Growth of Functional Nitride Surfaces by Alloy Oxidation Processes

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Symposium On Phase Stability & Defect Structures
In Honor Of Professor Austin Chang,
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Why an Alloy Oxidation Talk?

- Among his many research activities, Professor Chang has explored "Controlled Oxidation Processing"

  -***"Selective Oxidation of an Individual Layer in a Magnetic Tunnel Junction Through the Use of Thermodynamic Control"***, Ladwig PF, Yang JJ, Yang Y, Chang YA, Liu F, Pant BB, Schultz AE, Applied Physics Letters Aug 2005

  -Leverages oxygen potential control and the thermodynamic stability differences of metals in oxygen to selectively oxidize ultrathin metal layers

- The present talk will explore thermodynamic and kinetic control of oxidation to synthesize protective nitride surfaces of interest for fuel cells and other electrochemical devices

Why Would You Want to Form a Protective Nitride Layer?

•Many Nitrides (Carbides, Borides) are **Electrically Conductive** and **Corrosion Resistant**

•Of Interest for Fuel Cell and Battery Applications

•Protective Nitride Layer on Metallic Bipolar Plates in Proton Exchange Membrane Fuel Cells (PEMFCs)

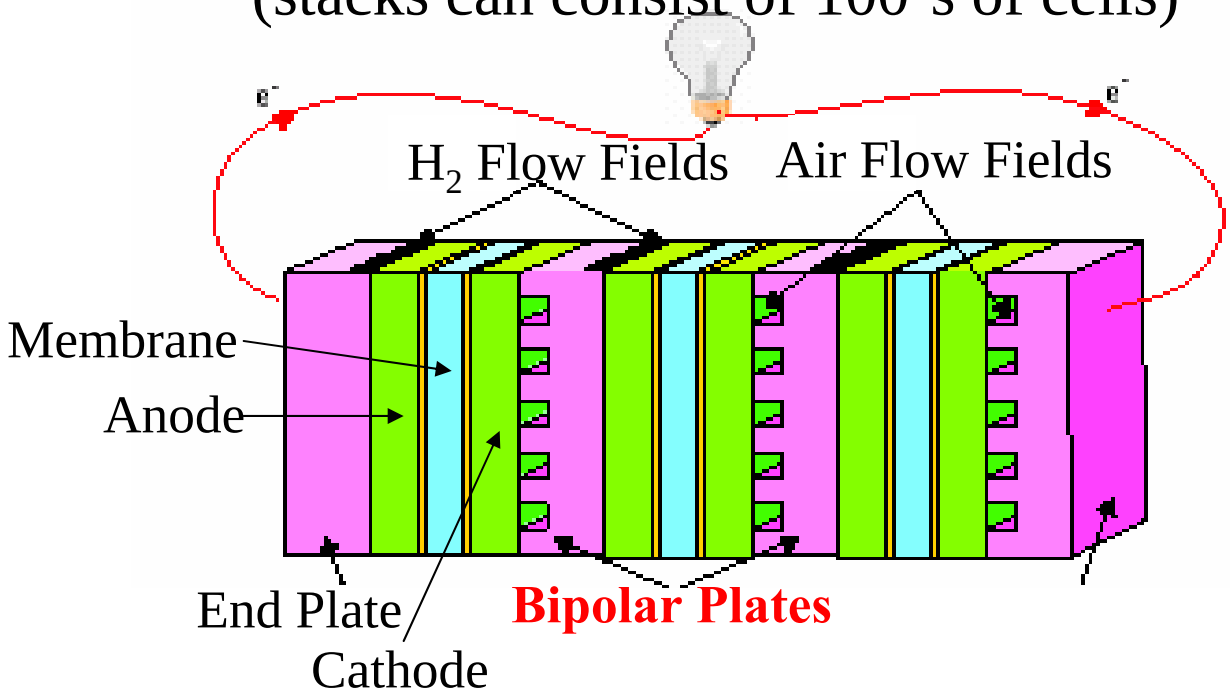
-These are l**ow-temperature** (60-90°C) fuel cells

-Acidic Environment

Bipolar Plates Connect Individual Fuel Cells in a Stack and Separate/Distribute H_2/O_2 Gases

3-Cell Portion of a PEM Fuel Cell Stack

(stacks can consist of 100's of cells)



- Connects anode of one cell to cathode of next, hence "bipolar"
- Same function as interconnect component in solid oxide fuel cells

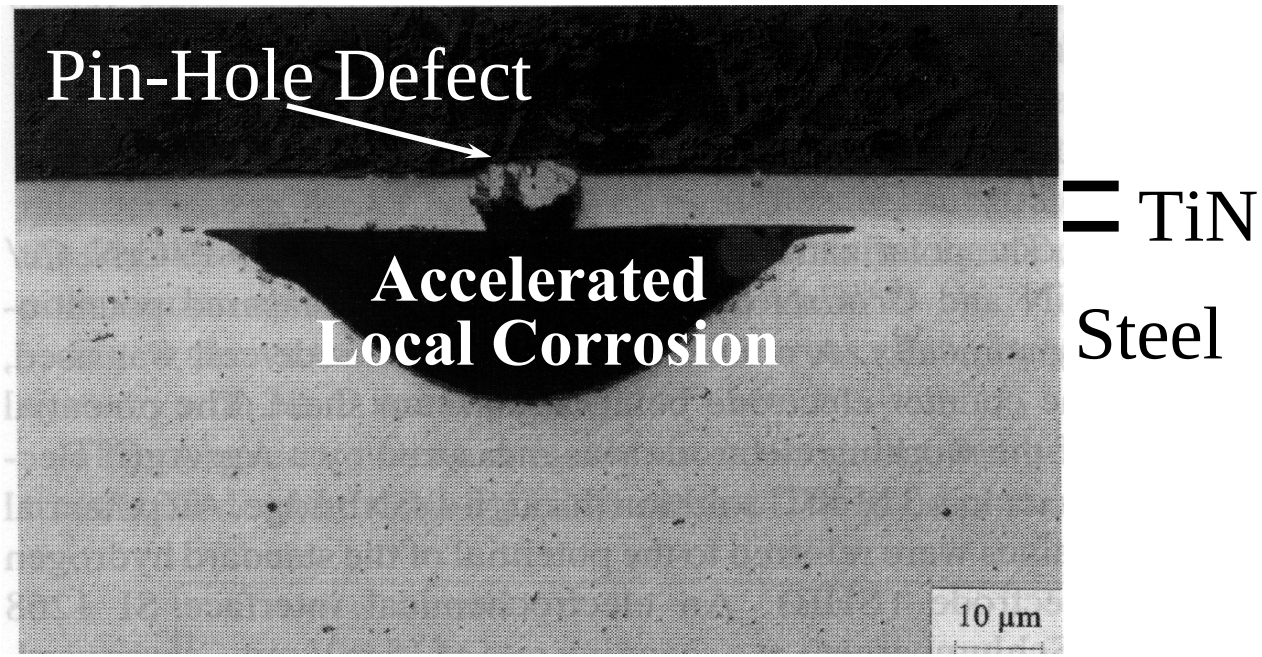
Thin Metallic Bipolar Plates for Manufacturability and High Power Density

- Replacement for Currently Used Graphite Plates
  - -Brittle: thick (low stack power density), expensive to machine
- Problem: Metals Corrode in Acidic Fuel Cell Environments
  - -Cathode side: oxides that form increase contact resistance
  - -Anode side: metal ion dissolution contaminates membrane
- Nitrides are Candidate Protective Coatings for Metal Bipolar Plates
  - **-Our Goal is to Form a Protective Nitride Coating by Selective Oxidation**

Why Not Just Deposit a Nitride Coating?

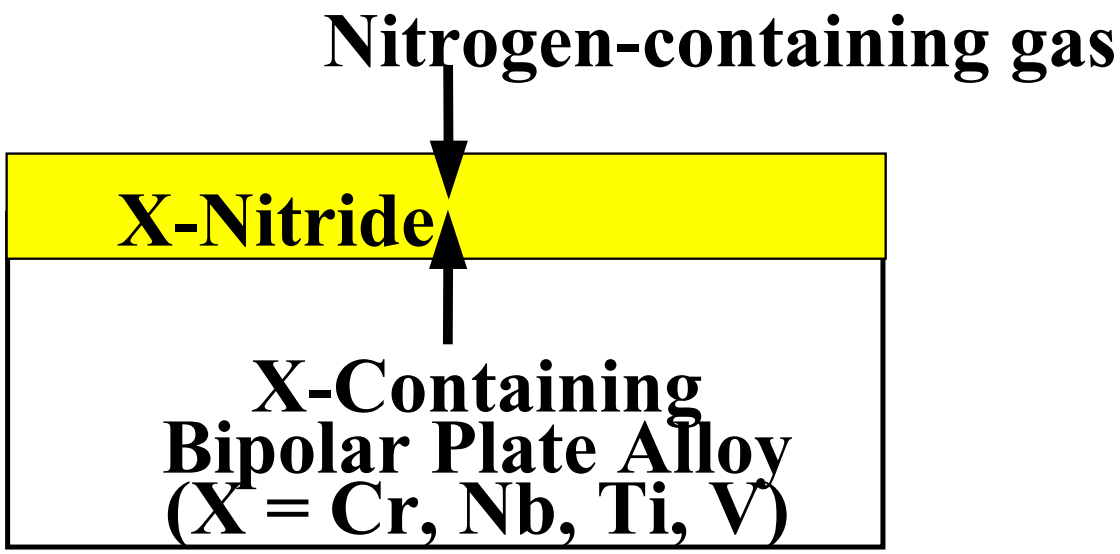
Deposited Coating Methods Typically Leave Pin-Hole Defects

Accelerated Local Corrosion in TiN Coated Steel
(Brandl and Gendig,1996)



- Pin-holes result in unacceptable corrosion resistance
  - -ppm levels of metal ions can degrade polymer membrane
- Good coverage of bipolar plate flow field grooves also difficult

