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-cm^2
  - corrosion < 1 x10^{-6} A/cm^2
  - cost < $6/kW

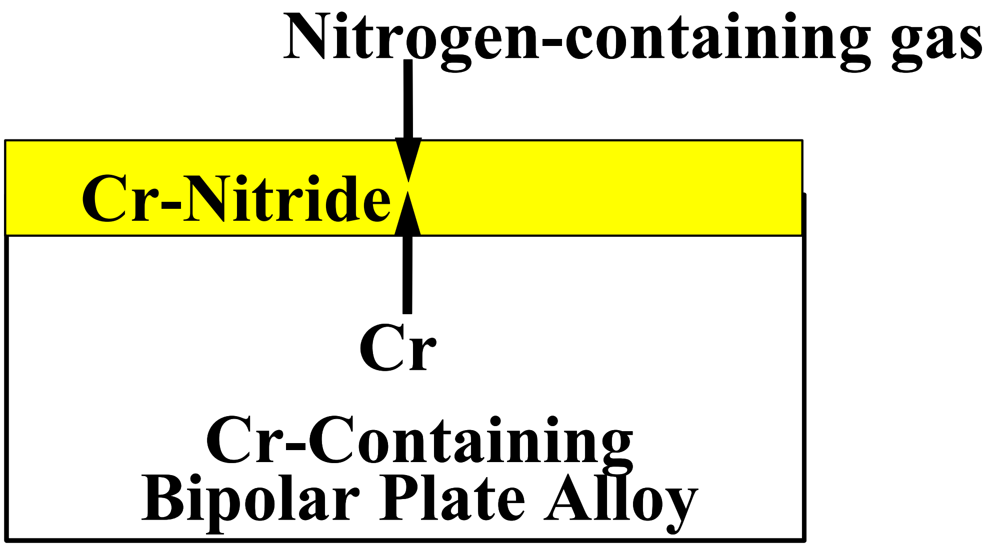
Primary Interactions

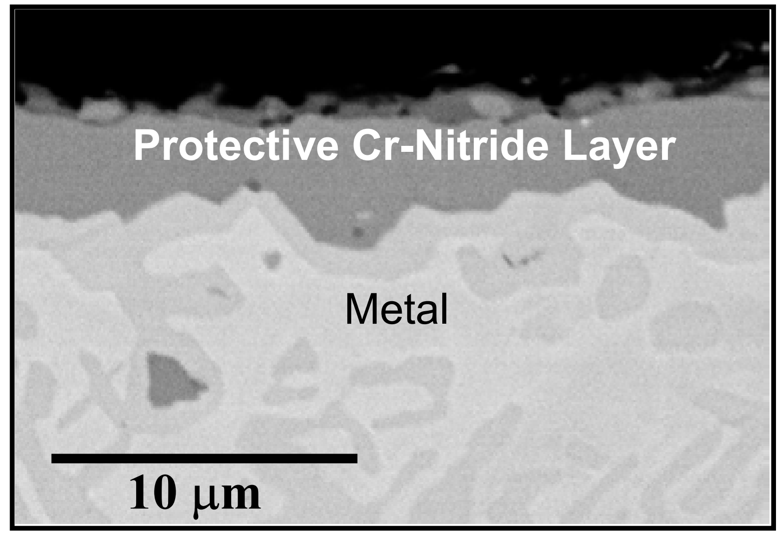
- DANA Corp., Fuel Cell Energy, GM, GenCell Corp., Jadoo Power Systems
- Los Alamos National Lab, TN Tech, Ecole des Mines de Paris (nitride characterization)

