# Nitrided Metallic Bipolar Plates

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Project ID
FC_40_Tortorelli

# 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

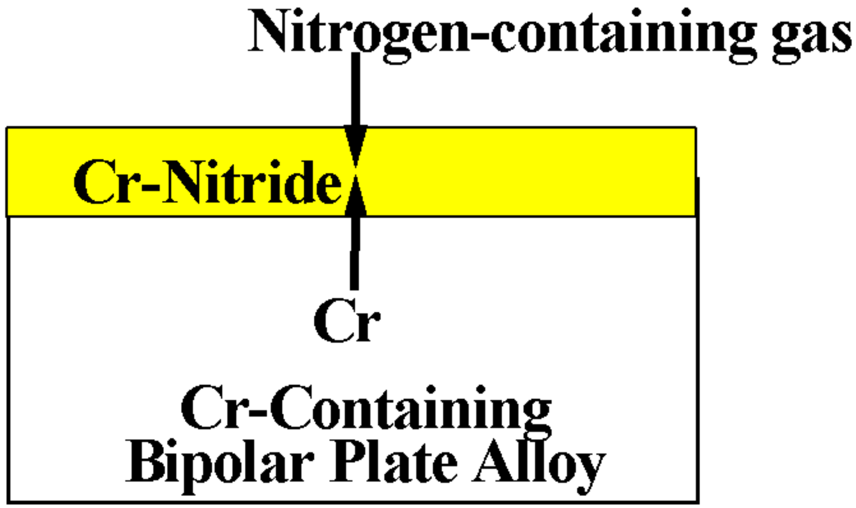
- ORNL (Lead)
- AGNI-GenCell
- Allegheny Ludlum
- Arizona State University
- LANL
- NREL

# Objective: Demonstrate Nitridation to Protect Stamped Metallic Bipolar Plates

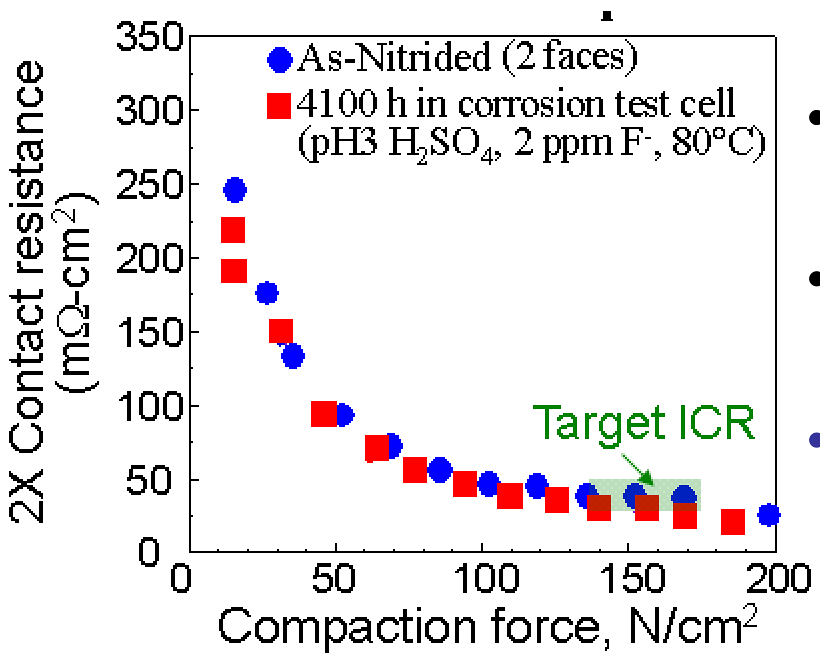
Overall Goal: Demonstrate potential for metallic bipolar plates to meet automotive durability goals at cost of < $5/kW

