Nitrided Metallic Bipolar Plates

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Project ID FC 27

Overview

Timeline

- Start: May 1, 2007
- Finish: Sept. 30, 2009
- ~30% complete

Budget

- Total project funding
  - \$4530k DOE share
  - \$400k Contractor share
- \$1200 k received in May 07
- \$1200 k expected for FY 08
- 5 month delay for 1st increment of FY08 funding (Feb 08)
- Delays/complications in subcontracting (~Sept 07 start)

Barriers

- Metallic bipolar plate durability and cost
- 2010 Targets
  - resistivity < 10 mohm-cm^2
  - corrosion $< 1 \times 10^{-6}$ A/cm^2
  - cost < \$5/kW

Partners

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

Objective: Demonstrate Nitridation to Protect Stamped Metallic Bipolar Plates

Overall Goal: Demonstrate potential for metallic bipolar plates to meet automotive durability goals at cost of < $5/kW

- **Milestone 1**: No significant warping or embrittlement of stamped 18 cm^2 active area plates by nitriding- **go/no go 1**
- **Milestone 2**: Single-cell fuel cell test performance for 18 cm^2 stamped and nitrided metallic bipolar plates equivalent to that of graphite (~1000 h, cyclic)- **go/no go 2**
- **Milestone 3**: 10 cell stack test of 250 cm^2 stamped and nitrided metallic bipolar plates under automotive drive-cycle conditions (~2000 h) -**project end**

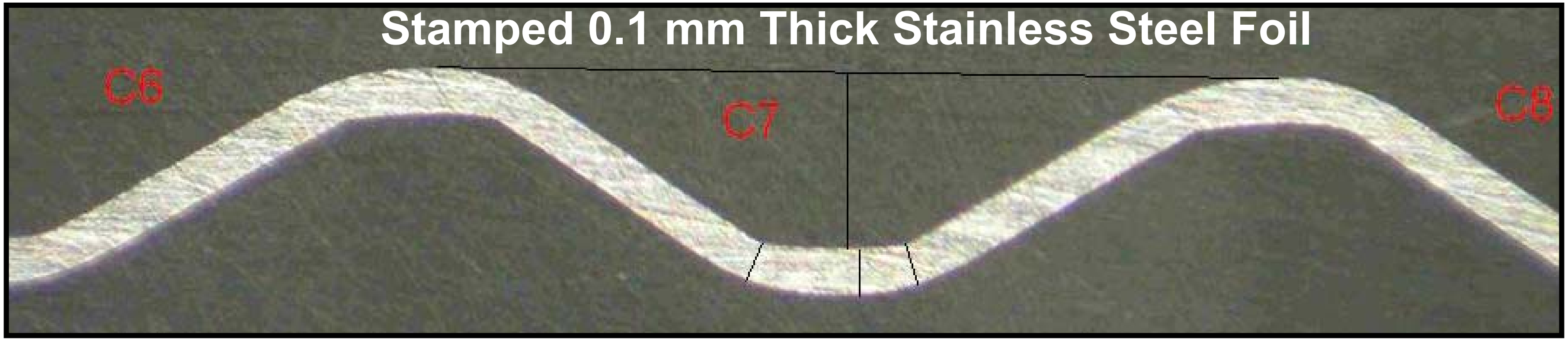
Stainless Steels As Bipolar Plates Have Some Advantages Over Graphite Composites

- **Better mechanical properties**
  - -can be stamped: *low cost/high volume manufacturing*
  - -can be made thin: *0.1 mm vs ~1 mm composite plates*
  - -not susceptible to brittle failure: *high graphite loadings in composites may result in brittleness*

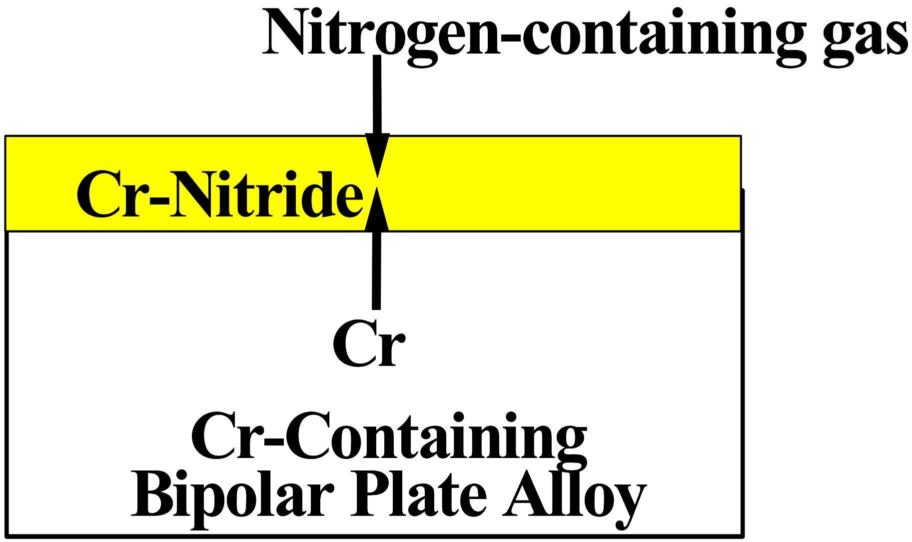
- **Lower gas permeation**: *better at keeping* H_2 *and air streams separate,* ***But…***

