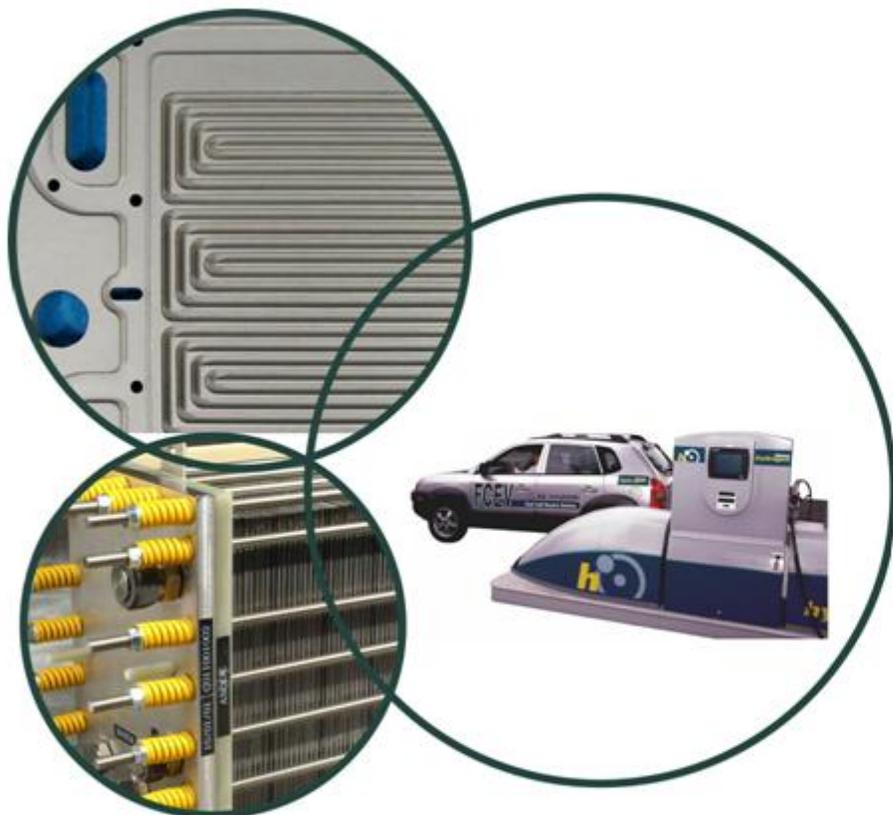


Nitrided Metallic Bipolar Plates



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Project ID FC 27

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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-cm²
 - corrosion < 1 x10⁻⁶ A/cm²
 - 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

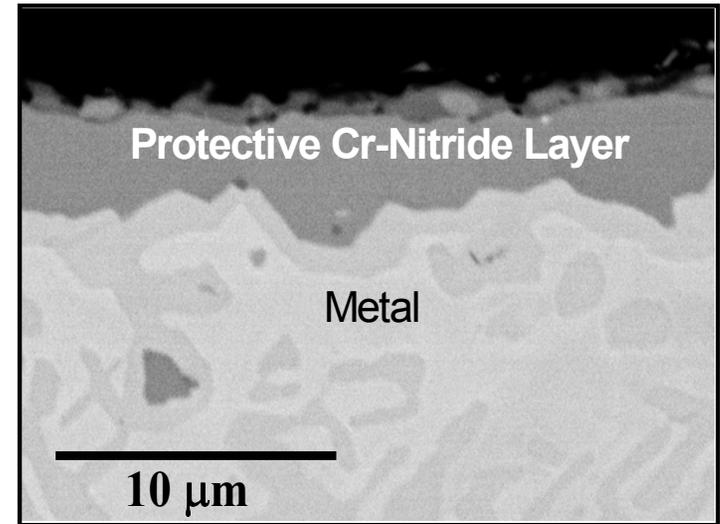
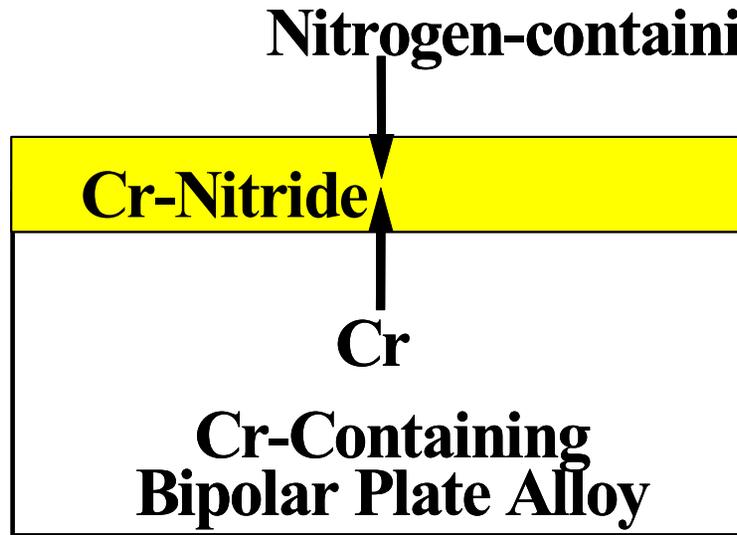
- **Milestone 1:** No significant warping or embrittlement of stamped 18 cm² active area plates by nitriding- **go/no go 1**
- **Milestone 2:** Single-cell fuel cell test performance for 18 cm² stamped and nitrided metallic bipolar plates equivalent to that of graphite (~1000 h, cyclic)- **go/no go 2**
- **Milestone 3:** 10 cell stack test of 250 cm² 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**

