Nitrided Metallic Bipolar Plates

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Project ID
FC_40_Tortorelli

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Overview

Timeline

- Start: May 1, 2007
- Finish: Sept. 30, 2010
- ~60% complete

Budget

- Total project funding
  - $4530k DOE share
  - $400k Contractor share
- $1700 k received in FY 08
- $350 k received in FY 09
- ~$700 k of planned FY09 $ deferred to FY 2010 pending milestone go/no go

Barriers

- Metallic bipolar plate durability and cost
- 2010 Targets
  - resistivity < 10 mohm-cm^2
  - corrosion < 1 $x10^{-6}$ A/cm^2
  - cost < $5/kW

Partners

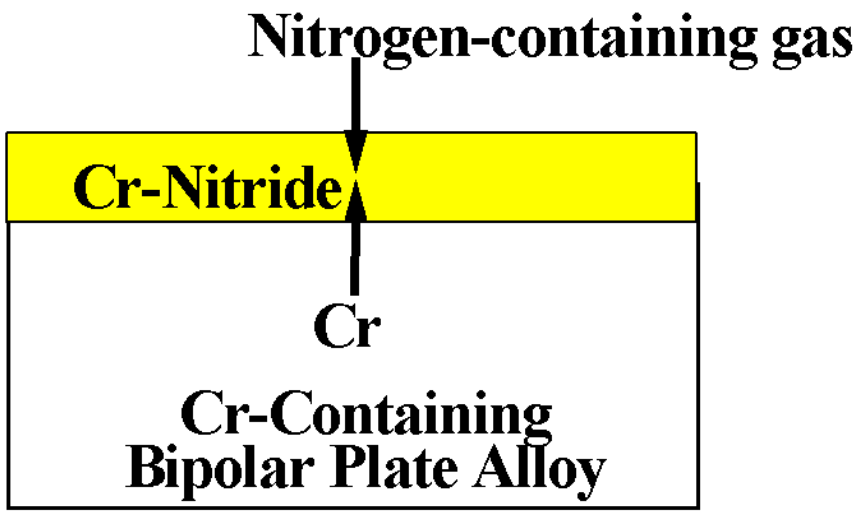
- ORNL (Lead)
- AGNI-GenCell
- Allegheny Ludlum
- Arizona State University
- LANL
- NREL

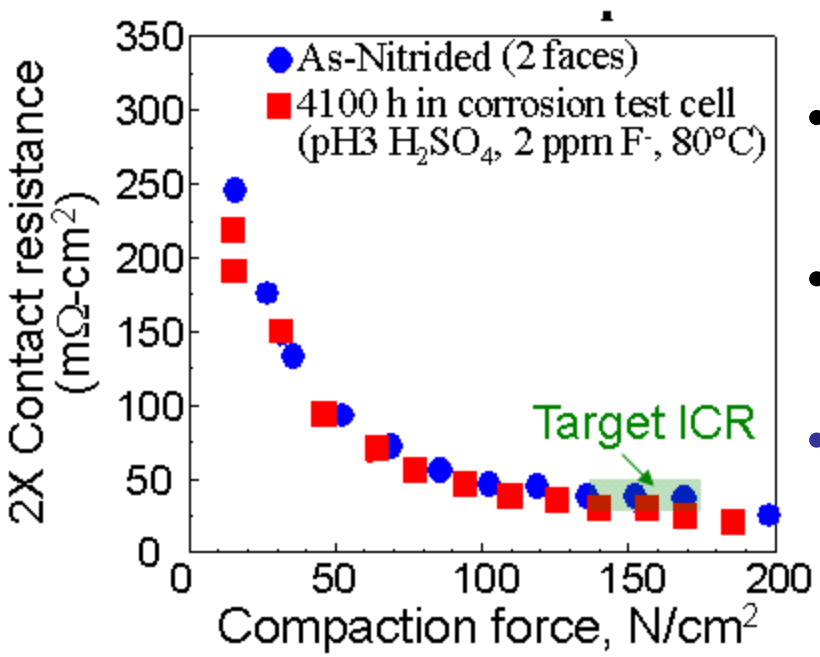
Objective: Demonstrate Nitridation to Protect Stamped Metallic Bipolar Plates

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 15 cm^2 active area plates by nitriding- **go/no go 1**
  -met April 08
- **Milestone 2**: Single-cell fuel cell test performance for 15 cm^2 stamped and nitrided metallic bipolar plates equivalent to that of graphite (~750-1000 h, cyclic) - **go/no go 2**
  -postponed to Sept 09
- **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 Sept 2010**

Nitride to Lower Contact Resistance and Protect Metallic Bipolar Plates from Corrosion