Selective Nitridation to Yield Dense, Pin-Hole Free Coatings

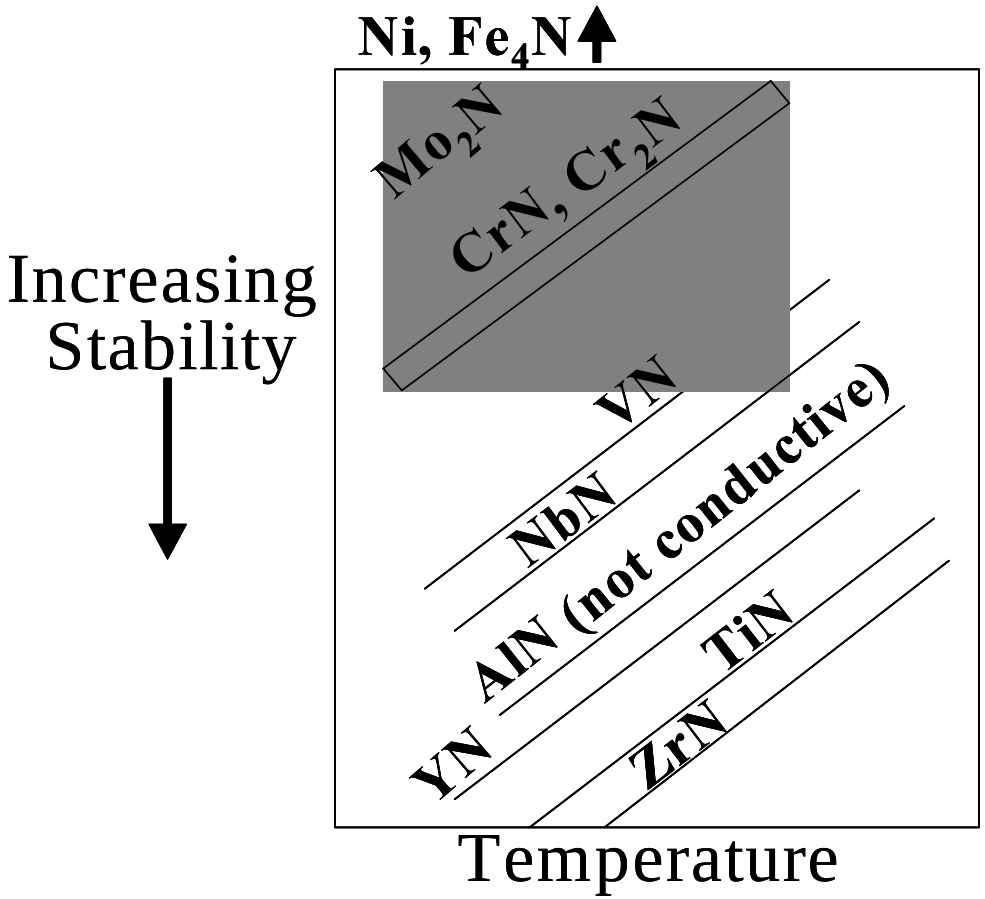


- High Temperature Favors Reaction of All Exposed Metal Surfaces
  - -No pin-hole defects
  - -Amenable to grooves/edges (not line of sight limited)
- Challenge is Getting External Scale of Desired Composition to Form

How Do We Design an Alloy to be Nitrided?

Nitride Formation on Ni- and Fe- Base Alloys

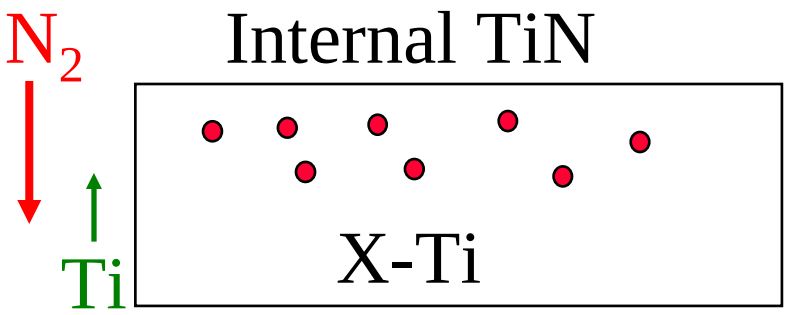
Schematic Ellingham Diagram for Nitridation

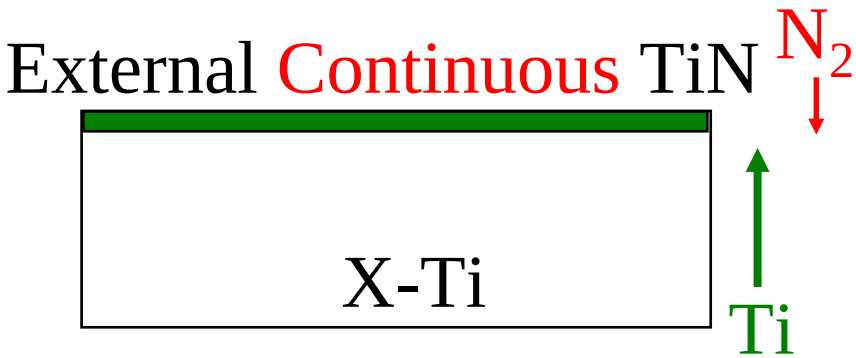


- Nitride-forming additions of Cr, Nb, Ti, V, Zr to Ni/Fe
- Nitridation from 800-1200°C in N_2 and N_2-$4H_2$

Kinetics: Alloy Design From Flux Criteria (Classical Wagner Oxidation Theory)

Shown for TiN: Holds for Any Nitride, Oxide, etc.





$$\text{Minimum Ti for Continuous TiN} \propto \left[N_{solubility} * \frac{N_{diffusivity}}{Ti_{diffusivity}} \right]^{1/2}$$

- Key is continuity: **continuous = protective**

- Continuous TiN favored by alloy additions/reaction conditions that decrease nitrogen permeability or increase Ti diffusivity

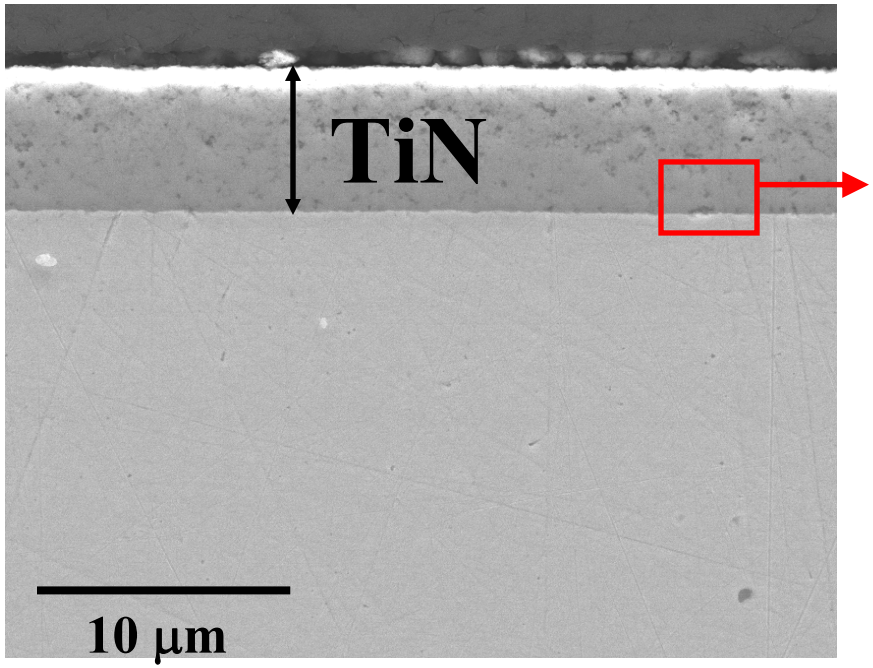
Nickel Ideal Alloy Base at Proof of Principle Stage

- Unstable nitride (won’t interfere with nitride-forming element we add to the alloy)
- Low permeability to nitrogen - favors formation of external nitride
- Ductile

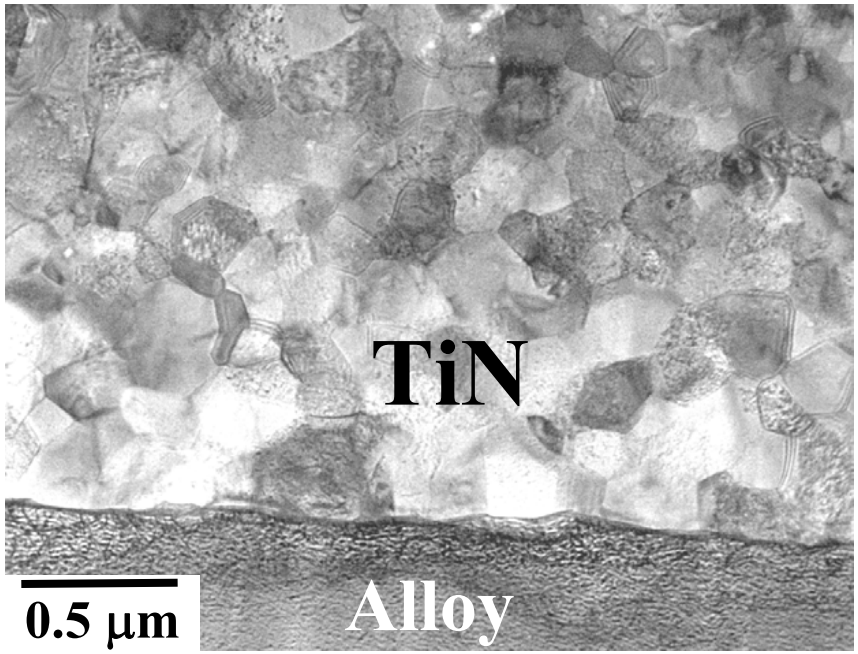
Initial Efforts Yielded Continuous TiN Surface Layer on a Model Ni-Ti Alloy

