Nitrided Metallic Bipolar Plates

M.P. Brady (project lead)

P. F. Tortorelli

Oak Ridge National Laboratory

Oak Ridge, TN 37831-6115

Feb 14, 2007 Kick-Off Meeting

Effort Devoted to Scale Up and Demonstration of Thin Stamped Metallic Bipolar Plates

Timeline

- **Start- April, 2006 (estimated)**
- **Finish- April, 2008 (estimated)**

Budget

- Total project funding
  - **$4530 K (+ $400 K Match)**
- Funding for Year 1
  - **$2480 K**
- Funding for Year 2
  - **$2050 K**

Barriers

- **A. Durability**
- **B. Cost**
- **Targets (2010)**
  - **resistivity < 10 mohm-cm^2**
  - **corrosion < 1 x10^{-6} A/cm^2**
  - **cost < $5/kW**

Team Members

- **ORNL (Lead)**
- **Allegheny Ludlum**
- **Arizona State University**
- **GenCell Corp**
- **LANL**
- **NREL**

Objective: Surface Treatment to Protect Stamped Metallic Bipolar Plates

Overall Goal: ***Demonstrate potential for metallic bipolar plates to meet 5000 h automotive durability goal at cost < $5/kW***

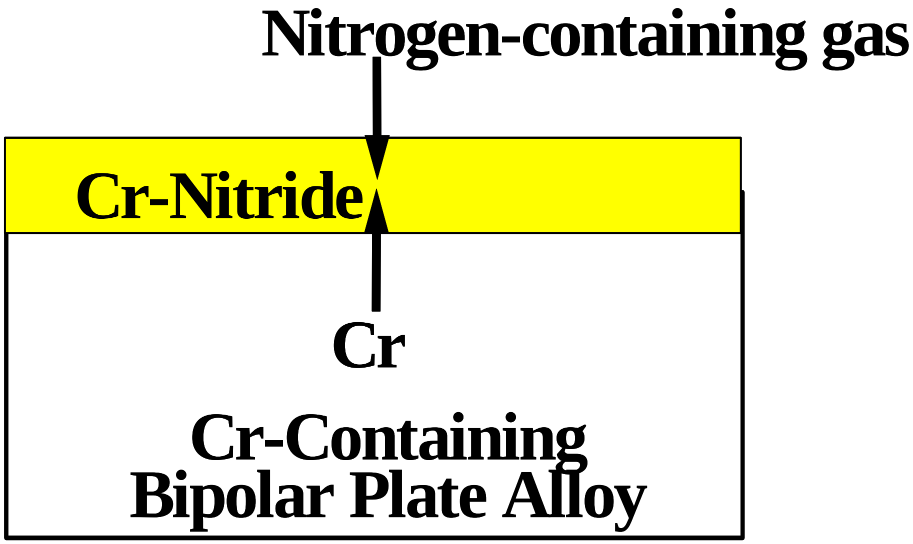
Year 1 Goals:

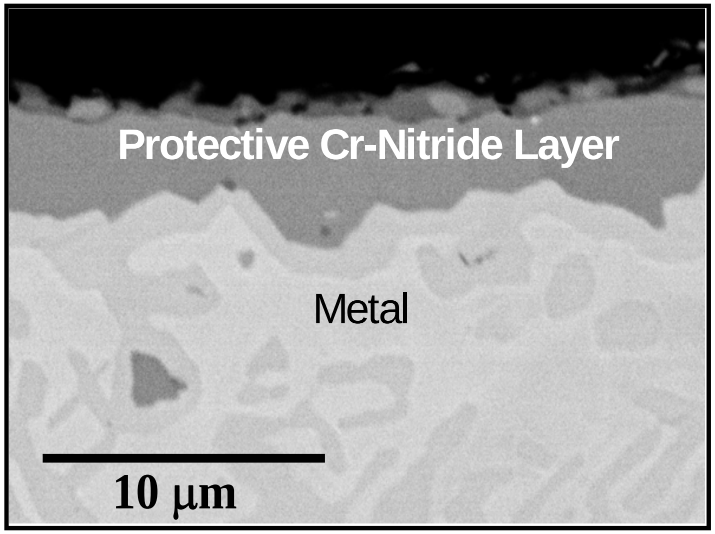
- **Single-cell fuel cell test performance for 25 cm^2 stamped and nitrided metallic bipolar plates equivalent to that of graphite (~1000 h, cyclic)**
- **No significant warping or embrittlement of the stamped plates by the nitriding**