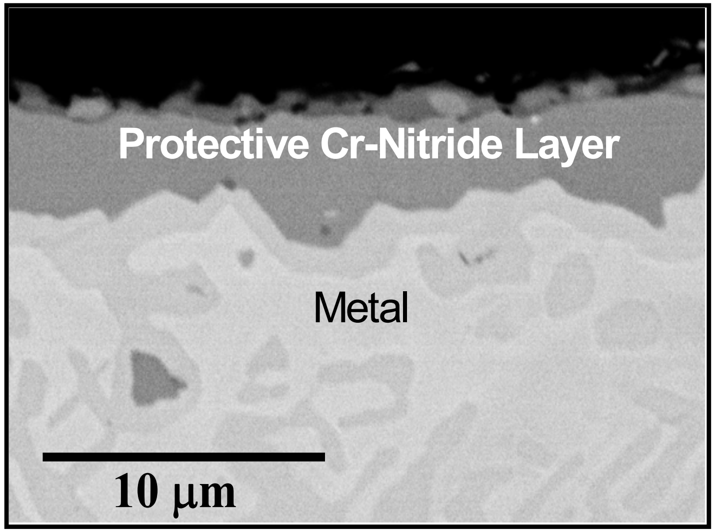
- Borderline corrosion resistance and high contact resistance

Stamped 0.1 mm Thick Stainless Steel Foil



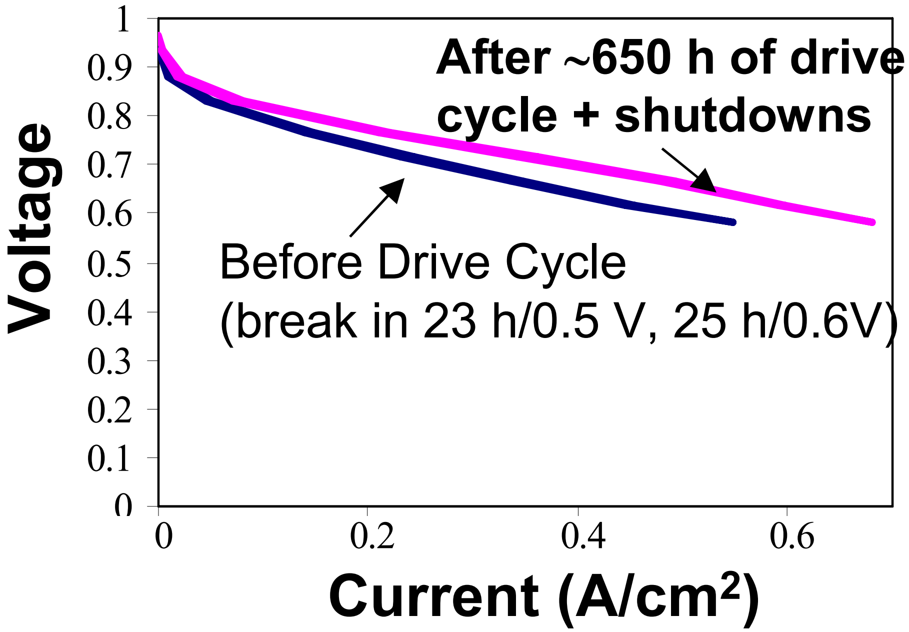
Approach: Thermally Grown Cr-Nitride for Corrosion Protection/Low Contact Resistance





- Nitrides are corrosion resistant with low surface contact resistance
- 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



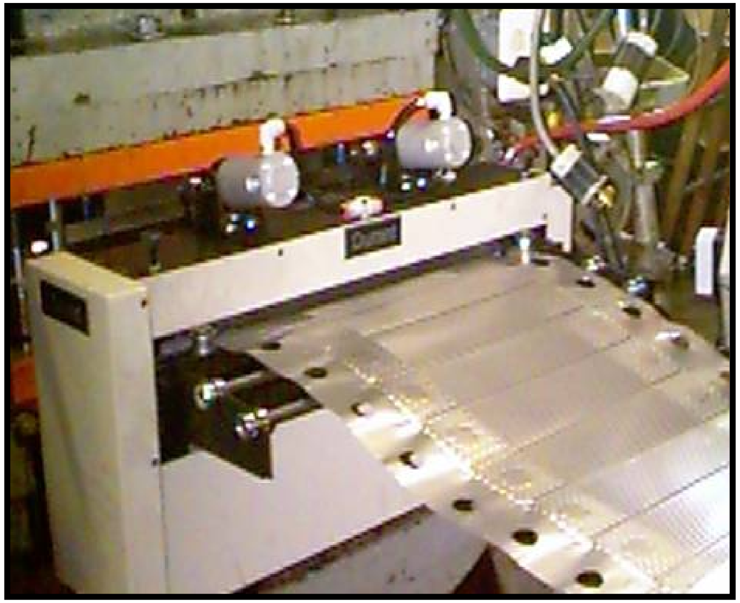
Collaboration with LANL
M. Wilson and F. Garzon

- **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

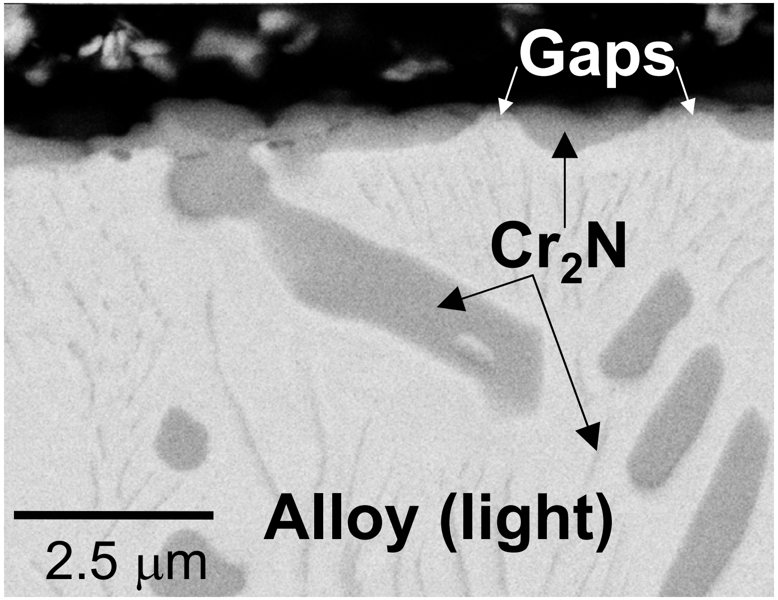
Need Fe-Base Stainless Steel to Meet $5/kW Bipolar Plate Cost Goals for Auto Applications

