Nitrided Metallic Bipolar Plates

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Project ID
FC022

Overview

Timeline

- Start: May 1, 2007
- Finish: Sept. 30, 2010
- ~85% complete

Budget

- Total project funding
  - $4530k DOE share
  - $400k Contractor share
- $1200 k received in FY 09
- $1000 k funding for FY10

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

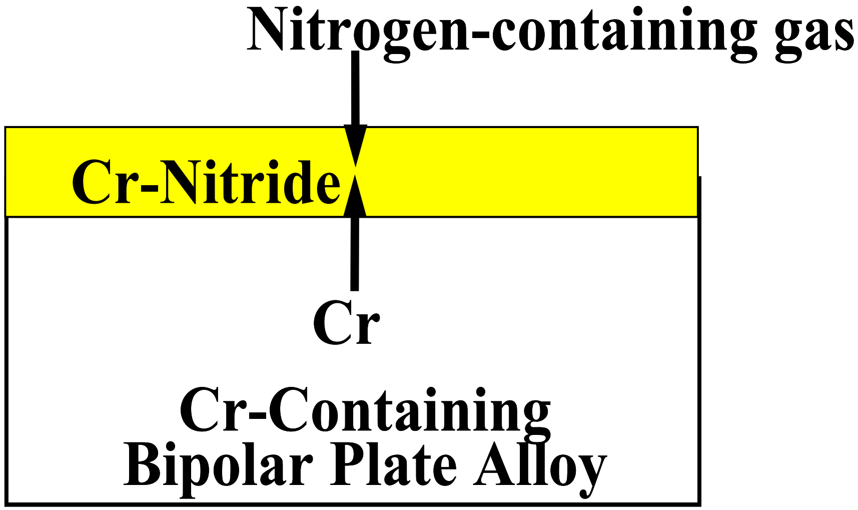
- ORNL (Lead)
- GM (new for FY10)
- AGNI-GenCell
- Allegheny Ludlum
- Arizona State University
- LANL
- NREL

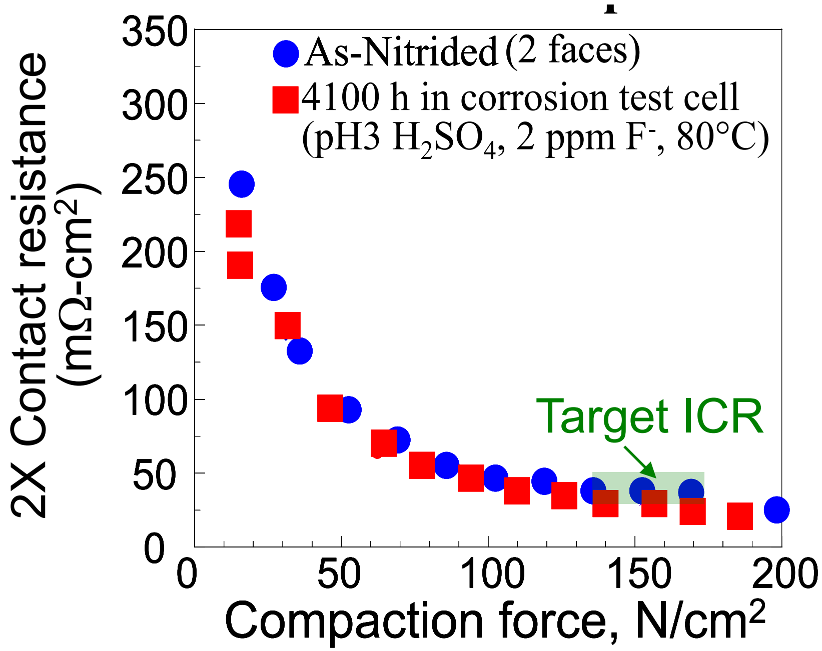
Objective: Demonstrate Nitridation to Protect Stamped Metallic Bipolar Plates

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 behavior for 15 cm^2 stamped and nitrided metallic bipolar plates equivalent to that of graphite (~750-1000 h, cyclic) - **go/no go 2**
  -met Sept 09 (details in this presentation)
- **Milestone 3 (Modified from original plan)**: Complete automotive OEM bipolar plate manufacturing assessment and single-cell, drive-cycle test protocol - **project end, Sept 2010**

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

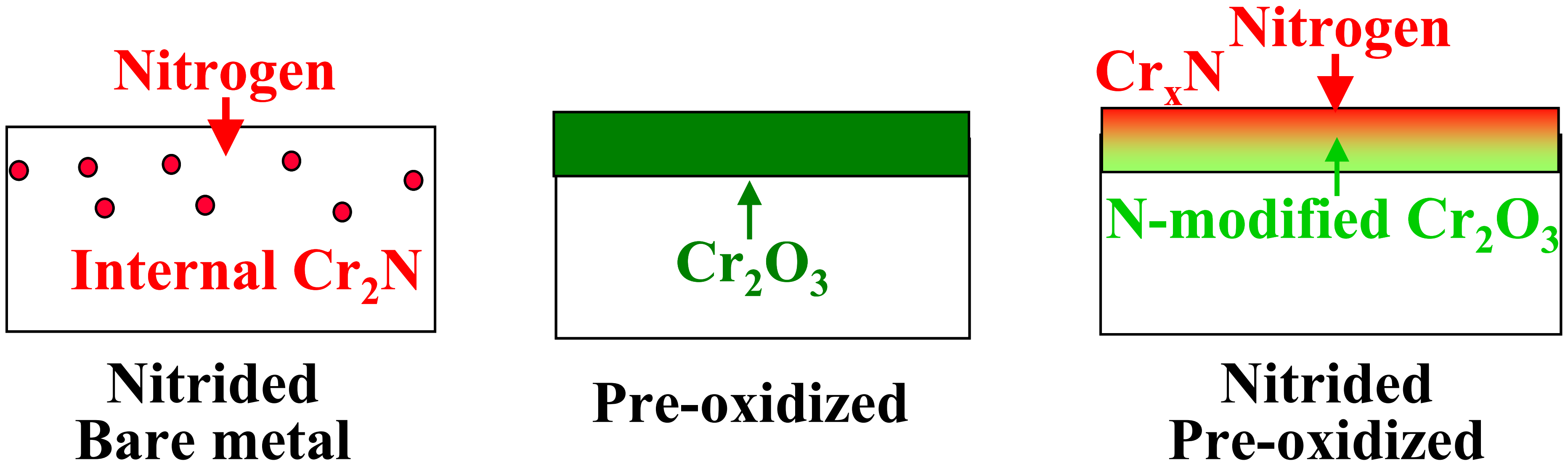




Nitrided Model Bipolar Plate

- 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 Cr2O3 to surface CrxN by nitridation
- V added to stainless steel assists conversion to nitride

