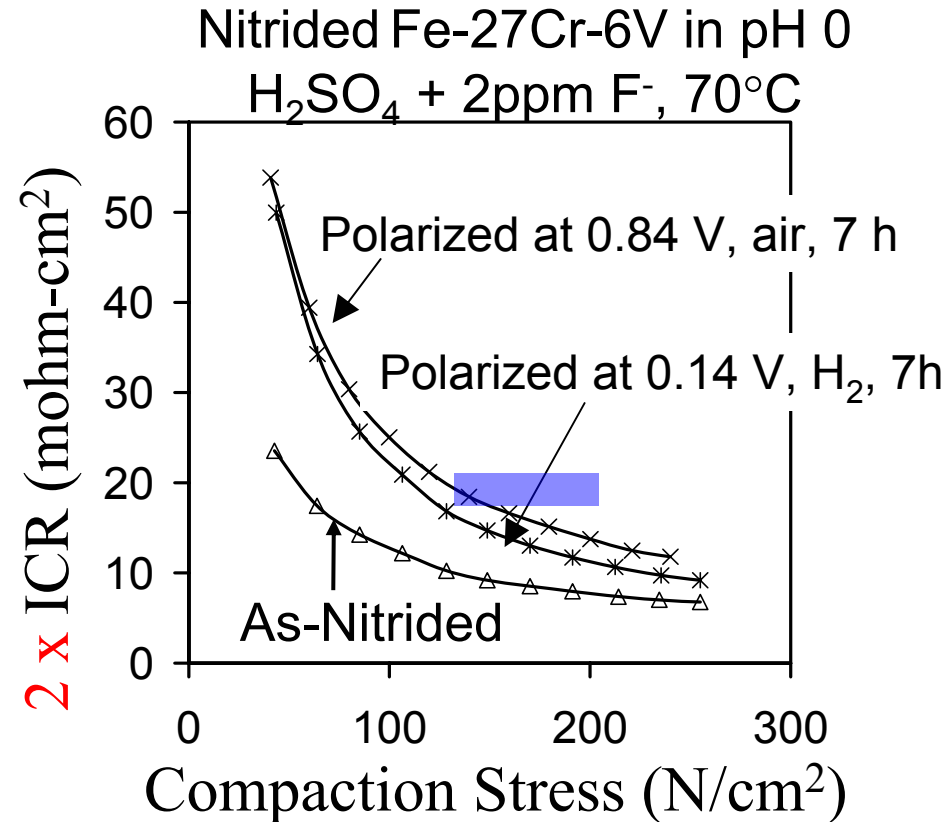
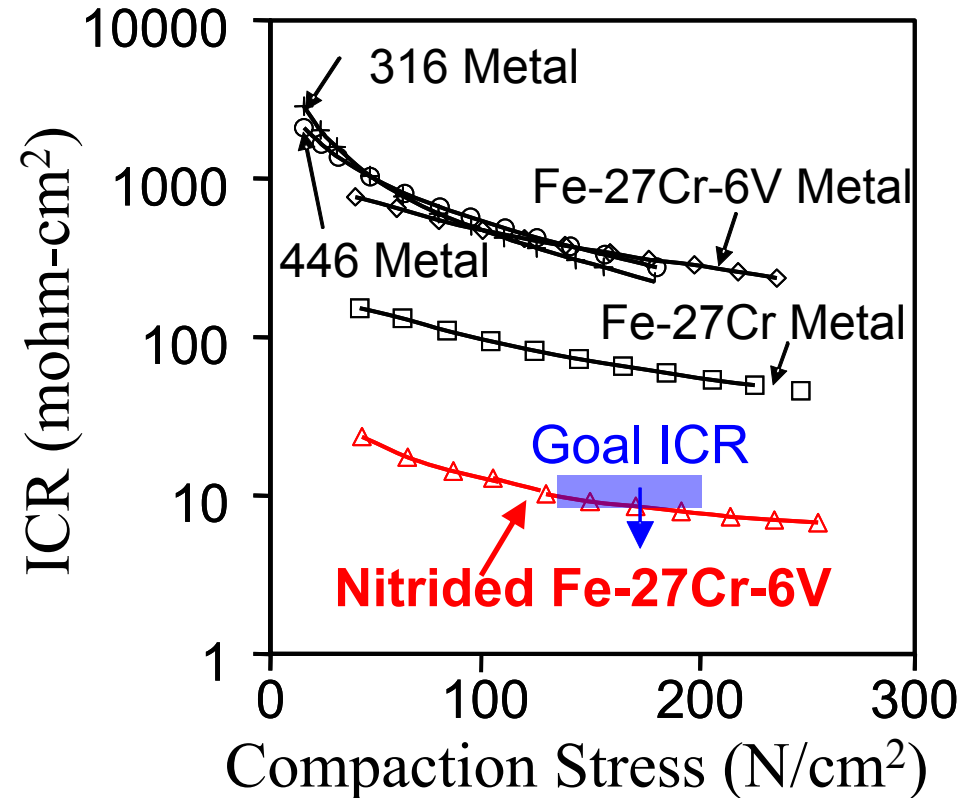
Vanadium Additions to Fe-27Cr Result in Protective Cr-Nitride Surface