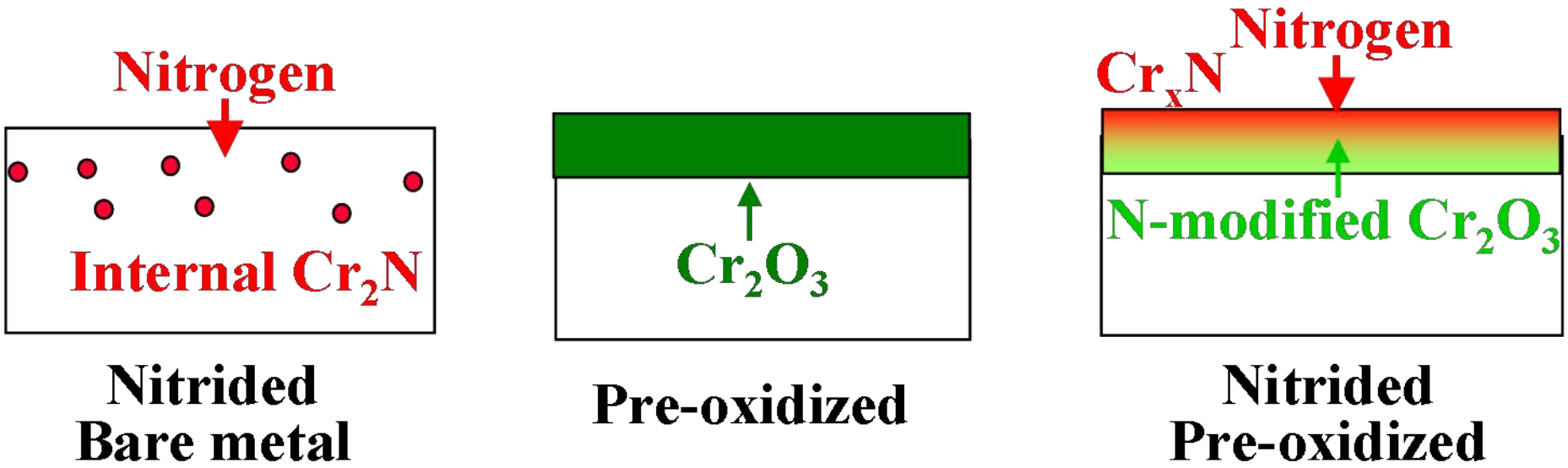


Nitrided Model Bipolar Plate

Collaboration w/DANA Corp, TN Tech, and USC

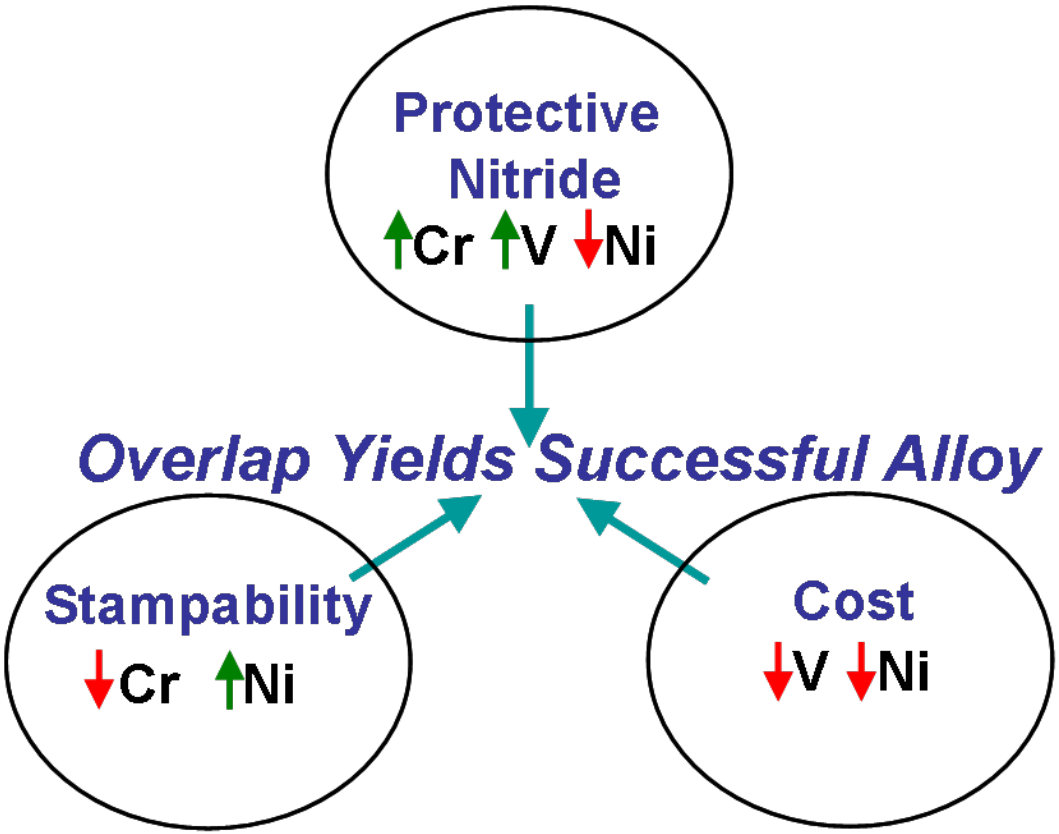
- Low-cost, scalable approach
  - -nitrides conductive and corrosion resistant
- Successful single-cell fuel cell testing with model nitrided Ni-Cr alloys ($)
- **Goal is to implement <u>stampings</u> of <u>low-cost stainless steel foils</u>**

Pre-Oxidation Followed by Nitridation to Form Cr_xN Surface on Stainless Steels



- Stainless steels internally nitride: corrosion
- Form Cr_2O_3 by preoxidation to keep N_2 at surface
  - -convert surface Cr_2O_3 to surface Cr_xN by nitridation
- V added to stainless steel assists conversion to nitride
  - -good ICR and corrosion results with model Fe-27Cr-6V alloy

Scale-Up From Model Alloy Sheet to Stamped and Nitrided Foils



Challenge: Co-optimize ductility (for stamping) and low alloy cost with protective Cr-nitride surface formation in developmental and commercial stainless steel foil

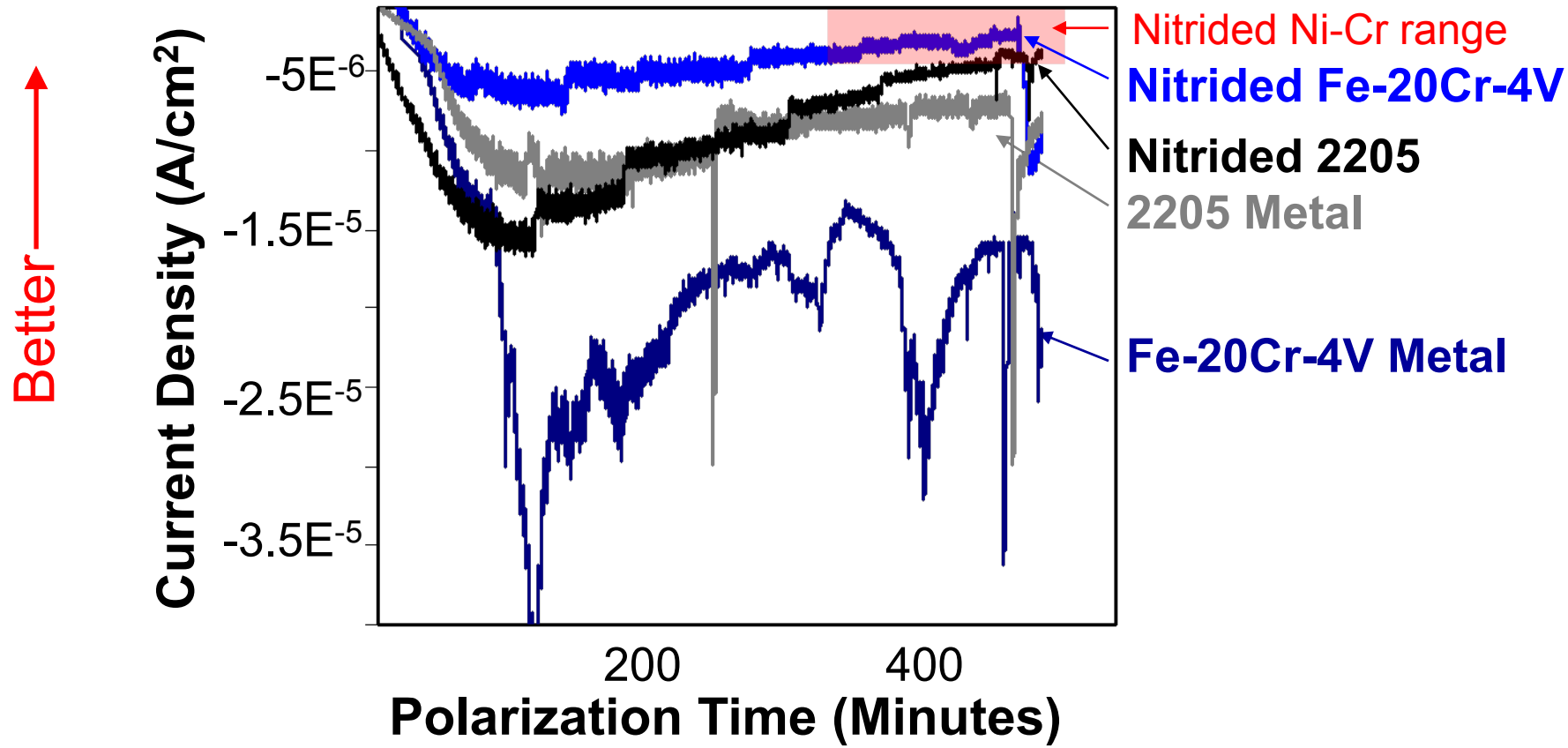
Where Did We Leave Off at Last Review?