Ni-10Ti wt.%, 1100°C, 48 h, N_2

SEM



TEM

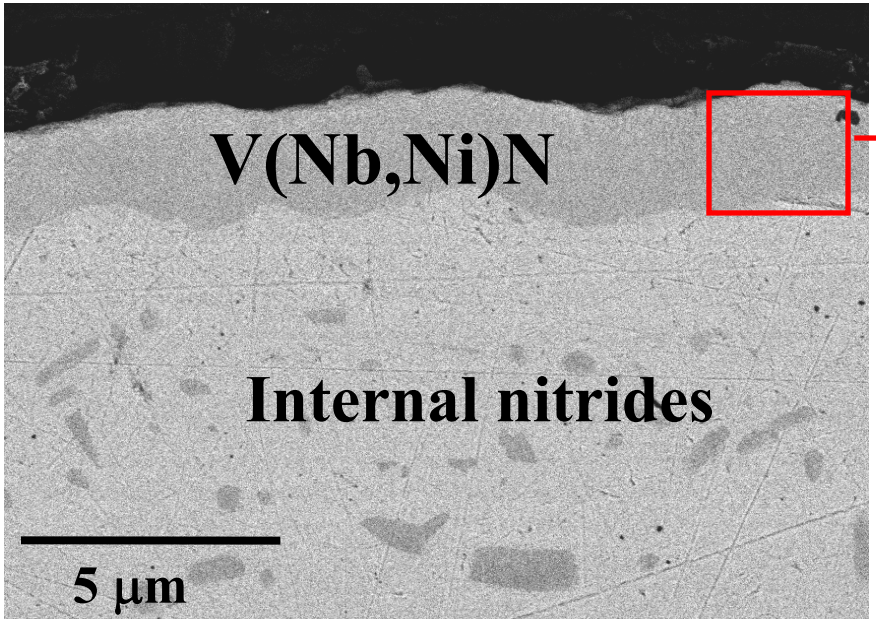


- Equiaxed TiN: 0.1 – 0.3 μm grain size and ~ (45-50) at.% N
- Strong driving force to form TiN on Ni-Ti alloys by gas nitridation- nucleation dominated yields fine equiaxed grains

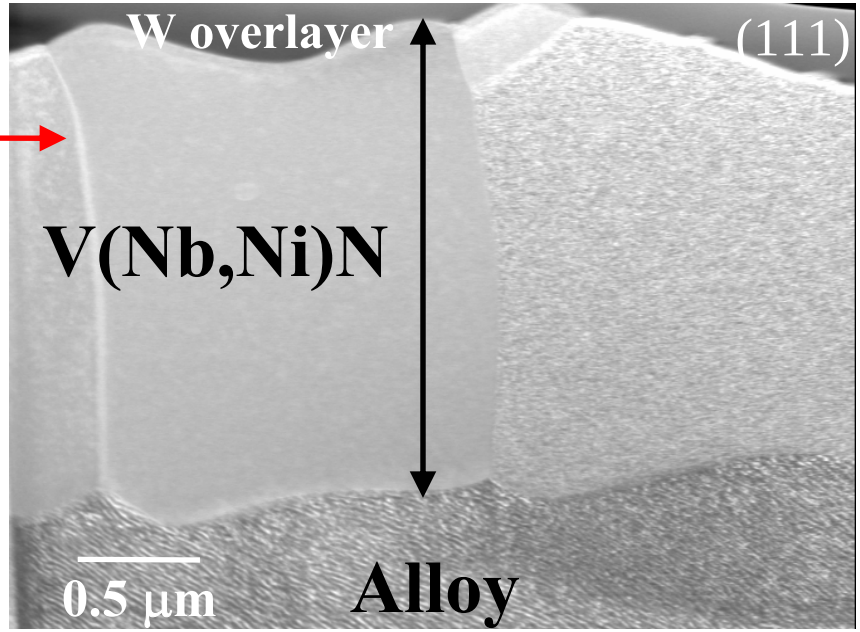
Complex (Multi-Element) Nitrides Also Possible

Ni-10Nb-5V wt.%, 1100°C, 24 h, N_2

SEM



STEM

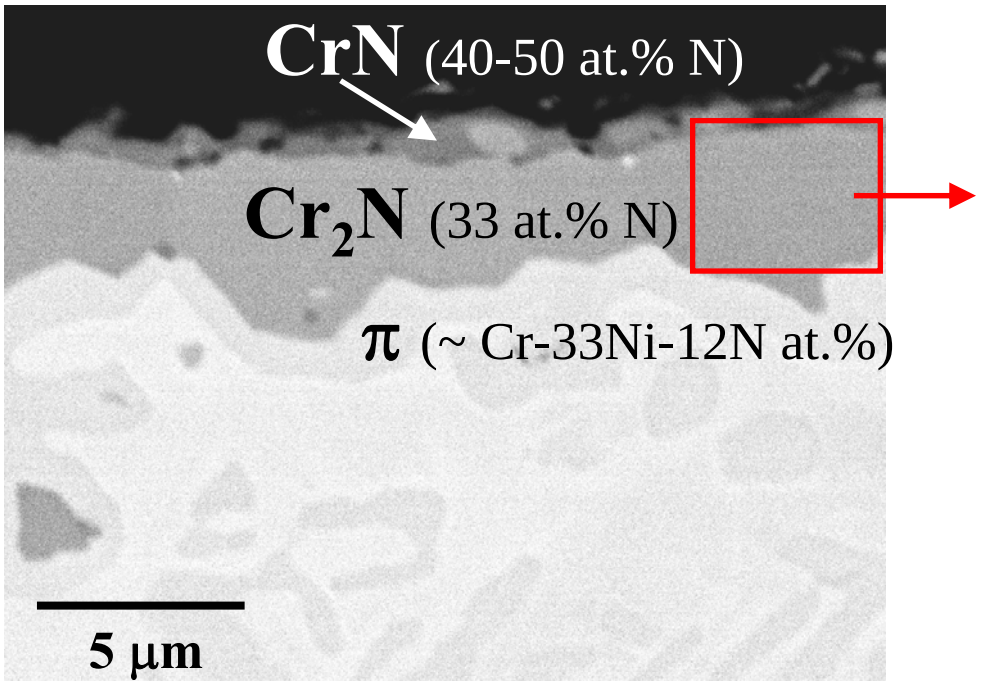


- Complex nitride directly formed (likely a solid solution)
  - -Scale composition: Ni-(12-15)V-(15-20)Nb-(20-30)N at.%
  - -Ni matrix and V(Nb,Ni)N both FCC (Fm3m)
- Point: Wide variety of nitrides (carbides, etc) accessible as surface layers by alloy/gas reactions

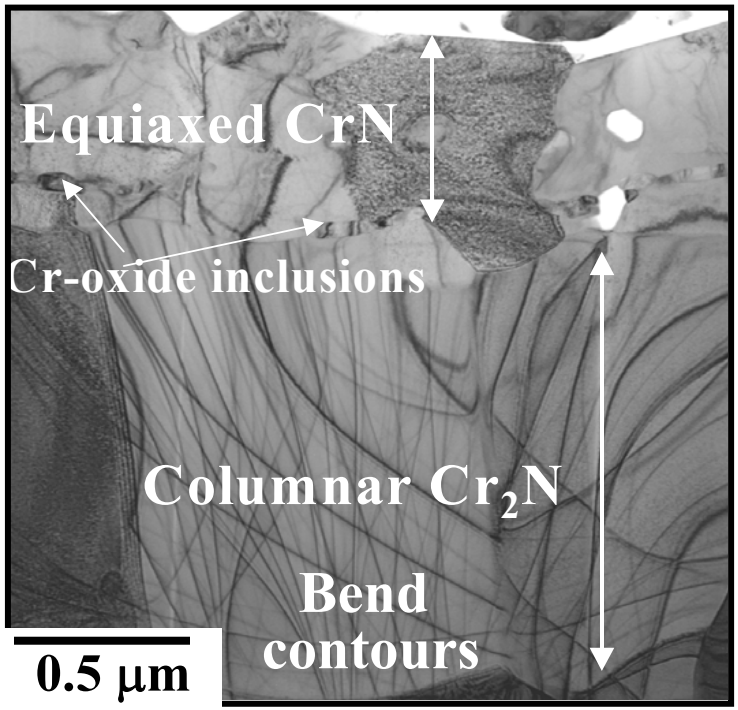
Best Success in PEMFC Environments by Nitridation to Form CrN/Cr_2N Surfaces

Model Alloy: Ni-50Cr wt.%, 1100°C, 2 h, N_2

SEM



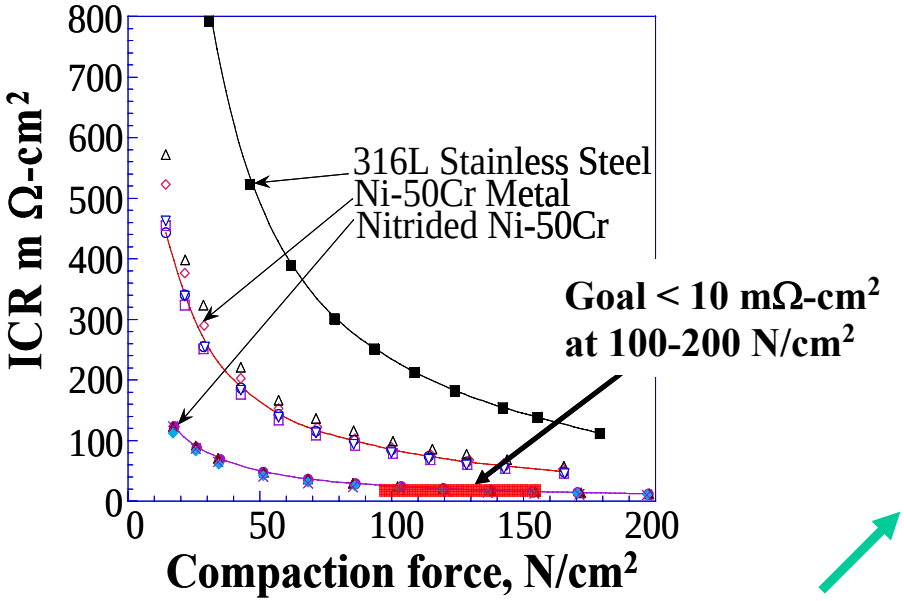
STEM



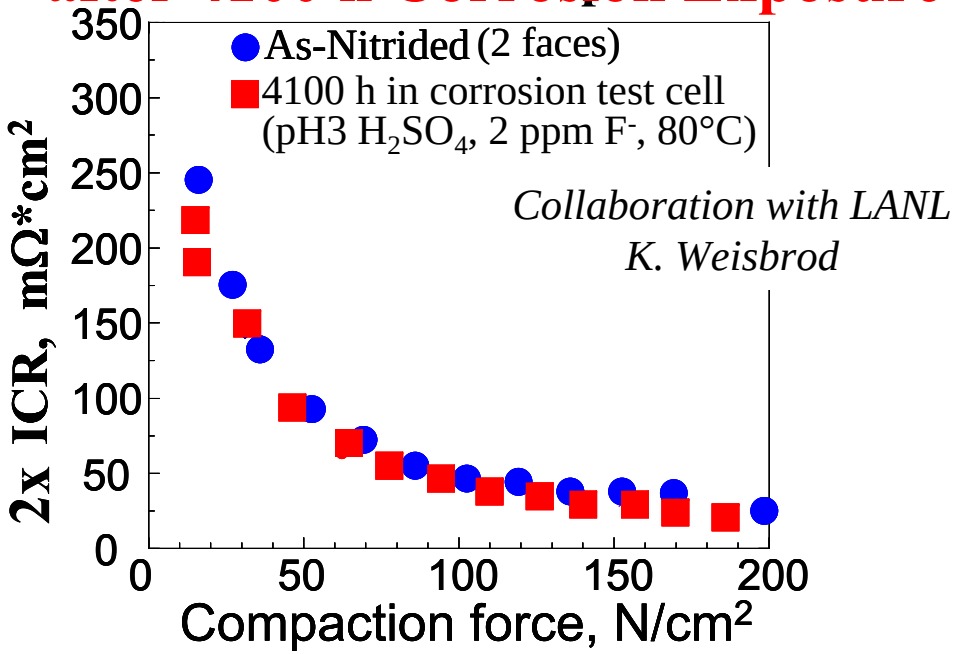
- Need > 30 wt.% Cr to form external Cr-nitride on Ni-Cr
- Inward growing and adherent nitride layer