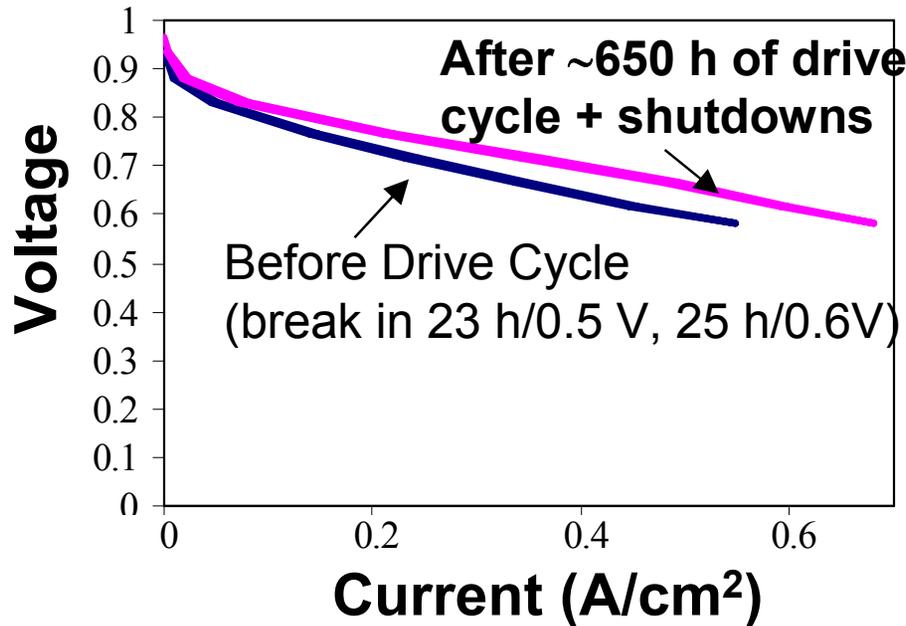


Approach: Thermally Grown Cr-Nitride for Corrosion Protection/Low Contact Resistance



- Nitrides are corrosion resistant with low surface contact resistance
- Surface conversion, not a deposited coating: 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

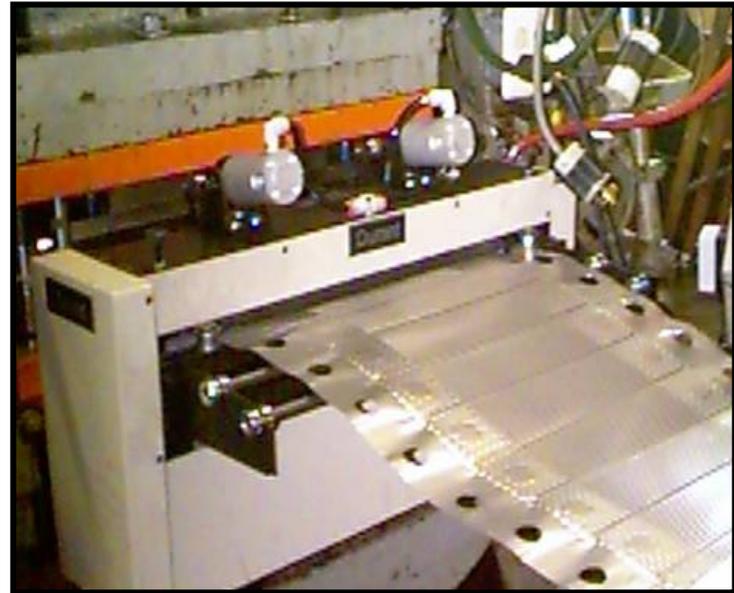
Good Single-Cell Drive-Cycle Durability Test Results for Model Nitrided Ni-50Cr Plates



- **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 (2×10^{-6} g/cm²) of Ni detected in MEA, suspect local CrNiN spots