- Ni-Cr Base Alloys in Range of ~$20-40/lb: far too costly
- Focus on Ferritic and Lower-Ni Duplex/Austenitic Stainless Steels, ~$2-10/lb
- Meeting Cost Goals Will Depend on Use of Thin Stamped Alloy Foil (less material/lower cost)



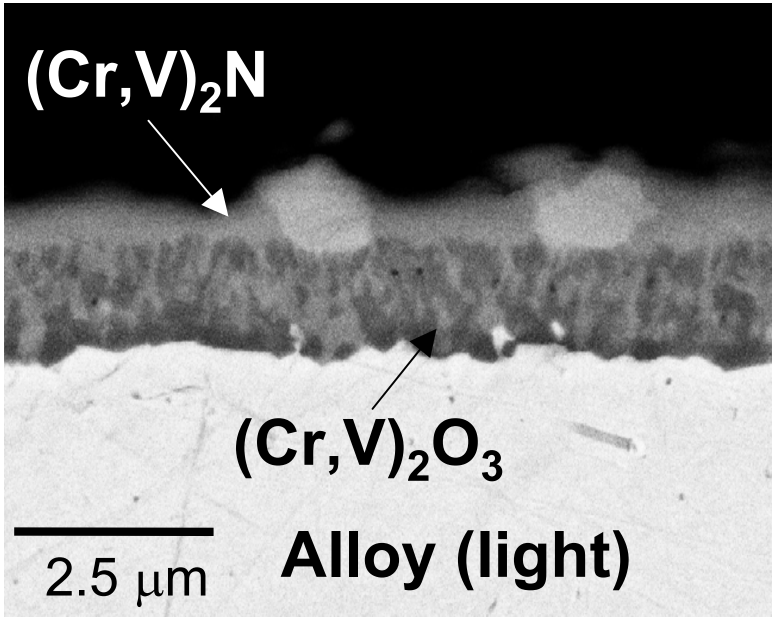
Pre-Oxidation/Nitridation Yields Protective Cr-Nitride Surface on Model Fe-27Cr-6V Alloy

Nitrided Fe-27Cr



- N_2 readily penetrates Fe-Cr
- Dense Cr-nitride surface not formed
- Poor corrosion resistance

Pre-Oxidized/Nitrided Fe-27Cr-6V



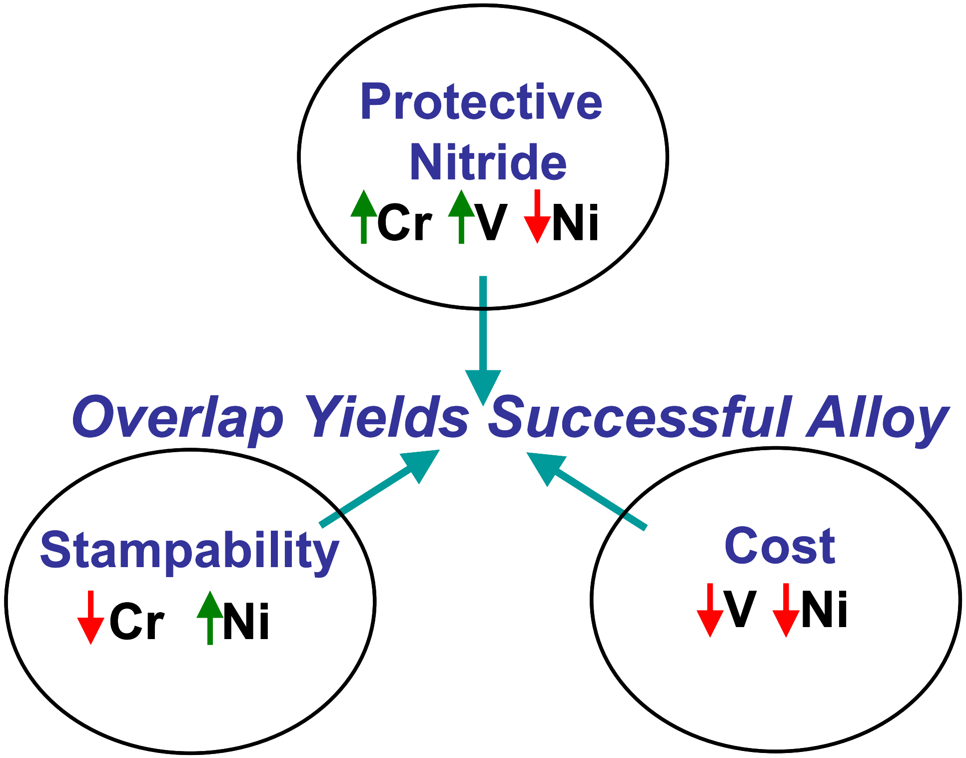
- Initial oxide keeps N_2 at surface
- V in Cr-oxide makes readily nitrided
- Excellent corrosion resistance and conductivity demonstrated

- Approach demonstrated for nitriding Fe-Cr base alloys

Scale-Up Considerations Focus of New Effort

- **Model Fe-27Cr-6V alloy not viable for scale up**
  -limited ductility and borderline cost
  -potentially embrittled by σ phase formation during nitridation

- **Challenge: Co-optimize ductility (for stamping) and low alloy cost with protective Cr-nitride surface formation**