Year 2 Goals:

- **10 cell stack test of 250 cm^2 stamped and nitrided metallic bipolar plates under automotive drive-cycle conditions (~2000 h)**
- **Potential to manufacture stamped and nitrided metallic bipolar plates at < $5/kW demonstrated**

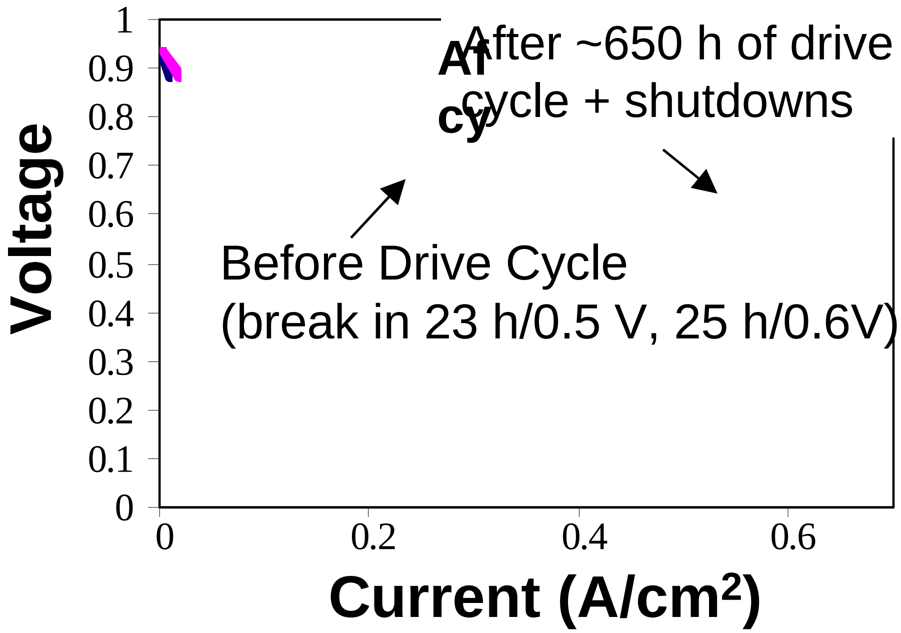
Approach: Thermally Grown Cr-Nitride for Protection





- **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 Single-Cell Drive-Cycle Durability Test Results for Model 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

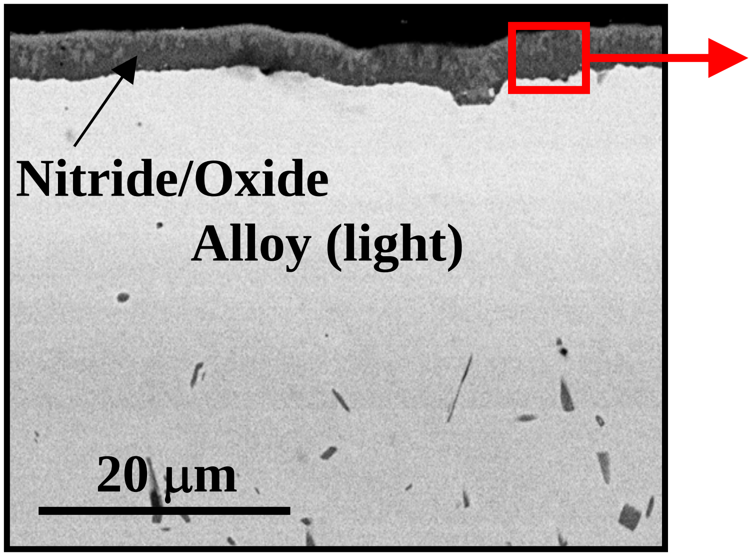
•No performance degradation/No attack of the Cr-nitride
  -trace level ($2x10^{-6}$ g/cm^2) of Ni detected in MEA, suspect local CrNiN spots