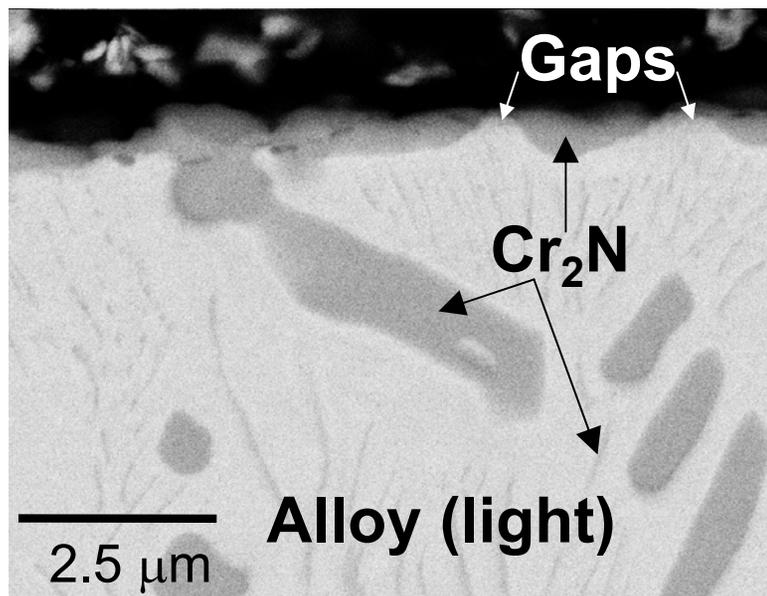
Need Fe-Base Stainless Steel to Meet \$5/kW Bipolar Plate Cost Goals for Auto Applications

- 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)



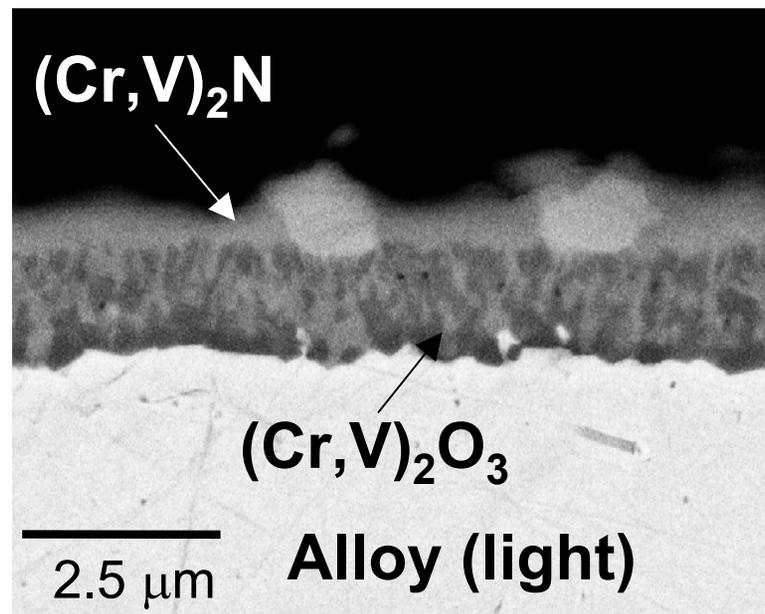
Pre-Oxidation/Nitridation Yields Protective Cr-Nitride Surface on Model Fe-27Cr-6V Alloy

Nitrided Fe-27Cr



- N₂ readily penetrates Fe-Cr
- Dense Cr-nitride surface not formed
- Poor corrosion resistance