- Down select to Fe-20Cr-4V wt.% and 2205 (Fe-22Cr-5Ni +N base) stainless steels based on nitridation studies of <u>sheet</u> material
  - -ICR goals met as-nitrided and after polarization (2205 ICR ~2x target)
  - -Good corrosion resistance in 1M H_2SO_4+2 ppm F^- at 70°C
  - -No brittle sigma phase formation during nitriding heat/cool cycle
- Allegheny Ludlum successfully manufactured 0.1 mm thick foils of series of developmental Fe-Cr-V base alloys
- AGNI-GenCell completed stamping assessment of a series of developmental and commercial stainless steel foils
  - -No significant warping or embrittlement with nitrided stampings
- Preliminary cost estimate by Directed Technologies: < 3 h, 1000°C nitriding cycle can potentially meet DOE cost targets

New FY09 work conducted with <u>0.1 mm stainless steel foils</u> using pre-oxidation and < 3 h, 1000°C nitriding cycle

Nitrided Foils Exhibit Good Corrosion Resistance Under Simulated Aggressive Anode Conditions

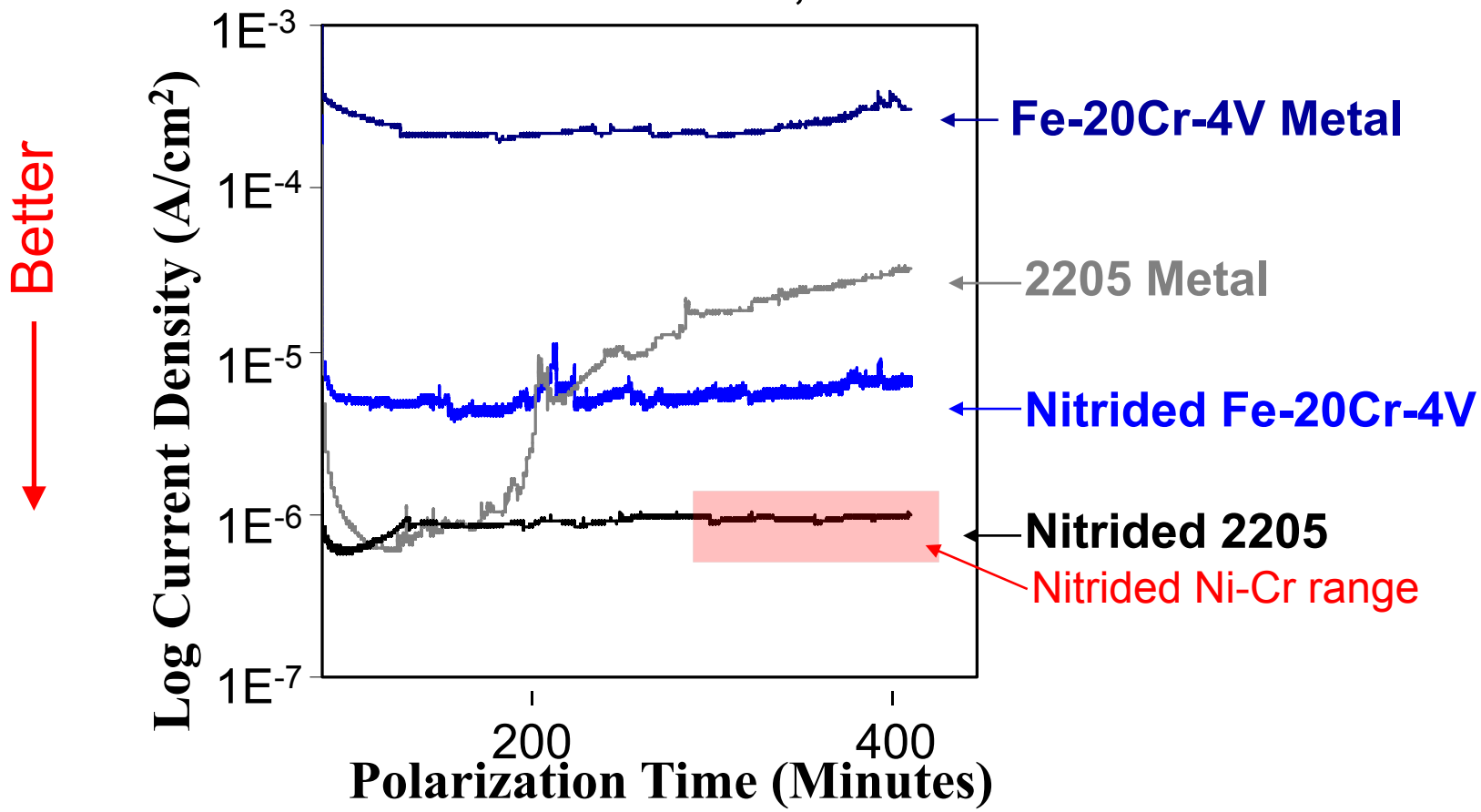
Polarization Evaluation at 70°C in 1M H_2SO_4+ 2 ppm F^- held at +0.14V vs SHE, H_2 purged



- Nitrided foil current densities comparable to nitrided model Ni-Cr and Fe-Cr base alloys: moderately better than untreated metal

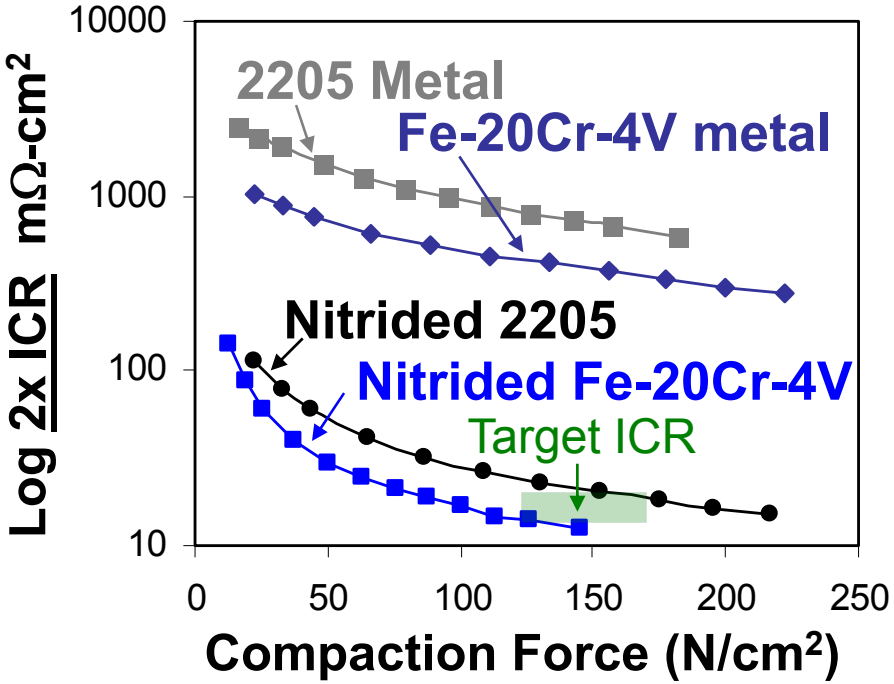
Nitrided Foils Exhibit Good Corrosion Resistance Under Simulated Aggressive Cathode Conditions