Polarization in Aerated pH 3 Sulfuric Acid at 80°C



- Corrosion resistance comparable to nitrided Ni-50Cr observed for nitrided Fe-27Cr-2V and Fe-27Cr-6V (850-900°C, < 24 h, N₂-4H₂)
 - Meets goal corrosion current density up to ~ 900mV range
 - Low corrosion current densities also observed under anodic conditions

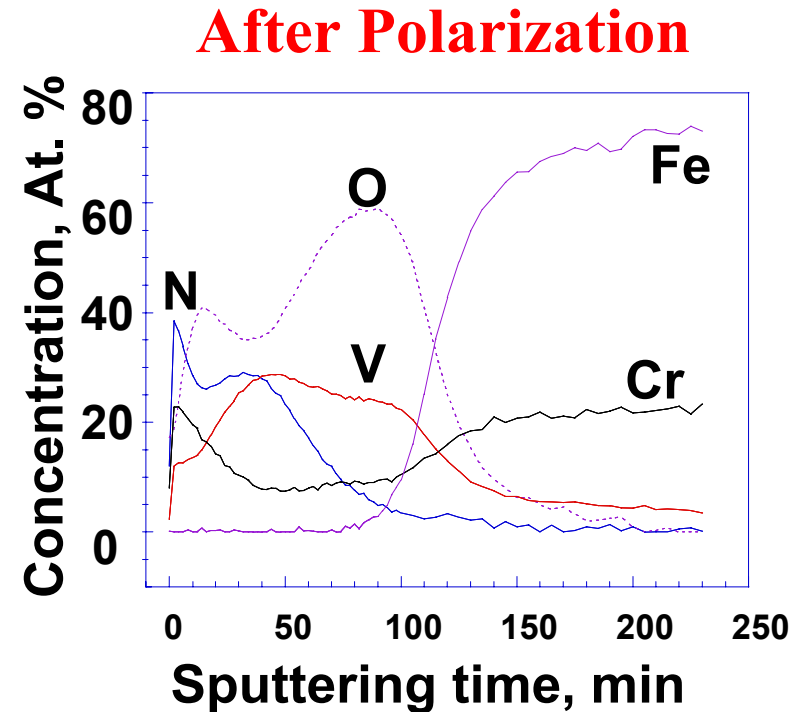
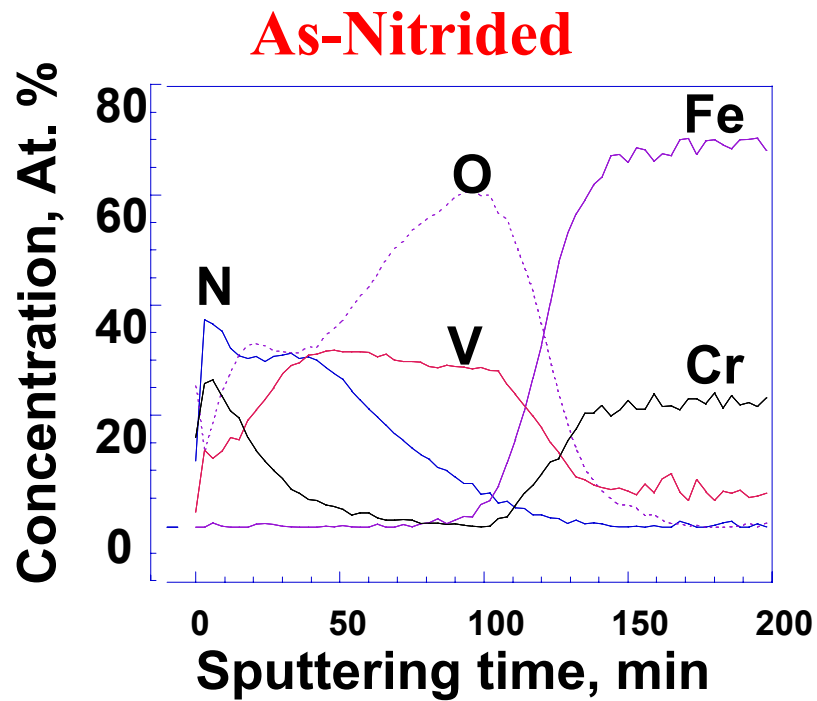
Nitrided Fe-27Cr+V Meets and Maintains Contact Resistance Goal