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

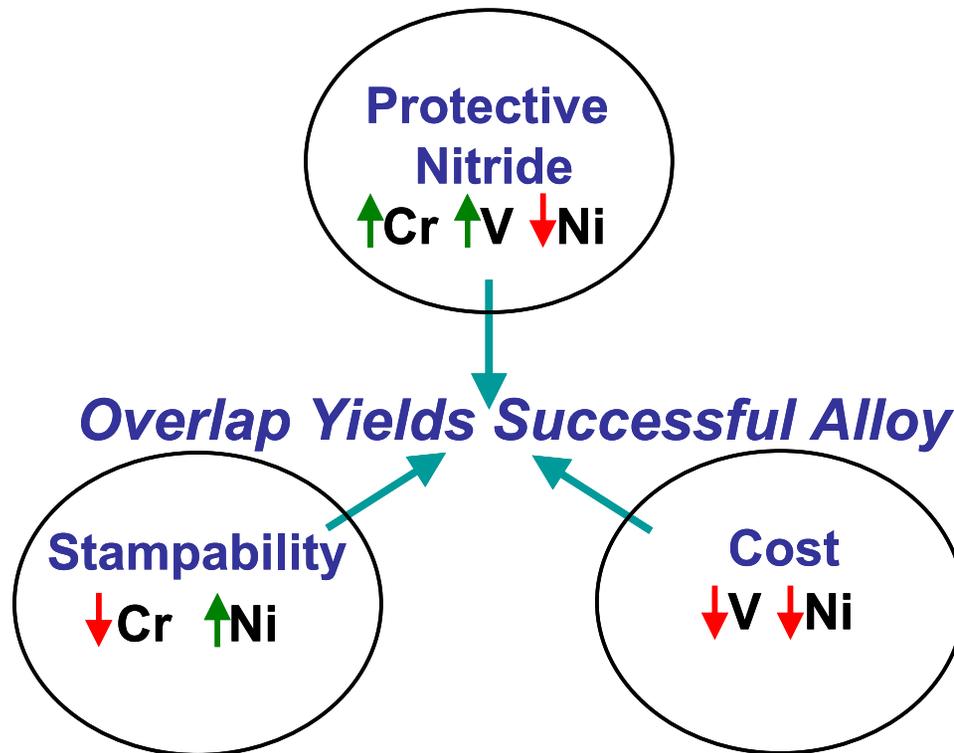


- Initial oxide keeps N₂ at surface
- V in Cr-oxide makes readily nitrided
- Excellent corrosion resistance and conductivity demonstrated

• Approach demonstrated for nitriding Fe-Cr base alloys

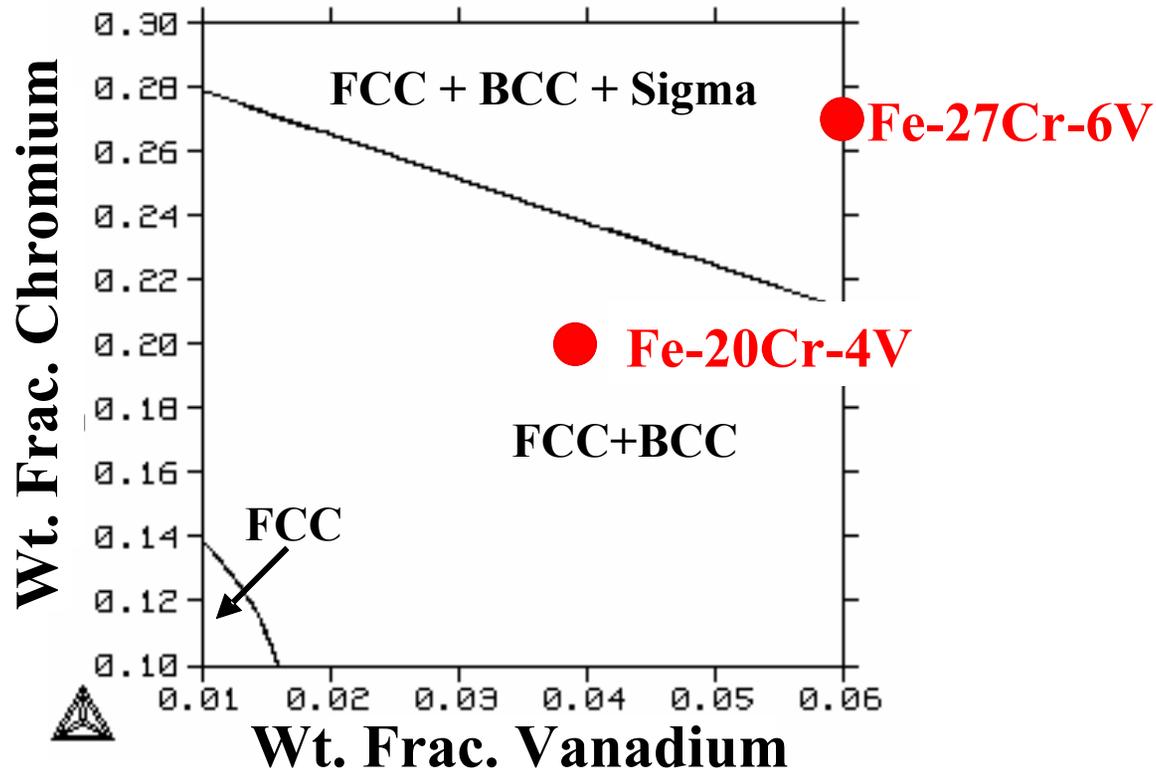
Scale-Up Considerations Focus of New Effort