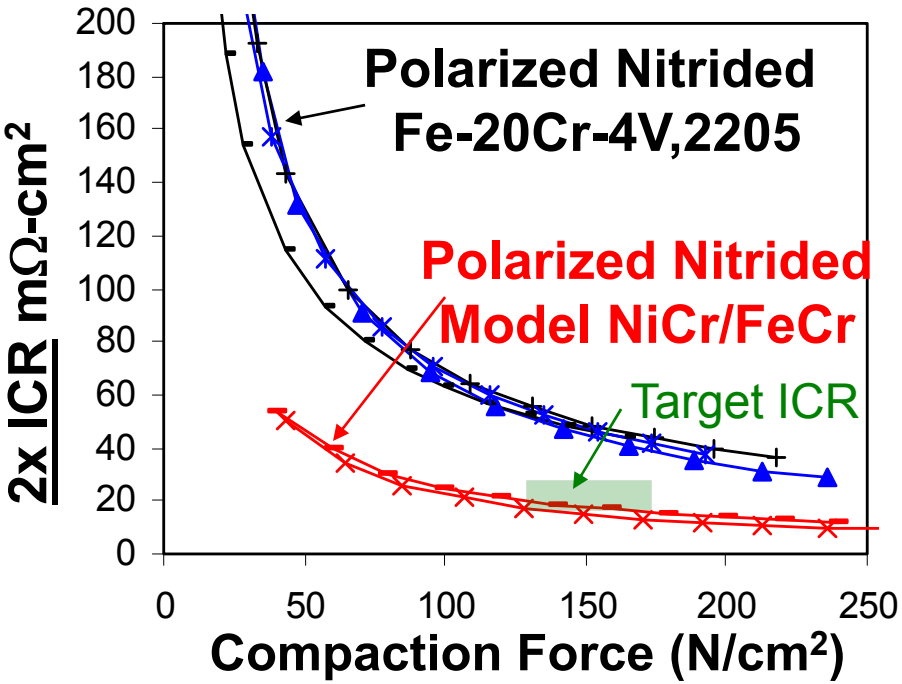
Polarization Evaluation at 70°C in 1M H_2SO_4+ 2 ppm F^- held at +0.84V vs SHE, aerated



- Current densities for nitrided Fe-20Cr-4V foil higher than model nitrided Ni-Cr/Fe-Cr alloys, still improved over untreated metal

Nitridation Significantly Reduces Foil Interfacial Contact Resistance (ICR)

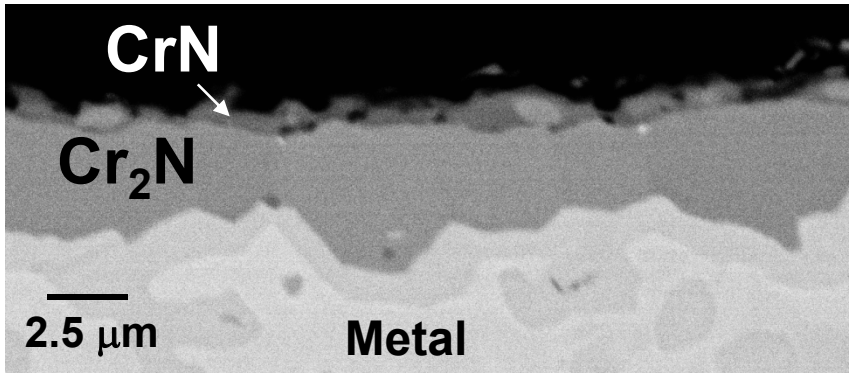




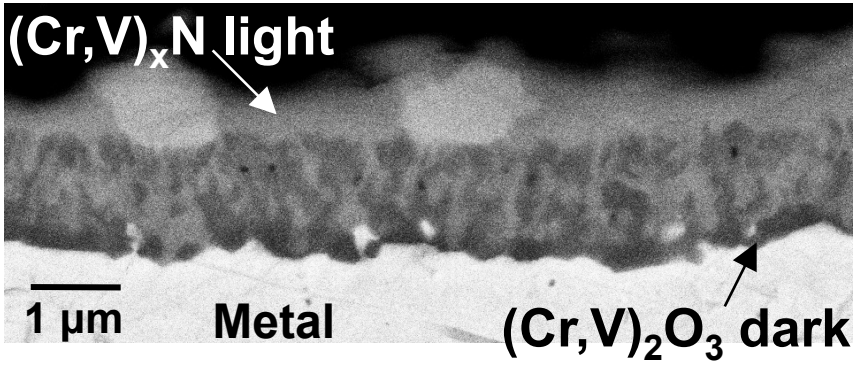
- 7h polarization of nitrided foils under simulated aggressive anode and cathode conditions raised ICR beyond target value
  - -remains order of magnitude lower than untreated metal
- 7h polarized nitrided model NiCr/FeCr alloys and nitrided Fe-20Cr-4V <u>sheet</u> material showed only small ICR increases

Continuous Cr-Nitride Surfaces Formed on Model Nitrided Ni-50Cr and Fe-27Cr-6V Alloys

Nitrided Ni-50Cr



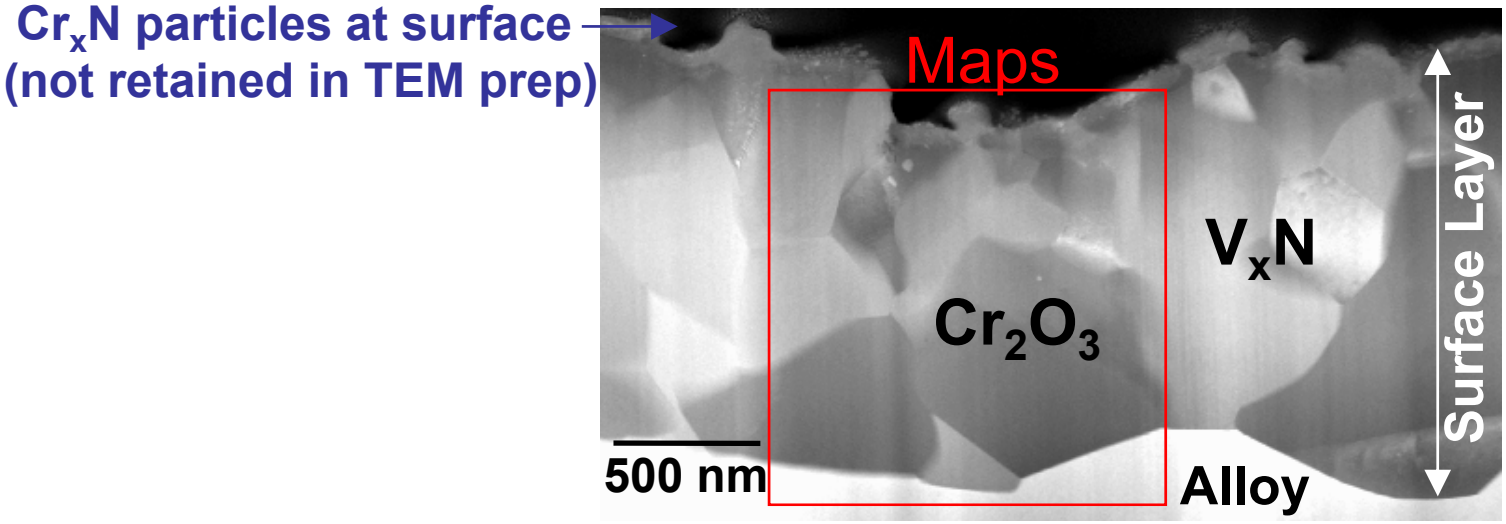
Nitrided Fe-27Cr-6V

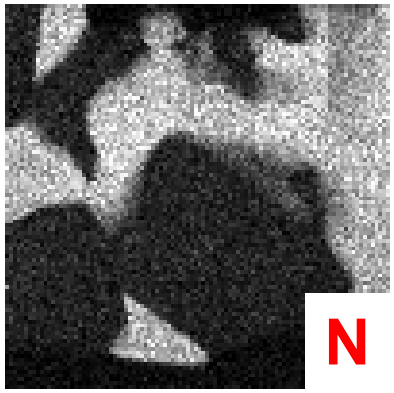


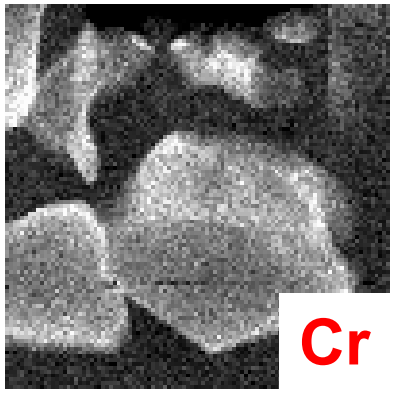
- Nitrided Fe-27Cr-6V Cr-nitride surface formed in mixed nitrogen/oxygen environment over 24 h nitriding cycle
  - -long cycle and mixed N_2/O_2 environment not practical for scale up
  - -used to understand and develop controllable pre-oxidation/nitridation approach with short nitriding cycles to meet cost targets
  - -structures shown above from sheet material