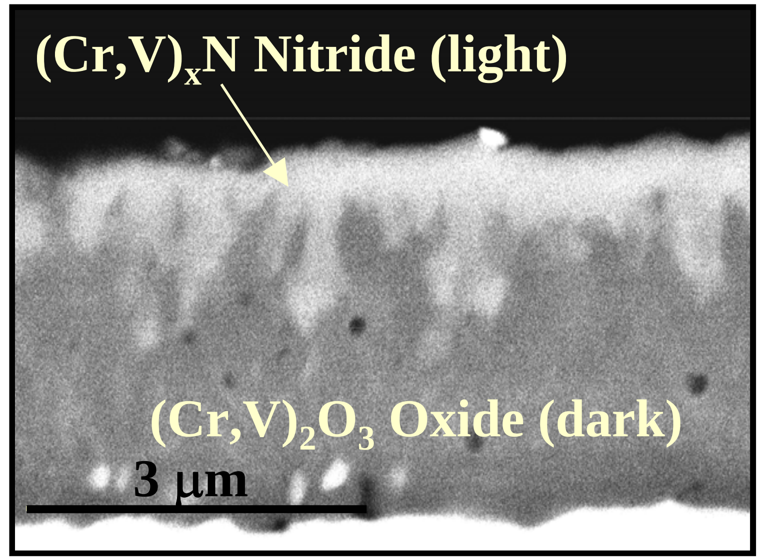
Need Fe-Base Alloys to Meet $5/kW Bipolar Plate Cost Goals

- **Dense Cr-nitride surface formation demonstrated on a model Fe-base alloy, Fe-27Cr-6V wt.%**
  - pre-oxidation key to protective surface nitride formation
  - V segregation into Cr-oxide makes it more readily nitrided
- **Alloy Challenges**
  - Lower Cr and V levels to reduce alloy cost
  - Co-optimize preoxidation/nitridation to segregate Cr, V to surface
  - Down select to ferritic (cheaper) or austenitic (more formable) alloy base

Dense, Continuous Nitride Surface Obtained

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





- Low contact/through-thickness electrical resistance
- Low corrosion current densities under simulated anodic and cathodic conditions

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: **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

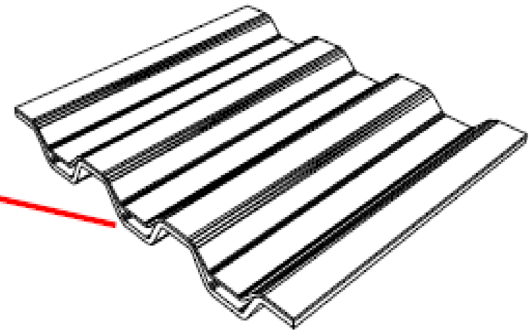
Teaming and Primary Responsibilities

- Oak Ridge National Lab:
  Alloy design, nitridation optimization, characterization
- National Renewable Energy Lab:
  Corrosion/contact resistance evaluation
- Allegheny Ludlum:
  Alloy foil manufacture
- GenCell Corp:
  Design and stamp bipolar plate flow field features
- Arizona State University:
  Single-cell testing (assisted by Gencell, ORNL)
- Los Alamos National Lab:
  Stack testing and performance assessment, characterization

