METALLIC BIPOLAR PLATES

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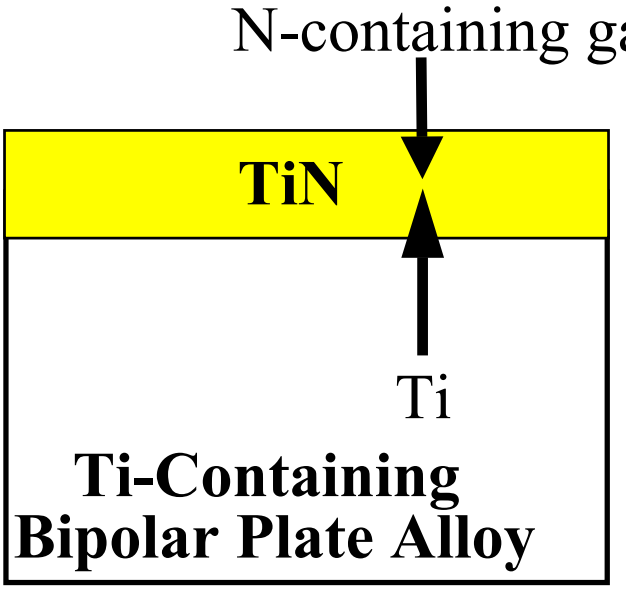
Objective

<u>Develop</u> a bipolar plate alloy which will form an electrical-conductive and corrosion-resistant nitride surface layer during thermal nitriding

Driver: Thin Metallic Plates Offer Potential for Greater Power Density/Performance than Polymer or Carbon Composite Plates

- Better thermal conductivity
- Amenable to high volume manufacturing
- Metals exhibit inadequate corrosion resistance
  - -poison polymer membrane
  - -electrically resistive surface oxides

Approach: Thermally Grown Nitride for Corrosion Protection



- Many metal-nitrides offer both high electrically conductivity and corrosion resistance (e.g. Cr-N, Nb-N, Ti-N, V-N)
- Diffusion Coating/Surface Modification- Not a Deposited Coating (higher likelihood of defect-free layer)
- Stamp to Final Form/Nitride (Industrially Established, Cheap)

Newer Effort

Timeline and History of Project

- 1999-2000: Small, Proof of Principle Effort

- September, 2000: Project Approved
  -Funded at 2/3 person-year for FY 2001, 2002

- Sept. 30, 2002 Milestone (Annotated) : Meet Corrosion Goal/Move to In-Cell Testing

Key Targets for Nitrided Metal Bipolar Plates

- Corrosion $\leq \sim 1 \times 10^{-6}$ A/cm^2 (pH3 Sulfuric, 80°C)
- Cost ~ $1-2 for a 0.1- 0.25 mm (≈ 5-10 mil) thick, 500 cm^2 (80 square inch) plate
- Amenable to high-volume, low cost manufacturing (e.g. rolling, stamping, etc.) prior to nitriding

What's Unique About Our Effort?

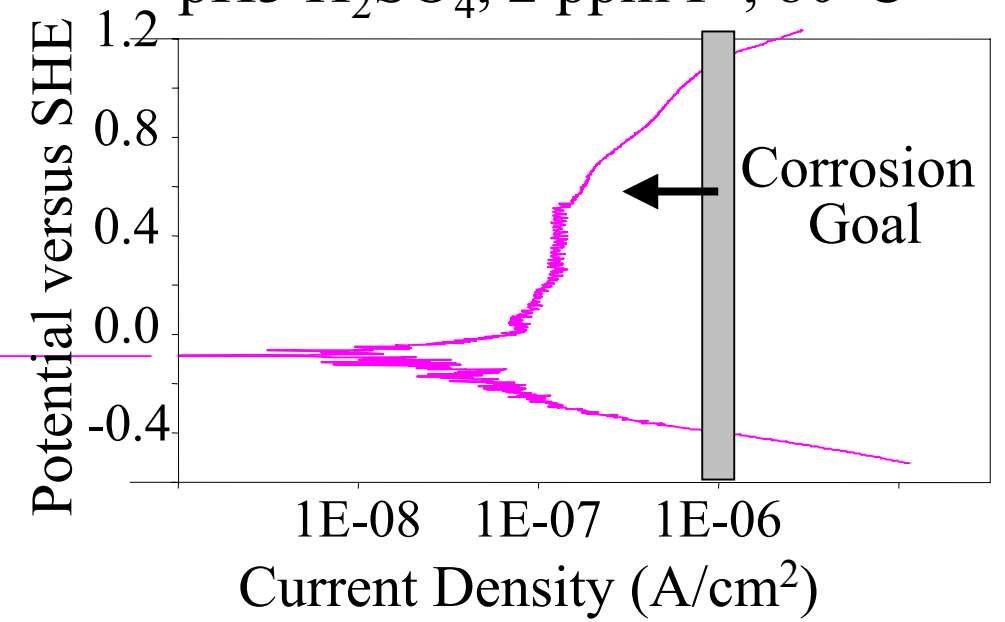
- **Alloy Design** to Form Dense, Corrosion-Resistant Nitride Surface Layers During Gas Nitridation
  - -Existing alloys typically do not form corrosion resistant nitride layers (designed to form protective oxides)