Protective Nitride
↑Cr ↑V ↓Ni

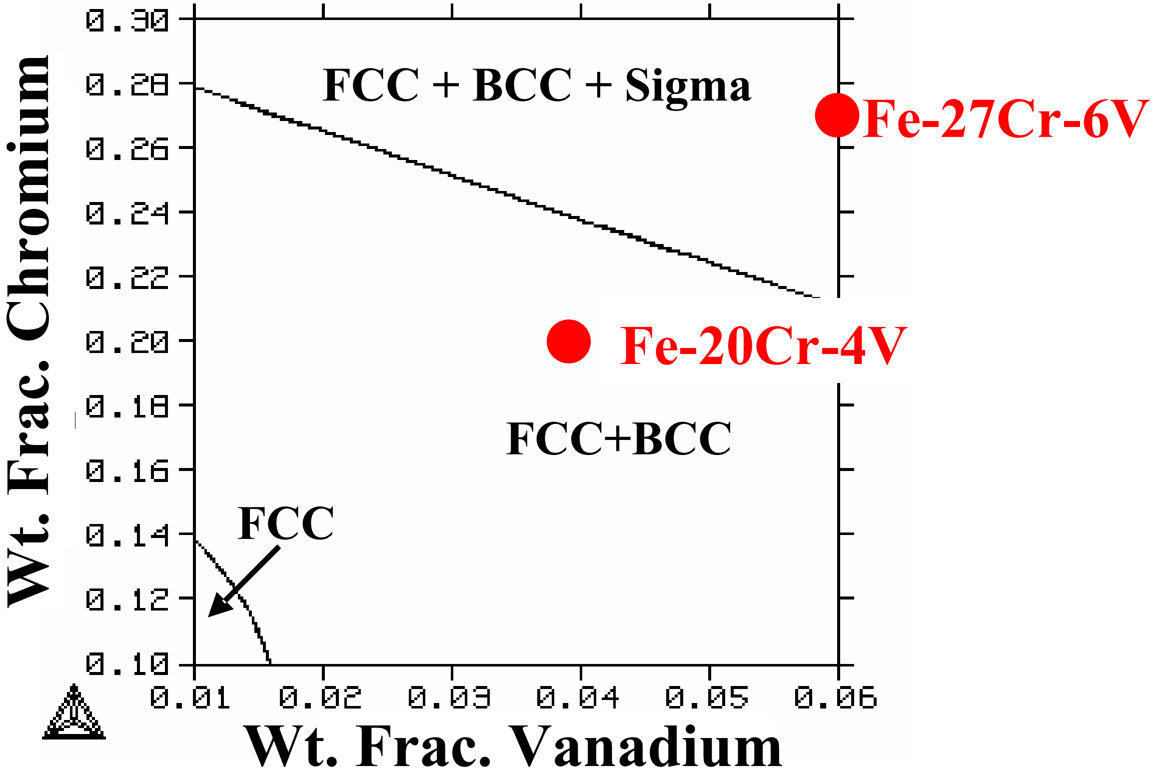
Overlap Yields Successful Alloy

Stampability
↓Cr ↑Ni

Cost
↓V ↓Ni

Computational Thermo. Guided Alloy Design

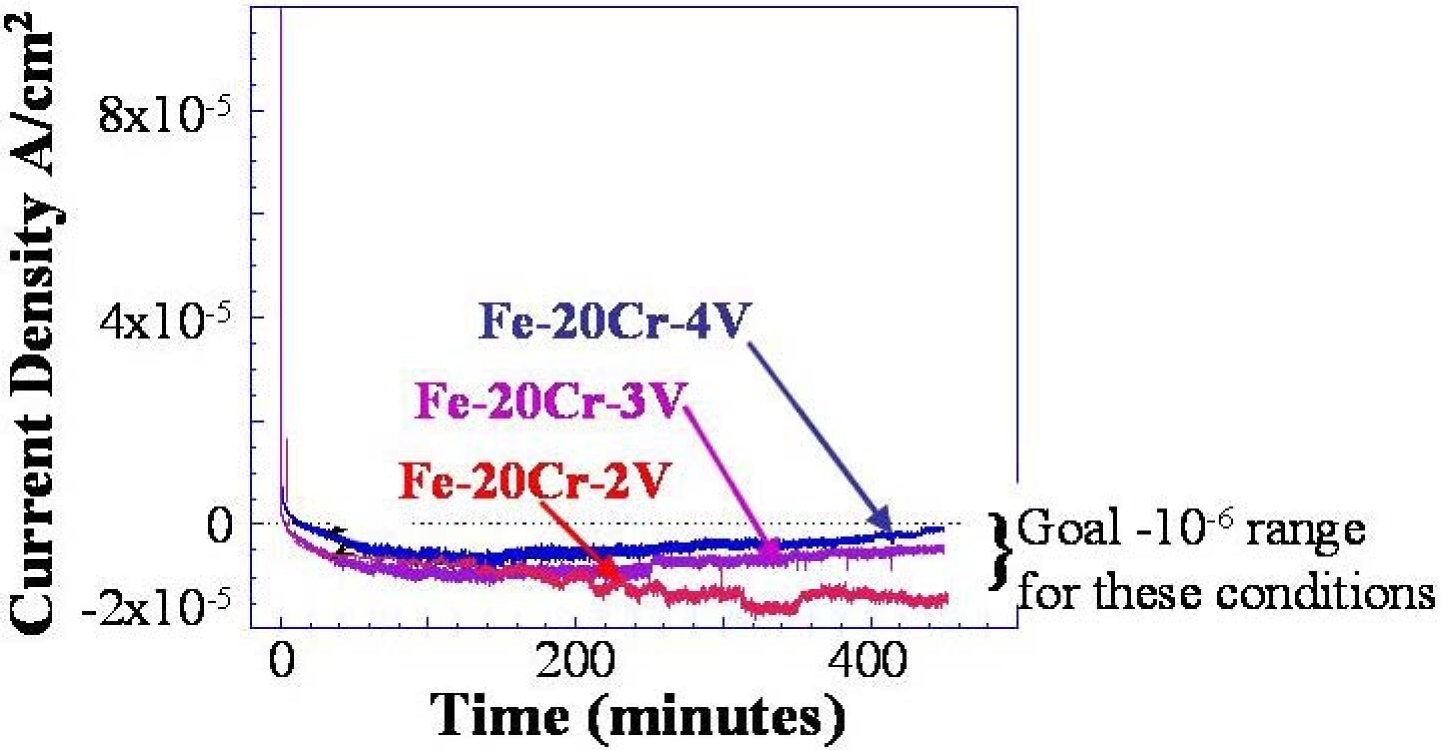
Calculated Phase Equilibria for Fe-Cr-V + 5 wt.% Ni at 800°C