- **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

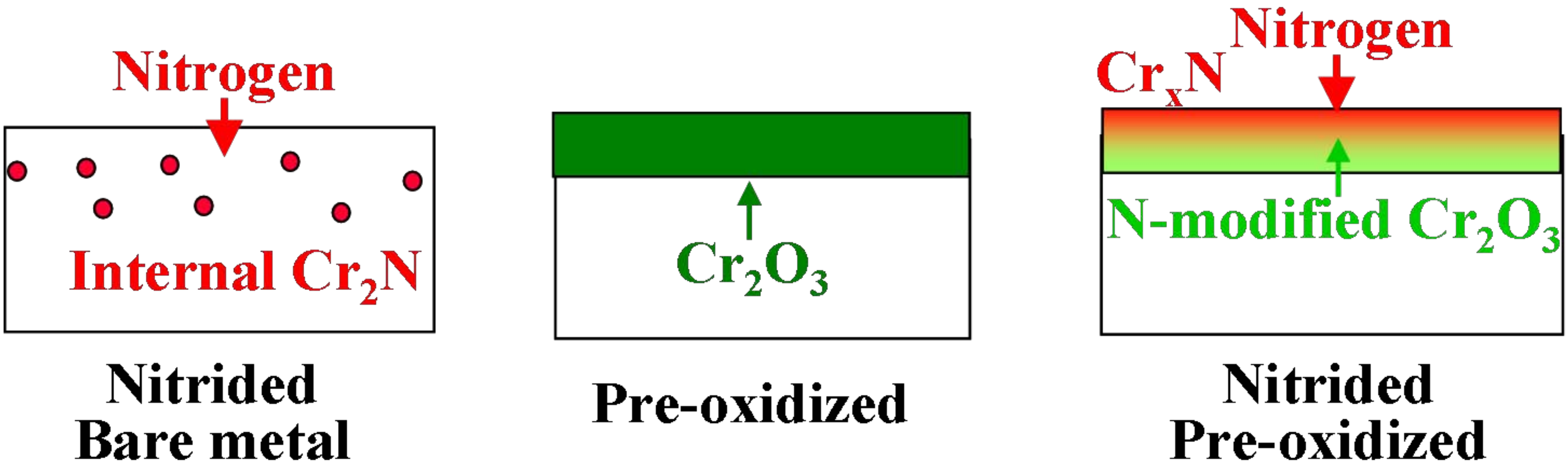



## Nitrided Model Bipolar Plate

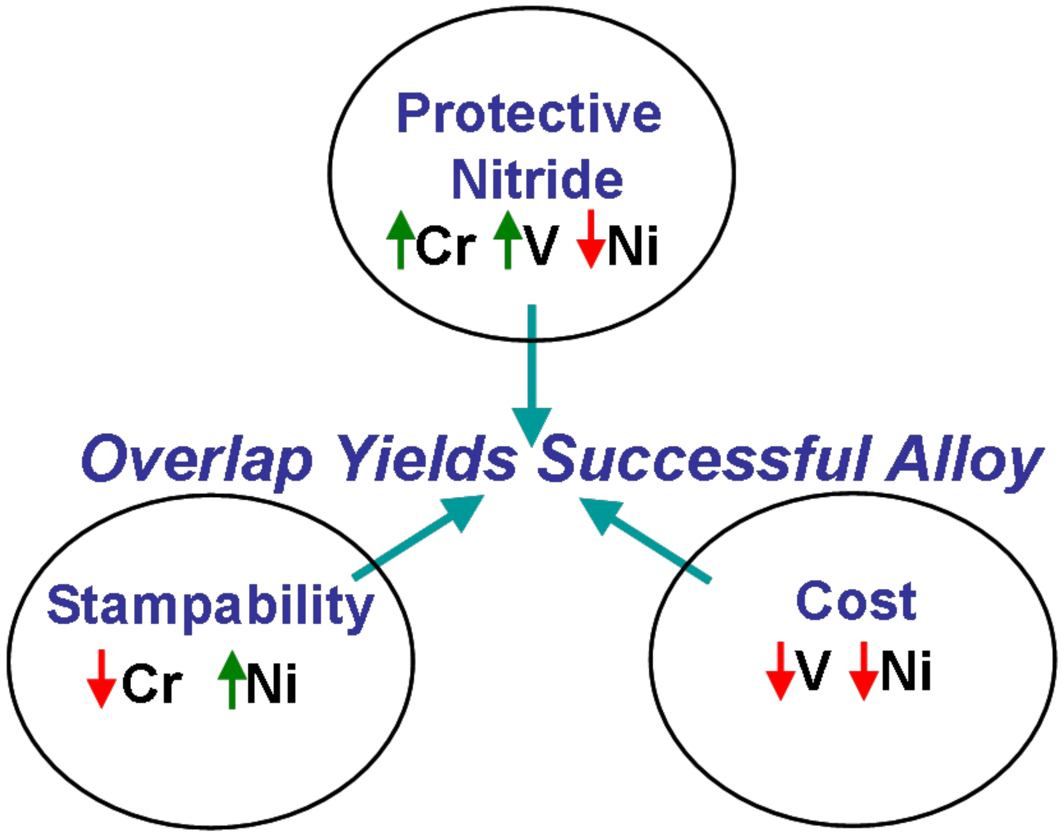

- Low-cost, scalable approach
  - -nitrides conductive and corrosion resistant
- Successful single-cell fuel cell testing with model nitrided Ni-Cr alloys ($)
- **Goal is to implement <u>stampings</u> of <u>low-cost stainless steel foils</u>**

# 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**

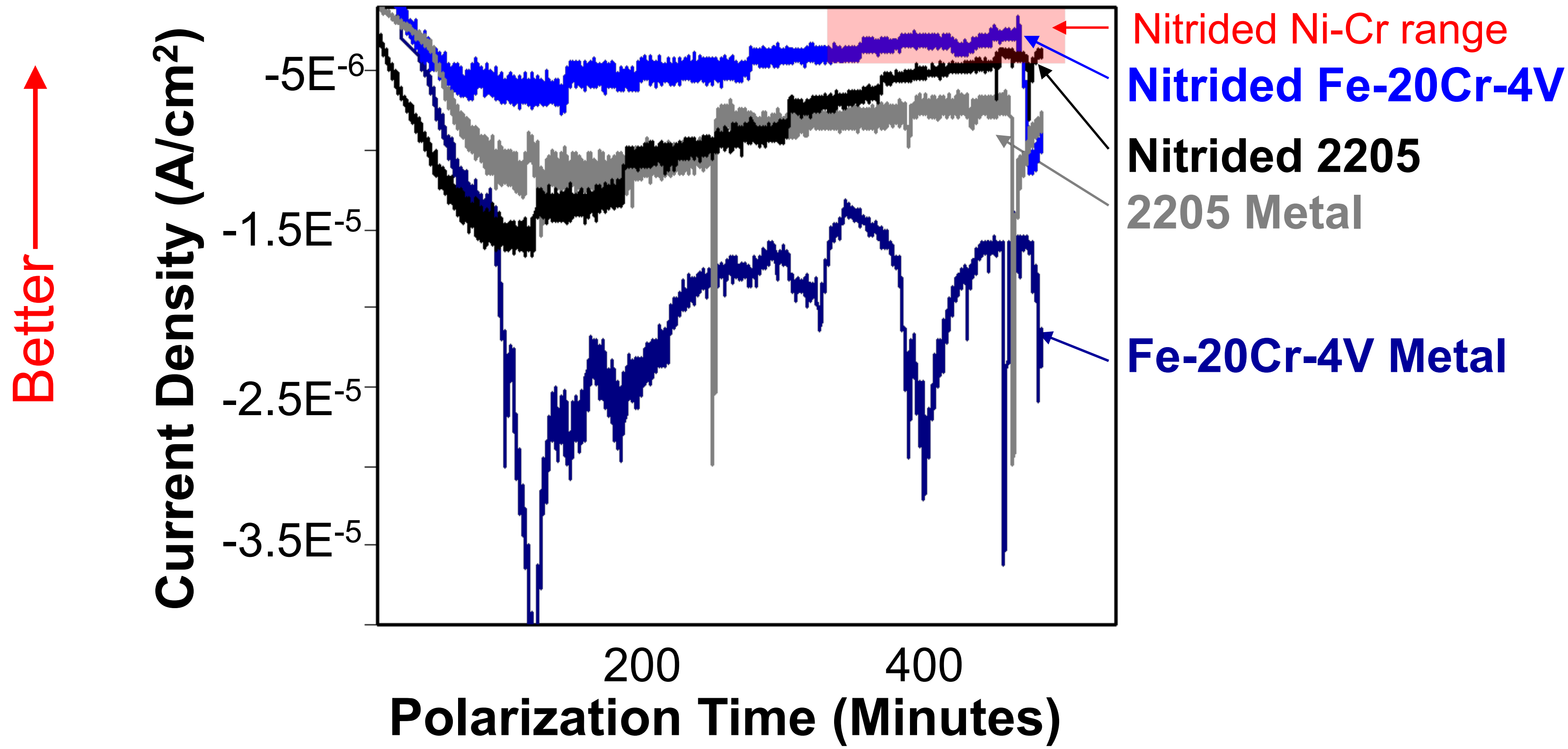
# Where Did We Leave Off at Last Review?