- Nitridation significantly reduces interfacial contact resistance (ICR)
- Slight increase in ICR on polarization-still meets goal
- Untreated stainless steels don't meet ICR goals

Little Effect of Polarization on Surface Chemistry of Nitrided Fe-27Cr-6V

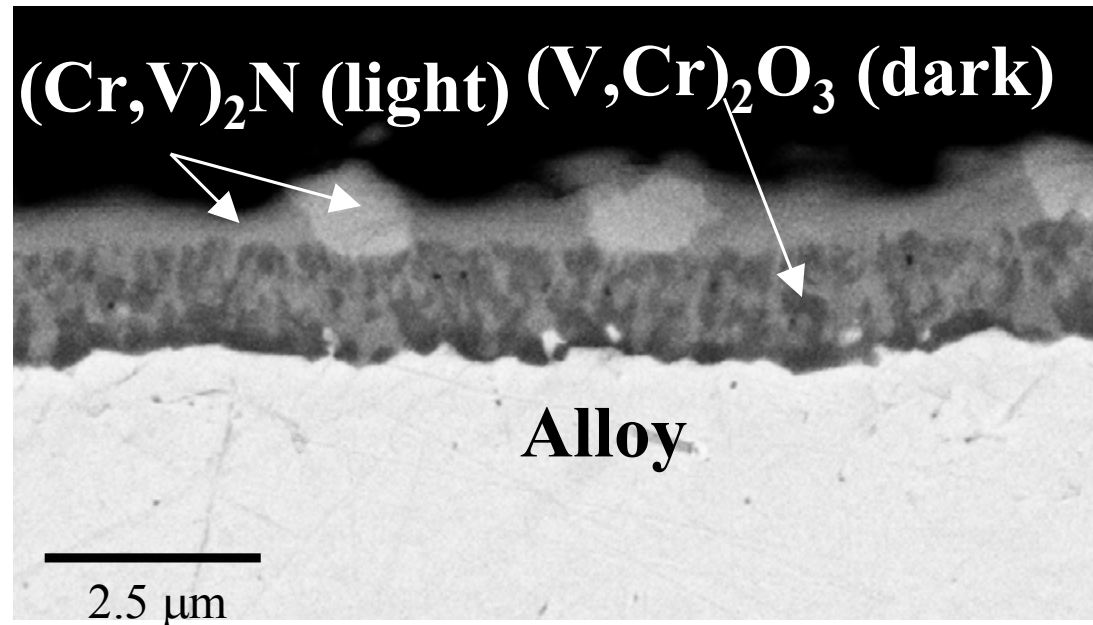
Auger Electron Spectroscopy of Nitrided Fe-27Cr-6V



- Polarized 7 h at 0.84 V SHE in pH 0 H_2SO_4 + 2 ppm F^- air purged at 70 °C (similar results under H_2 -purged anodic conditions)
- No Fe detected in nitrided surface, **oxygen present** in surface