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



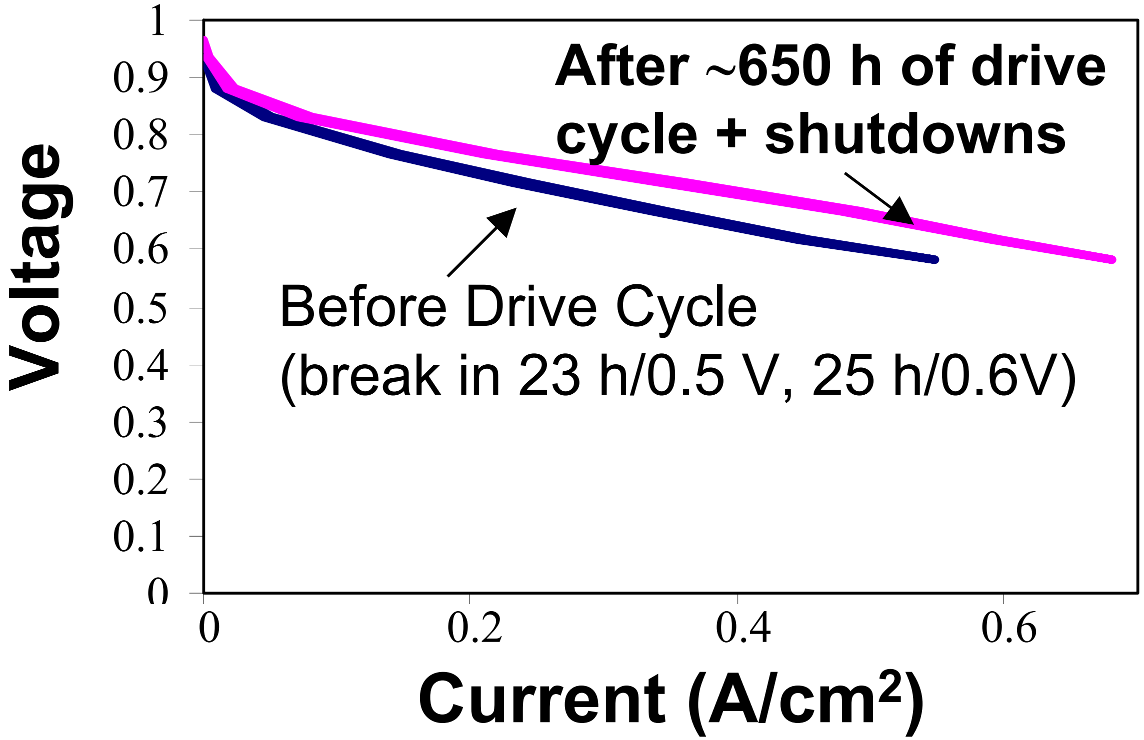


- **Surface conversion, <u>not a deposited coating</u>: High temperature favors reaction of all exposed metal surfaces**
  - -No pin-hole defects (other issues to overcome)
  - -Amenable to complex geometries (flow field grooves)
- **Stamp then nitride: Industrially established and cheap**

Durability/Performance Studied with CrN/Cr_2N 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/Cr_2N 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



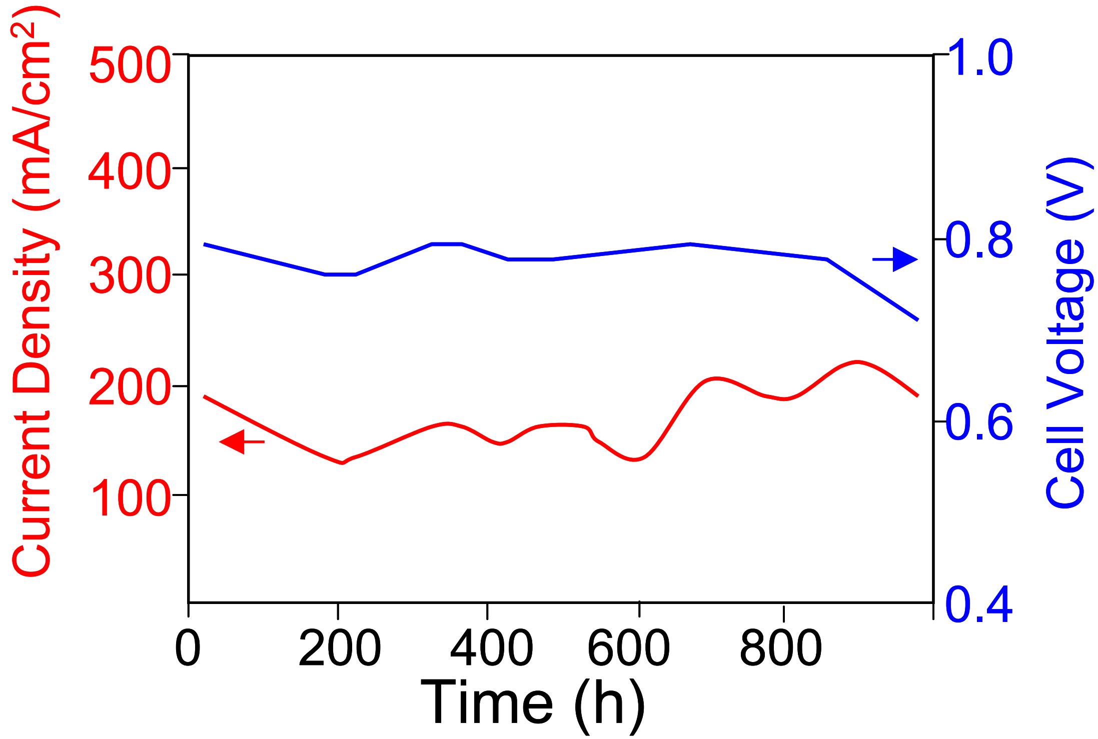
Collaboration with LANL
M. Wilson and F. Garzon

- **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 ($2x10^{-6}$ g/cm^2) 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