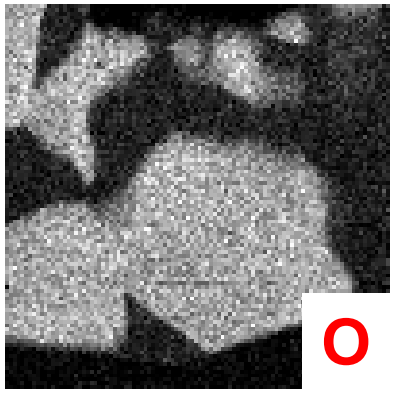
V_xN Dispersed in Cr_2O_3 Formed on Fe-20Cr-4V Sheet and Foils

Cross-Section TEM Analysis of Pre-Oxidized/Nitrided Fe-20Cr-4V





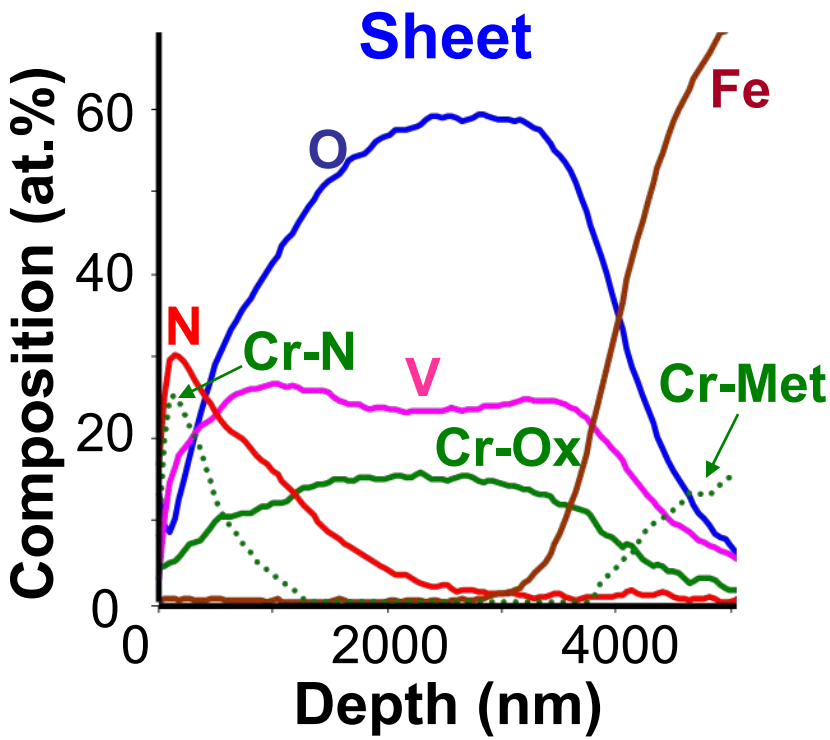


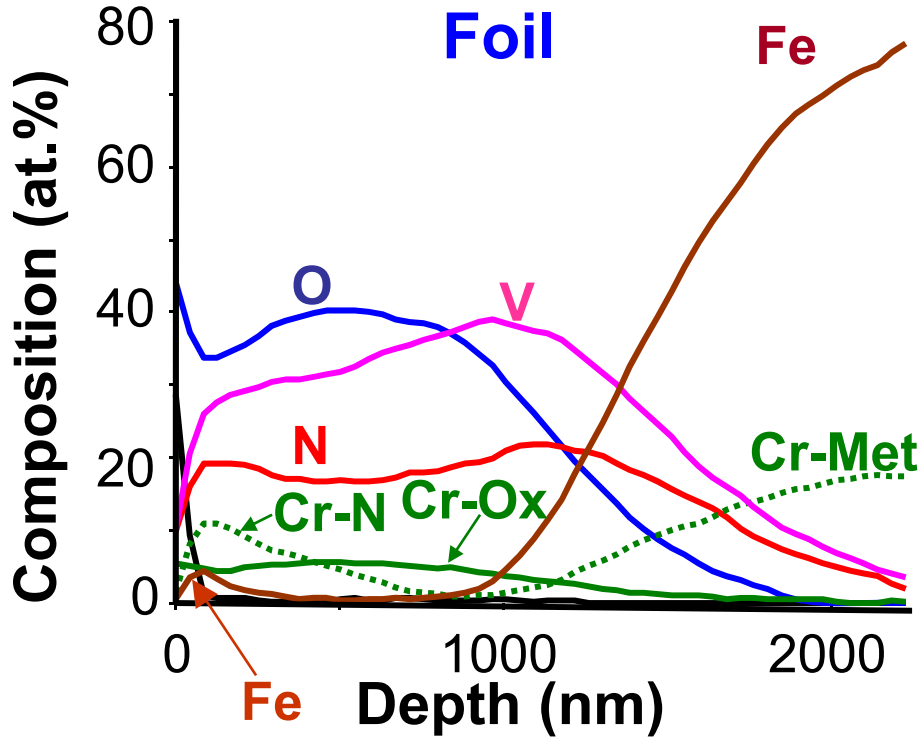


- <u>Through thickness V_xN paths</u> but no continuous Cr_xN as with model alloys
- Consequence of pre-oxidation/nitridation cycle to meet cost goals

Pre-Oxidized/Nitrided Fe-20Cr-4V Foils Tend to Exhibit Less N at Surface than Sheet Material