- 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

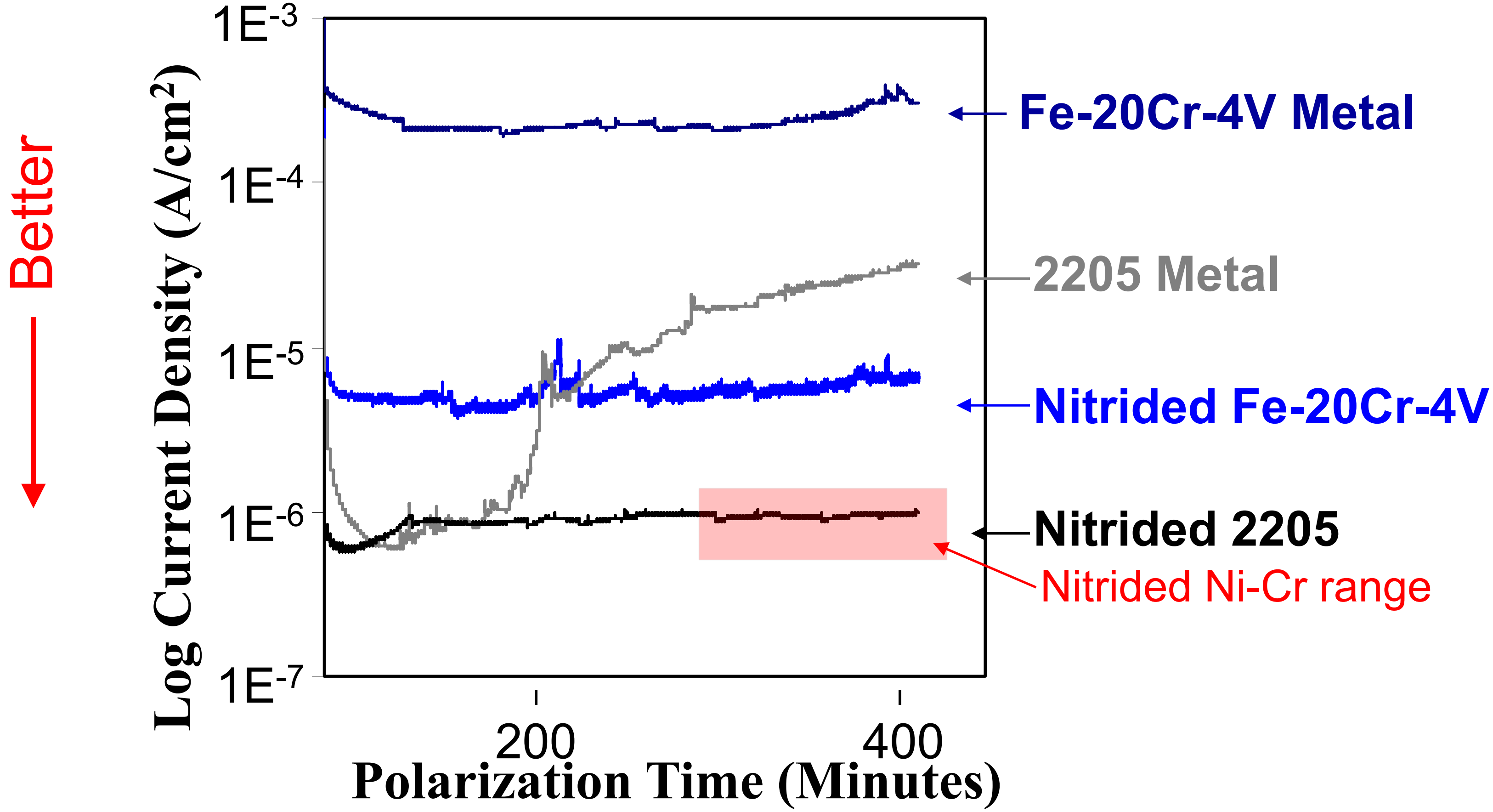
Polarization Evaluation at 70°C in 1M $H_2SO_4$+ 2 ppm $F^-$ held at +0.14V vs SHE, $H_2$ purged




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

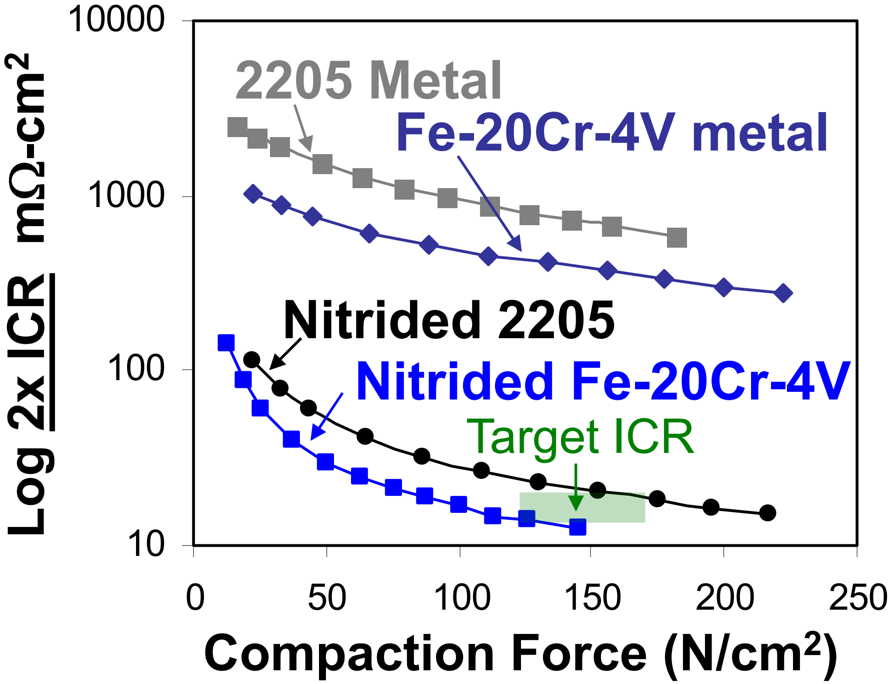
# Nitrided Foils Exhibit Good Corrosion Resistance Under Simulated Aggressive Cathode Conditions