  good ICR and corrosion results with model Fe-27Cr-6V alloy

Last Review

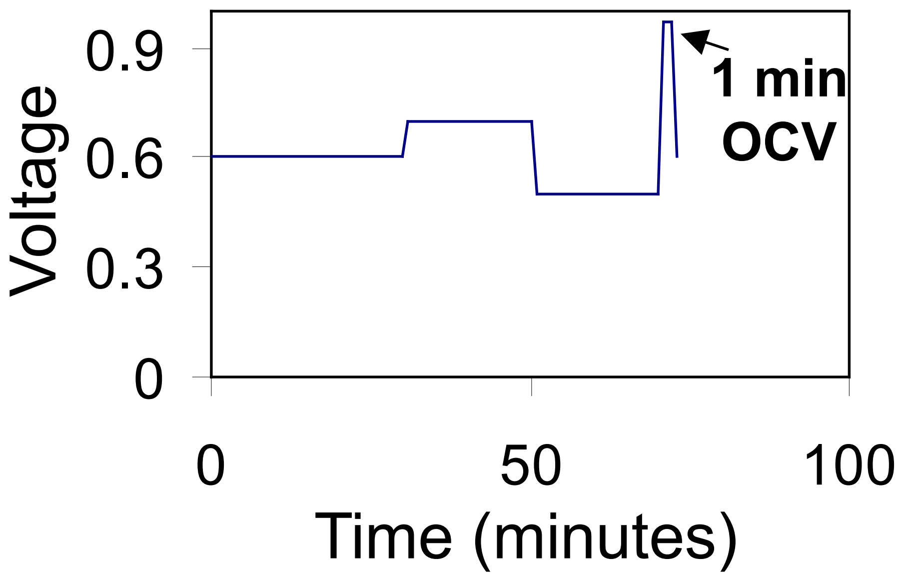
- Low-cost Fe-20Cr-4V alloy amenable to nitridation developed
  - 1 to 2 h nitriding at 1000°C yielded V_xN dispersed in Cr_2O_3 (15 min pre-oxidation)
  - low ICR and good corrosion resistance obtained in ex-situ testing of foils
- Single-cell fuel cell testing initiated for stamped and nitrided Fe-20Cr-4V relative to stamped 904L and machined graphite plates
  - ~15 cm^2 active area stampings successfully made from 0.1 mm foil
  - Initial performance curves showed promising behavior by nitrided material

New FY10 Work (Based on 09 Review and Tech Team Input)

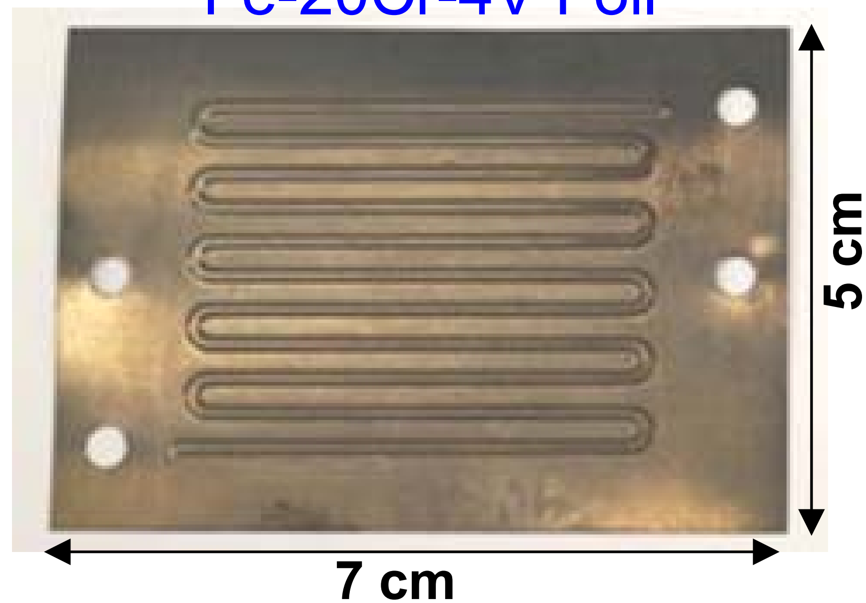
- 1000 h single-cell durability testing of stamped/nitrided 15cm^2 plates
- Evaluation of rapid heating/cooling cycles with quartz infrared lamp technology for nitriding (shorter cycle = lower cost)
- Teaming with GM for manufacturability assessment and single-cell, drive-cycle testing with state-of-the-art stamped plates

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

Fuel Cell Test Cycle
(1000-1200 total h)



Stamped and Nitrided
Fe-20Cr-4V Foil



- Operating conditions: 80°C, 25 psig
  performance curves (V-I):0.9-0.4V, 0.05V steps, 20 min./step, repeat 3x
- Simple serpentine ~15 cm^2 active area stamped foils for metals, machined graphite block of similar flow-field design