- **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**



Computational Thermo. Guided Alloy Design

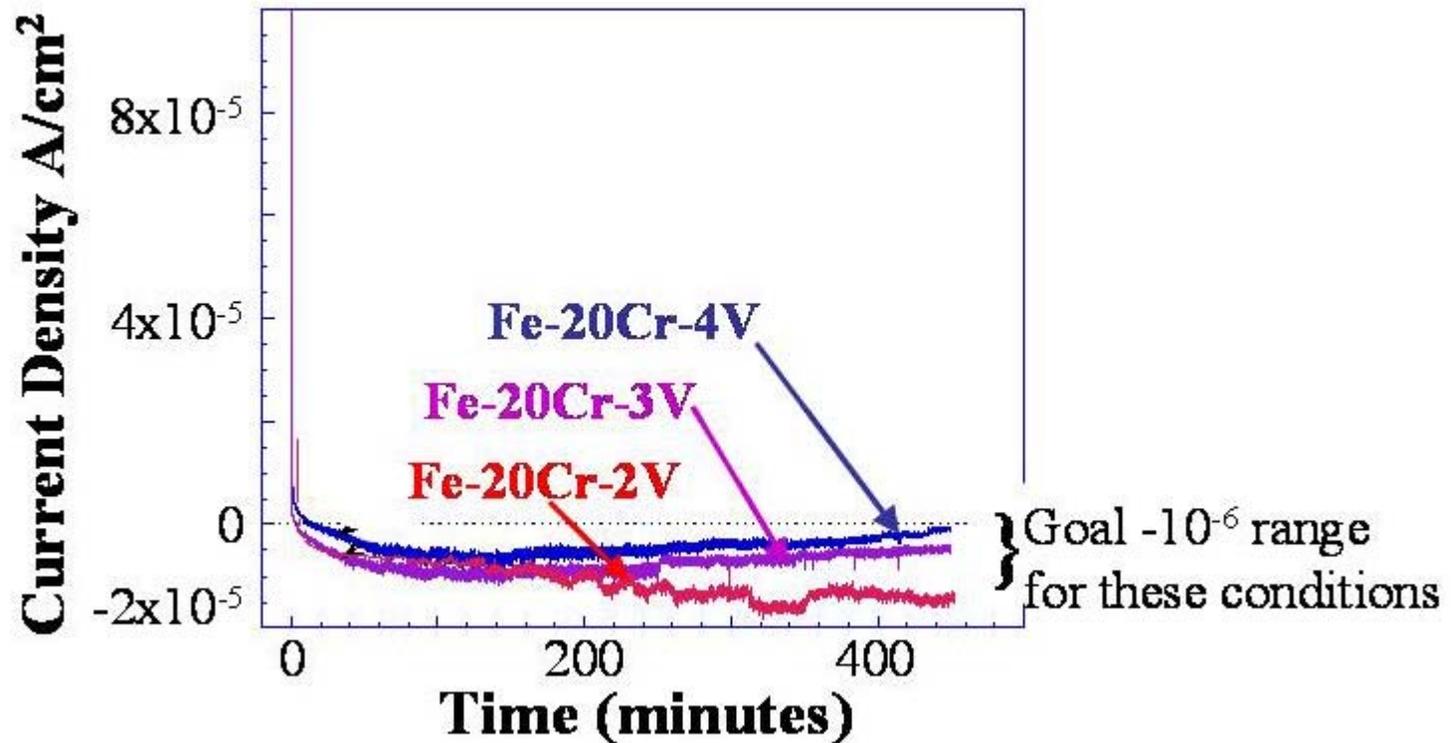
Calculated Phase Equilibria for Fe-Cr-V + 5 wt.% Ni at 800°C