Thermally Grown Nitride Can Behave Well in PEM Environment

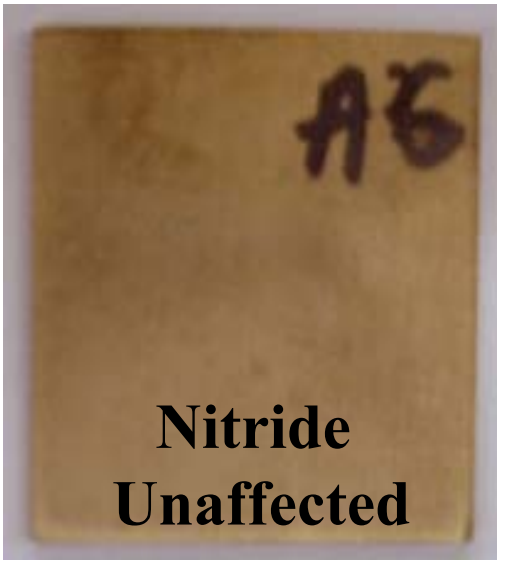
Model Alloy: Nitrided Tribocor (Nb-30Ti-20W wt.%)

(Data of K. Weisbrod/C. Zawodzinski)

Polarization Data
pH3 H_2SO_4, 2 ppm F-, 80°C



300 h pH2/pH6
H_2SO_4 (Air/H_2) 80°C

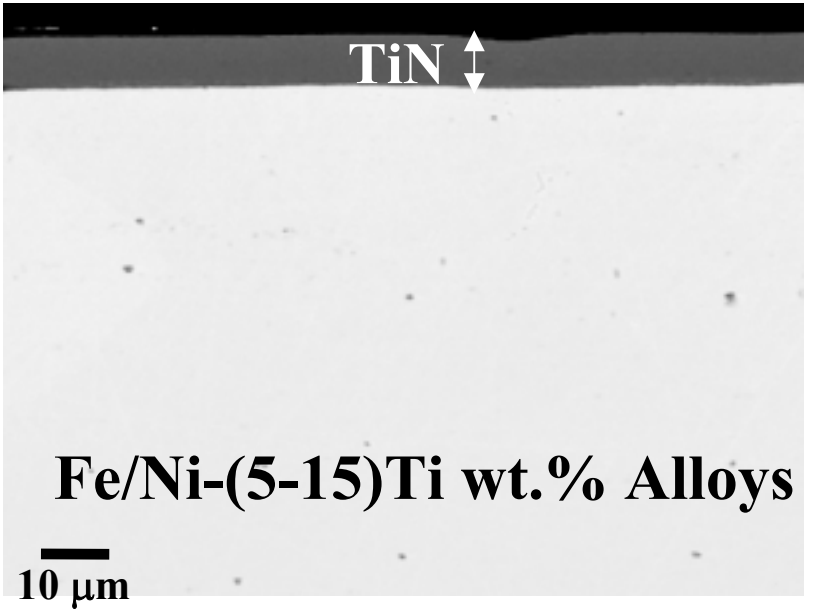


- Stable behavior for >1000 h in Corrosion Test Cell
- <1% Active site blockage in Nafion membrane after 300 h immersion screening in H_2SO_4 at 80 ° C

Can a Sufficiently Inexpensive Alloy be Developed Which Forms a Corrosion Resistant Nitride Surface?