- Brittle σ phase formation during nitriding a concern
- Ferritic (BCC), duplex (FCC+BCC), austenitic (FCC) compositions computationally explored as a function of Fe, Cr, V, and Ni content
  - -ferritic lowest cost but lowest ductility
  - -austenitic best ductility but highest cost due to Ni content

Protective Cr-Nitride Base Surface Successfully Formed on Ferritic Fe-20Cr-(2-4)V Wt.%

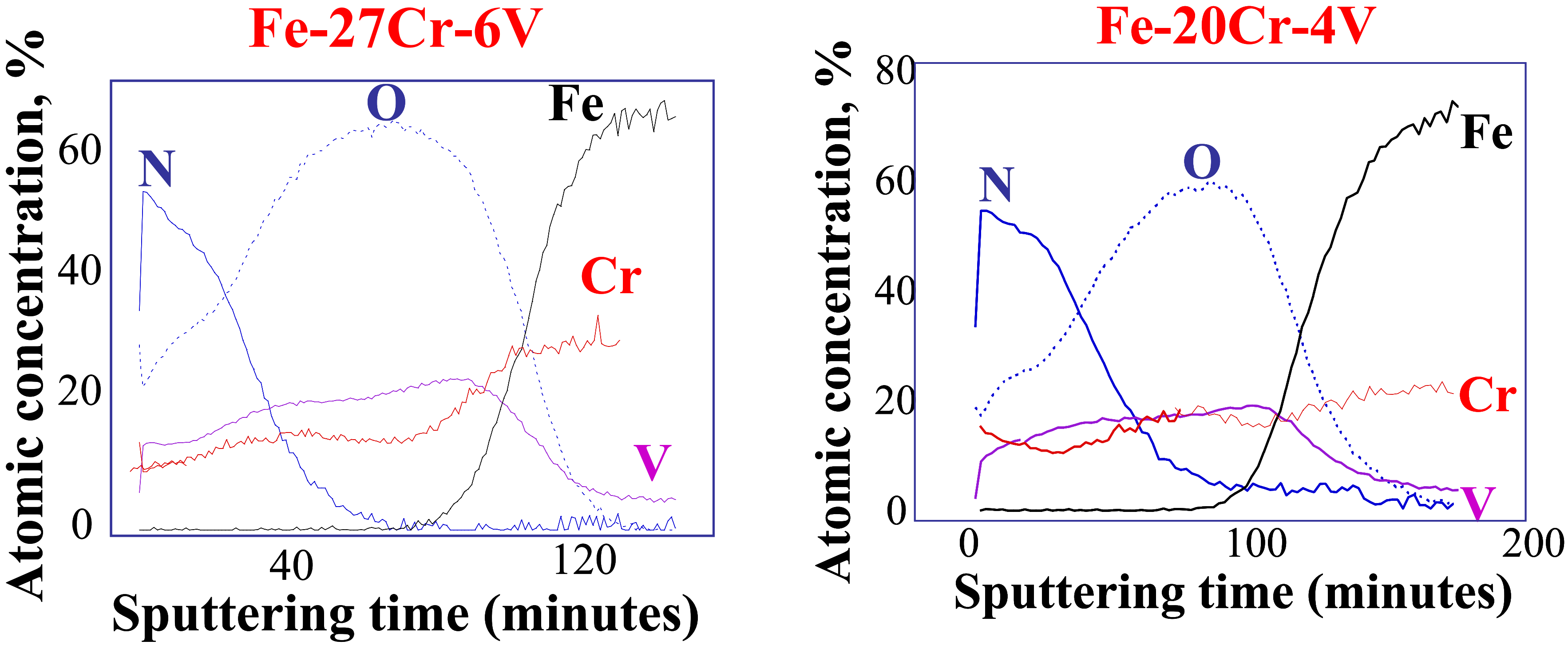
Static Polarization in H_2-Purged 1M H_2SO_4+2 ppm F^-/70°C/0.14 V vs SHE



- Highly-aggressive simulation for anode-side environment
- Higher V content alloys more robust
  - -readily repeated with cast and nitrided Fe-20Cr-4V
  - -some reproducibility issues with cast and nitrided Fe-20Cr-2V