Surface Layer on Nitrided Fe-27Cr-6V Contained Nitrides and Oxides

Cross-Section of Fe-27Cr-6V wt.%, 900°C, 24 h, N₂-4H₂

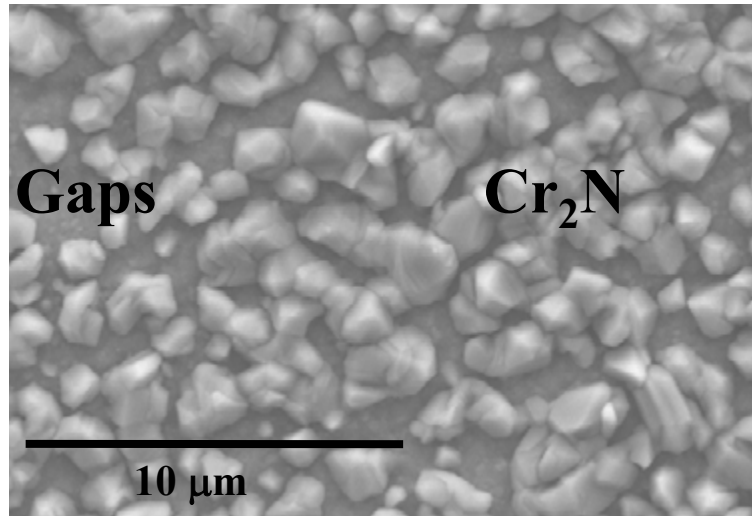


- O₂ Impurity level in nitriding gas sufficient to form oxides
- Nitrogen stayed at surface, no internal nitridation
- (Cr,V)₂N overlying mixed (V,Cr)₂O₃ + (Cr,V)₂N at 900°C

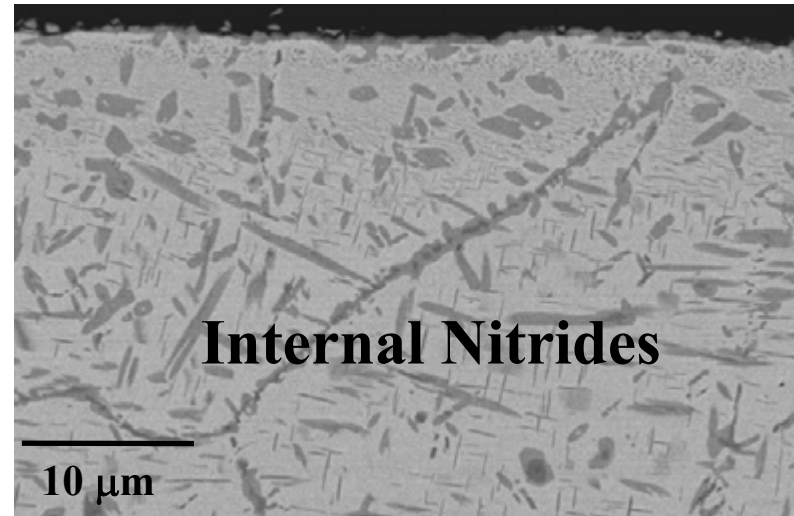
Reducing O_2 in Nitriding Gas Resulted in Surface Gaps/Extensive Internal Nitridation

Fe-27Cr-6V Nitrided at 900°C for 4 h in Purified N_2-4H_2

Surface



Cross-Section

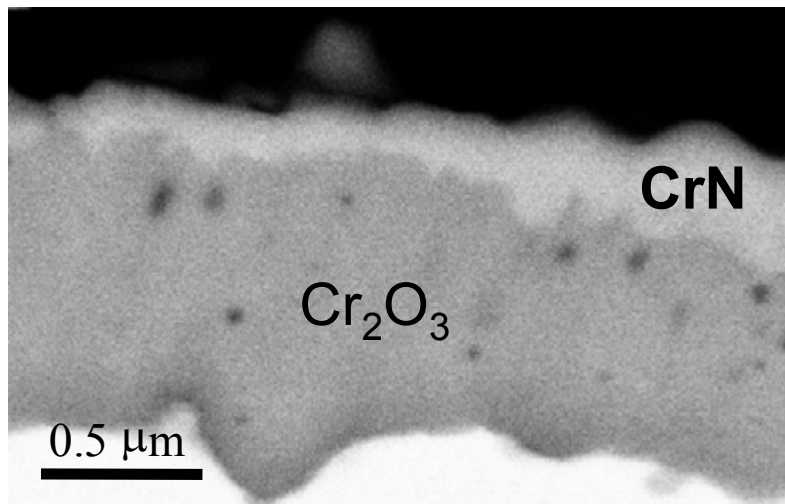


- Indicates O_2 impurity/oxide formation favors dense Cr-nitride surface formation by reducing N_2 penetration into the alloy
- Variations in O_2 impurity level cause of initial repeatability issues