Materials Evaluated in Single-Cell Fuel Cell Testing

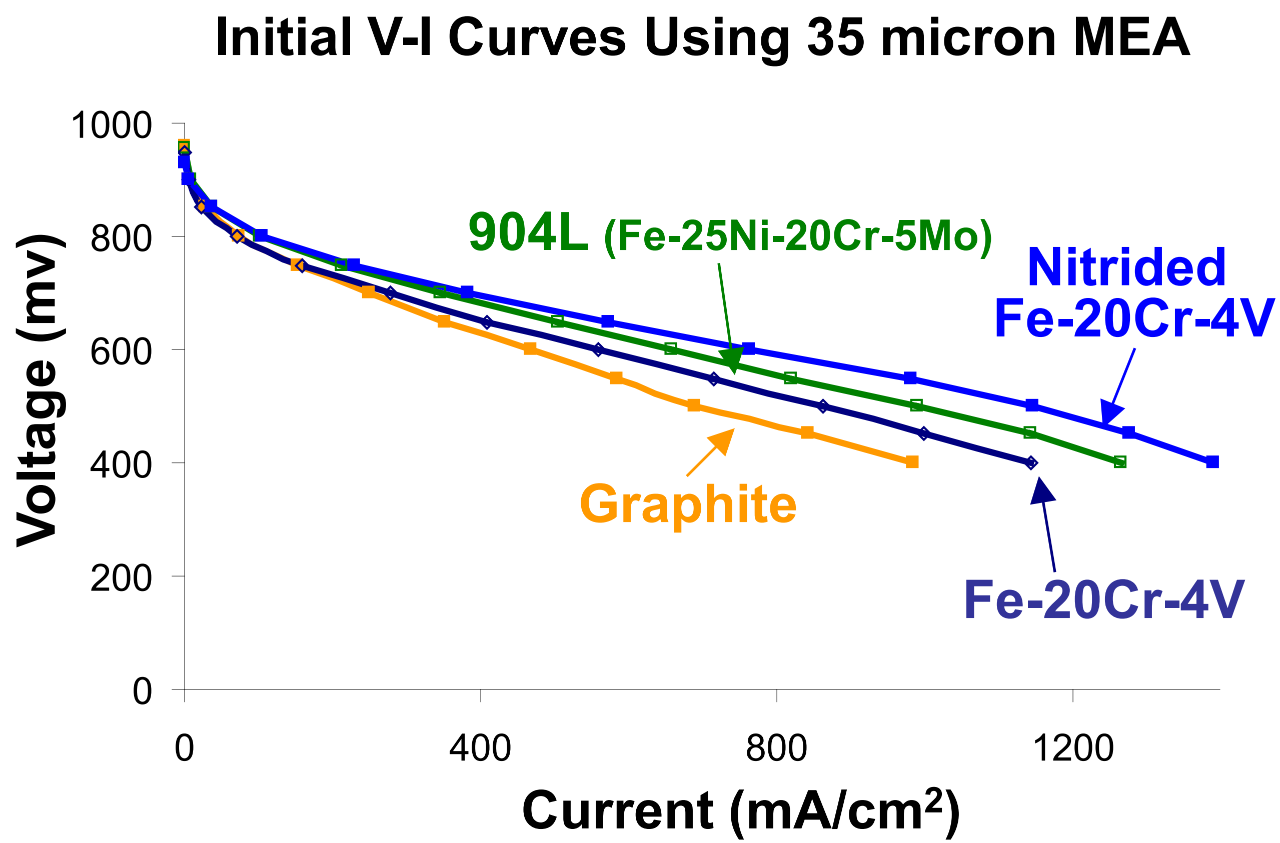
- Stamped and pre-oxidized/nitrided Fe-20Cr-4V and 2205 stainless steel foils

- Stamped Fe-20Cr-4V, 2205, and 904L stainless steel foils (not treated)
  - 904L is Fe-25Ni-20Cr-5Mo base
  - Reported to exhibit excellent corrosion resistance in PEMFC environments

- Machined graphite of similar flow-field design to stampings

Cycle: 30 min at 0.6 V - 20 min at 0.7V - 20 min at 0.5V - 1 min @ Open Circuit Voltage (OCV)

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



- Nitridation significantly increased performance of Fe-20Cr-4V
- Lower performance of graphite attributed to flow-field differences w/stampings
- <u>All tests</u> experienced ~100 h MEA failure due to gasketing/integration issues

Cyclic Single-Cell Fuel Cell Durability Evaluation

Initial Assessment Using High-Performance 35 micron MEA

↓

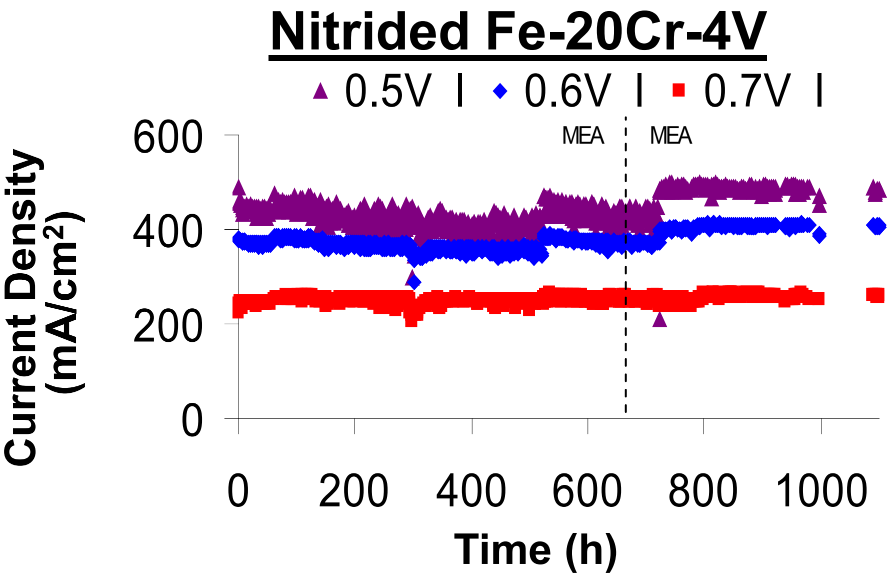
1000⁺ h Evaluation Using More Durable 175 micron MEA