TiN Formation on Cheap Ni/Fe Base Alloys Demonstrated at FY01 Review

SEM Cross-Section of Typical Nitrided Alloy



- **Unacceptably High Corrosion Rates in 1st Generation of Alloys**

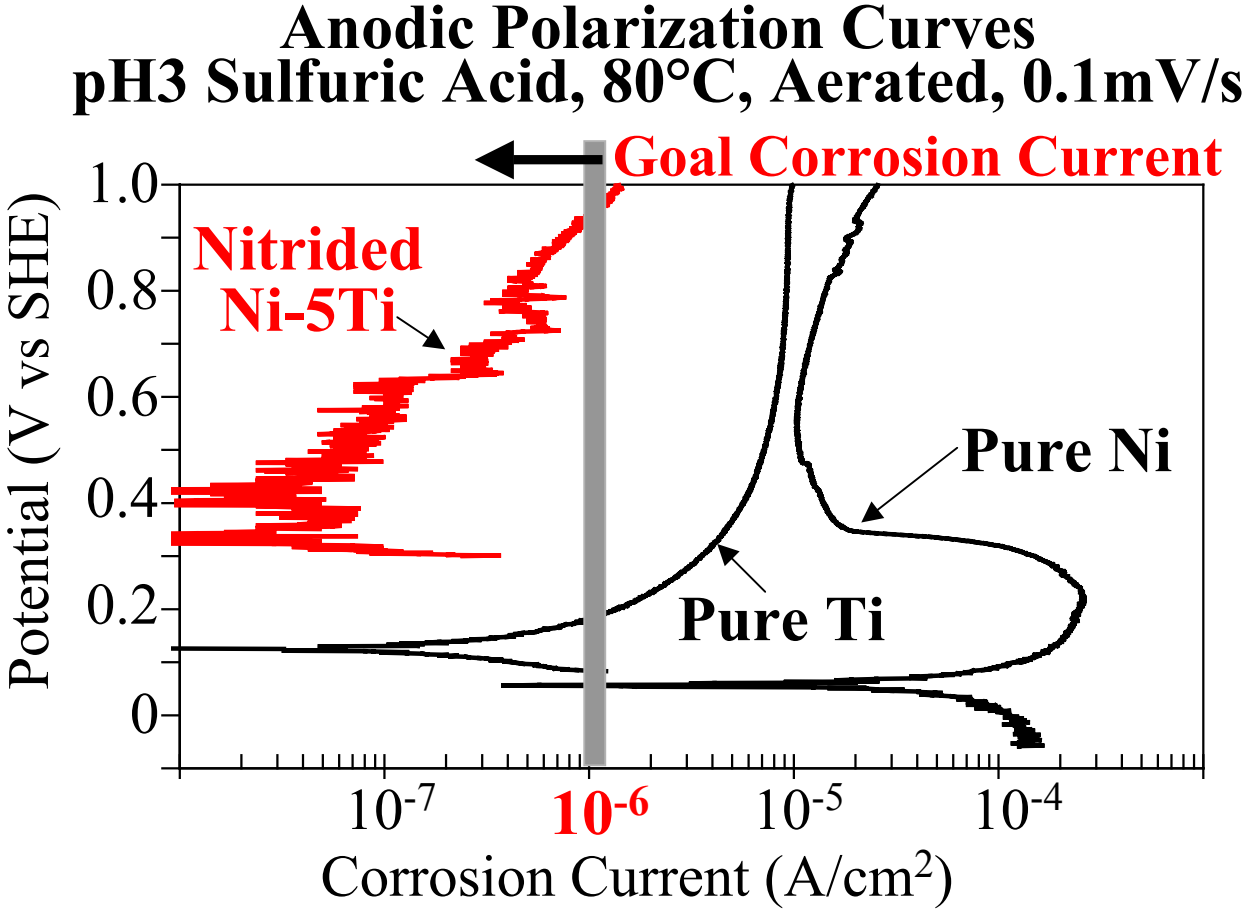
Response to FY 01 Review Comments

- Technically Strong/Sound Approach
  - -Good Scientific/Technological Progress
    - Thanks

- Must Achieve Corrosion Resistance Goals
  - We Approached Corrosion as Go/No Go Decision in FY 02
  - Teamed with U. Tennessee for Polarization Corrosion Studies of Nitrided Alloys (Master's thesis project)

- Move to In-Cell Testing/Coverage of Flow Field Features
  - Incorporated in FY02 Milestone

Corrosion Current Goal Met with Optimized Nitrided Ni-5Ti wt.% Alloys



- **BUT issues remain with poor reproducibility and local corrosion attack at edges and some nitride surface sites(?)**