AES Depth Profile of Pre-Oxidized/Nitrided Fe-20Cr-4V



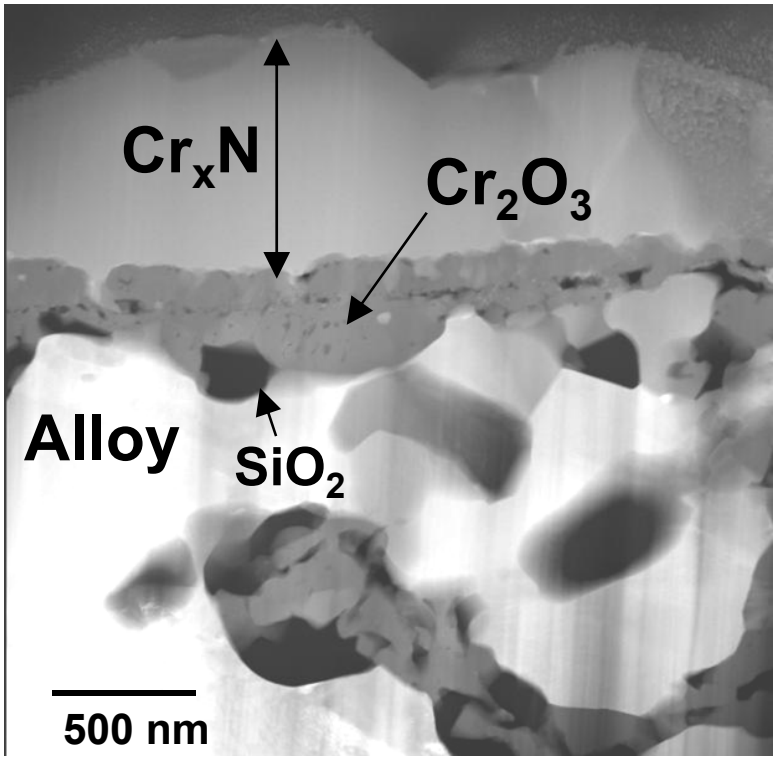


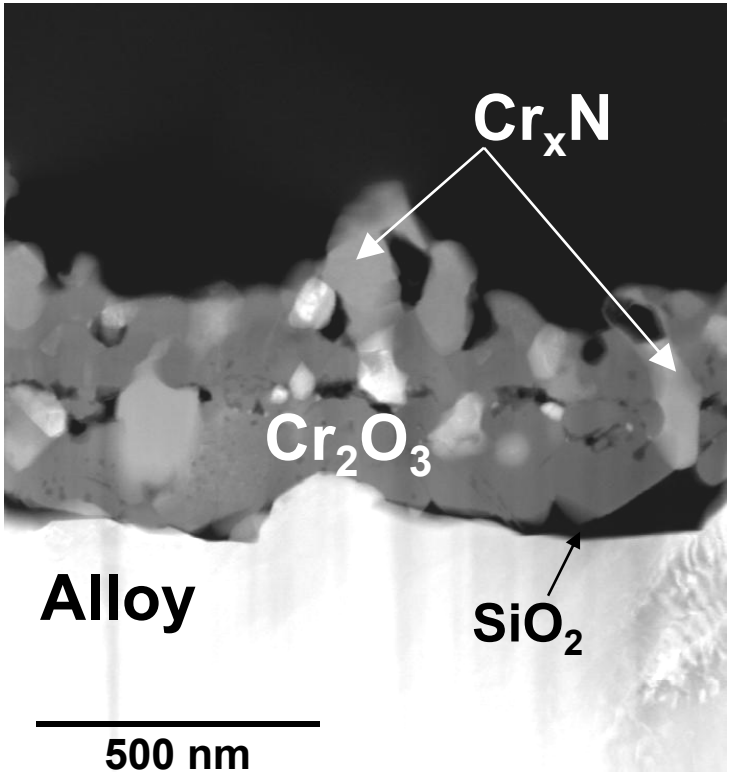
- Foils more sensitive to O_2 impurities in N_2-$4H_2$, more oxide at surface
  - -foil surface finish and microstructure/diffusion effect?
- Foils show small surface Fe peak-not observed in sheet material
  - -may contribute to observed ICR increase on polarization

Continuous Cr-Oxide Regions Formed on Pre-Oxidized/Nitrided 2205

Cross-Section TEM Analysis of Pre-Oxidized/Nitrided 2205

Two Runs/Similar Conditions

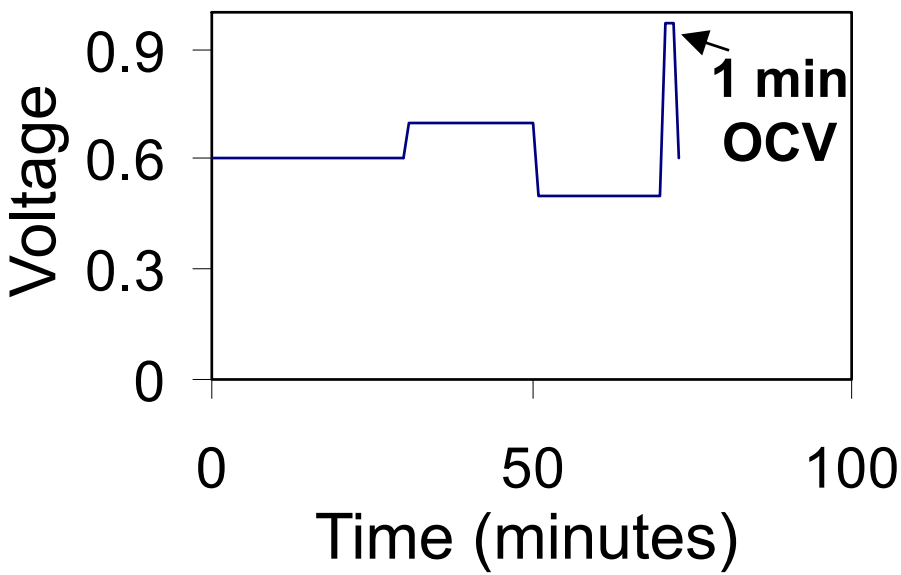




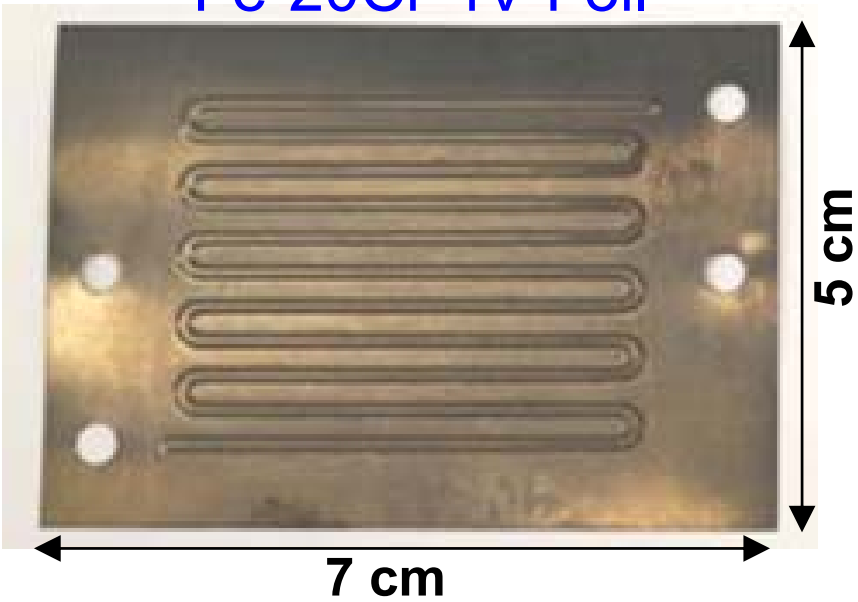
- Significant scatter in run-to-run surface O/N content
  - -consequence of lack of strong nitride-forming element in 2205 (only Cr)
- Few through-layer thickness nitride paths
  - -continuous inner oxide could compromise electrical conductivity

Single-Cell Fuel Cell Testing of Nitrided Foils Benchmarked to Stainless Steels and Graphite

Fuel Cell Test Cycle
(750-1000 total h planned)