GenCell Corp Stamped Bipolar Plate Approach

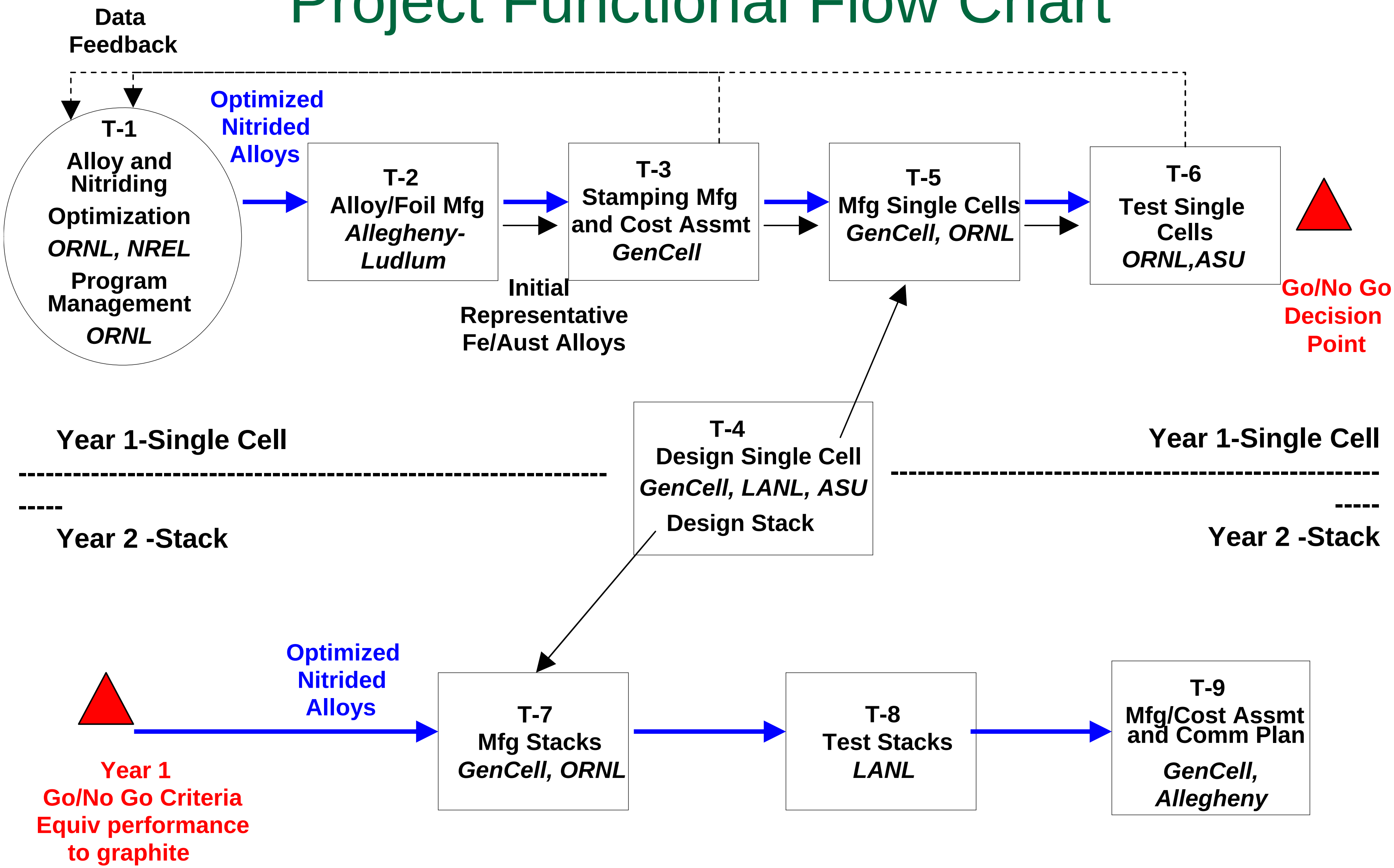
Internal Chamber (patented)

- "Heat exchanger in each cell"
- Thin wall, high surface area
- From same tooling using nested sheet metal