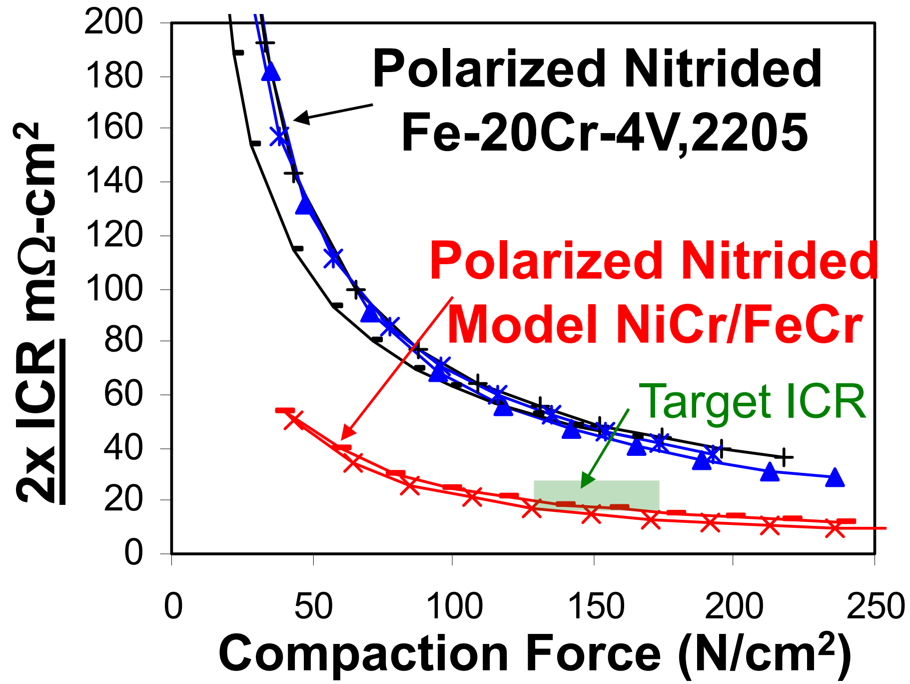
Polarization Evaluation at 70°C in 1M $H_2SO_4$ + 2 ppm $F^-$ held at +0.84V vs SHE, aerated




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

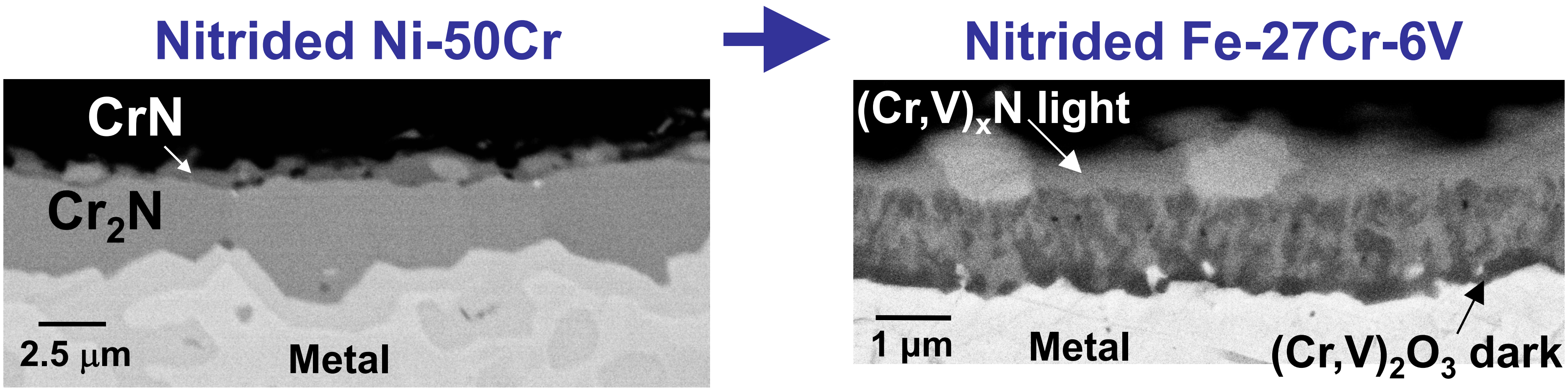
# Nitridation Significantly Reduces Foil Interfacial Contact Resistance (ICR)




- 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 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

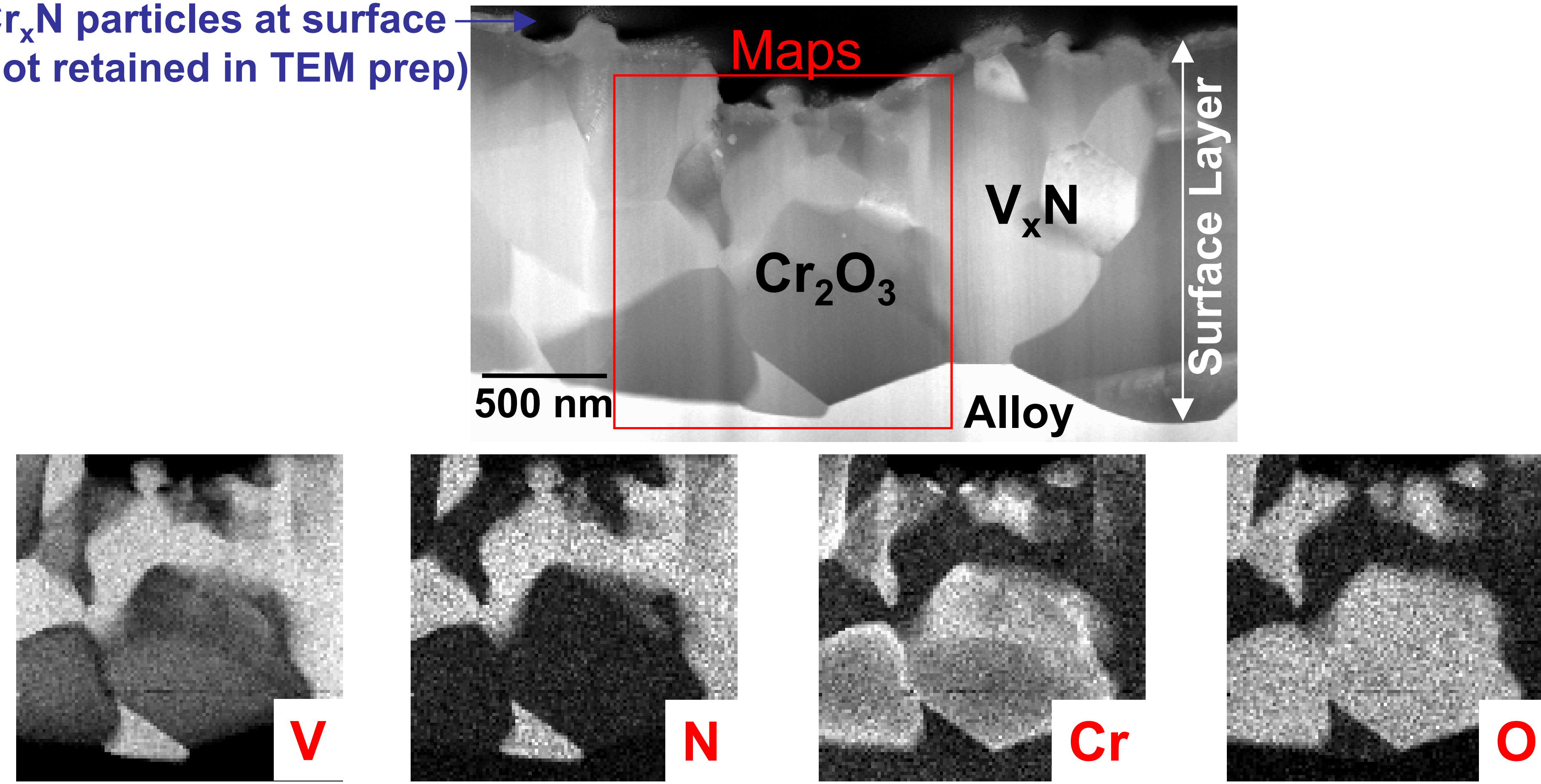
-used to understand and develop controllable pre-oxidation/nitridation approach with short nitriding cycles to meet cost targets