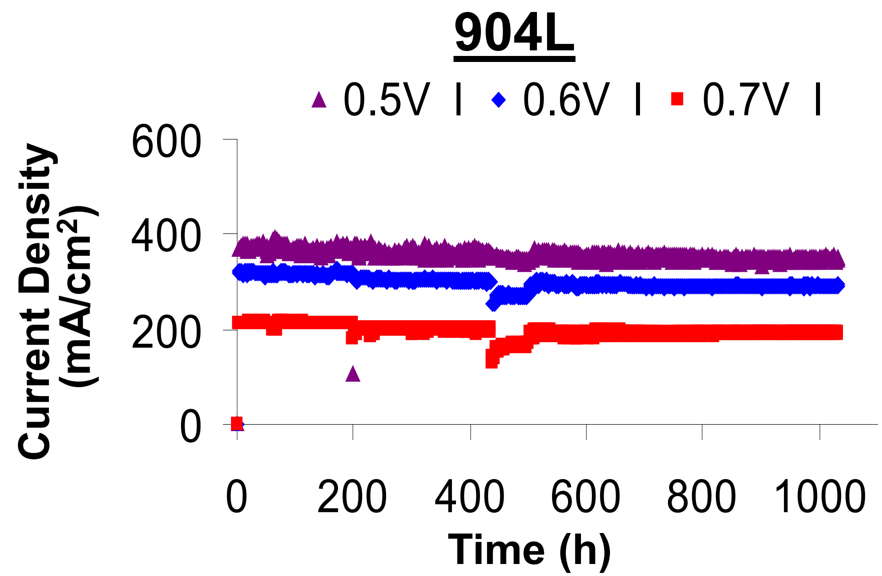
↓

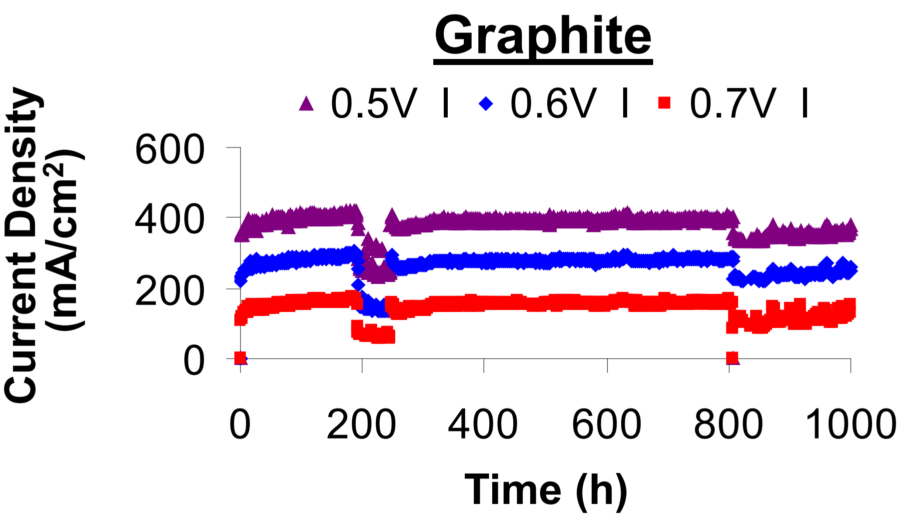
Re-Evaluate Performance of 1000 h Durability Tested Plates with Fresh 35 micron MEA (Cell Rebuild)

Use of Thicker, More Mechanically Robust MEA Solved Premature MEA Pin-Hole Failure Issue (sufficient for plate materials assessment)

Lower but Stable 1000 h Cyclic Performance for All Plate Materials with 175 micron MEA

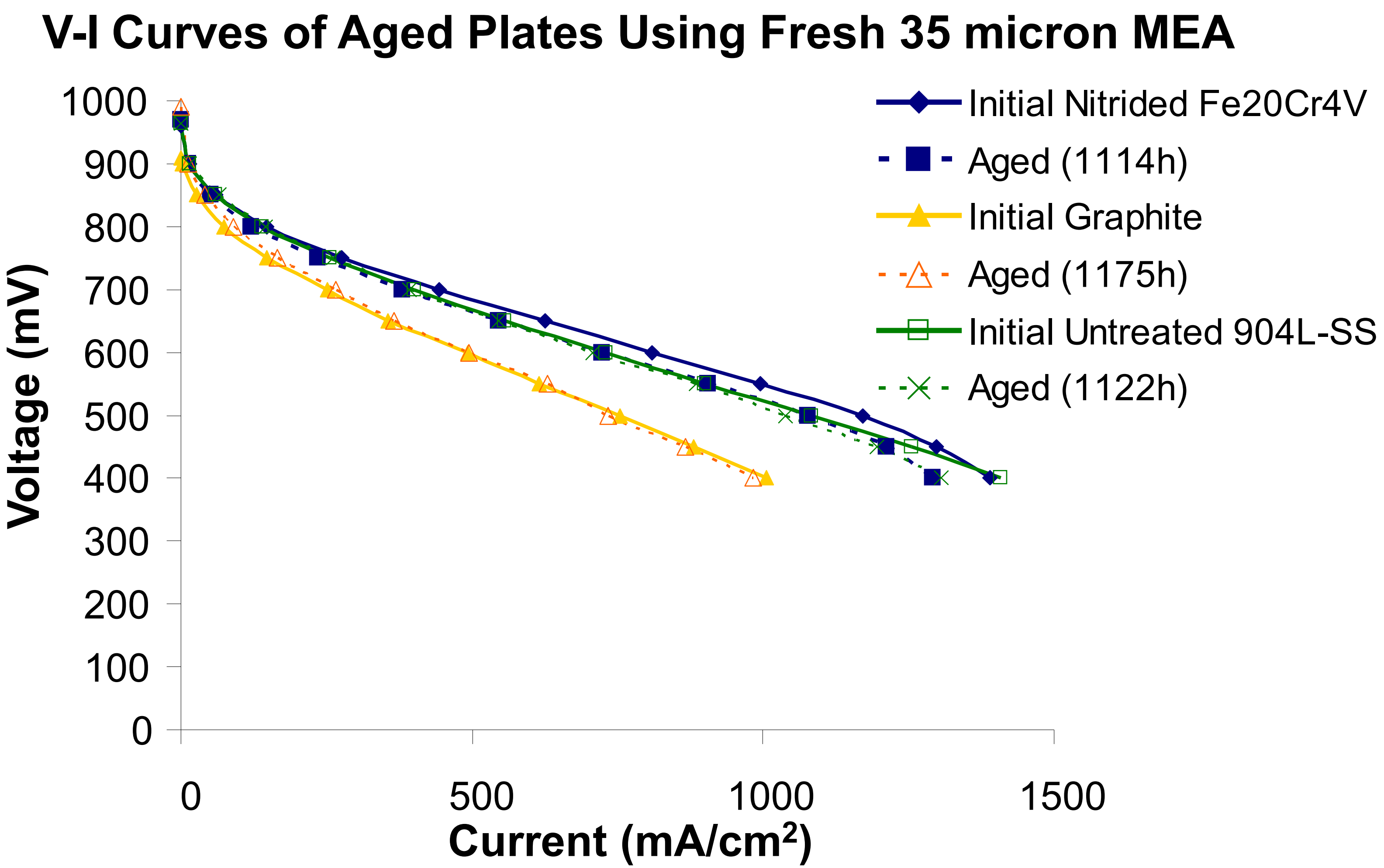






- No appreciable loss in performance for all 3 plate materials
- Cycle included OCV (not shown)
- Discontinuities in data from power outages, back pressure loss, etc