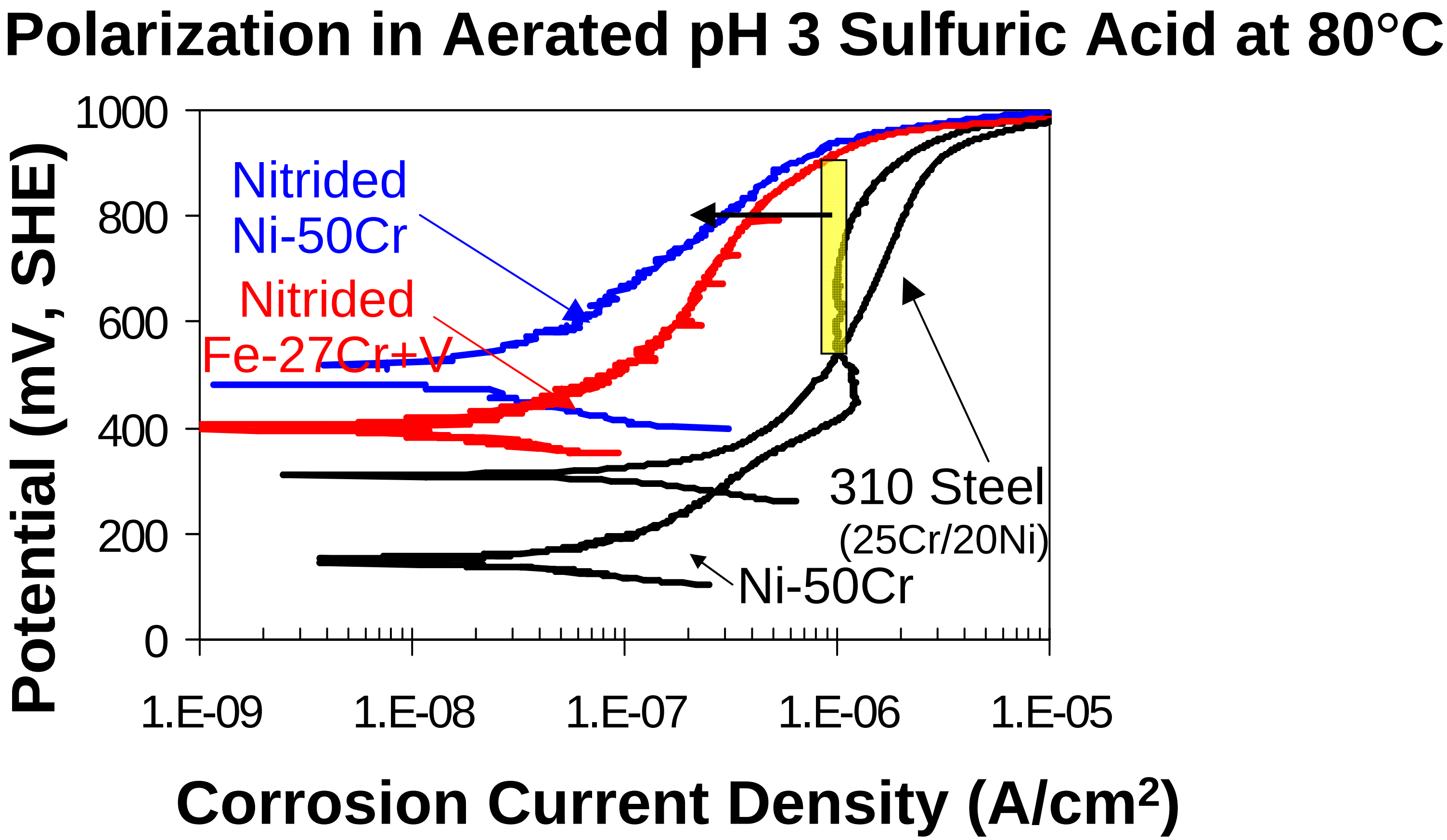
Above shown for molten carbonate fuel cell bipolar plates, approach currently being extended to PEM and SOFC

Project Functional Flow Chart



Extra Slides for Q and A

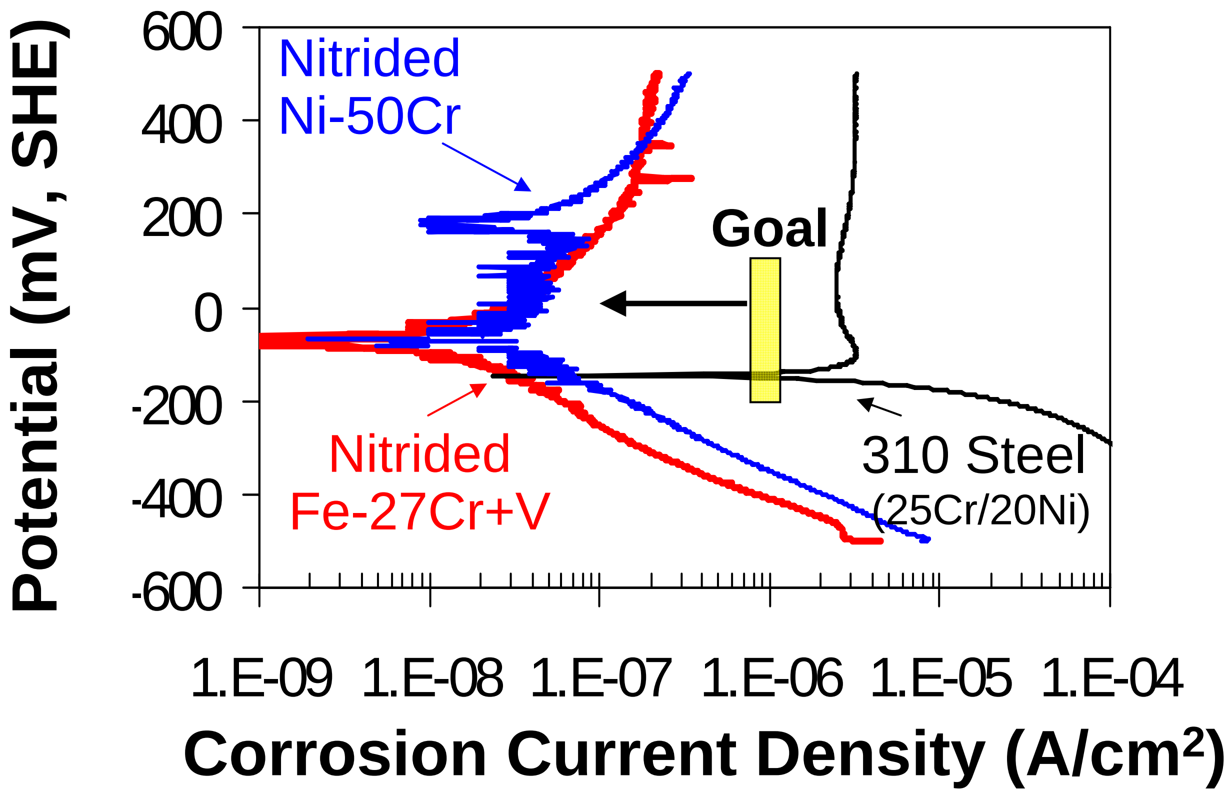
Vanadium Additions to Fe-27Cr Result in Protective Cr-Nitride Surface