-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

$Cr_xN$ particles at surface (not retained in TEM prep)

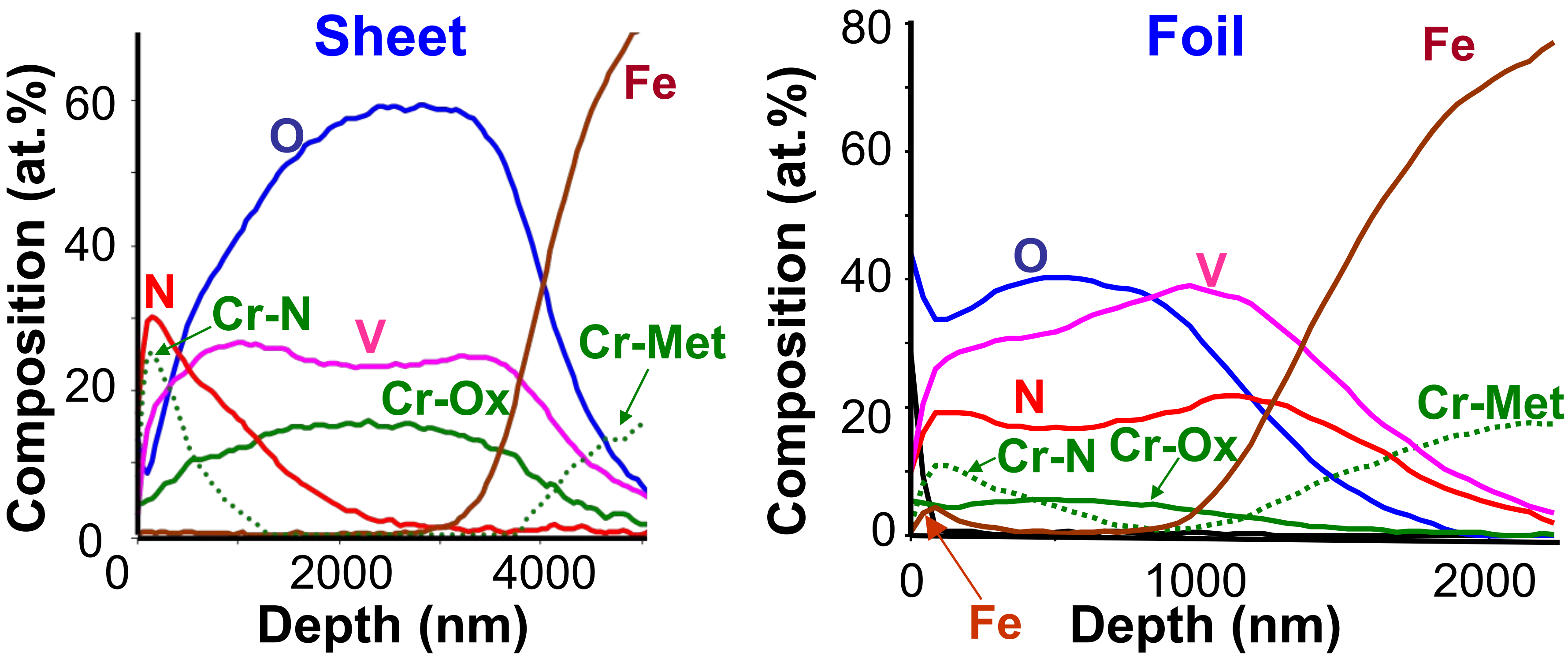



•<u>Through thickness $V_xN$ paths</u> but no continuous $Cr_xN$ as with model alloys