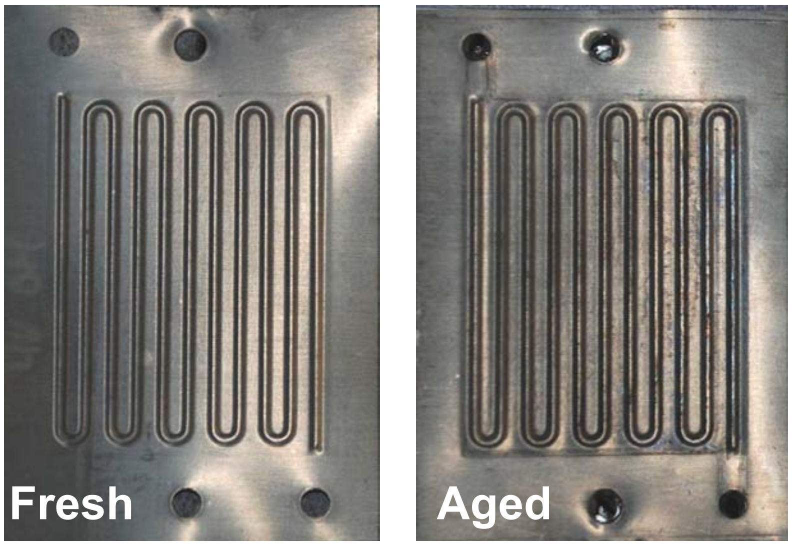
1000-h Aged Nitrided Fe-20Cr-4V, 904L, and Graphite Plates All Showed Good Durability



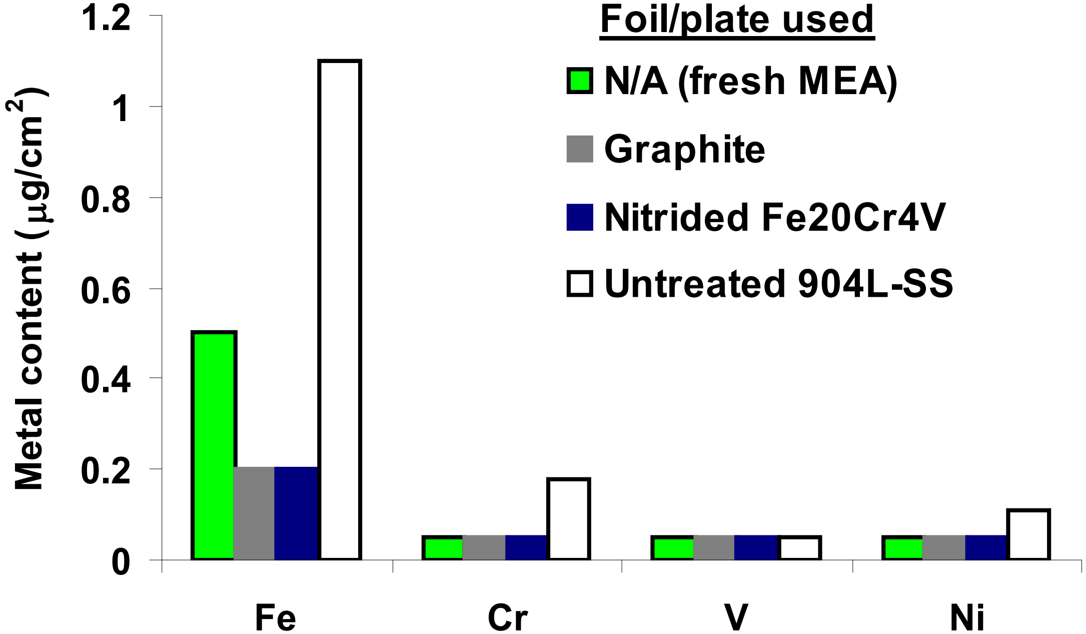
Slight decline in nitrided Fe-20Cr-4V data within fuel cell build-to-build variation (< 5-10% variation of peak power output)

<u>Milestone Met:</u> Nitrided Surface on Fe-20Cr-4V Protected MEA from Metal Contamination

Nitrided Fe-20Cr-4V Plates



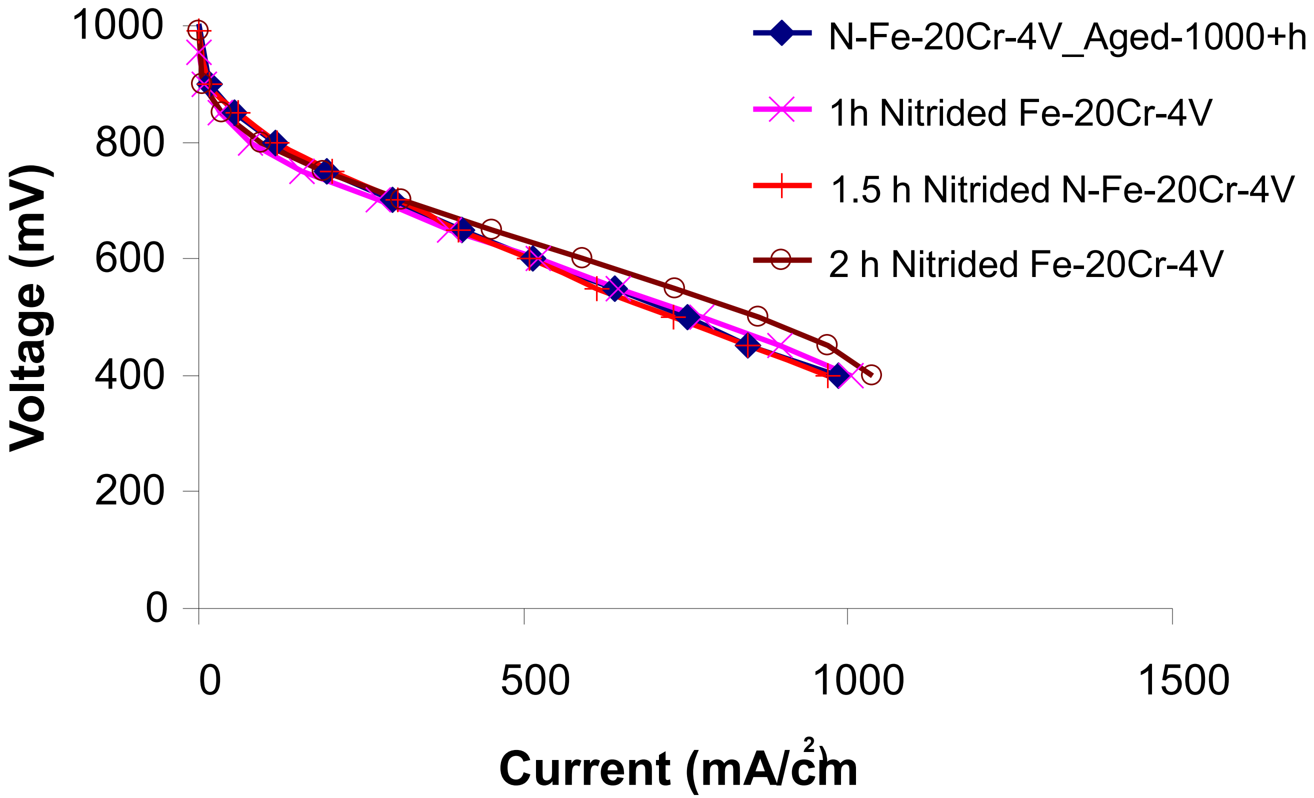
X-ray Fluorescence (XRF) of MEAs



- No visible attack of nitrided Fe-20Cr-4V plates (slight staining-GDL contact)
- XRF found MEAs from graphite and nitrided Fe-20Cr-4V plates “clean”
- Small (~1 $\mu g/cm^2$) level of metal ion contamination with 904 L