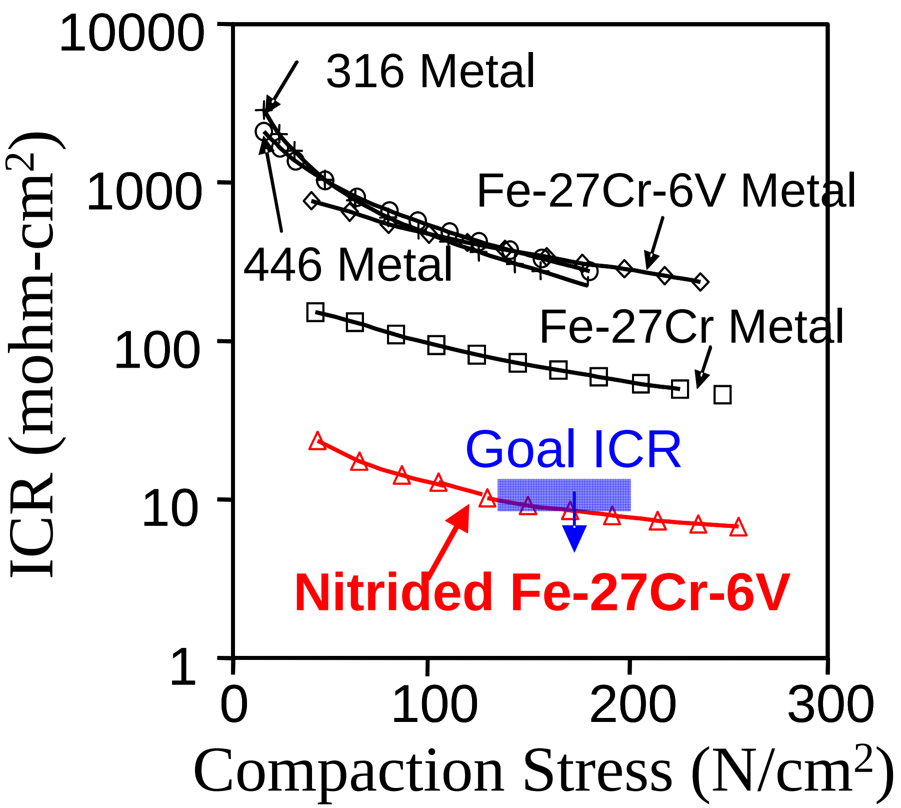
Corrosion resistance comparable to nitrided Ni-50Cr observed for nitrided Fe-27Cr-2V and Fe-27Cr-6V (850-900°C, < 24 h, N_2-$4H_2$)