•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

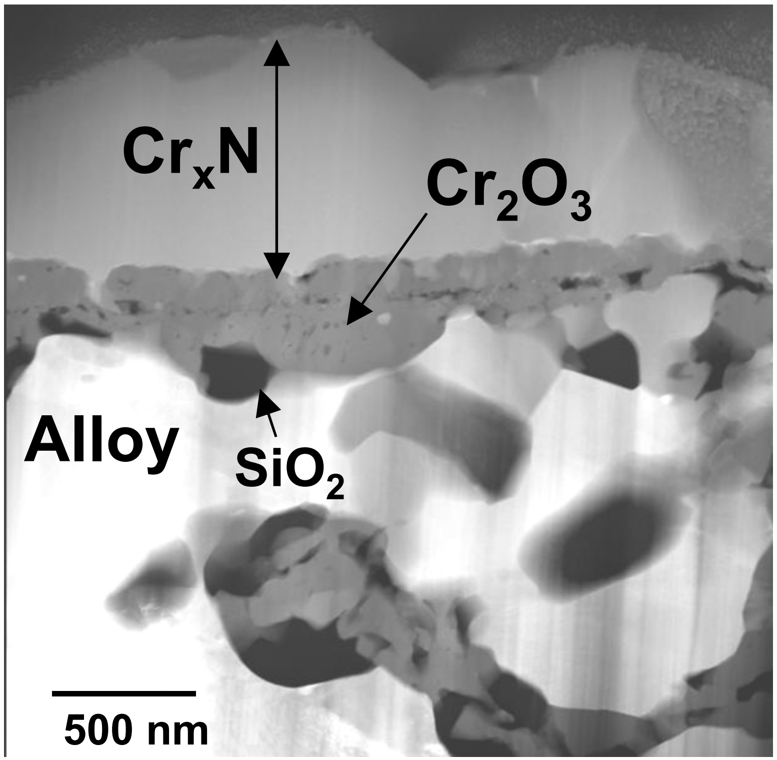


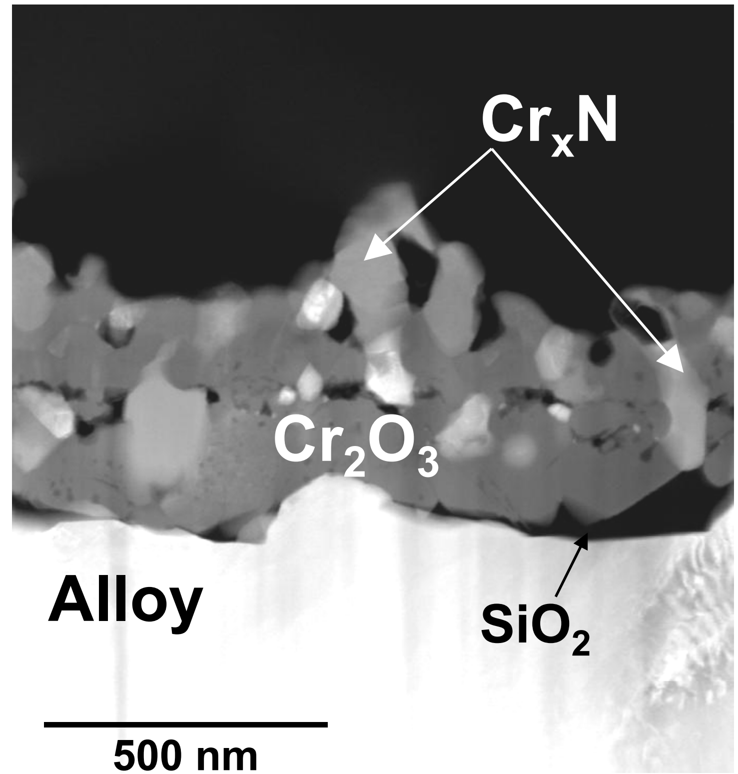

- Foils more sensitive to $O_2$ impurities in $N_2$-$4H_2$, more oxide at surface
  - -foil surface finish and microstructure/diffusion effect?
- Foils show small surface Fe peak-not observed in sheet material
  - -may contribute to observed ICR increase on polarization

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

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

### Two Runs/Similar Conditions

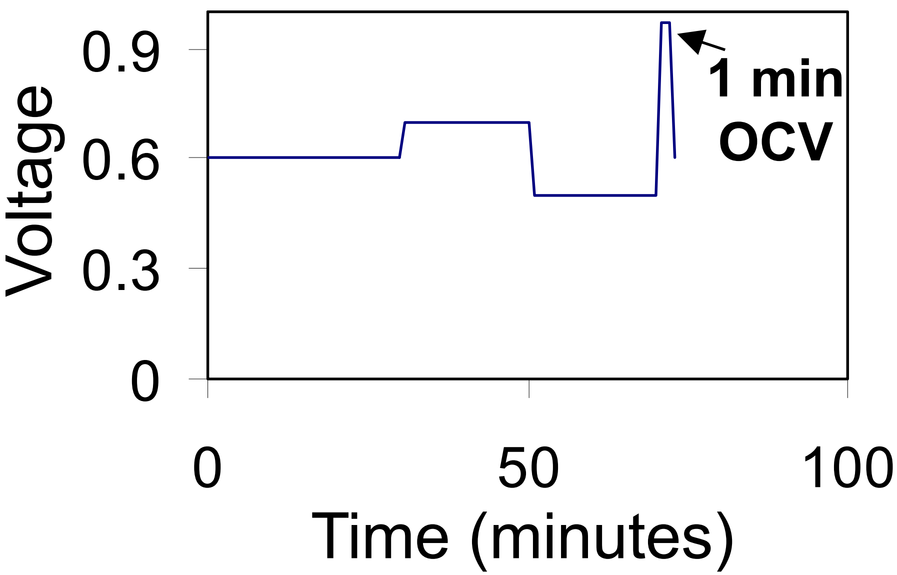


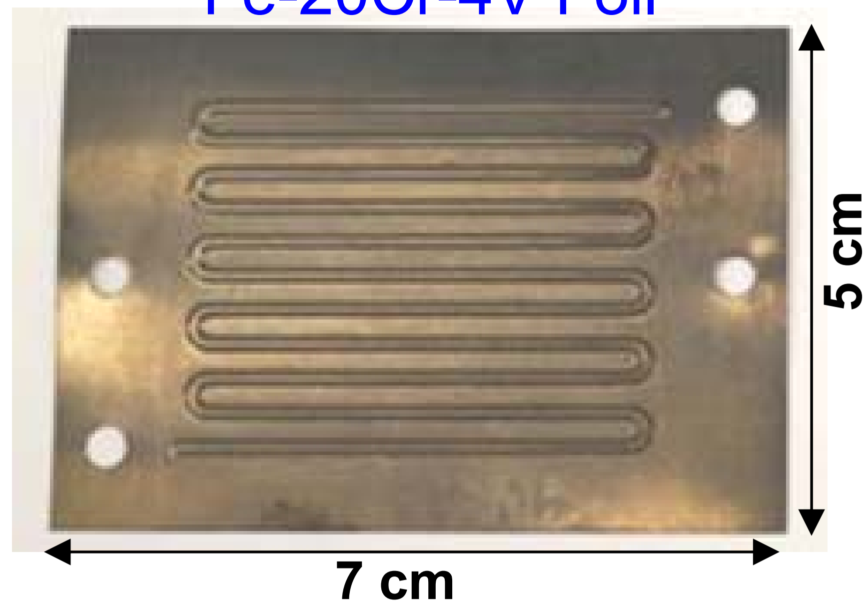

- Significant scatter in run-to-run surface O/N content
  - -consequence of lack of strong nitride-forming element in 2205 (only Cr)
- Few through-layer thickness nitride paths
  - -continuous inner oxide could compromise electrical conductivity