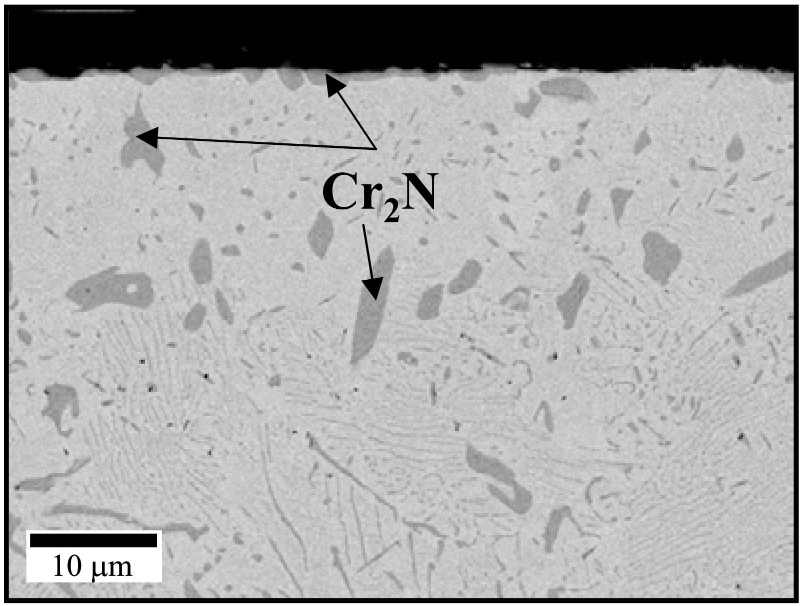
Status at FY05 Review

- Dense Cr-nitride formation demonstrated on Fe-Cr base alloy
  - -low corrosion current densities in 1st polarization screenings
  - -low interfacial contact resistance

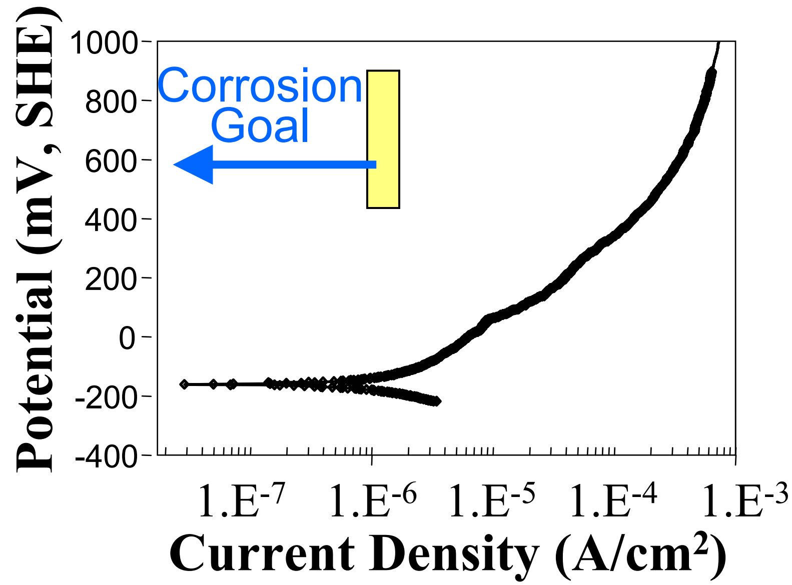
- At that time:
  - -repeatability issues encountered
  - -surface layer microstructure not well characterized
  - -mechanism of formation not well understood (needed to improve repeatability and optimize)