CrN/Cr_2N Surface on Nitrided Ni-50Cr Exhibits and Maintains Low Contact Resistance

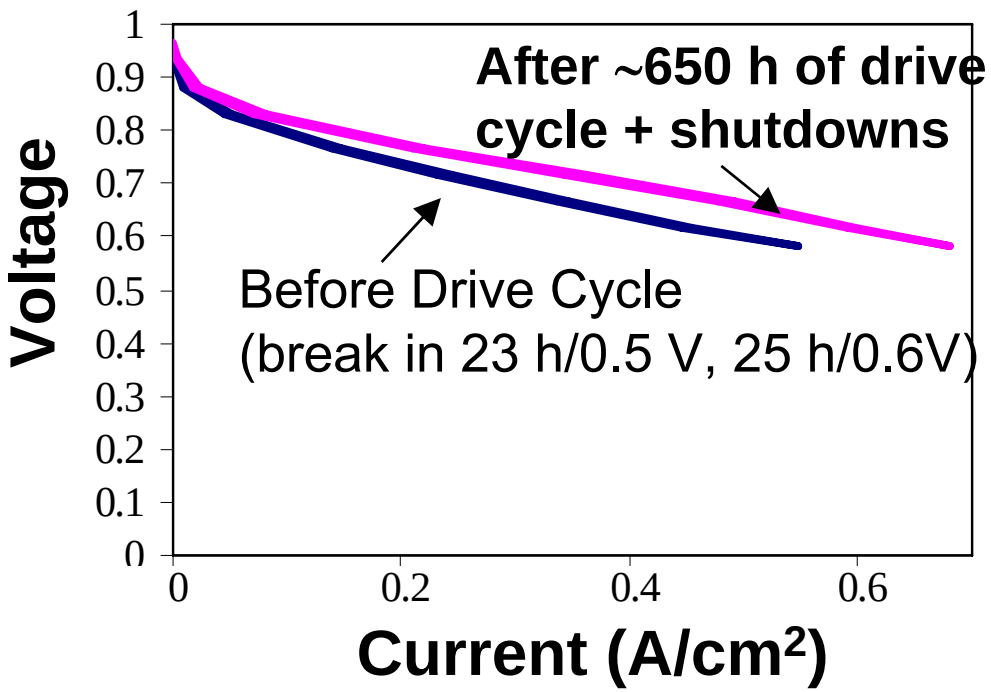
Low Initial Contact Resistance



No Contact Resistance Increase after 4100 h Corrosion Exposure



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 significant attack of the Cr-nitride

Need Fe-Base Alloys to Meet $5/kW Bipolar Plate Cost Goals for Automotive Applications

- **Commercial Ni-30Cr Base Alloys in Range of ~$20-40/lb- far too expensive**

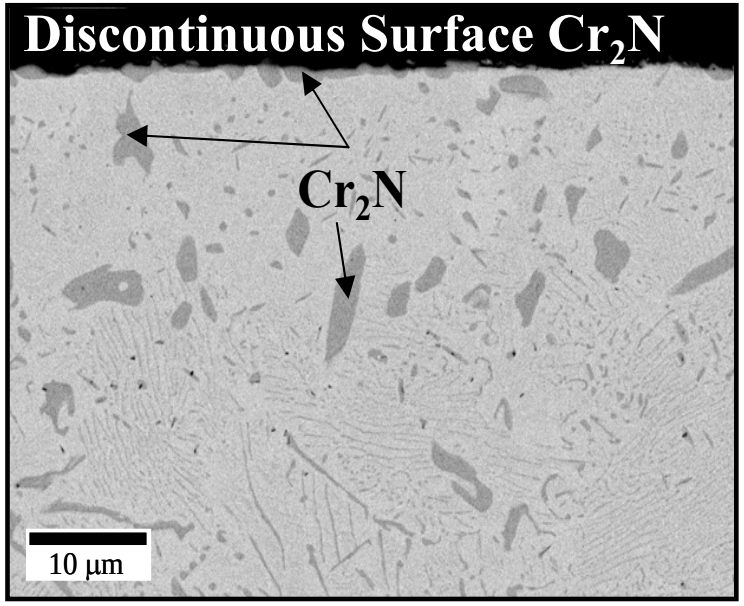
- **Fe-(15-30)Cr Base Alloys in Range of ~$2-10/lb**

- **Meeting Cost Goals Will Depend on Use of Thin Stamped Foil (less material/lower cost)**

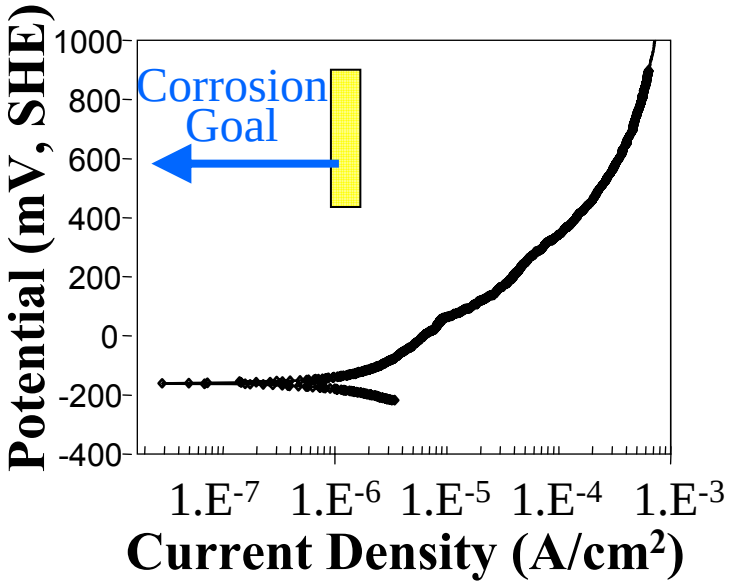
- **Initial Focus on Ferritic Stainless Steels**
  - -Little to no Ni so relatively cheap ($3-7/lb range)

Problem: Ferritic Stainless Steels are Internally Nitrided

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



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



- High alloy N_2 permeability prevents dense Cr-nitride surface formation
  - corrosion resistance is poor

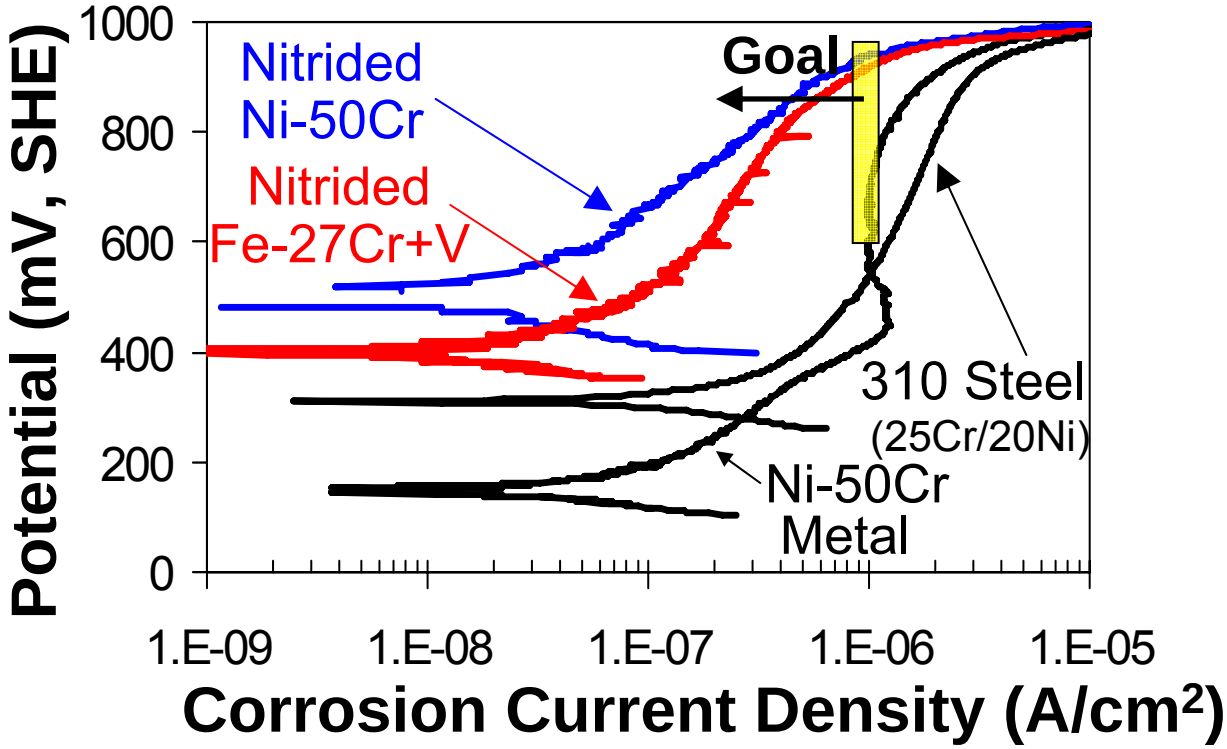
Study Initiated of Nitridation of Fe-27Cr Base Alloys to Form a Dense Cr-Nitride Surface