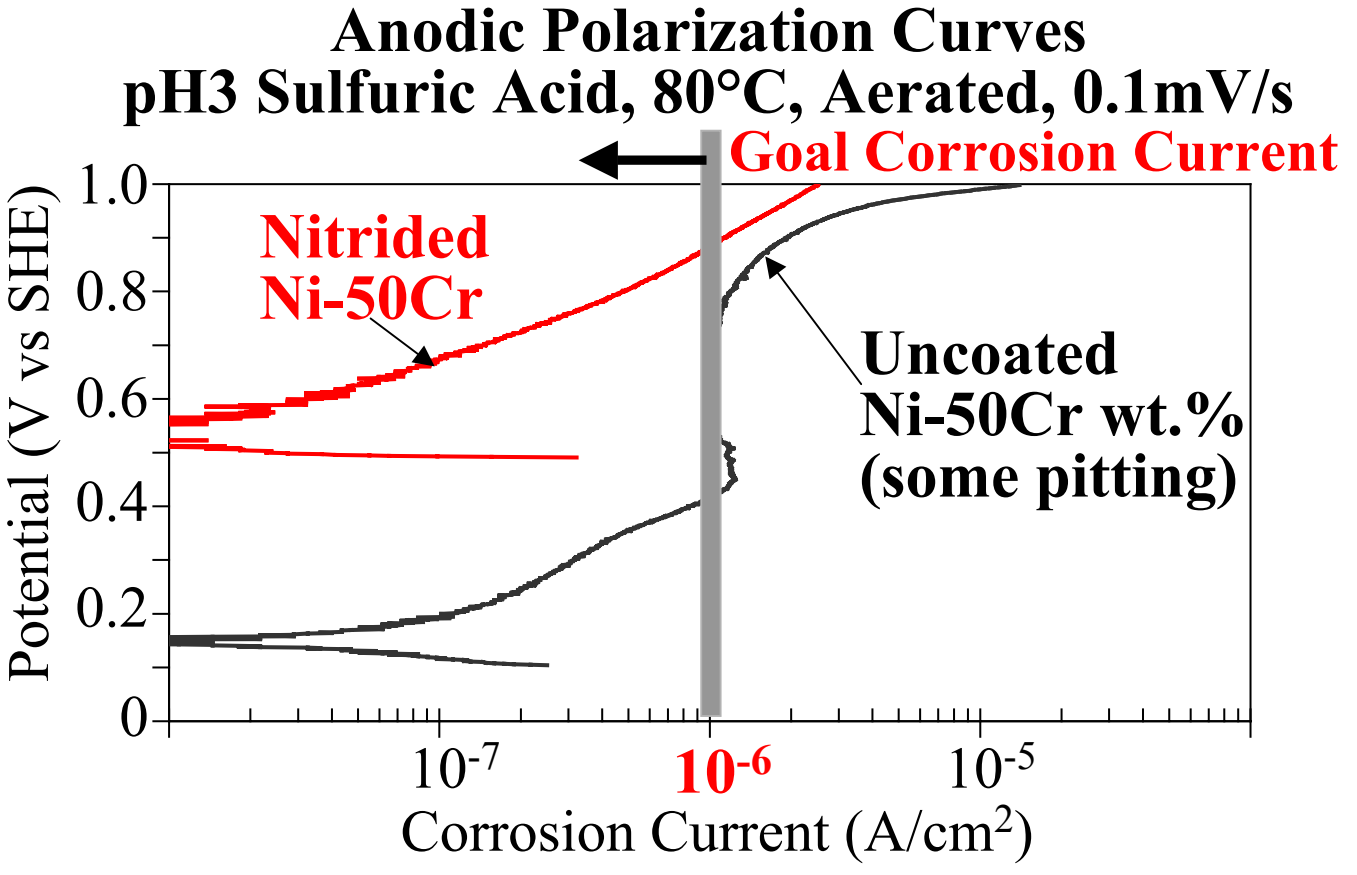
Extensive Alloy Development/Corrosion Screening Pursued

Corrosion Screened with Sharp Edged/Cornered Nitrided Coupons By One Week Immersion in pH2 Sulfuric at 80°C
(follow-on polarization studies of promising alloys)

- **Ni/Fe – (5-15)Ti- X** (X = Cr, Hf, La, Mn, Mo,Nb, V, Y, Zr)
  - -X based on thermodynamic considerations/Wagner theory
  - -Not successful/not clear if sufficiently robust TiN-based layer possible on Ni/Fe

- Cr-N, Nb-N, Nb(V)-N, V-N Formation Explored on Ni/Fe Base Alloys
  - **-Nitrided Ni-Nb-V and Ni-Cr showed promise**