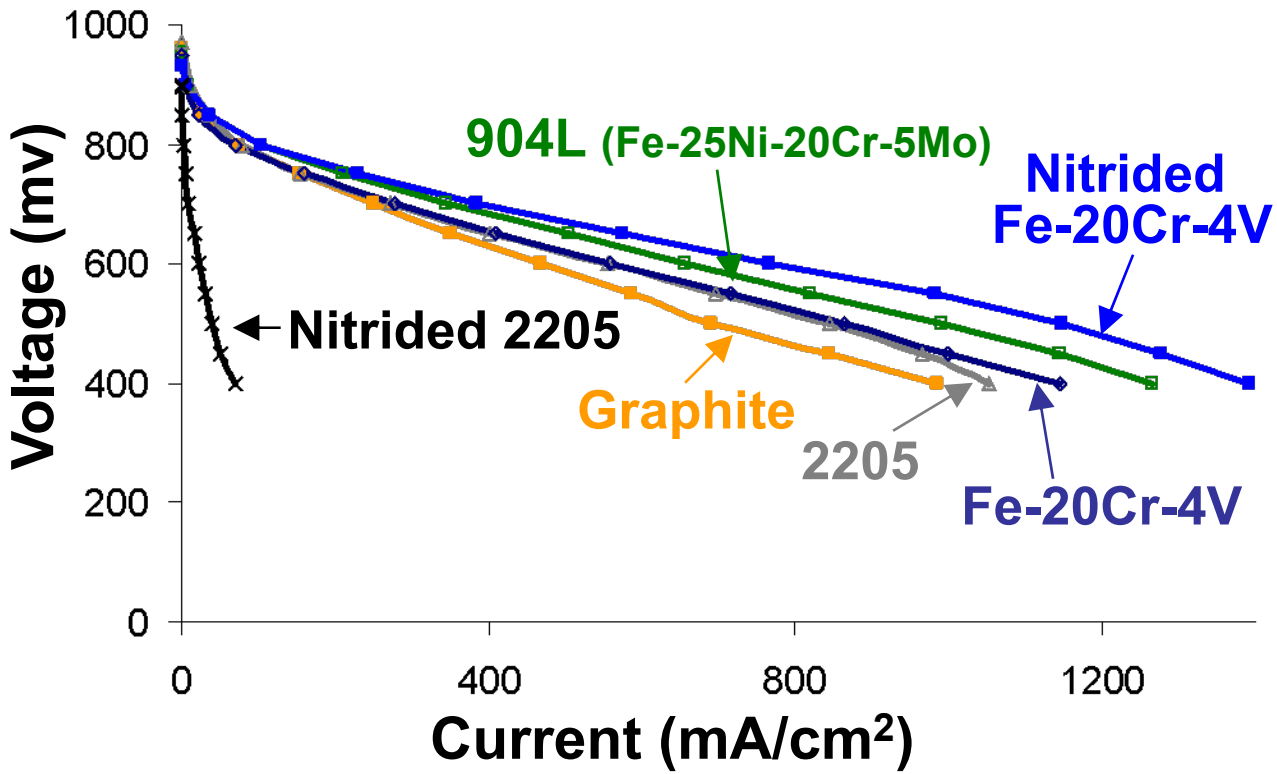
Stamped and Nitrided Fe-20Cr-4V Foil



- Operating conditions: 80°C, 25 psig, stoichiometry $2.5O_2/1.25H_2$
  - -performance curves (V-I):0.9-0.4V, 0.05V steps, 20 min./step, repeat 3x
- Serpentine ~15 cm^2 active area stamped foils for metals, machined graphite block of similar flow-field design
- Significant learning curve for stamped foil design and testing

Good Initial Single-Cell Fuel Cell Performance For Nitrided Fe-20Cr-4V

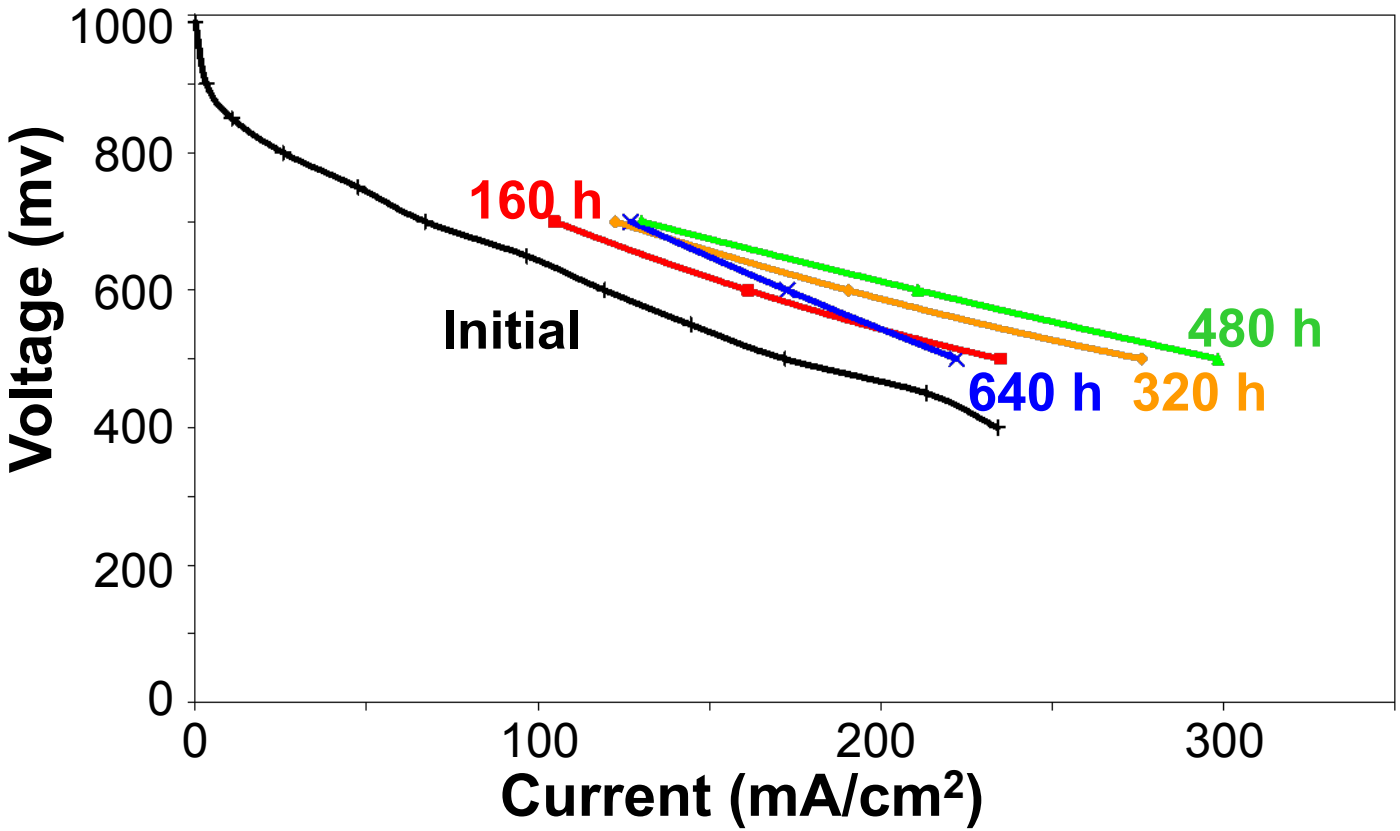
Initial V-I Curves Using 50 micron MEA (0.8 mg Pt/cm^2)



- Nitrided Fe-20Cr-4V exhibited best behavior (some discoloration cathode side)
- Nitrided 2205 exhibited poor behavior- continuous oxide areas suspected
- MEA failure at gas inlet/outlet due to foil/MEA design integration issues