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

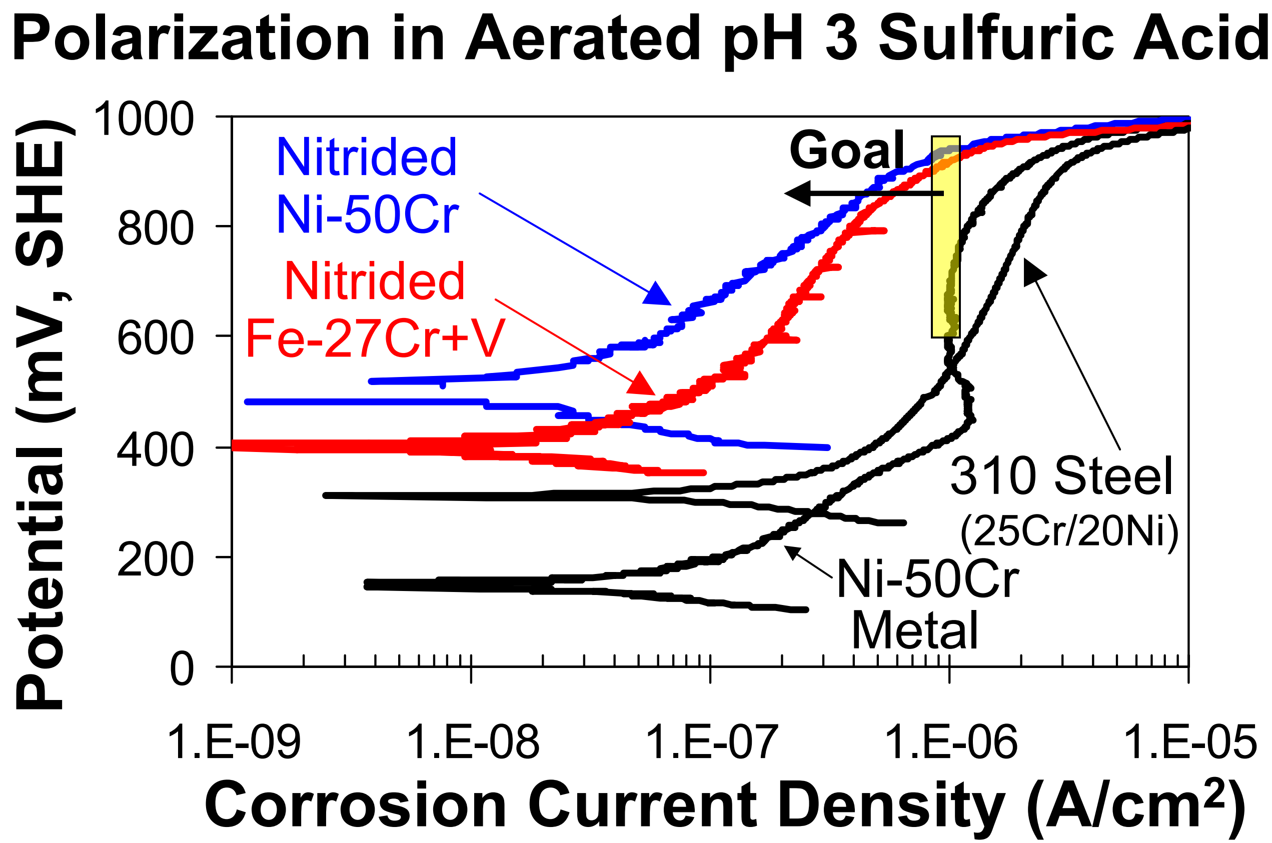


Typical Nitrided Fe-27Cr Polarization (aerated pH3 H_2SO_4 80°C)



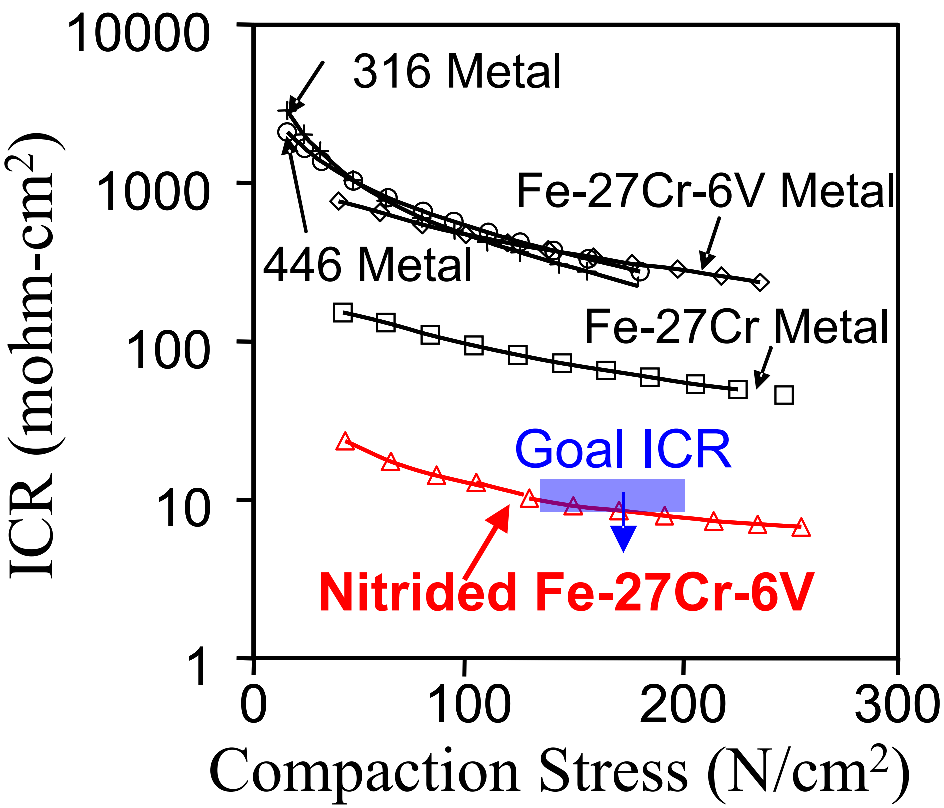
- Mechanical property, cost, and phase stability issues limit viable range of Fe-Cr base alloys to < 30 wt.% Cr
- High alloy N_2 permeability prevents dense Cr-nitride surface