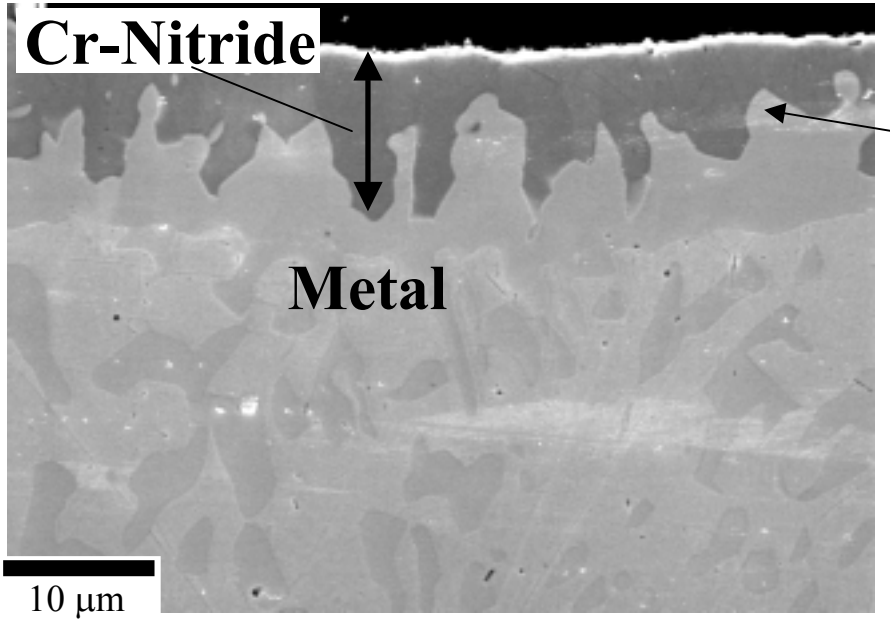
Nitrided Ni-50Cr Shows Goal Corrosion Current ≤ 10^{-6} A/cm^2 up to ~ 0.9V vs SHE



- Nitrided Ni-50Cr coupons show **no evidence of corrosion** after testing (optical/SEM only- surface analysis planned)
- **Provisional patent disclosure submitted**

Inward Growing Cr_xN Layer on Ni-50Cr

SEM Cross-Section of Nitrided Ni-50Cr



- Growth/morphology of Cr-nitride layer appears favorable for coverage and protection of irregular features (e.g. flow fields)
- More diffuse metal/nitride interface than initial Ni/TiN alloys (suggested by FY 01 reviewer for better adherence)

Nitridation of Ni-50Cr Very Robust

Macrograph of Stamped and Nitrided Ni-50Cr Coupon After 1 Week Immersion in pH2 Sulfuric at 80°C

- Inward-growing nitride layer shows good promise to handle flow field features
- Electrical conductivity in the $10^4 \Omega^{-1}cm^{-1}$ range (preliminary)

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

- Minimize Cr level/switch to Fe, Ni(Fe) base for low cost
  -apply lessons learned from nitriding Ni-Ti-X base alloys

- Cladding of 10-25 micron thick Ni-Cr on cheap substrate
  -Preliminary discussions with TMI Inc./Visit to ORNL (TMI already produces Nb clad Cu for bipolar plates)

Plans

- Priority One: **In-Cell Testing of Nitrided Ni-50Cr**
  - **Determine if promising corrosion resistance translates to in-cell performance**
    - Preliminary discussions with Plug Power
    - Joint proposal led by Dana-Plumley, Tenn. Tech, U. Minn (State Energy Program)

- Optimization of Ni-Cr base composition/nitriding
  - U. Tenn. study of corrosion mechanism
  - Nitrided coupons to Los Alamos for evaluation

- Examine issues with nitriding thin sheet/flow fields/ claddings/alloy scale up (not trivial but stand good chance)

Collaborations Significant Part of Effort

- **Corrosion Evaluation**
  - **Los Alamos National Lab** (**K. Weisbrod, Christine Z.**)
  - **U. Tennessee** (Supporting Master's Thesis Effort)
- **Alloy Scale-Up Issues**
  - Input from **Special Metals, Allegheny Ludlum,** others
- **Metal Processing/Cladding**
  - Recent prelim. discussions for collaboration with **TMI Inc.**
- **PEM Fuel Cell/Bipolar Plate Issues**
  - Past Input from **T. Rehg** of **Honeywell**/G.E.
- **In-Cell Testing (Actively Seeking Partners!!!)**
  - Recent prelim. discussions with **Plug Power**
  - Part of State Energy Call Proposal with **Dana-Plumley**