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

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



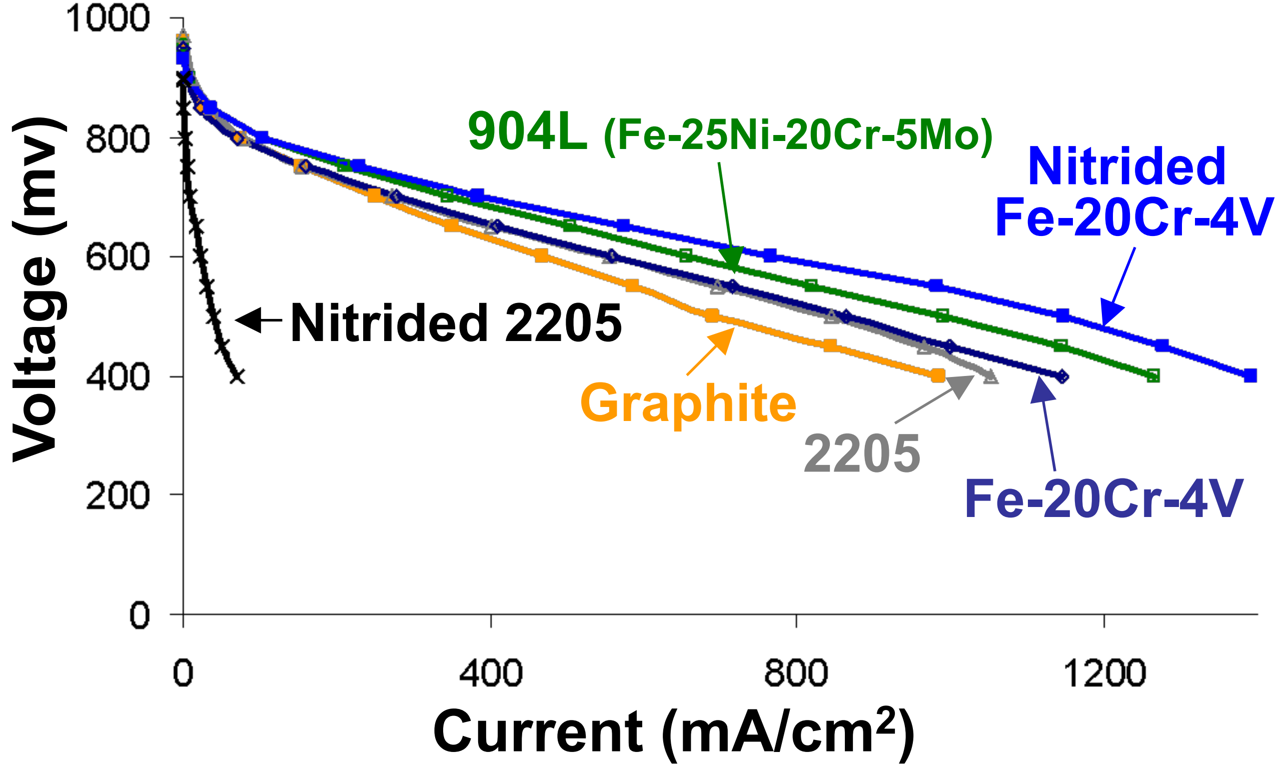

## Stamped and Nitrided Fe-20Cr-4V Foil




- 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

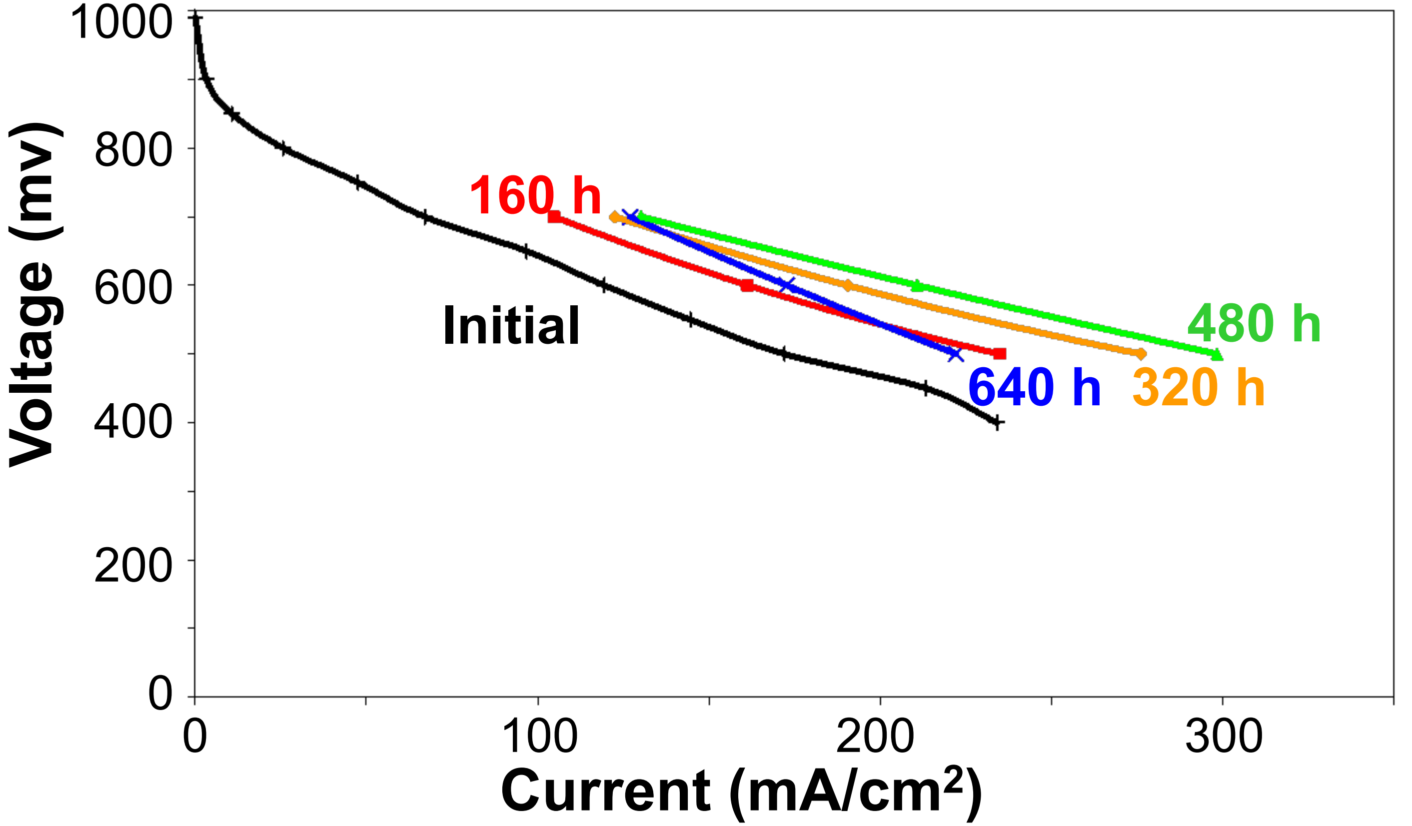
## Initial V-I Curves Using 50 micron MEA (0.8 mg Pt/cm$^2$)