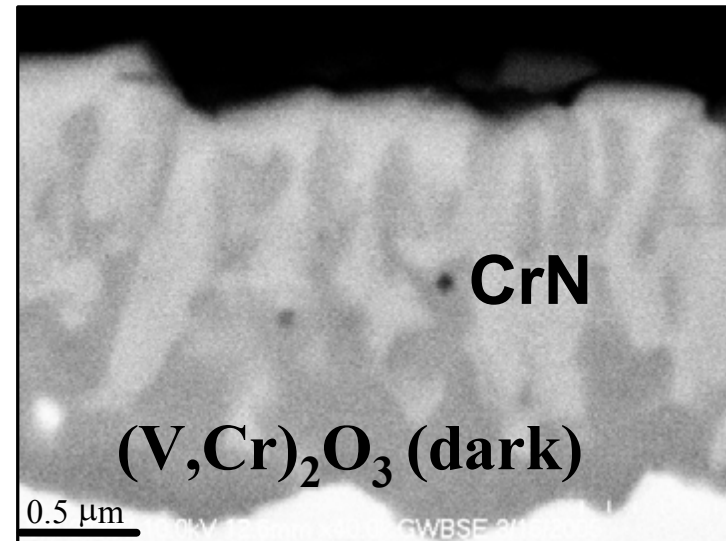
Initially Formed Oxide Converted to Nitride: Easier with Vanadium

SEM Cross-Sections after 24 h at 850°C in N₂-4H₂

Fe-27Cr



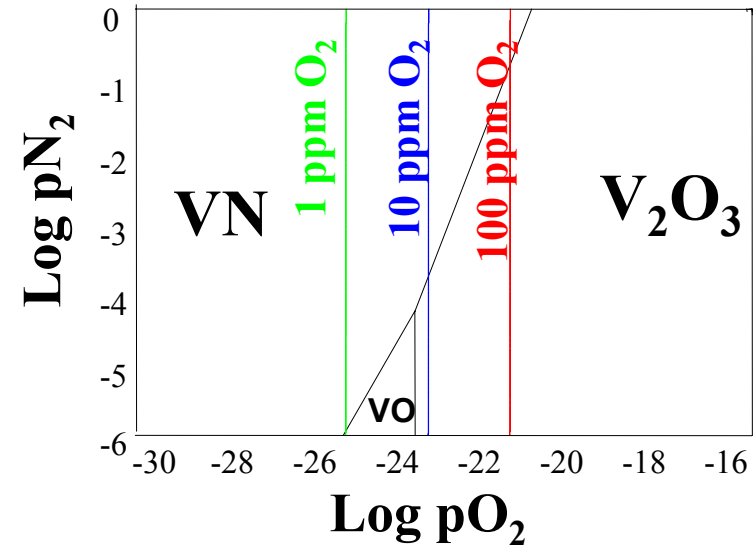
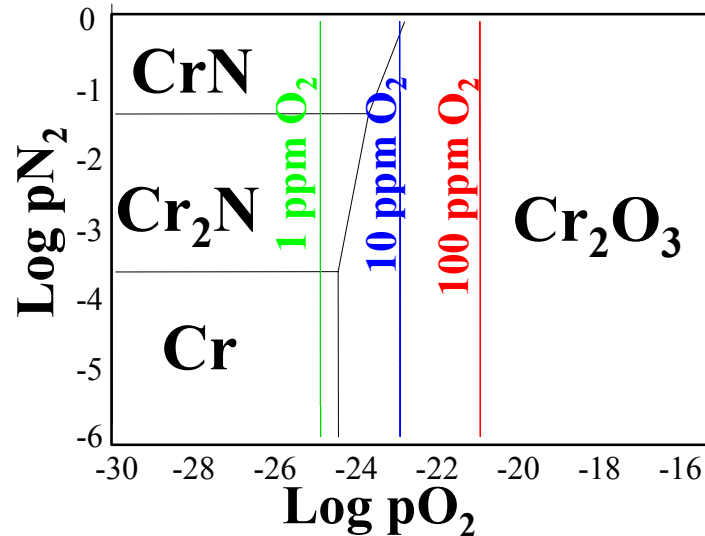
Fe-27Cr-6V