- Nitridation as a function of alloy additions to Fe-27Cr
  -Al, Mn, Mo, Nb, Ni, Si, Ti, V, Zr

- Systematic variation of nitridation temperature, nitrogen partial pressure, and oxygen impurity level

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

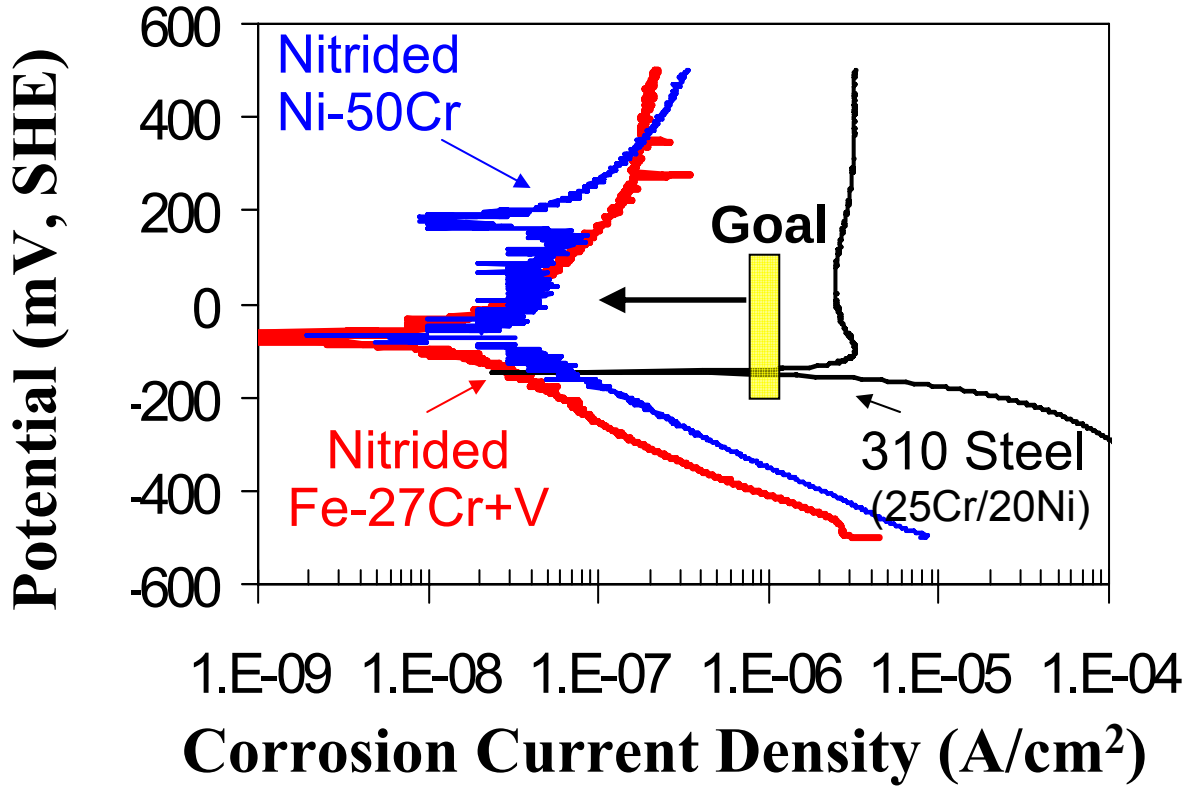
Polarization in Aerated pH 3 Sulfuric Acid at 80°C



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

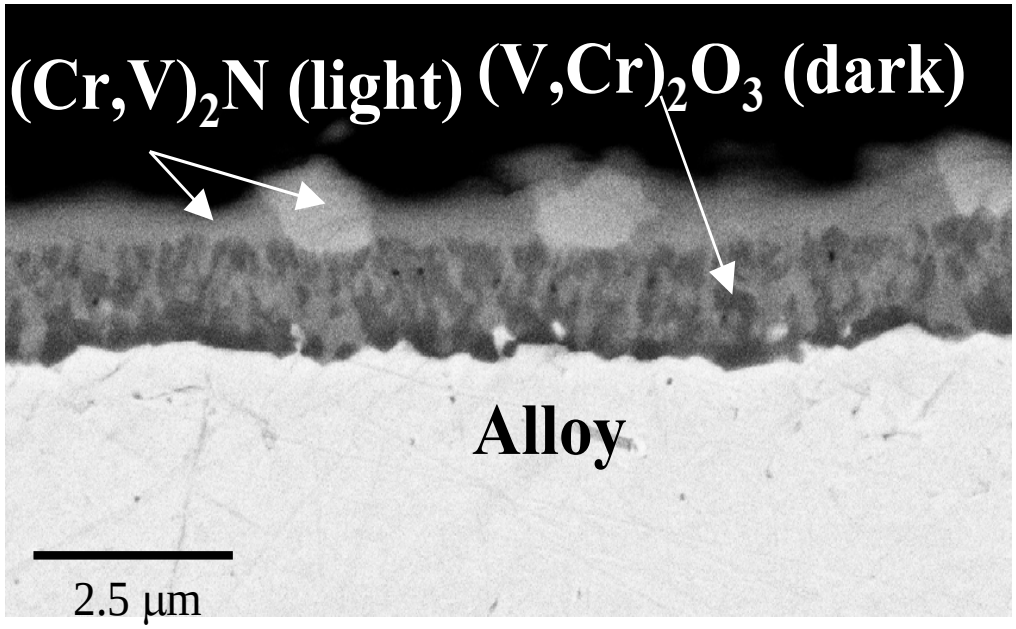
Good Corrosion Resistance Also Observed Under Simulated Anode Conditions

Polarization in Ar-4H_2 Purged pH 3 Sulfuric Acid at 80°C



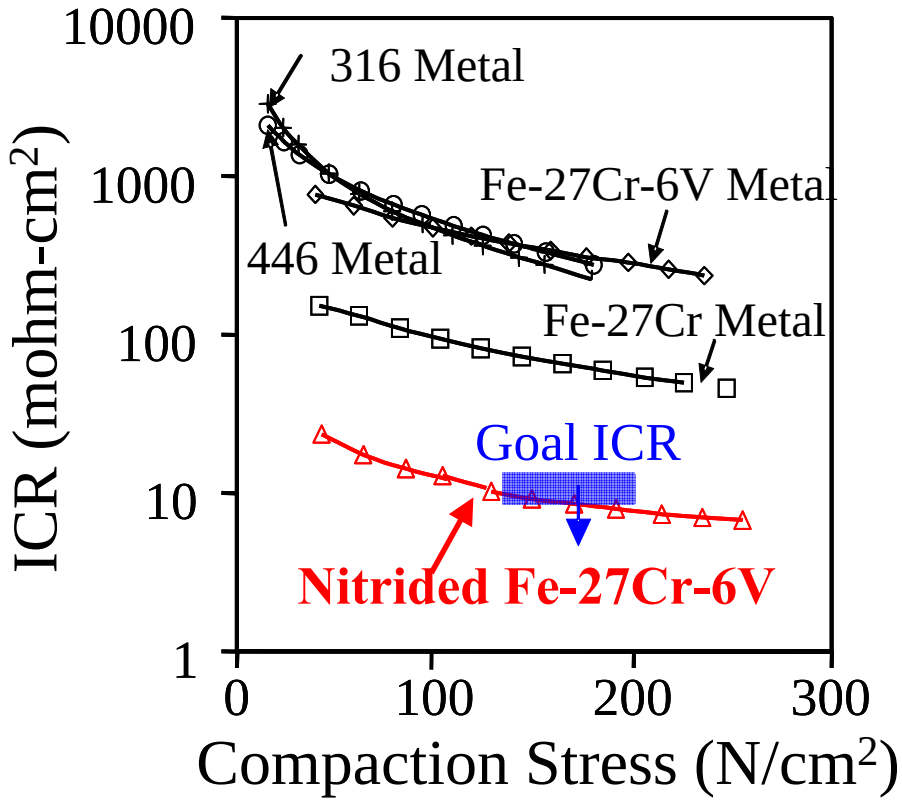
Surface Layer on Nitrided Fe-27Cr-6V Contained Nitrides and Oxides

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

Nitrided Fe-27Cr-6V Meets Contact Resistance Goal Despite Oxide

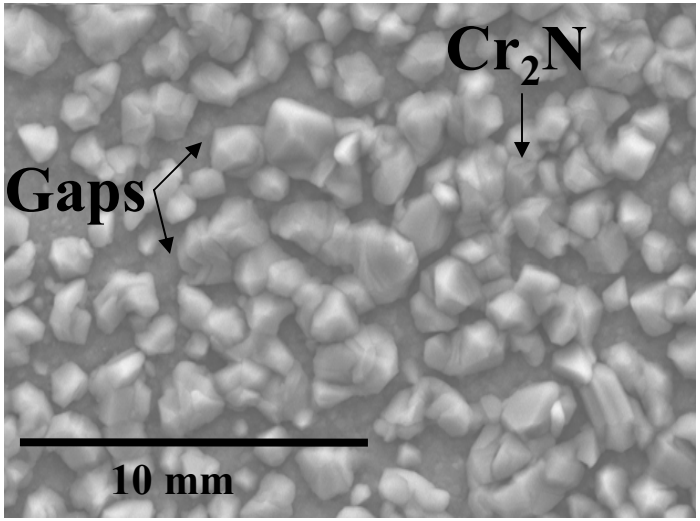


- V_2O_3 is electrically conductive
- AES suggests $(V,Cr)_2O_3$ phase also contains nitrogen