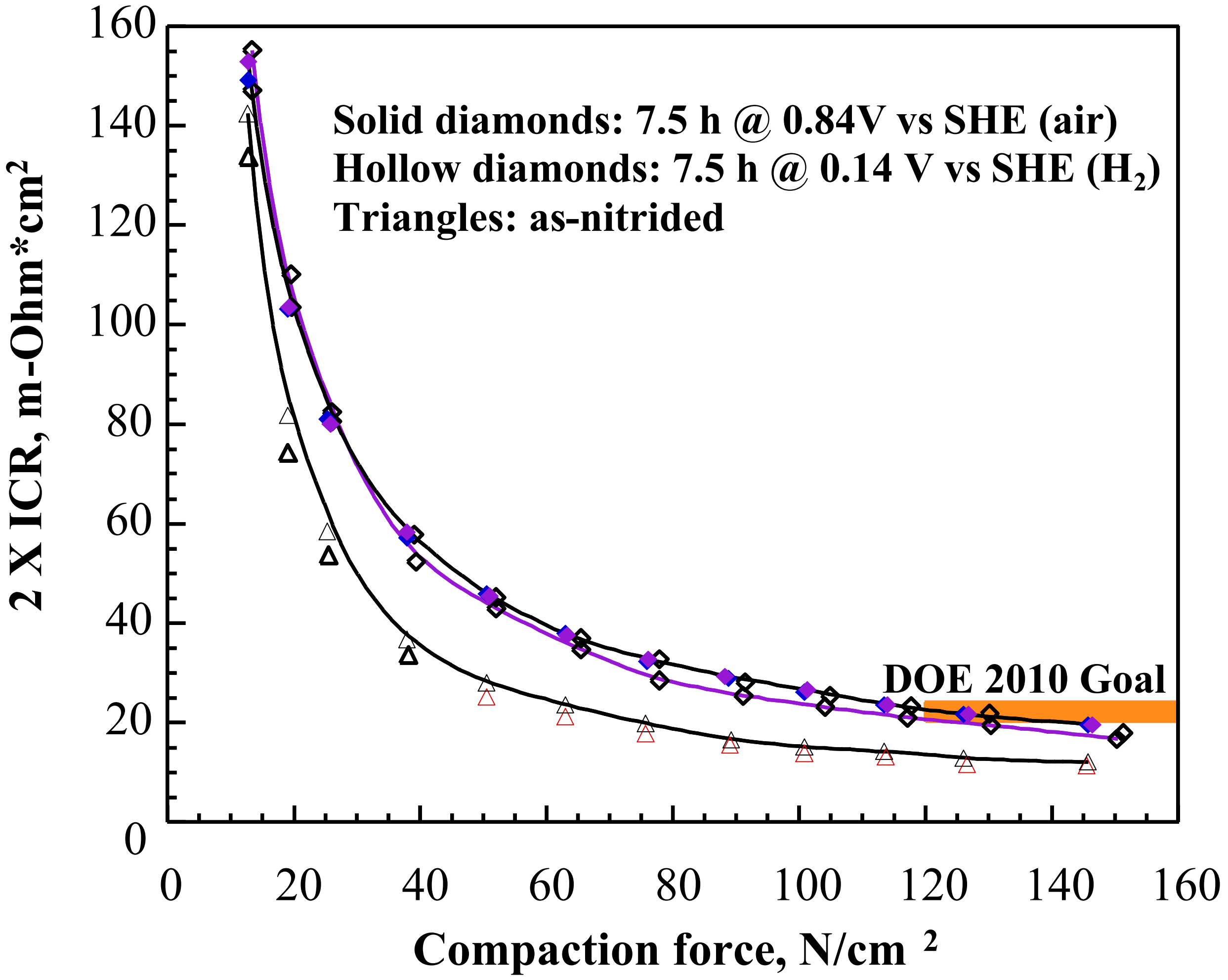
Nitrided Fe-20Cr-4V Surface Similar to That Formed on Nitrided Fe-27Cr-6V

AES Depth Profiles After Polarization for 7.5h in Aerated
1M H_2SO_4+2 ppm F^-/70°C/0.84 V vs SHE
(*Highly aggressive simulation for cathode-side environment*)



- Pre-oxidation/nitridation yields mixed nitride + oxide structure
  - -similar surface before/after polarization
- Surface is free of Fe: correlates with good PEMFC behavior in our studies

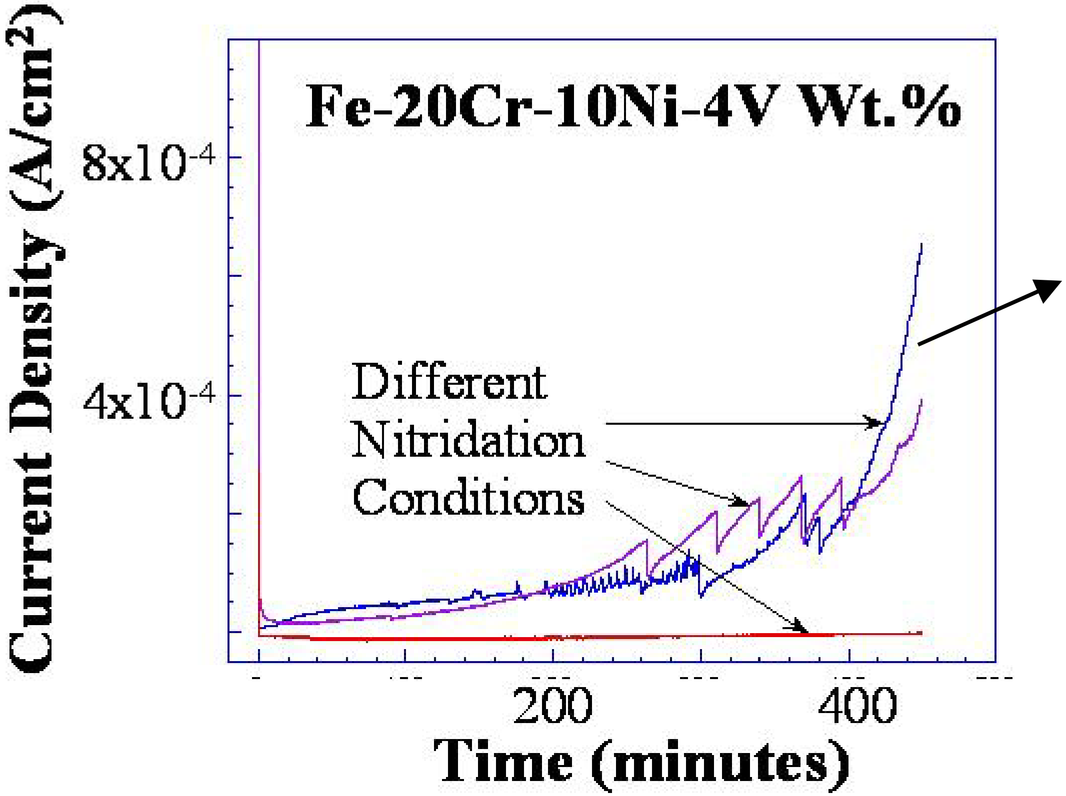
Nitrided Fe-20Cr-4V Meets DOE Interfacial Contact Resistance Goal