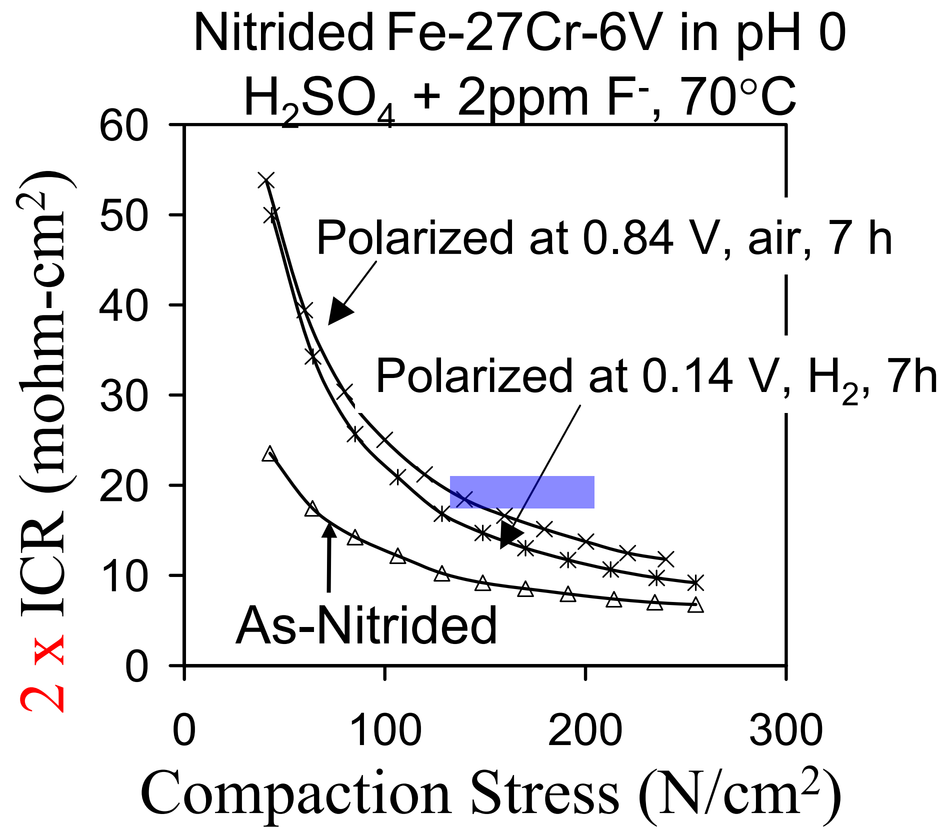
Vanadium Additions to Fe-27Cr Result in Protective Cr-Nitride Surface



- Corrosion resistance comparable to nitrided Ni-50Cr observed for nitrided Fe-27Cr-2V and Fe-27Cr-6V (850-900°C, < 24 h, N_2-$4H_2$)
  - -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

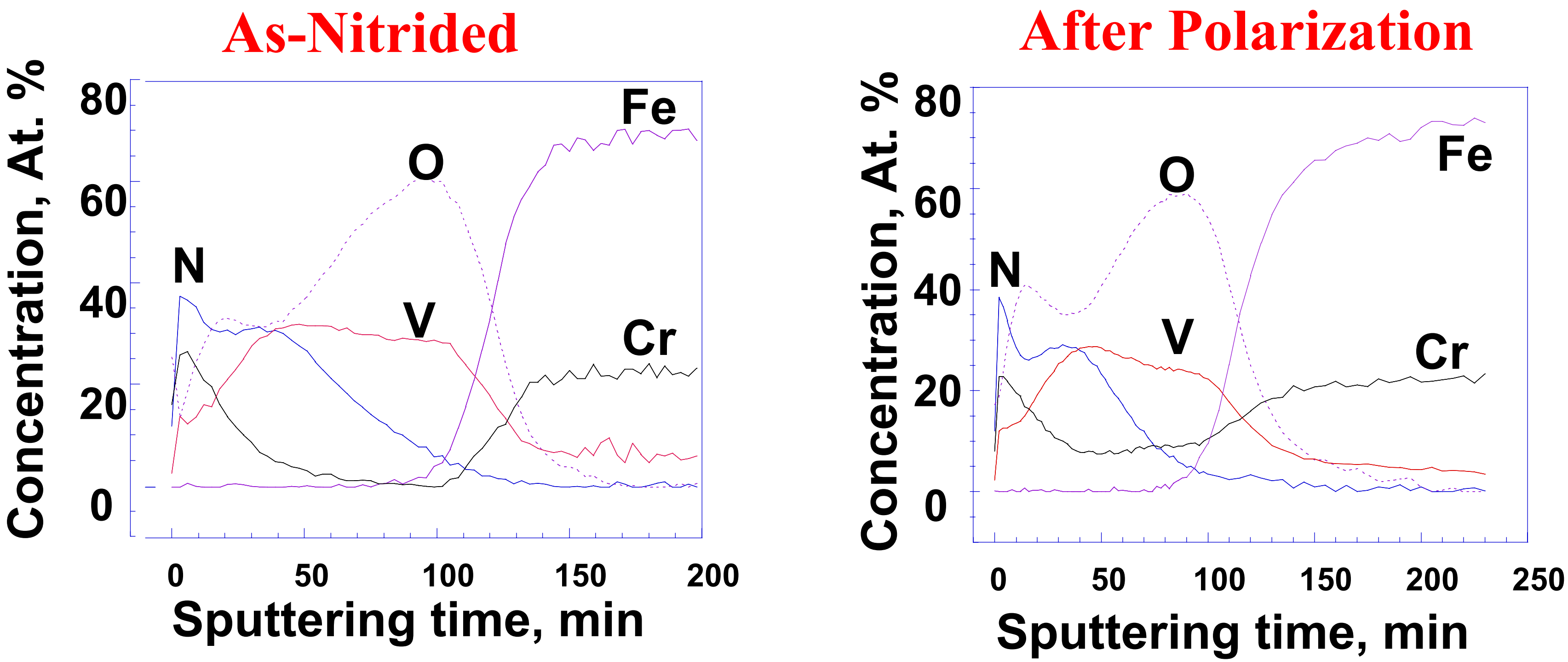




- Nitridation significantly reduces interfacial contact resistance (ICR)
- Slight increase in ICR on polarization-still meets goal
- Untreated stainless steels don’t meet ICR goals