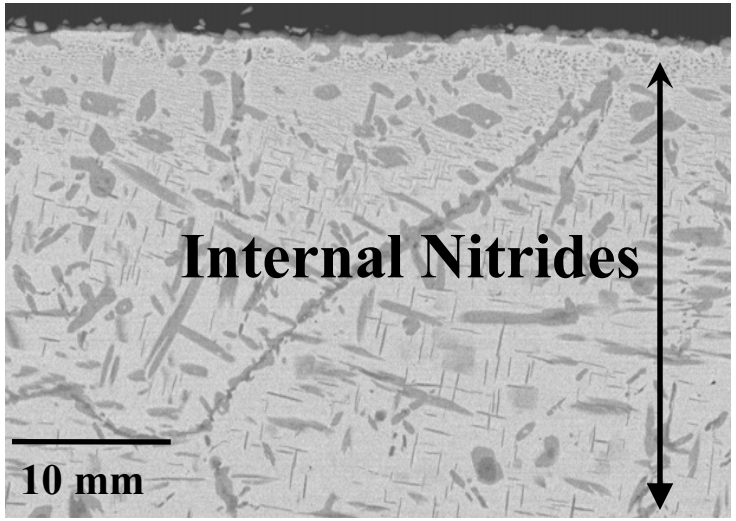
Reducing O_2 in Nitriding Gas Resulted in Surface Gaps/Extensive Internal Nitridation

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

Surface



Cross-Section

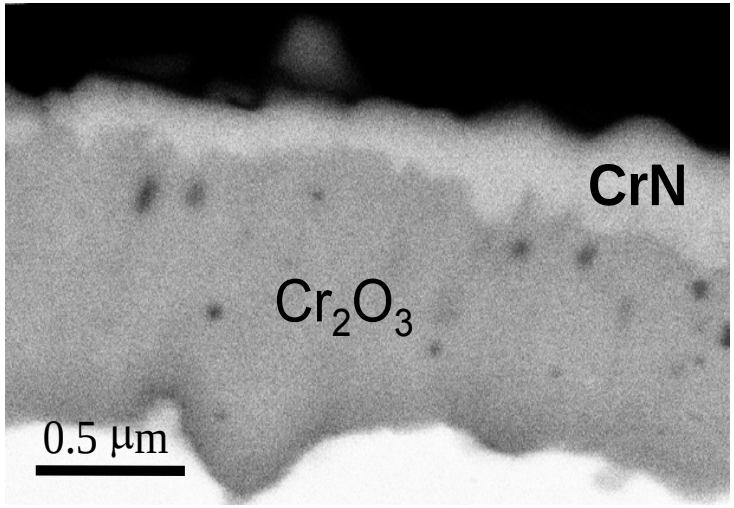


- Indicates O_2 impurity/oxide formation favors dense Cr-nitride surface formation by reducing N_2 penetration into the alloy

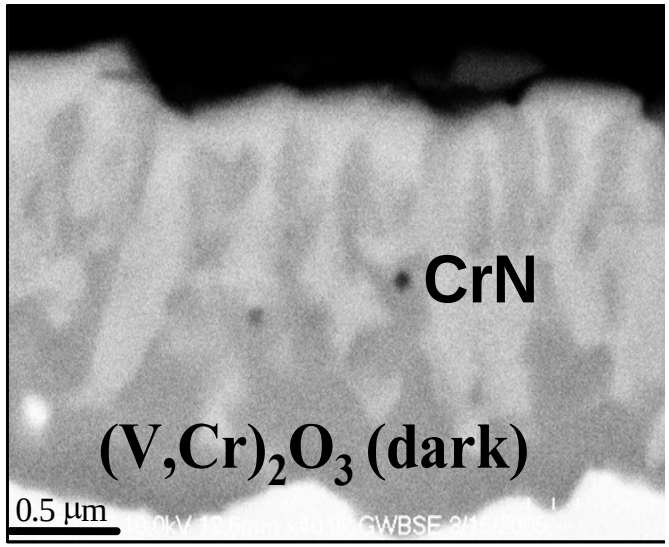
Initially Formed Oxide Converted to Nitride: Easier with Vanadium

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

Fe-27Cr



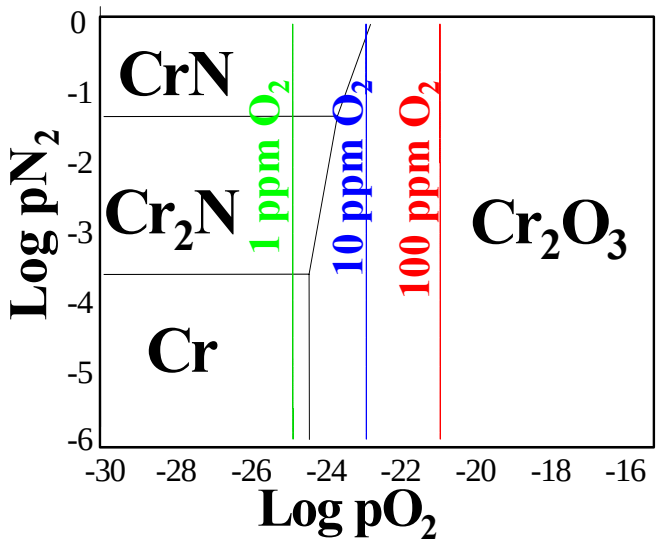
Fe-27Cr-6V

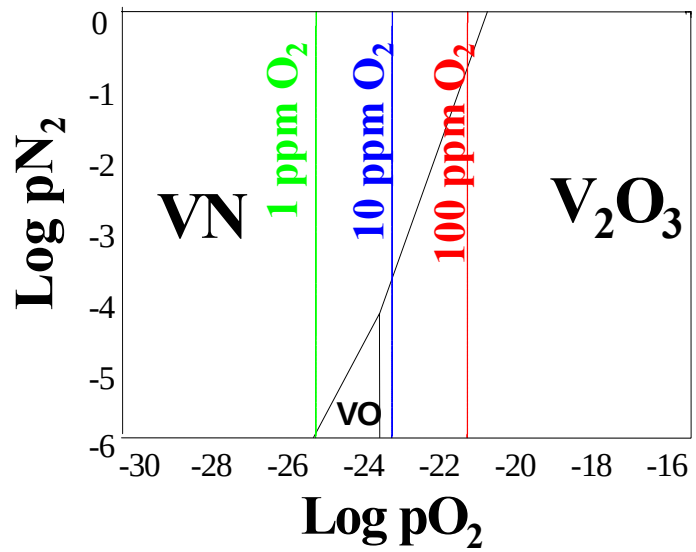


- Oxide formed initially followed by conversion to nitride
- Nitrided binary Fe-27Cr showed inadequate corrosion resistance due to many non-uniform areas and thin spots: sluggish conversion of oxide

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

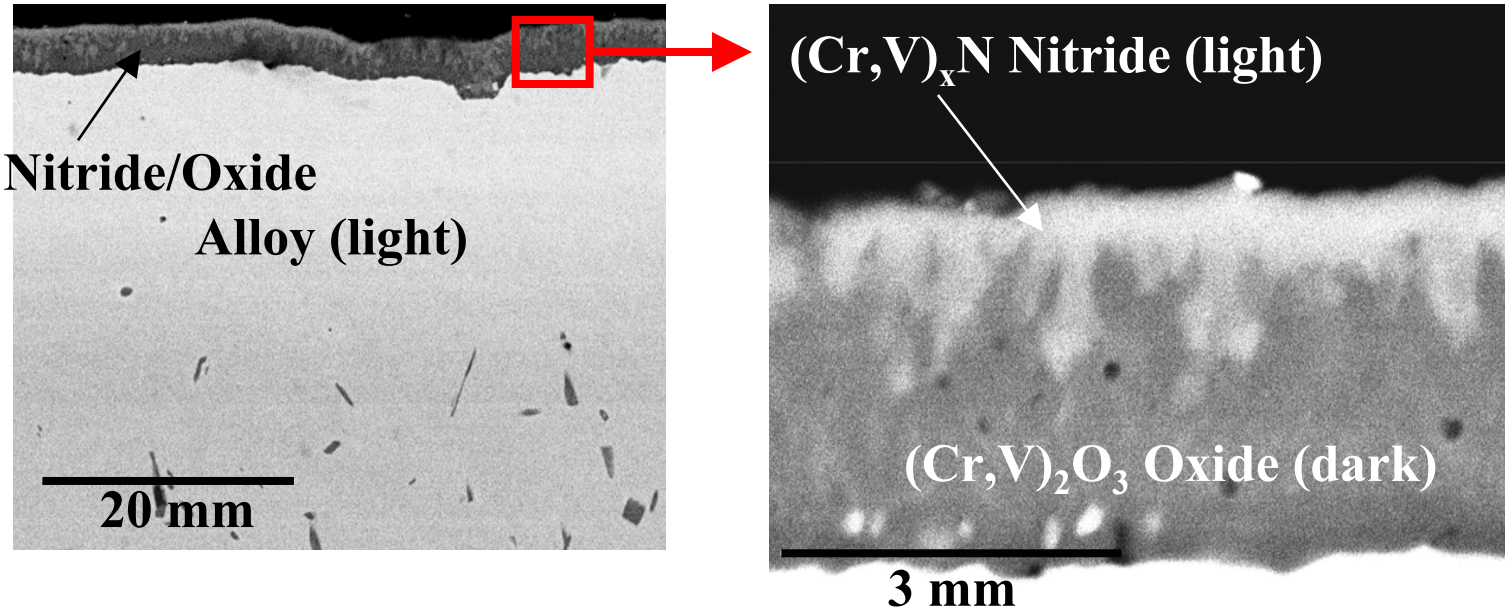
Insights for Alloy/Nitridation Optimization

- 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

- Positive early results with pre-oxidation followed by nitridation
  - -800-900°C, < 2h to form oxide (want ≤ 0.2-0.5 micron thick)

Dense, Continuous Nitride Surface Obtained via Pre-Oxidation Followed by Nitridation

SEM Cross-Sections of Preoxidized and Nitrided Fe-27Cr-6V



- Similar interpenetrating oxide/nitride morphology to that observed in single-step N_2-$4H_2$+O_2 impurity conditions
- Preoxidation approach can potentially be extended to form nitride phase layers on other alloys with high nitrogen permeabilities

Summary

- Selective nitridation can be used to form dense, continuous nitride surface layers (analogous to protective oxide scale formation)

- CrN/Cr_2N surfaces formed on Ni-50Cr show excellent potential to protect metallic bipolar plates

- High nitrogen permeability of Fe-Cr base alloys can be overcome by preoxidation in combination with V alloying additions
  - -Fe-base alloys low cost, key fuel cell consideration

- Future efforts will focus on scale up and evaluation of stamped and nitrided alloy foils in fuel cell stacks

Congratulations to Professor Chang!