- Oxide formed initially during heat up followed by conversion to nitride
 - V and Cr co-segregate into initially-formed (V,Cr)₂O₃ oxide
 - V addition adds extra degree of freedom- intermixed morphology
- Nitrided Fe-27Cr showed inadequate corrosion resistance due to many non-uniform areas and thin spots

V Additions Destabilize Oxide Relative to Nitride Compared to Cr

900°C Predominance Diagrams



- Order of magnitude greater O_2 impurity stability for VN relative to CrN at 900°C in $\text{N}_2\text{-4H}_2$ (100 vs 10 ppm O_2)
- V works because $\text{Cr}_2\text{O}_3\text{-V}_2\text{O}_3$; $\text{Cr}_2\text{N-V}_2\text{N}$; CrN-VN all mutually soluble
- V_2O_3 and Cr-doped V_2O_3 also conductive-combined with intermixed morphology and N_2 -doping yields good ICR values

Insights for Alloy/Nitridation Optimization

- Use of O_2 to segregate Cr and V to the surface may permit significant decrease in Cr and V level to minimize alloy cost
 - Fe-27Cr-6V studied as model (Fe-27Cr-2V also worked)
 - Decrease to 18-20 wt.% Cr and 1-2 wt.% V likely, possibly lower (Cr-V oxides very stable, low O_2 permeability in Fe)
- Positive early results with pre-oxidation followed by nitridation
 - 800°C, < 20 minutes to form oxide (want \leq 0.2-0.5 micron thick)
 - May be accomplished on commercial scale by heat up in O_2 containing purge gas followed by introduction of nitriding gas (can also leverage shifting oxide/nitride boundary with temperature)
- Total temp./time cycle < 900°C and < 24 h
 - cost estimates difficult at this stage
 - not a conventional hardening cycle (cheaper), only need few microns
 - very dependent on # and size of plates, furnace size, exact cycle,...

Stamped Fe-Cr-V Alloys Can Meet \$6/kW Transportation Cost Goals

GenCell Corp Cost Estimates for Stamped Bipolar Plates (Nitriding Costs Not Included)

Foil Thick. (in)	Density kg/kW	Bipolar Plate Cost (\$/kW)		
		<u>\$3/lb Alloy</u>	<u>\$5/lb Alloy</u>	<u>\$7/lb Alloy</u>
0.002	0.26	\$2.31	\$3.47	\$4.58
0.004	0.38	\$3.15	\$4.26	\$6.57
0.008	0.64	\$4.86	\$7.69	\$10.51

- High Cr ferritic alloys \$3-7/lb: **potentially viable nitriding costs**
 - E-BRITE® (Fe-26Cr-1Mo wt.%): \$5-7/lb commercial price for foil
 - Alloy 444 (Fe-18Cr-2Mo wt.%): \$3-5/lb commercial price for foil
 - Above alloys comparable to Fe-Cr-V alloys as Mo and V costs similar

Assumptions: 360 cm² active area plate (494 cm² total area), 2 mil secondary foil for cooling (nested stacking), parallel flow field 0.025" depth, 2010 MEA target power density

Future Work

- Delivery of nitrated Fe-27Cr-6V plates for fuel cell testing with collaborators (thick machined plates for comparison with graphite)
- Better establish range of oxygen-nitrogen conditions that lead to protective Cr-nitride base surfaces
 - Includes exploration of lower Cr and V alloys
- Manufacture foil for stamping assessment with GenCell Corp
- Complete post fuel cell test microstructure analysis of nitrated Ni-Cr plates run with collaborators
 - Establish limits of Cr-nitride by cycling nitrated Ni-50Cr plates at $> 1V$ (such conditions can be encountered in stacks)
- Project ends in Sept 2006: Go/No Go decision for scale up via proposal submitted for recent DOE fuel cell call