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

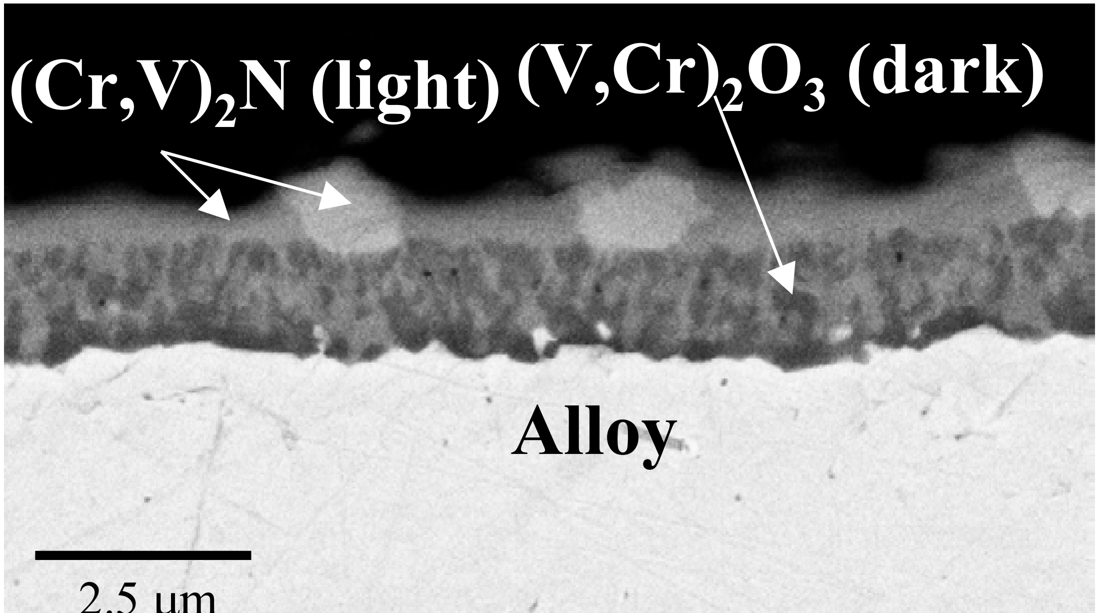
Auger Electron Spectroscopy of Nitrided Fe-27Cr-6V



- 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, **<u>oxygen present</u>** in surface

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

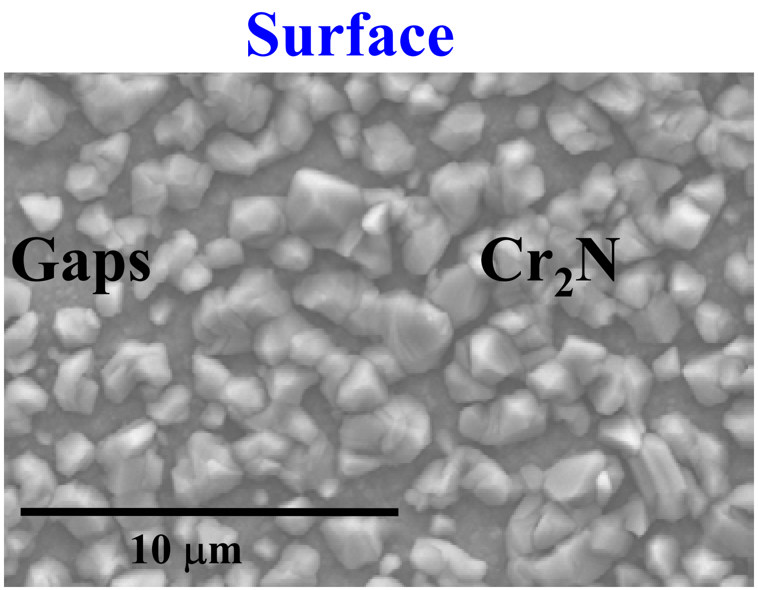
Cross-Section of Fe-27Cr-6V wt.%, 900°C, 24 h, N_2-$4H_2$