- 10^{-5} to 10^{-6} A/cm^2 range current densities typically observed
- Testing in 1M H_2SO_4 + 2ppm F^- (typically, 0.001M H_2SO_4)

Ni Additions Make Protective Cr-Nitride Base Surface Harder to Achieve

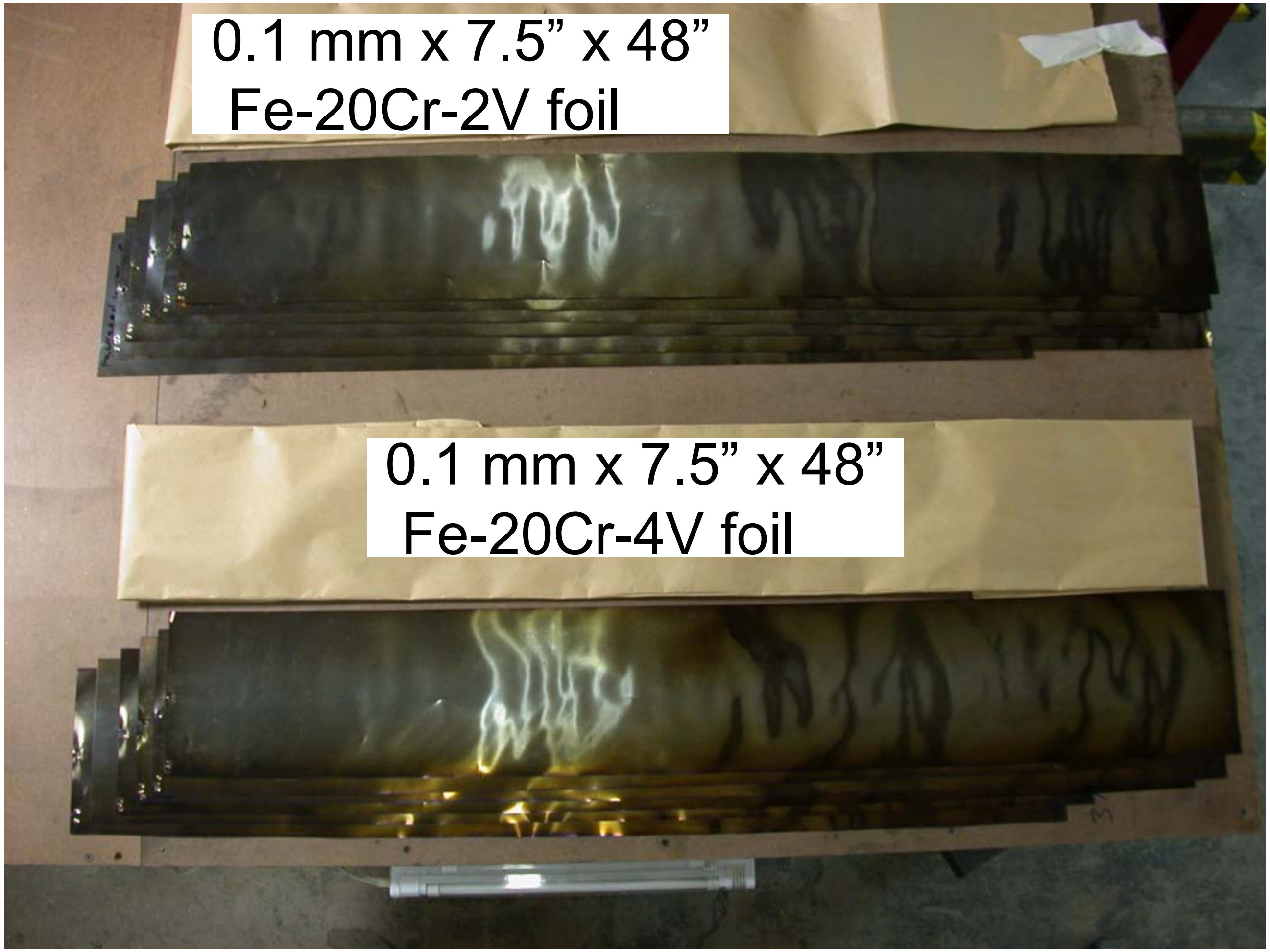
Static Polarization in H_2-Purged 1M H_2SO_4+2 ppm F^-/70°C/0.14 V vs SHE



"+" currents under simulated anode conditions suggests metal dissolution

- Ni additions may yield better foil manufacture and stampability
- Drawback is increased cost and difficulty in forming nitride surface
- Results to date: possible to form desired nitride with 5-10% Ni

Allegheny Ludlum Successfully Produced Developmental Ferritic Alloy Foil



0.1 mm x 7.5” x 48”
Fe-20Cr-2V foil

0.1 mm x 7.5” x 48”
Fe-20Cr-4V foil

- Developmental duplex and austenitic V-modified Fe-Cr alloy foil also successfully manufactured

20 Cr Ferritics Performed Well in GenCell Stamping Assessment

Alloy	Description	Flow-Field Stampability (channel depth/foil thick)
444	Fe-18Cr-2Mo Ferritic	**6**
316L	Fe-18Cr-12Ni Austenitic	**5.25**
904L	Fe-20Cr-25Ni-5Mo Aust.	**5.25**
Fe-15Cr-10Ni-3V	**Near-Austenitic**	**5.25**
Fe-20Cr-4V	**Ferritic**	**4.38**
Fe-20Cr-2V-5Ni	**Duplex**	**4.25**
Fe-20Cr-2V	**Ferritic**	**4.13**
2205	Fe-22Cr-5Ni-3Mo Duplx.	**3.75**
E-brite	Fe-26Cr-1Mo Ferritic	**2.5**