Summary

- Single-cell fuel cell testing of model nitrated Ni-Cr alloys indicates good performance and durability of thermally grown CrN/Cr₂N surfaces under cyclic test conditions (voltage, relative humidity)
- Promising results with protective Cr-nitride formation on V-modified Fe-Cr alloys that can meet DOE cost goals
 - Behavior in range of contact resistance and polarization corrosion screening targets met
 - Dense Cr-nitride surface formation aided by oxide formation to reduce nitrogen penetration/internal nitridation
 - Key to V effectiveness is mutual solubility in Cr-V-O and Cr-V-N, and high relative stability of V-nitride, V₂O₃ also conductive

Responses to Previous Year Reviewers' Comments

- Need for coatings for metal plates not established/no baseline fuel cell tests with untreated metal plates
 - Under some mild/static conditions and applications uncoated metals may be acceptable: not the case for automotive applications which is primary focus of this program
 - Limited \$/time prevent fuel cell testing of untreated control metal plates (collaborators use past graphite plate performance as benchmark)
 - i) extensive corrosion and ICR studies of untreated coupons
 - ii) no untreated stainless steel can meet ICR goals
- Limited alloy, cost estimate, road mapping details, good collaborations but proactively seek more stack developers
 - Project wrapping up development stage, not yet in scale up
 - Cost estimate details added this year with GenCell Corp
 - i) Input also obtained from alloy manufacturers
 - ii) Exploratory discussions w/many fuel cell OEM's (not all listed)

Publications

Publications/Manuscripts: 9 journal papers published, in press, or in manuscript for effort since 2002

Since Last Review ↑

- 1) M.P. Brady, B. Yang, H. Wang, J.A. Turner, K.L. More, M. Wilson, F. Garzon, “Growth of Protective Nitride Layers for PEM Fuel Cell Bipolar Plate Applications”, invited overview paper for the August 2006 Issue of JOM
- 2) B. Yang, M.P. Brady, D.J. Young, K.L. More, P.F. Tortorelli, E.A. Payzant, H. Wang, and J.A. Turner, “Growth of Multi-Functional Protective Nitride Layers on Fe-Cr Base Alloys for PEM Fuel Cell Bipolar Plates”, to be submitted to *Acta Materialia*
- 3) M.P. Brady, H. Wang, B. Yang, J.A. Turner, K.L. More, M. Bordignon, R. Molins, “Nitridation of Commercial Ni-Cr and Fe-Cr Base Alloys for PEM Fuel Cell Bipolar Plate Applications”, to be submitted to *International Journal of Hydrogen Energy*
- 4) I. Paulauskas, M.P. Brady, H. M. Meyer III, R.A. Buchanan, L.R. Walker, “Corrosion Behavior of CrN, Cr₂N and π Phase Surfaces Formed on Nitrided Ni-50Cr with Application to Proton Exchange Membrane Fuel Cell Bipolar Plates”, *Corrosion Science* (in press)
- 5) 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”, *Materials and Corrosion*, 56 (11), 748-755 (2005)
- 6) 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).
- 7) 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)
- 8) 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 349TM alloys”, *Journal of Power Sources*, 138 (1-2), 86 (2004)
- 9) 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)

Presentations

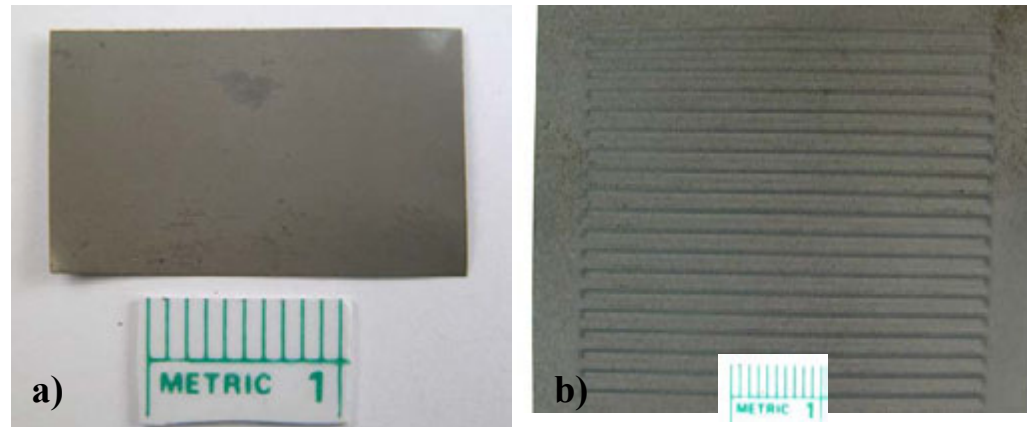
Presentations: 2 Conference Presentations with Proceedings Papers, 9 total oral presentations not including DOE Hydrogen Program Reviews, 3 poster presentations, several additional university/student presentations not listed for effort since 2002