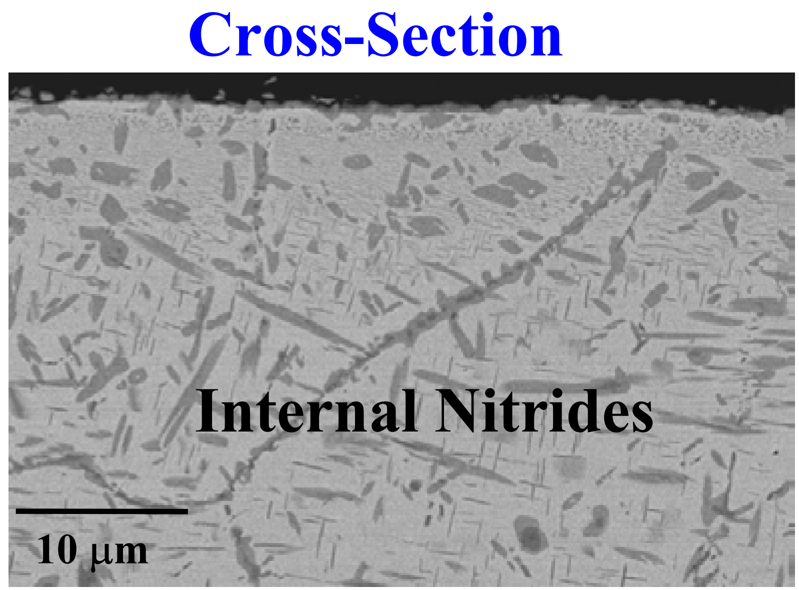


- O_2 Impurity level in nitriding gas sufficient to form oxides
- Nitrogen stayed at surface, no internal nitridation
- $(Cr,V)_2N$ overlying mixed $(V,Cr)_2O_3$ + $(Cr,V)_2N$ at 900°C

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-$4H_2$



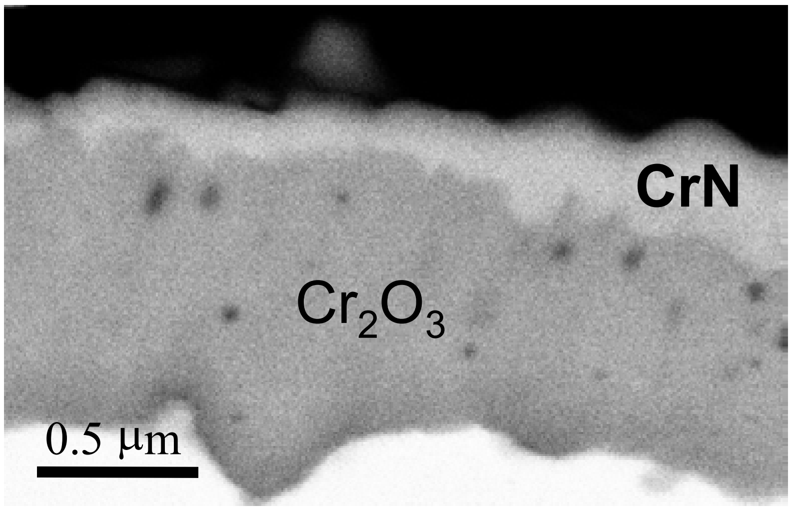


- Indicates O_2 impurity/oxide formation favors dense Cr-nitride surface formation by reducing N_2 penetration into the alloy
- Variations in O_2 impurity level cause of initial repeatability issues

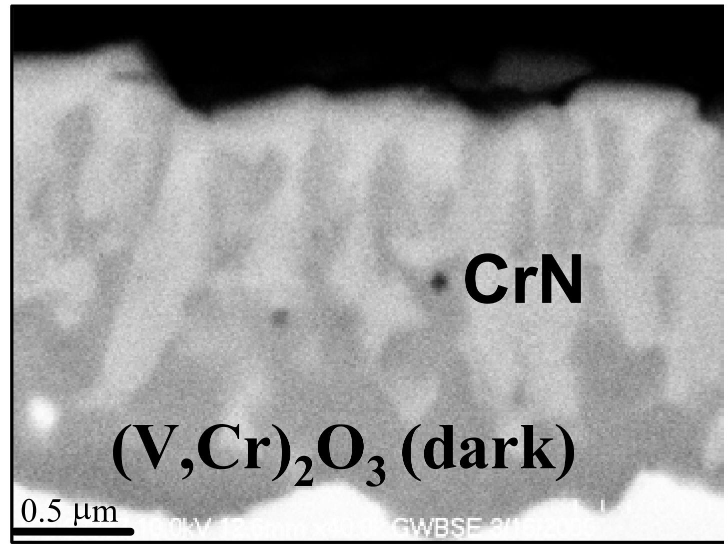
Initially Formed Oxide Converted to Nitride: Easier with Vanadium