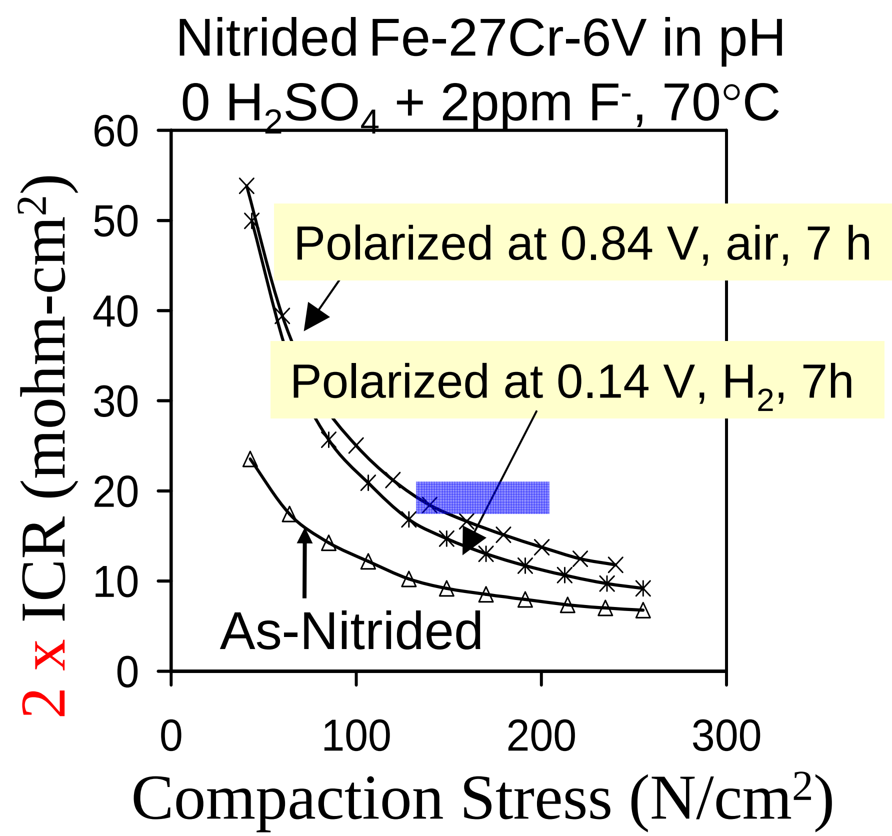
Good Corrosion Resistance Also Observed Under Simulated Anode Conditions