MEA Durability Issue Solved by Moving to Thicker MEA

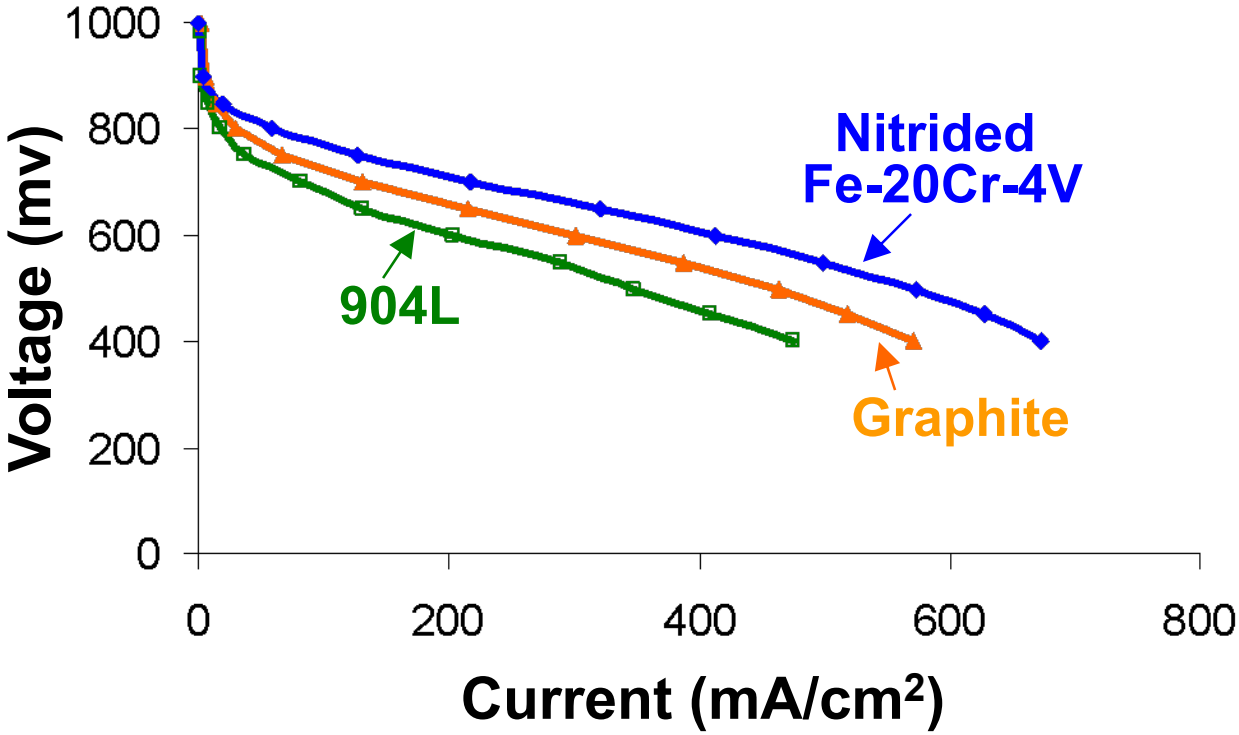
V-I Curves from 700 h Test of Untreated 904L Foil Using 125 micron MEA (0.5 mg/cm^2 Pt)



- Some discoloration on anode-side plate, MEA will be analyzed by XRF
- 175 micron MEA selected for ~750-1000 h durability studies

Cyclic Durability Tests Underway Using 175 Micron MEA with Integrated GDL

Initial V-I Curves Using 175 micron MEA (0.5 mg/cm^2 Pt)



- Significant initial performance advantage of nitrided Fe-20Cr-4V over that of untreated 904L stainless steel (ICR effect?)
- Machined flow-fields may be source of lower graphite performance
- Durability assessed by V-I curves and MEA analysis for metal ions

Summary

- Nitridation of stainless steel foils using short pre-oxidation and nitriding cycle yielded mixed nitride/oxide surface layer
  - -significant improvement in ICR and corrosion behavior compared to untreated stainless steel foils
  - -not as protective as continuous Cr-nitride layers formed on model alloys (some concern for ICR and cathode-side corrosion)
- Promising initial performance of stamped and nitrided Fe-20Cr-4V in cyclic single-cell fuel cell tests
- Durability studies of stamped and nitrided foils benchmarked to untreated stainless steels and graphite underway
  - -Go/no go decision at end of FY09
  - -Criteria are comparable resistivity and performance to graphite, no more than 5 ppm MEA metal ions beyond MEA from graphite test

Future Work

- Incorporation of nitrided Fe-23Cr-4V foil into test matrix
  - -higher Cr may improve surface ICR and corrosion resistance
- Evaluation of commercial stainless steel foil compositions containing Ti and related strong nitride-forming additions
  - -goal would be to form similar through thickness nitride/Cr_2O_3 surface to nitrided Fe-20Cr-4V (commercial alloys more accessible to developers)
- Evaluation of rapid heating/cooling using plasma arc lamp and related quartz infrared lamps for nitriding
  - -fast heat/cool may favor more nitride-rich surface, minimize Fe
  - -fast heat/cool minimizes brittle σ phase formation in higher Cr alloys which may yield more corrosion-resistant nitrided surfaces
  - -lower cost nitriding approach
- If go/no go milestone reached move to full-size plates and stack testing in FY 2010

Additional Slides

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

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

2006 GenCell Cost Estimates for Stamped Bipolar Plates

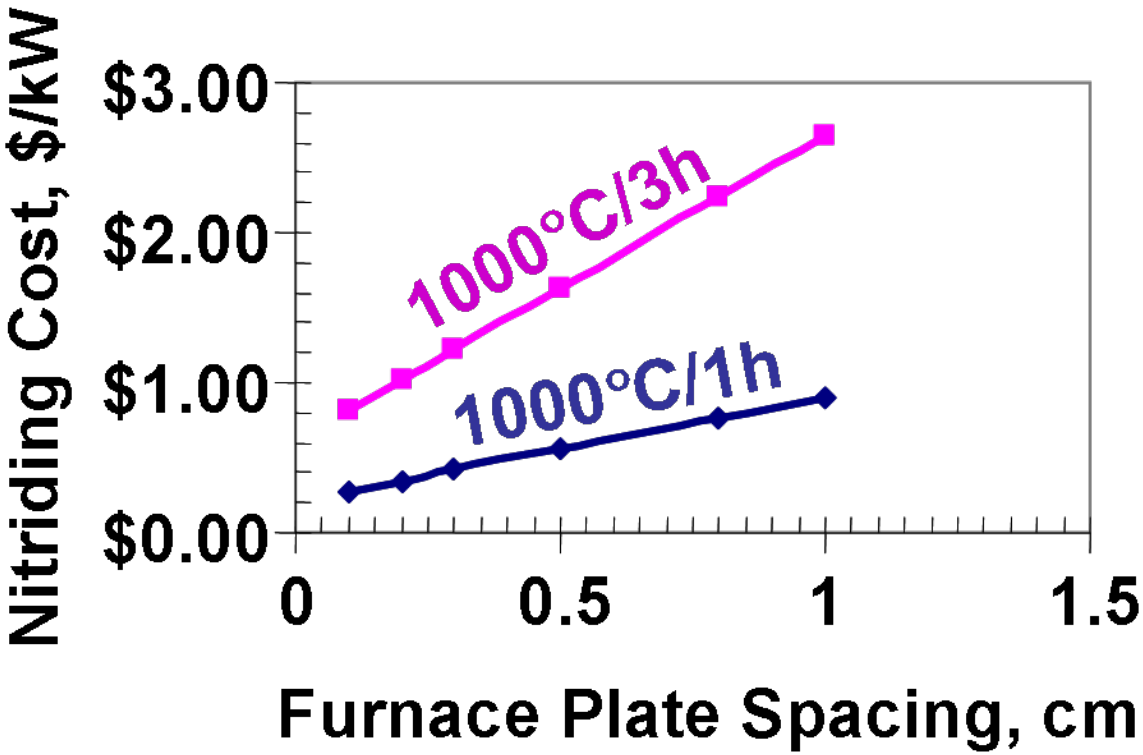
(Nitriding Costs Not Included)

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