- 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.%

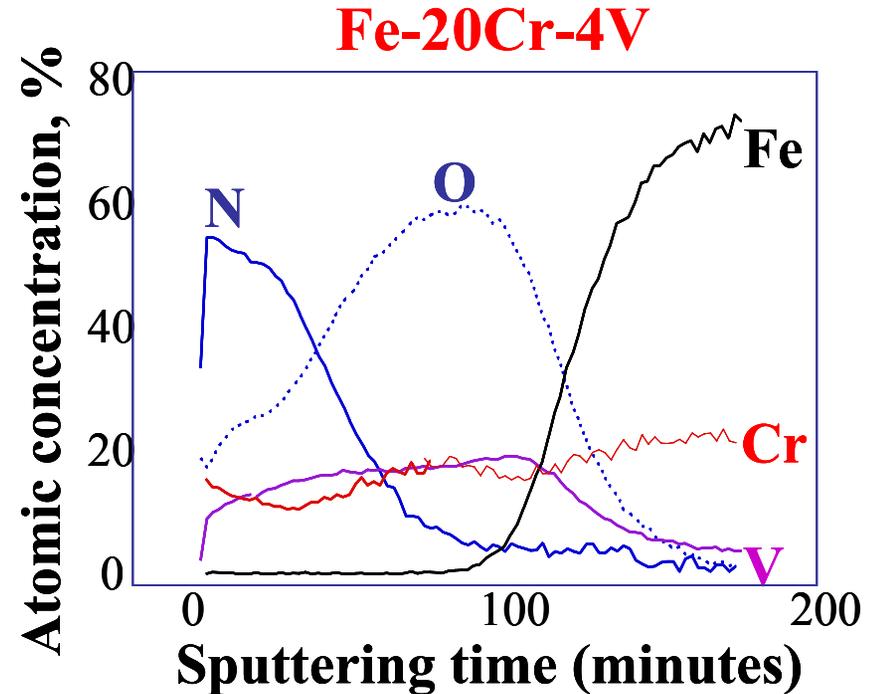
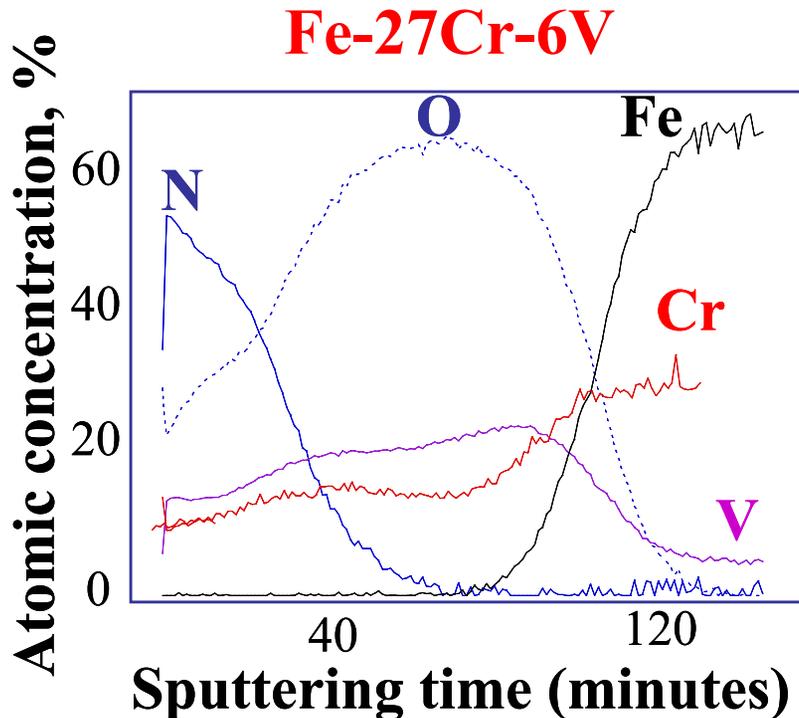
Static Polarization in H₂-Purged 1M H₂SO₄+2 ppm F-/70°C/0.14 V vs SHE



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

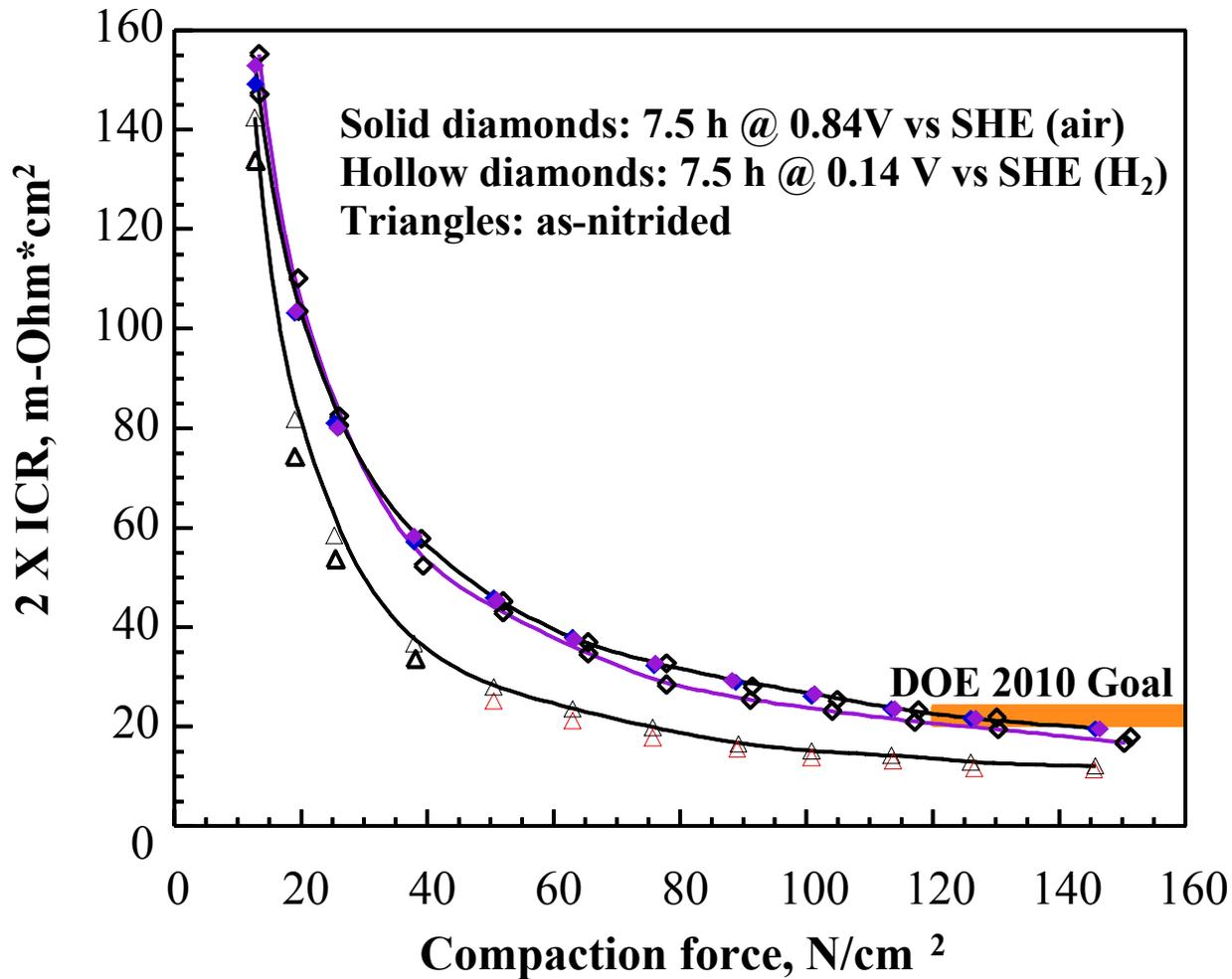
Nitrided Fe-20Cr-4V Surface Similar to That Formed on Nitrided Fe-27Cr-6V