Extra Slides

Stamped Fe-Cr-V Alloys Can Meet $5/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

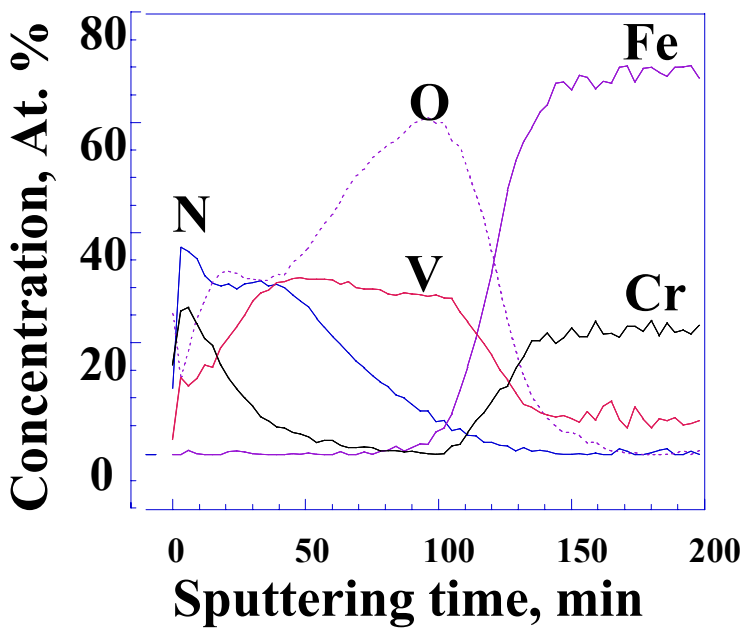
- High Cr ferritic alloys $3-7/lb: **potentially viable nitriding costs**
  - -E-BRITE® (Fe-26Cr-1Mo wt.%): $5-7/lb commercial price for foil
  - -Alloy 444 (Fe-18Cr-2Mo wt.%): $3-5/lb commercial price for foil
  - -Above alloys comparable to Fe-Cr-V alloys as Mo and V costs similar

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

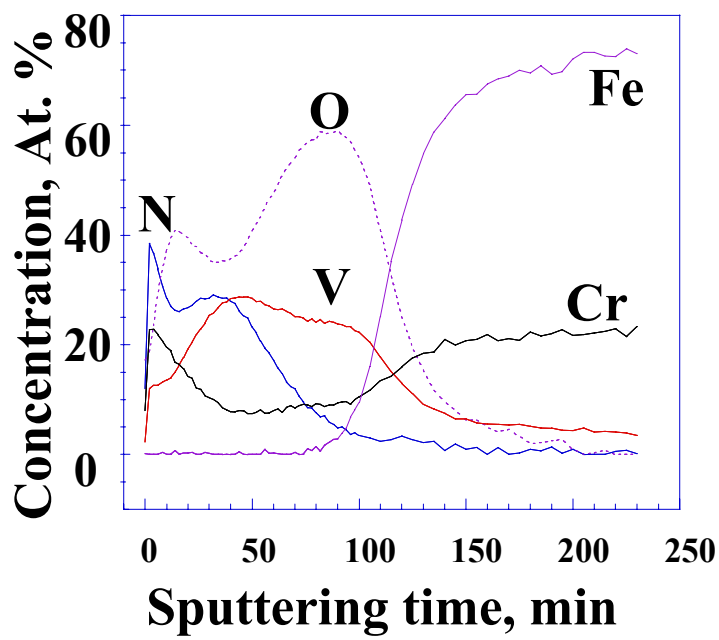
Little Effect of Polarization on Surface Chemistry of Nitrided Fe-27Cr-6V

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

As-Nitrided



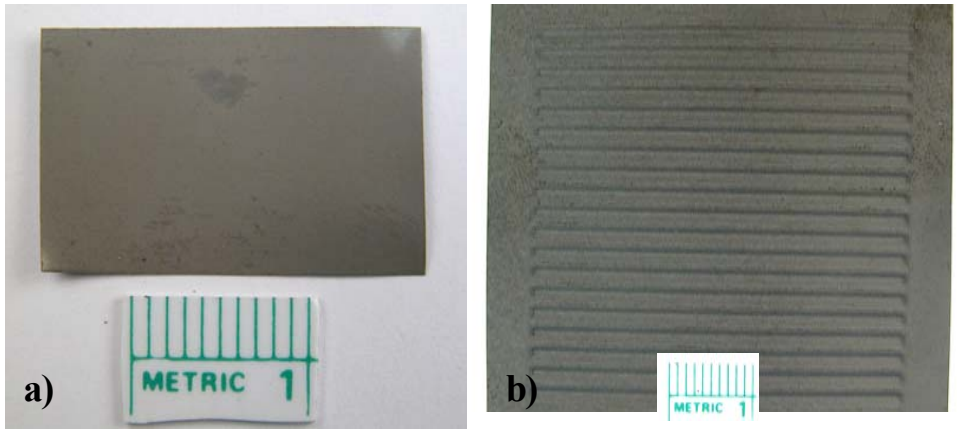
After Polarization



- 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

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)

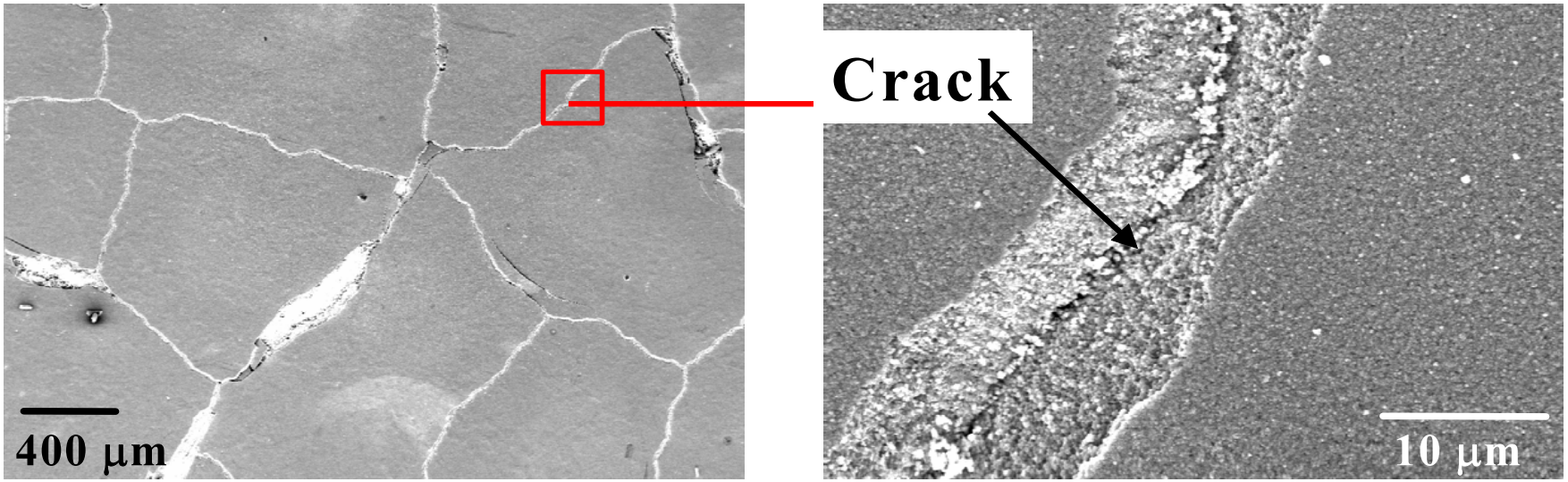
Critical Assumptions and Issues (Cont).

- 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

Local Surface Attack of TiN Layer on Nitrided Ni-Ti and Fe-Ti Alloys

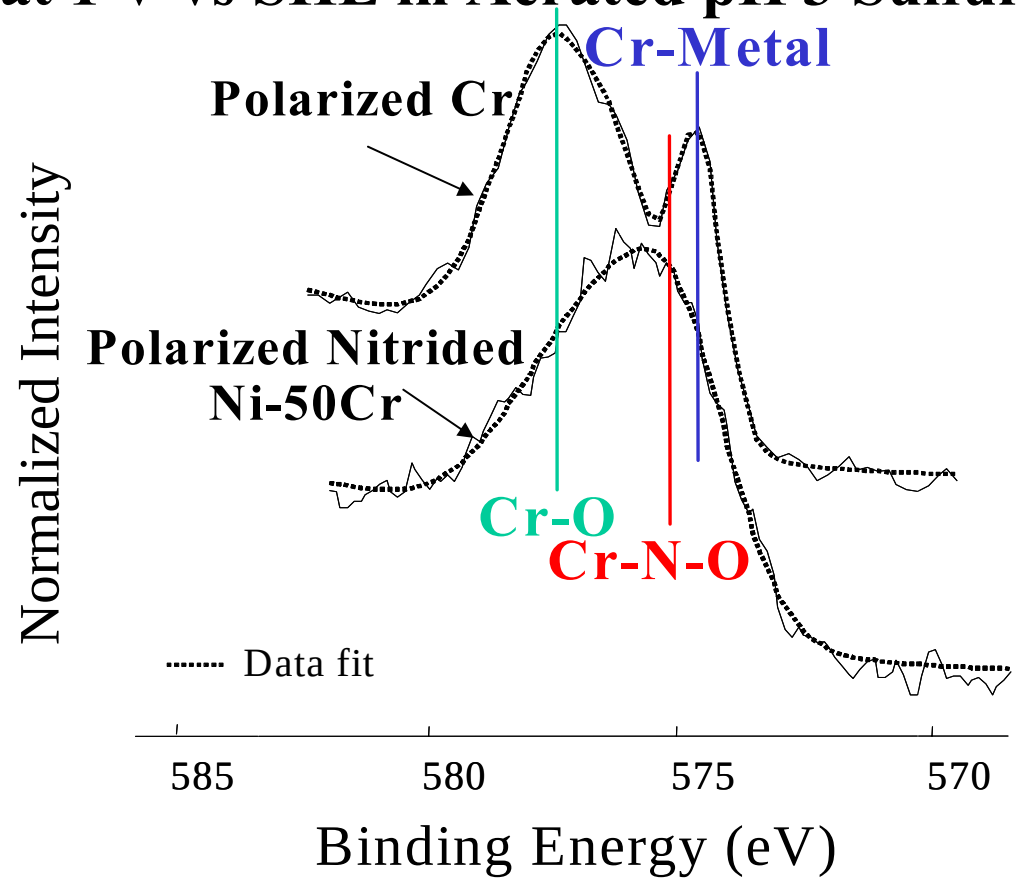
Surface SEM of TiN on Nitrided Ni-10Ti after 1 Week in pH2 Sulfuric Acid at 80ºC