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



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

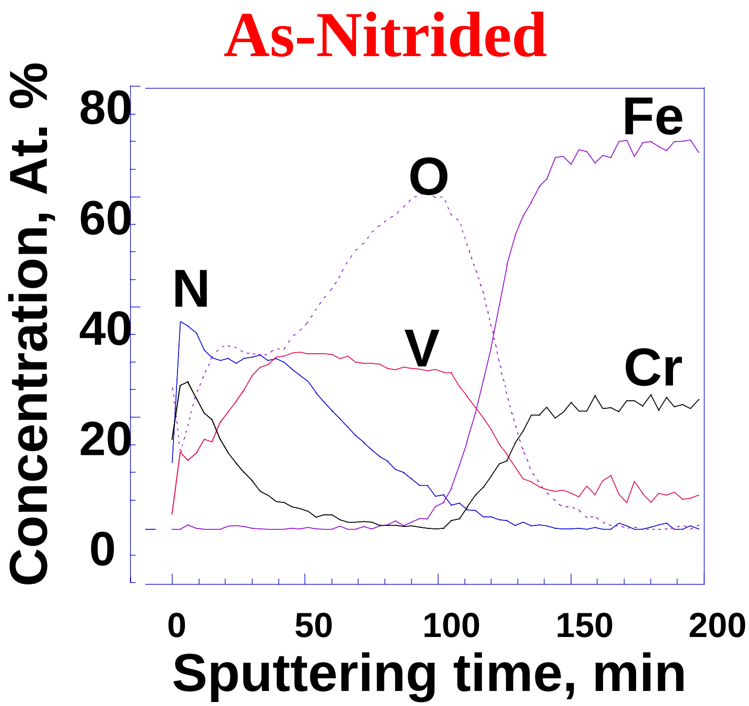


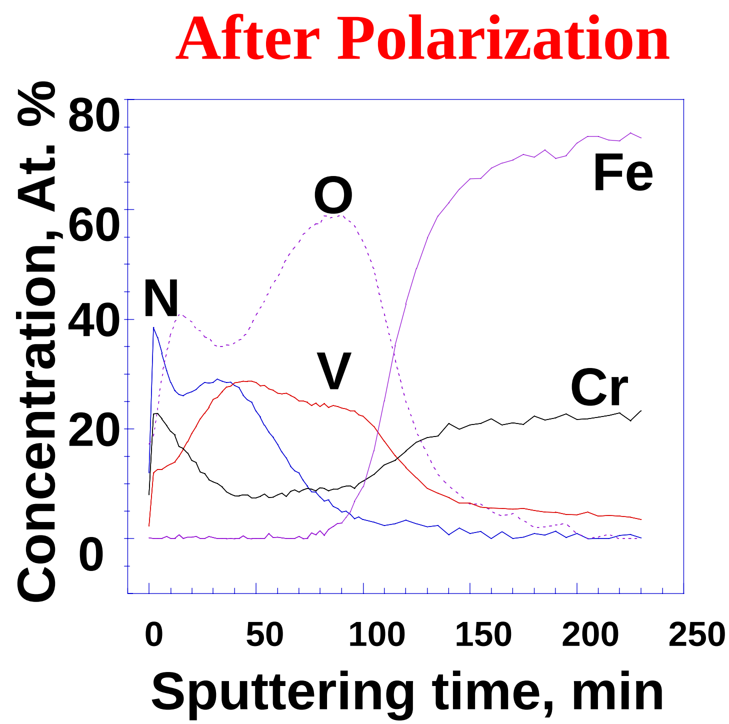


- Nitridation significantly reduces interfacial contact resistance (ICR)
- Slight increase in ICR on polarization-still meets goal
- Untreated stainless steels don't meet ICR goals

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

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

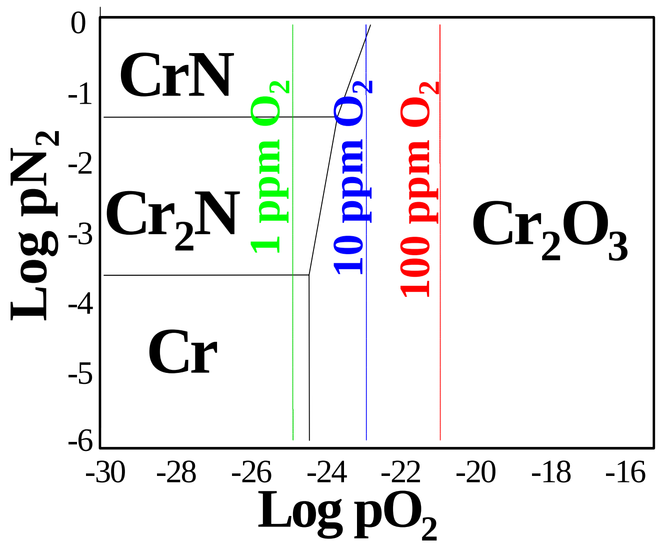


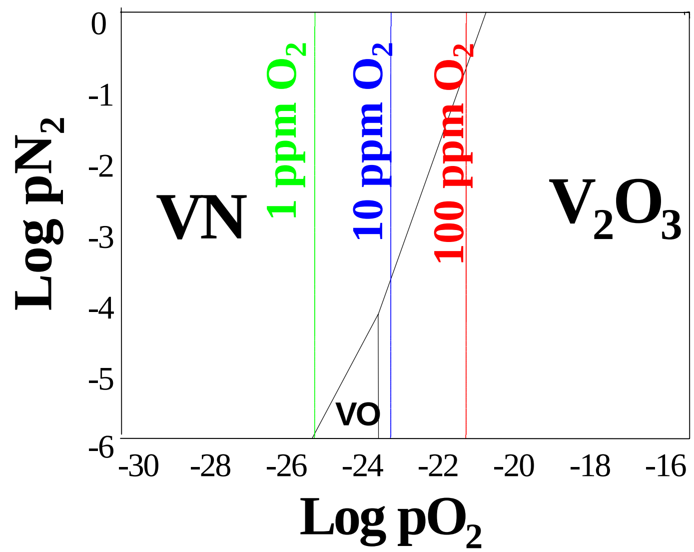


- Polarized 7 h at 0.84 V SHE in pH 0 H_2SO_4 + 2 ppm F^- air purged at 70 °C (similar results under H_2-purged anodic conditions)
- No Fe detected in nitrided surface, **oxygen present** in surface

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