AES Depth Profiles After Polarization for 7.5h in Aerated
1M H₂SO₄+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

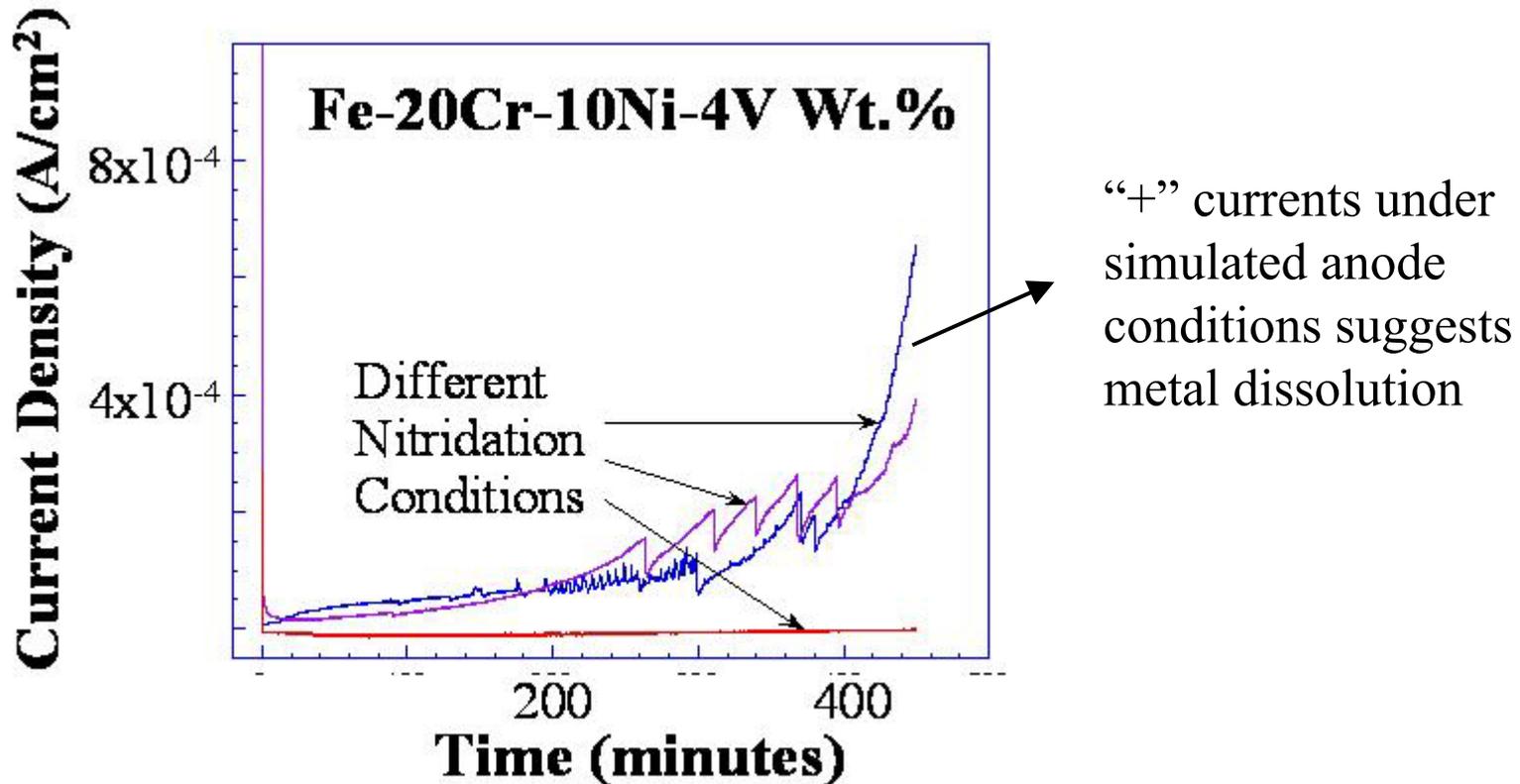
Nitrided Fe-20Cr-4V Meets DOE Interfacial Contact Resistance Goal