- Suspect stress corrosion cracking type mechanism
- Corrosion rates also high for V(Nb,Ni)N and related nitrides formed on Ni/Fe base alloys in PEMFC environments

Graded "Oxy-Nitride" Formation on CrN/Cr_2N Surface After Polarization

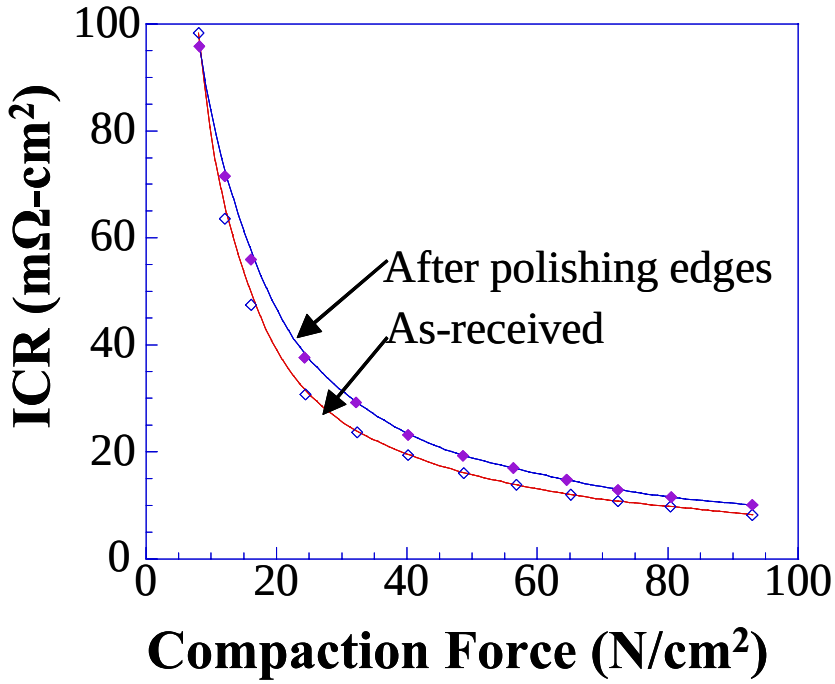
XPS data for Cr Metal and Nitrided Ni-50Cr After Short Term Polarization at 1 V vs SHE in Aerated pH 3 Sulfuric Acid at 80°C



- No increase in resistance for nitrided Ni-50Cr on polarization
- Suggests oxygen incorporation as conductive "oxy-nitride"

No Detrimental Effect of Inner Oxide-Rich Layer on Conductivity Detected

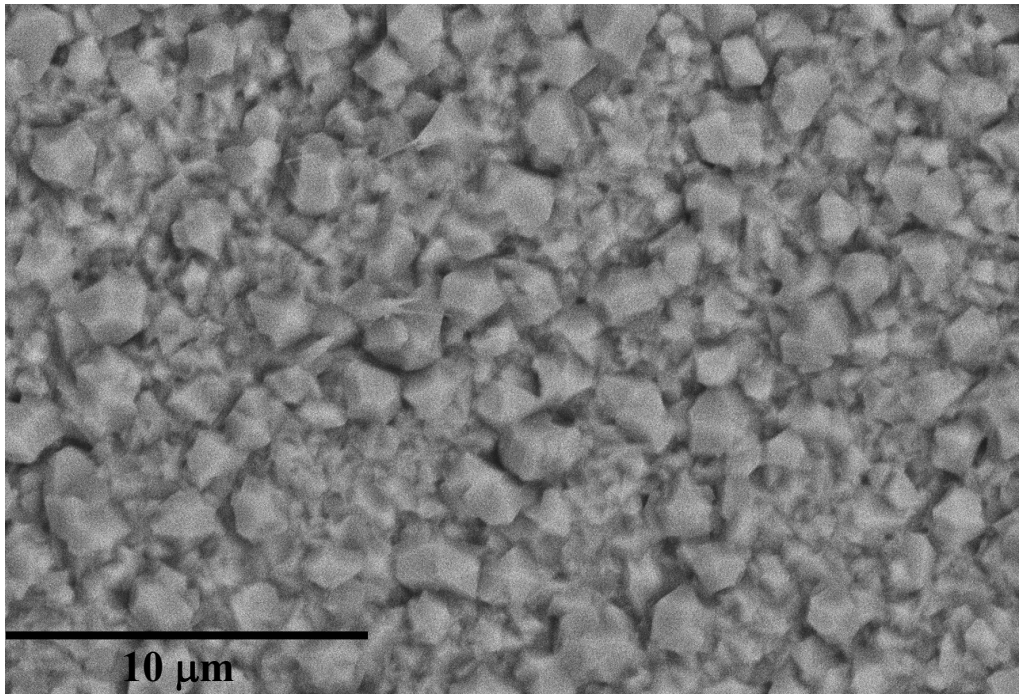
Contact Resistance of Nitrided Fe-27Cr-6V



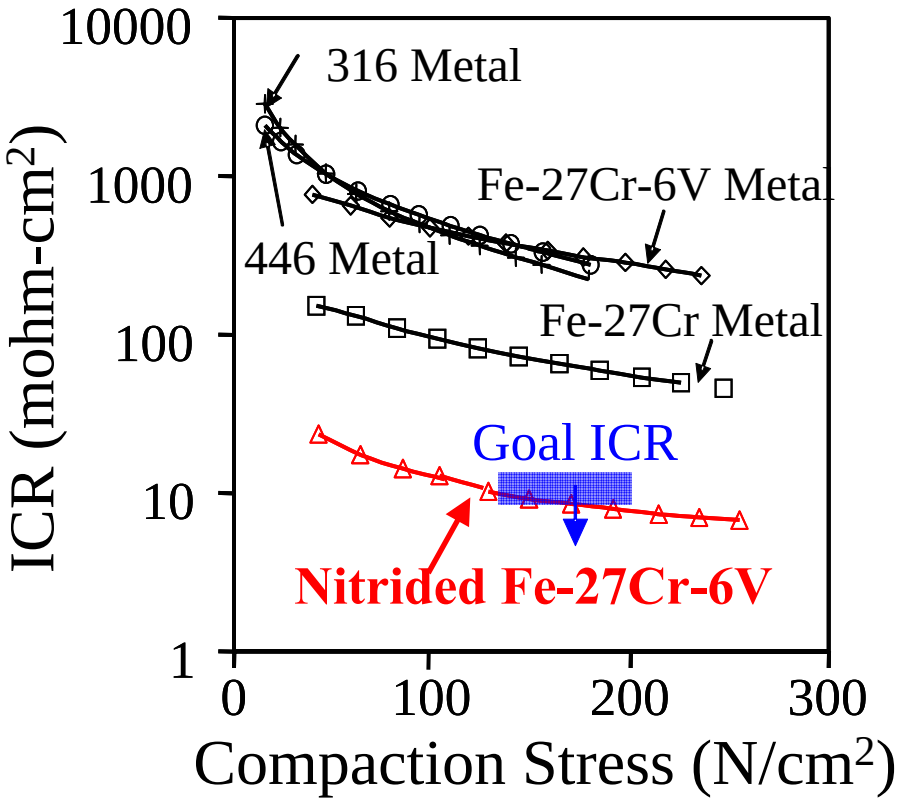
- Nitride at coupon edges removed to reduce possibility of conduction across surface via edge instead of through thickness
  - -difficult to definitively determine
- Suspect many local continuous through thickness nitride paths

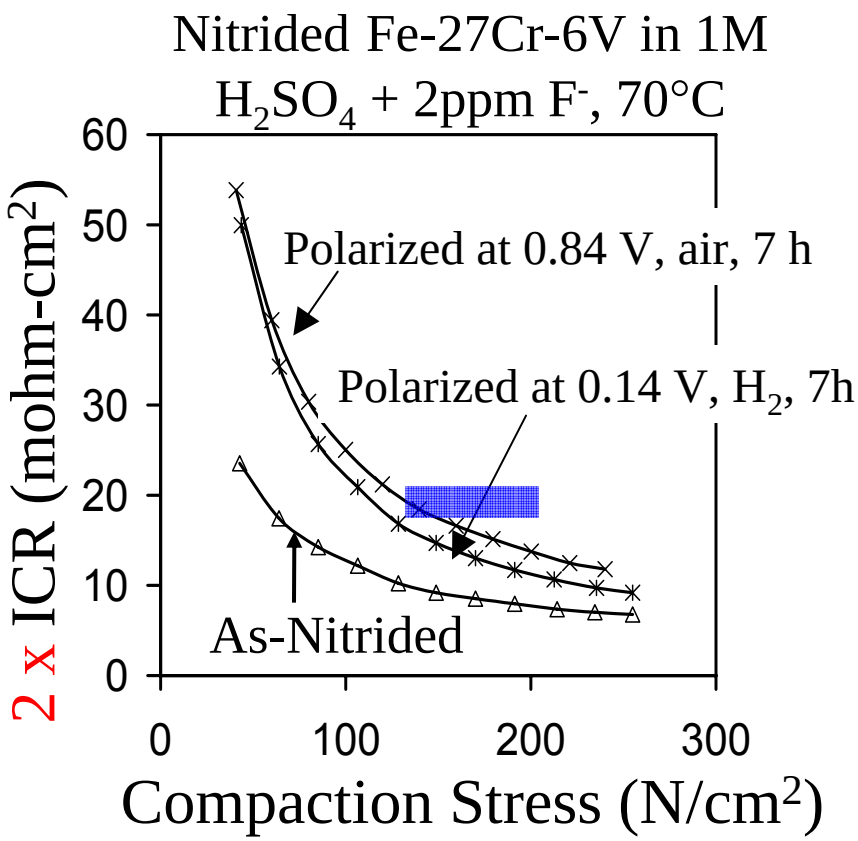
Dense Cr-Nitride Surfaces Most Readily Achieved on V-Modified Alloys

SEM Surface of Fe-27Cr-4Mo-2V After 900°C/24 h/N_2-4H_2



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





- Slight increase in ICR on polarization under aggressive conditions
  - still meets goal