- 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

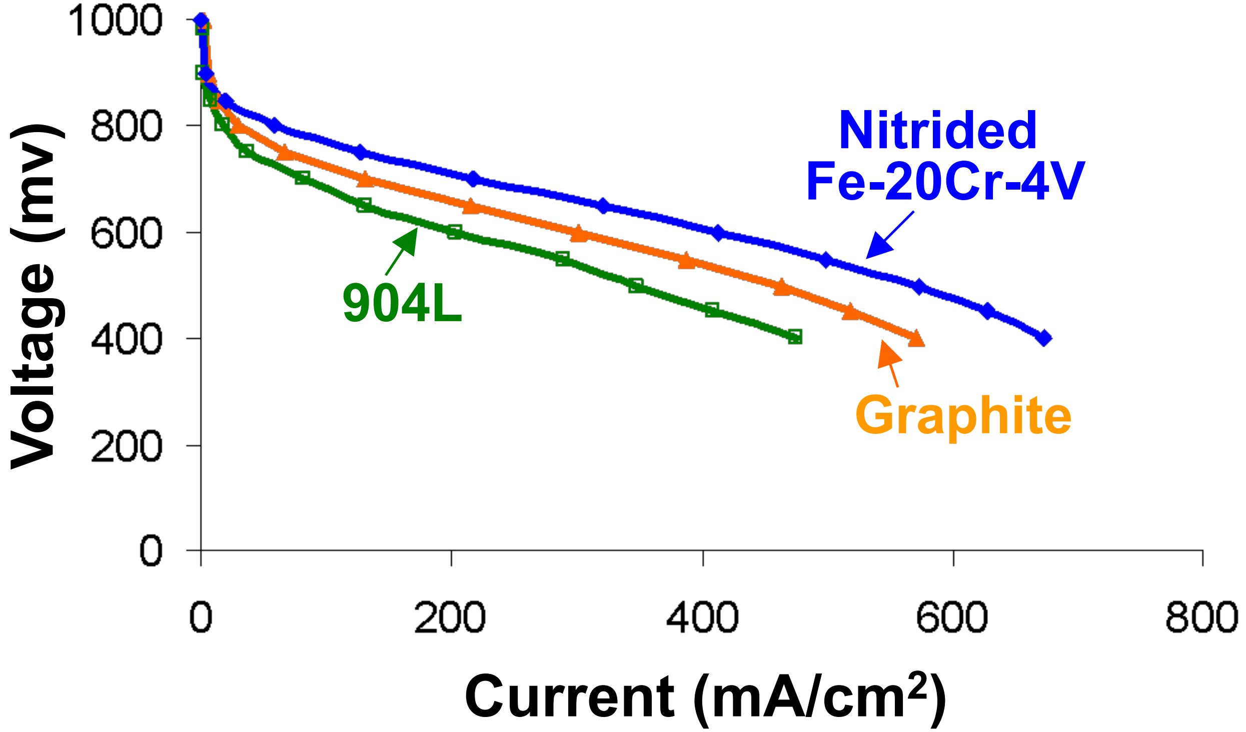
**V-I Curves from 700 h Test of Untreated 904L Foil Using 125 micron MEA (0.5 mg/cm$^2$ Pt)**




- 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

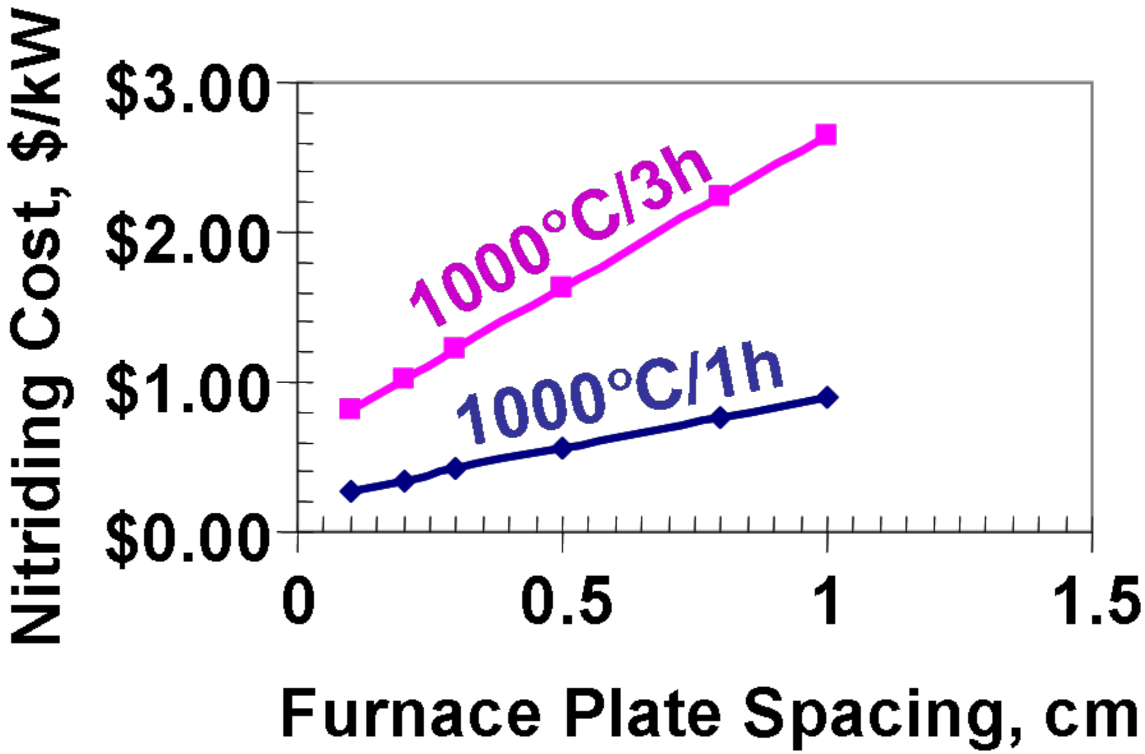
**(Nitriding Costs Not Included)**

| 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