- 10^{-5} to 10^{-6} A/cm^2 range current densities typically observed
- Testing in $1\text{M H}_2\text{SO}_4 + 2\text{ppm F}^-$ (typically, $0.001\text{M H}_2\text{SO}_4$)

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

Static Polarization in H₂-Purged 1M H₂SO₄+2 ppm F-/70°C/0.14 V vs SHE



- 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



- 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 cm² active area parallel flow-field stamping of commercial and developmental stainless steel foils

No Embrittlement and Little Warping of Stamped 18 cm² 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 N₂-4H₂

-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, nitrated metal, and graphite single-cell comparison

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

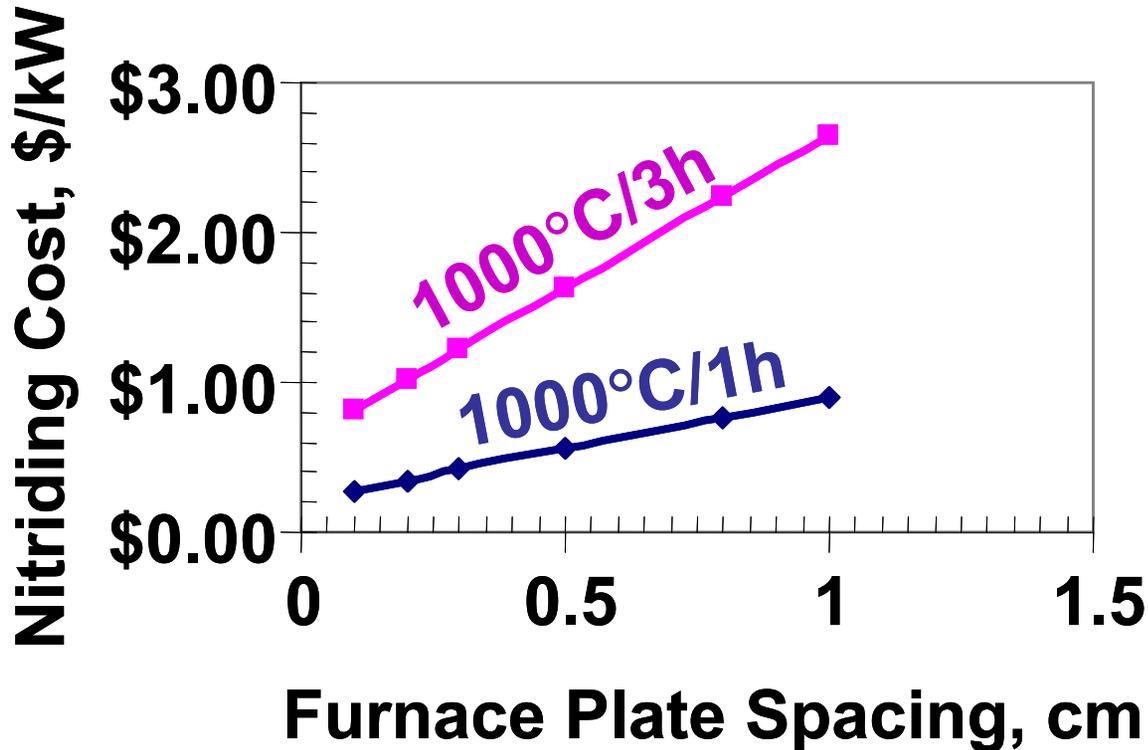
2006 GenCell Cost Estimates for Stamped Bipolar Plates (Nitriding Costs Not Included)

Foil Thick. (in)	Density kg/kW	Bipolar Plate Cost (\$/kW)		
		<u>\$3/lb Alloy</u>	<u>\$5/lb Alloy</u>	<u>\$7/lb Alloy</u>
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 nitrated Fe-Cr-V developmental foils (corrosion and ICR data to date from lab-scale castings)
 - Finalization of baseline 18cm² active area plate design for single-cell testing (modeling and shakedown testing)
 - Single-cell testing of stamped and nitrated 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 250cm² active area plates for 10-cell drive-cycle stack test.
 - Project ends with post-test characterization and assessment