Initial Single-Cell Performance Not Degraded by Anticipated Variation in Nitriding on Scale Up

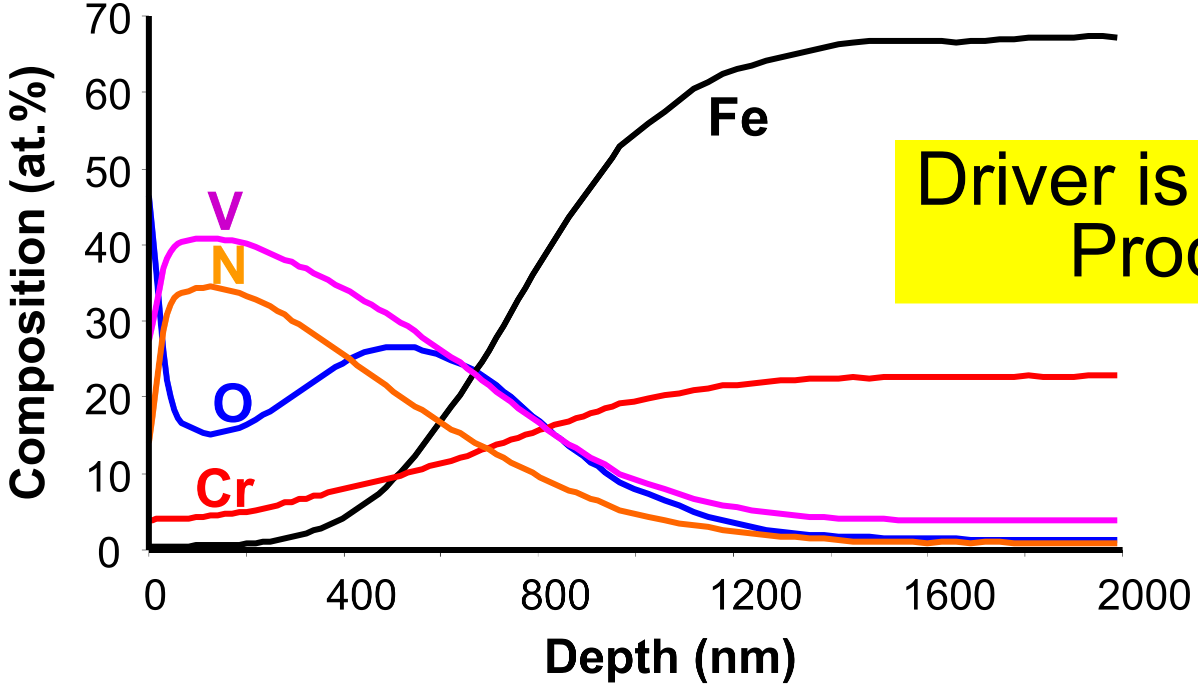
Initial V-I Curves of Nitrided Fe-20Cr-4V Stampings Using 50 micron MEA



- Suggests robustness by alloy/nitridation processing
- Durability runs needed to fully assess (planned)

Desired Surface Formed by Rapid Nitriding Using Quartz Lamp Heating Technology

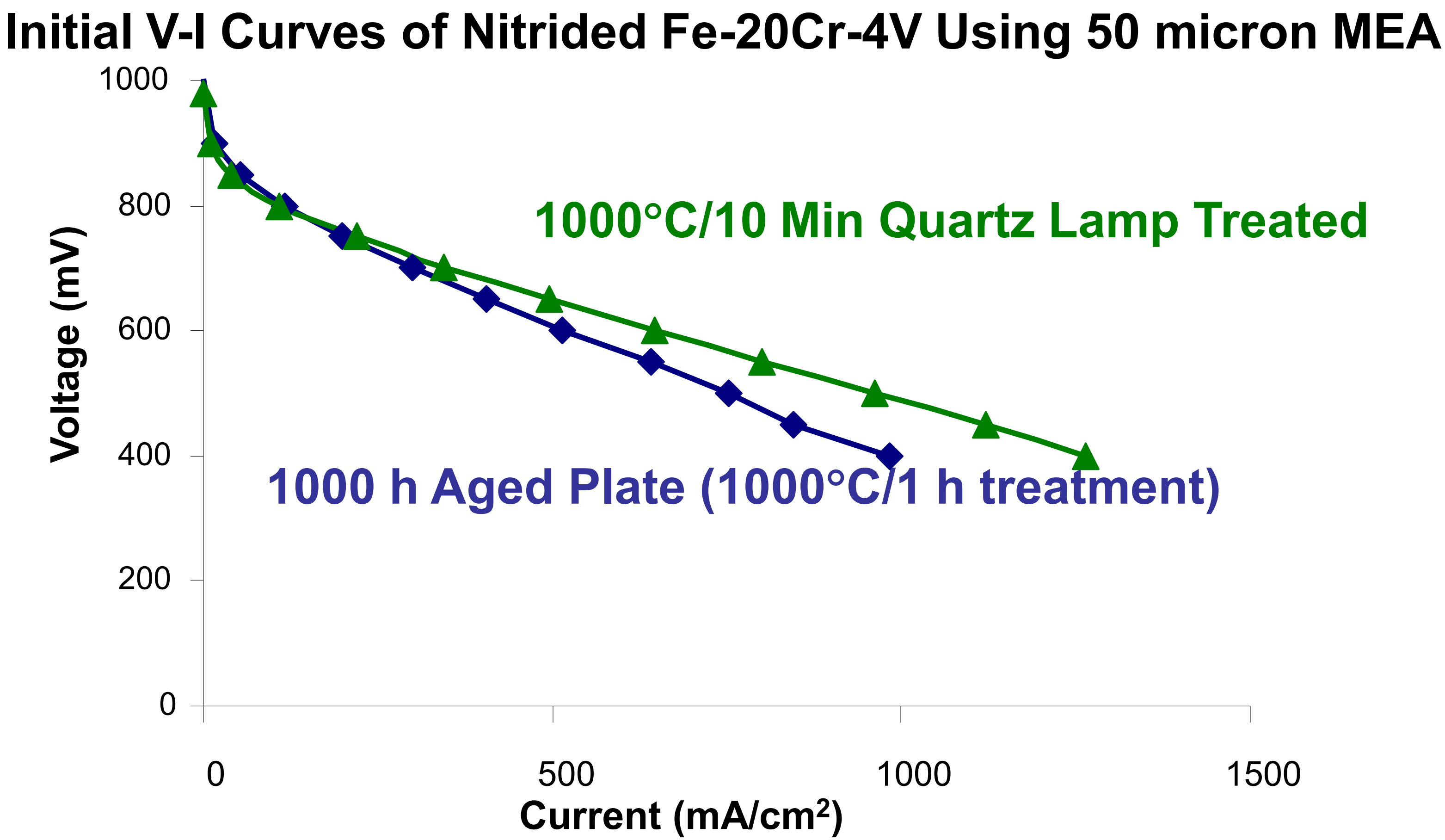
XPS Surface Chemistry of <u>1000°C/10 min</u> Treated Fe-20Cr-4V