SEM Cross-Sections after 24 h at 850°C in N_2-$4H_2$

Fe-27Cr



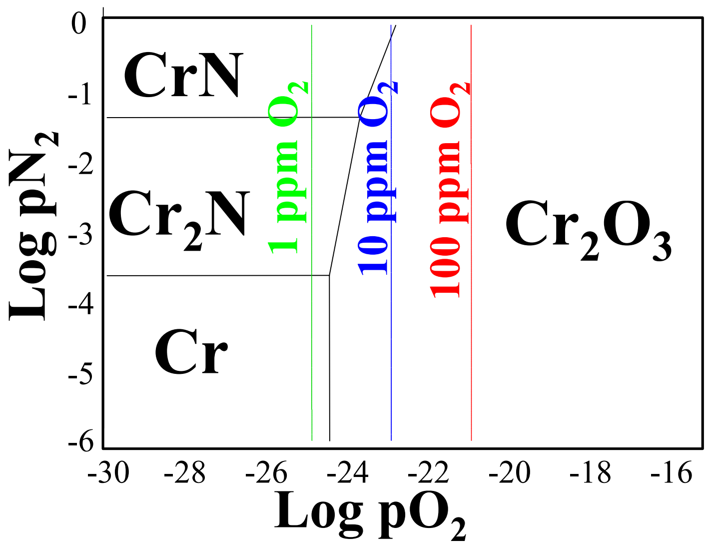
Fe-27Cr-6V

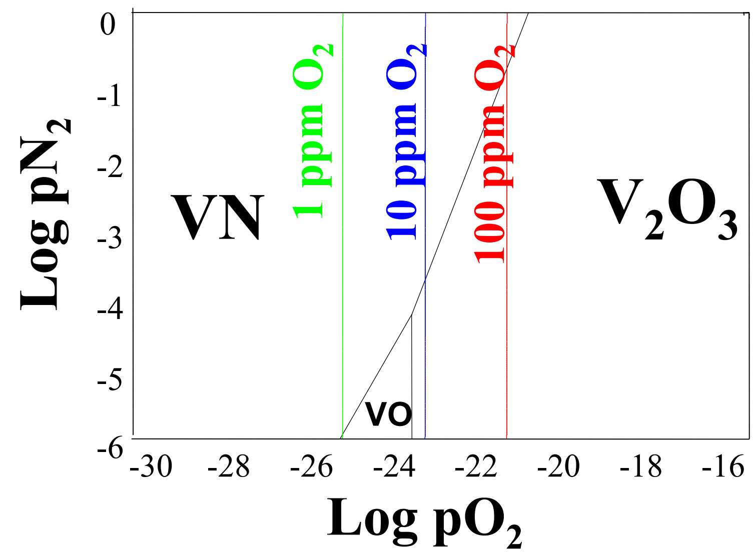


- Oxide formed initially during heat up followed by conversion to nitride
  - -V and Cr co-segregate into initially-formed $(V,Cr)_2O_3$ oxide
  - -V addition adds extra degree of freedom- intermixed morphology
- Nitrided Fe-27Cr showed inadequate corrosion resistance due to many non-uniform areas and 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 N_2-$4H_2$ (100 vs 10 ppm O_2)
- V works because Cr_2O_3-V_2O_3; Cr_2N-V_2N; 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 ≤ 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) $3/lb Alloy	$5/lb Alloy	$7/lb Alloy
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 cm^2 active area plate (494 cm^2 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 nitrided 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 nitrided Ni-Cr plates run with collaborators
  - -Establish limits of Cr-nitride by cycling nitrided 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 nitrided Ni-Cr alloys indicates good performance and durability of thermally grown CrN/Cr_2N 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, V_2O_3 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 Comercial 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, Cr_2N 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 349™ 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. 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 Antonio, TX, March 15, 2006
2) (Invited) 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.
3) 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”, 208th Meeting of the Electrochemical Society, October 22-26, Los Angles, 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.

Since Last Review ↑

5) 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).
6) 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.
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

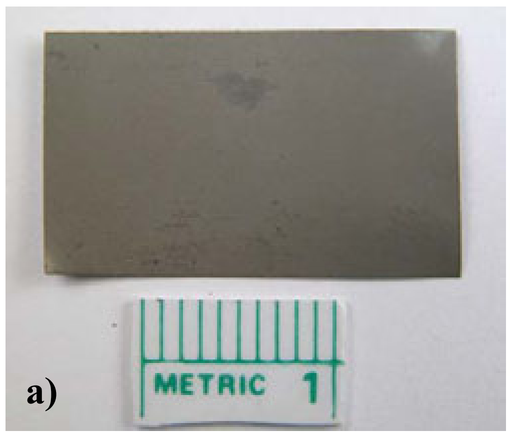
Critical Assumptions and Issues

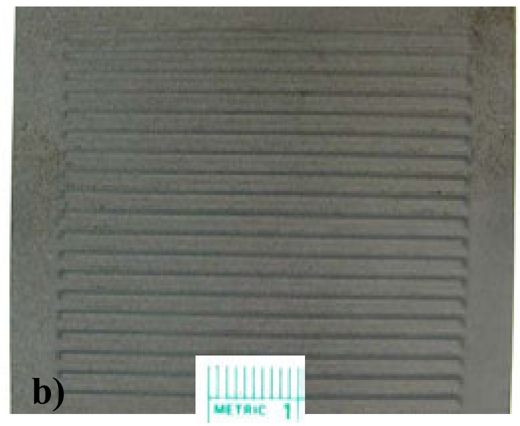
•Potential for warping of thin stamped foil during nitriding

-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°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