Better Flow-Field Stamping

- 18 cm^2 active area parallel flow-field stamping of commercial and developmental stainless steel foils

No Embrittlement and Little Warping of Stamped 18 cm^2 Active Area Plates on Nitriding

Fe-20Cr-4V Ferritic

Stamped and Nitrided **As-Stamped**

2205 Duplex (Fe-22Cr-5Ni-3Mo base wt.%)

Stamped and Nitrided **As-Stamped**

- Nitridation at 1000°C for 2 h in N_2-$4H_2$
  - promising initial corrosion results also with nitrided 2205 stainless steel

Parallel and Serpentine Design Refinement Underway to Establish Baseline for Single-Cell Evaluation

GenCell Exploratory Serpentine Flow-Field Stampings

- Serpentine flow-fields successfully stamped in austenitic 904L (above) and ferritic Crofer 22 APU foils

- Modeling and single-cell/hardware design “shakedown” studies underway

-platform for metal, nitrided metal, and graphite single-cell comparison

Stamped Fe-Cr-V Alloys Can Meet $5/kW Transportation Cost Goals

2006 GenCell Cost Estimates for Stamped Bipolar Plates

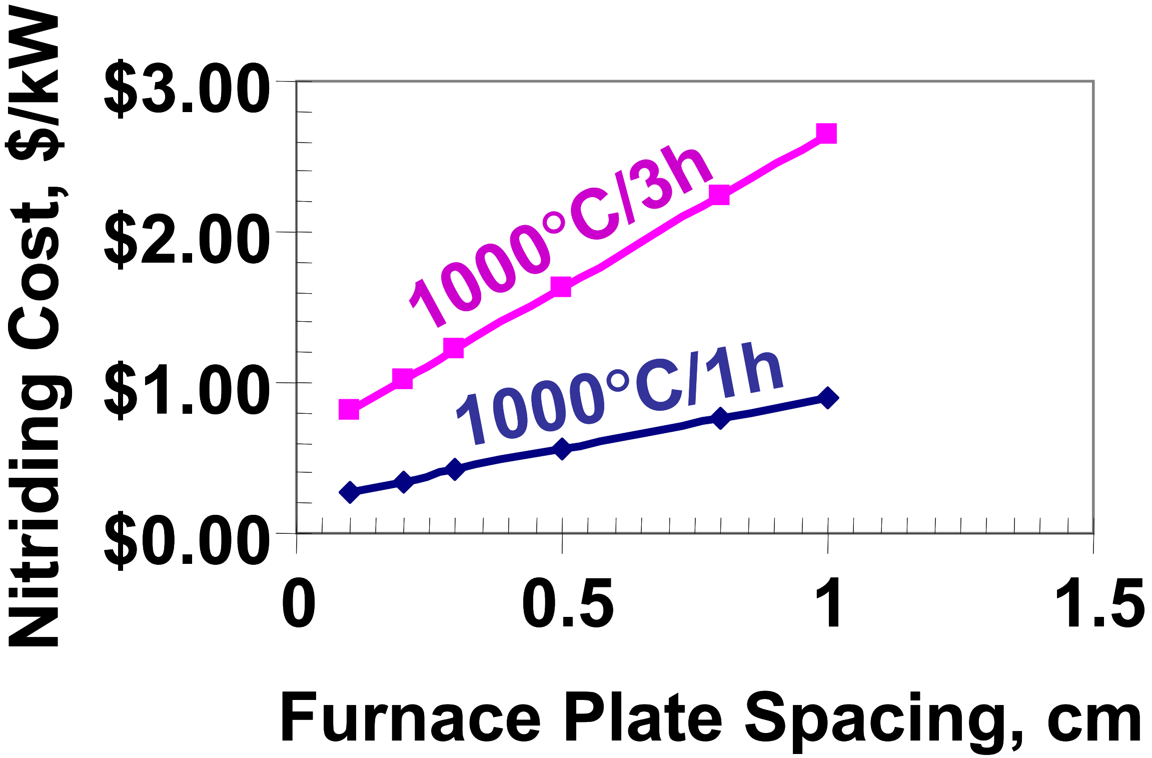
(Nitriding Costs Not Included)

Foil	Density	Bipolar Plate Cost ($/kW)		
Thick. (in)	kg/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

- Higher-Cr ferritic commercial alloy foils ~$3-7/lb :
  - 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 likely comparable to Fe-Cr-V alloy range
- Alloy/stamping costs leaves < ~75 cents/kW for nitriding costs

75 cents/kW Nitriding Costs Potentially Feasible

Preliminary Cost Analysis by B. James, Directed Technologies



- Automated, step-continuous conventional nitriding system at 500,000 systems per year, mark up not included
  - -keys are short nitriding cycle and high furnace plate stacking density
- Nitriding by pulsed plasma arc lamp in range of 16-44 cents/kW
  - -feasibility to nitride Ti in "seconds" previously demonstrated

Summary

- Ferritic and duplex compositions amenable to both stamping and nitriding have been identified

- Alloy/nitriding envelope capable of imparting low ICR and high corrosion resistance at potentially acceptable nitriding cost identified (all in range of DOE targets)

- Potential to nitride stamped alloy foils without embrittlement and with little warping demonstrated
  - -meets 1st milestone go/no go decision point

Future Work

- **FY 2008** (Funding delays have jeopardized work-plan schedule)
  - -Detailed characterization of corrosion and electrical properties of nitrided Fe-Cr-V developmental foils (corrosion and ICR data to date from lab-scale castings)
  - -Finalization of baseline 18cm^2 active area plate design for single-cell testing (modeling and shakedown testing)
  - -Single-cell testing of stamped and nitrided alloys compared to untreated stainless steel and graphite control plates
    2nd Go/No go decision point for project
- **FY 2009**
  - -Modeling, shakedown testing, and down select for stamped 250cm^2 active area plates for 10-cell drive-cycle stack test.
  - -Project ends with post-test characterization and assessment