Driver is Lower-Cost Processing

- Surface consistent with $V(Cr)_xN$ dispersed in $(Cr,V)_2O_3$
- Virtually no Fe in treated region (correlates with good corrosion behavior)
- Currently investigating 700-1000°C; 1 to 10 min cycles

Quartz-Lamp-Treated Stamping Shows Promising Single-Cell Fuel Cell Behavior



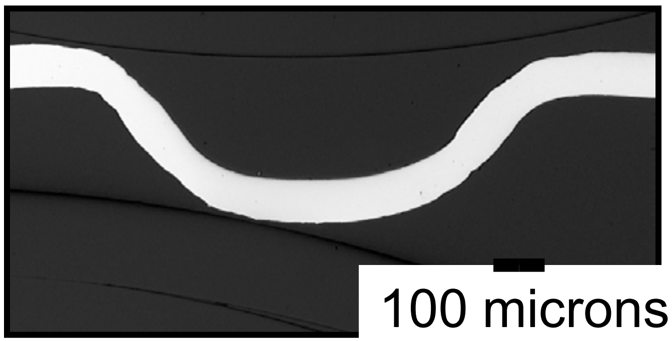
- Better behavior than standard nitriding procedure (higher N/O at surface yields even lower contact resistance?)
- Long-term durability testing planned

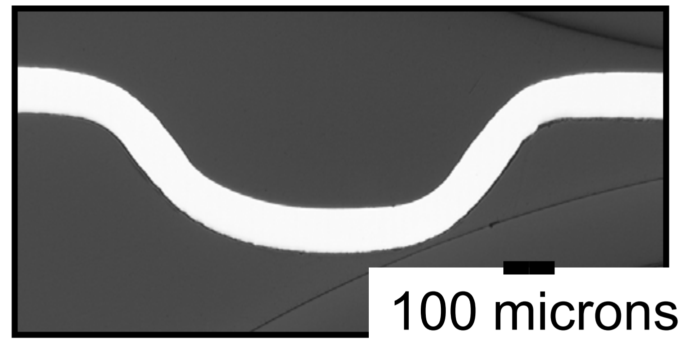
Promising Initial Stamping Assessment by GM

Small Stamping Section Test Pieces

Fe-20Cr-4V

316 L (Fe-18Cr-12 Ni base)





- Appears ferritic Fe-20Cr-4V may be sufficiently amenable to stamping of automotive flow-field designs (recent industry shift to austenitic focus)
- Fe-20Cr-4V to be nitrided after stamping

Collaborations and Future Work

- General Motors New Partner in Program
  - 09 Review/Tech Team suggested automotive OEM
  - Planned GM Activities
    - Stamping and bipolar plate manufacturing assessment of Fe-20Cr-4V and related ORNL alloys
    - Laser welding assessment (metal and/or nitrided metal)
    - ORNL will nitride state-of-the-art 50cm^2 active area FeCrV alloy GM stampings with welded cooling channel
    - GM single-cell drive cycle test protocol of nitrided plates with full diagnostics
    - Findings will be made available/Overall project end
- Continued Evaluation of Quartz Lamp Nitriding
  - Lower temperatures, shorter cycles
  - Work into GM test matrix if warranted

Project Summary

- Relevance: Metallic Bipolar Plate Durability and Cost Goals
- Approach: Thermal Nitridation of Thin Metal Stampings
- Accomplishments:
  - 1000 h single-cell durability test of nitrided stamping with no metal contamination of MEA (key milestone)
  - Potential for lower-cost/short duration nitriding with quartz lamp technology established
  - Developed Fe-20Cr-4V alloy amenable to stamping in GM screening
- Technology Transfer/Collaborations:
  - Teaming with Allegheny Ludlum, ASU, LANL, NREL, and GenCell
  - New partnership with General Motors
  - IP available for license to interested parties
- Future Research (Project End FY 10):
  - Complete GM manufacturing and test protocol
  - Complete assessment of rapid quartz lamp nitriding

Supplemental Slides

Teaming and Primary Responsibilities

- Oak Ridge National Lab: (Brady, McCarthy, Meyer, More, Pihl, Toops, Tortorelli)
  Alloy design, nitridation optimization, characterization, single-cell fuel cell design and testing
- Arizona State University: (Gervasio, Kosaraju, Mada Kannan, Mylan)
  Single-cell fuel cell design and testing
- ATI Allegheny Ludlum: (Rakowski)
  Alloy foil manufacture
- AGNI-GenCell: (Estevez, Connors)
  Design and stamping of bipolar plate flow-field features
- Los Alamos National Lab: (Garzon, Rockward)
  Stack testing/performance assessment, characterization, single-cell fuel cell design and test protocol
- National Renewable Energy Lab: (Turner, Wang)
  Corrosion/contact resistance evaluation