- 1) B. Yang, M. P. Brady, P.F. Tortorelli, K. L. More, H. Wang, J. A. Turner and D.J. Young, “Nitrated Stainless Steels for PEM Fuel Cell Bipolar Plates”, TMS Annual Meeting San Antonio, TX, March 15, 2006
- 2) (Invited) M.P. Brady, B. Yang, Peter Tortorelli, K. L. More, H. Wang and J. A. Turner, “Thermally Nitrated Metallic Bipolar Plates for PEM Fuel Cells”, Materials Science and Technology 2005, Pittsburgh, PA, September 26, 2005.
- 3) B. Yang, M. P. Brady, D. J. Young, K. L. More, H. Wang and J. A. Turner, “Thermally Nitrated Stainless Steel Bipolar Plates for Proton Exchange Membrane Fuel Cells”, 208th Meeting of the Electrochemical Society, October 22-26, Los Angeles, CA, USA, 2005, paper No. 1007.
- 4) (Invited) M.P. Brady, “Multi-component/multi-phase alloys as precursors to protective/functional surfaces via gas reactions”, Gordon Research Conference on High Temperature Corrosion”, July 2005 Colby Sawyer, NH.
- 5) M.P. Brady, H. Wang, I. Paulauskas, B. Yang, P. Sachenko, P.F. Tortorelli, J.A. Turner, R.A. Buchanan, “Nitrated 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).
- 6) M. P. Brady, I. Paulauskas, R. A. Buchanan, K. Weisbrod, H. Wang, L. R. Walker, L. S. Miller “Evaluation of Thermally Nitrated Metallic Bipolar Plates for PEM Fuel Cells “, in Proceedings of 2nd European Fuel Cell Forum, Lucerne, Switzerland, June 30-July 4, 2003.
- 7,8) Two presentations at Spring Electrochemical Society, Orlando, FL (2003).
- 9) ASM, Pittsburgh, PA (2003)
- 10) Fall Meeting of The Materials Research Society (2002).
- 11,12) Fuel Cell Seminar 2003, 2004 poster presentations

Since Last Review ↑

Critical Assumptions and Issues

- **Potential for warping of thin stamped foil during nitriding**
 - significant warping not observed thus far
 - slight warping at corners: could cause stack sealing issues (not expected)
 - bigger issue appears to be nitridation embrittlement of foil: can be controlled by limiting internal nitridation



- a) Oxidized 2 mil FeCrAlY Foil (20-500 h cycles/800°C/10,000 h total)
- b) Stamped and nitrided G-35™ foil (Ni-30Cr alloy; collaboration w/GenCell)

Critical Assumptions and Issues (Cont).

•Durability of Cr-nitride surface under stack conditions

- transient excursions $> 1V$ could degrade nitride surface
- $10^{-5} A/cm^2$ corrosion current densities in coupon tests: pH 0 H_2SO_4 + 2 ppm F^- at $70^\circ C$ and 1.4 vs SHE (dynamic scan, not hold)
- literature suggests transpassive dissolution via $Cr_2O_7^{2-}$ above 1.2 V
- vanadium additions may further stabilize Cr-nitride
- will examine via $> 1V$ cycling at LANL
- current MEAs and carbon supports degrade at $> 1V$

•Repeatability of protective nitride on Fe-Cr-V alloys on scale up

- a concern but use of initial formation of oxide to control appears promising