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

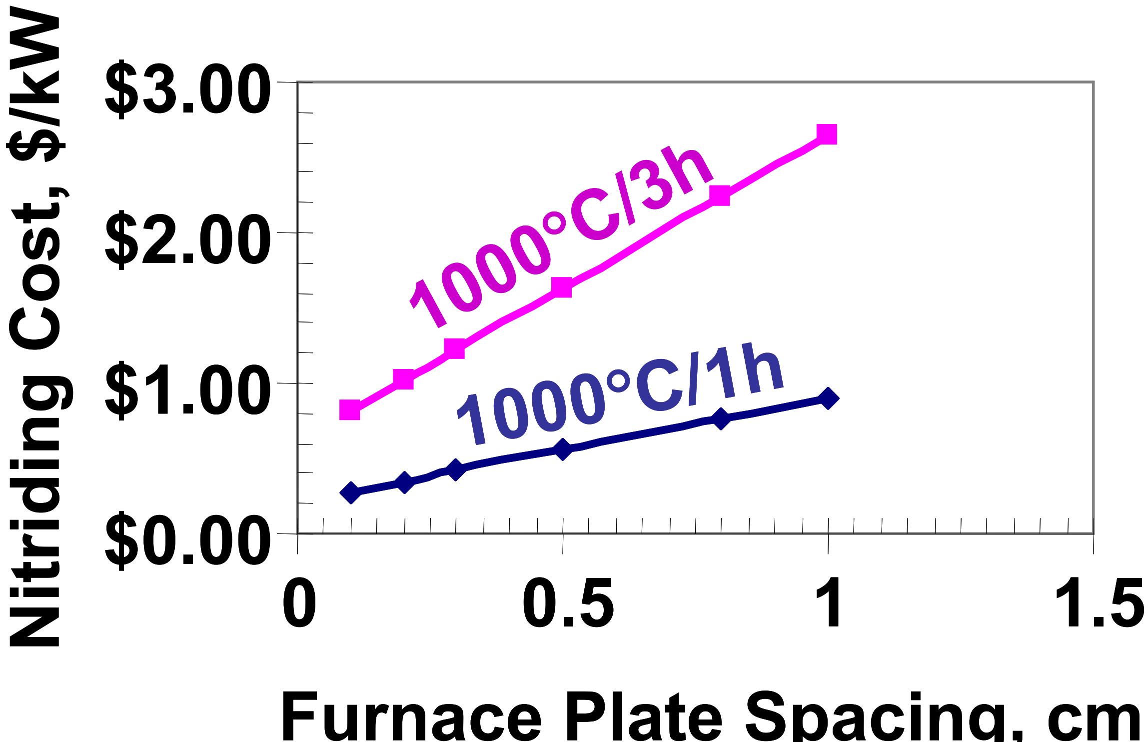
2006 GenCell Cost Estimates for Stamped Bipolar Plates
(Nitriding Costs Not Included)

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

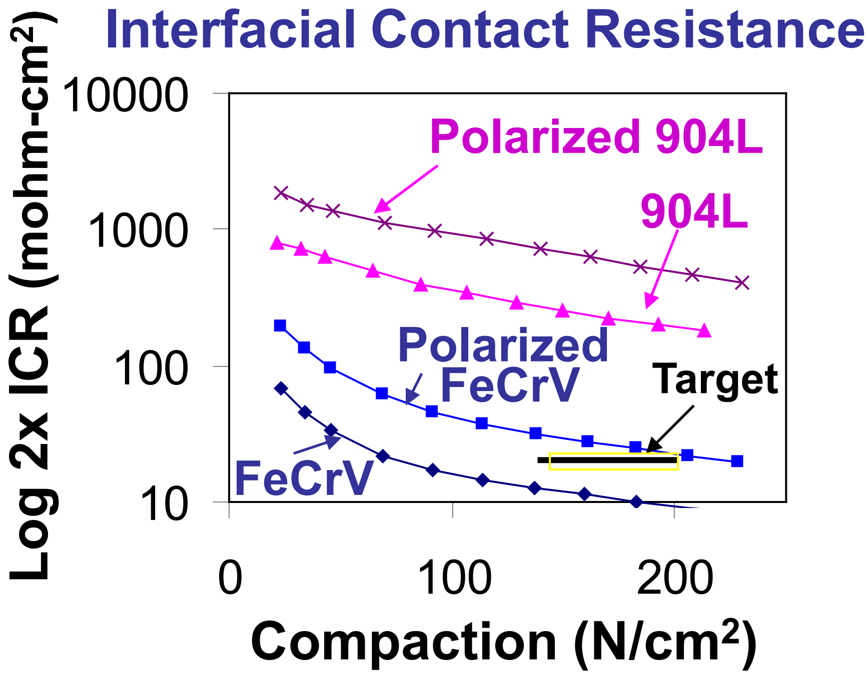
75 cents/kW Nitriding Costs Potentially Feasible

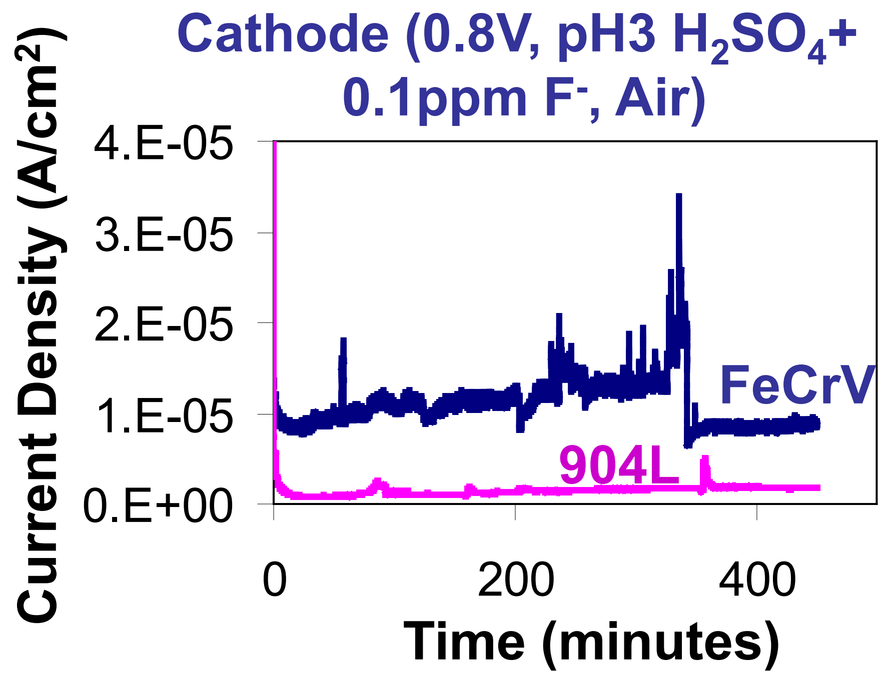
Preliminary Cost Analysis by B. James, Directed Technologies

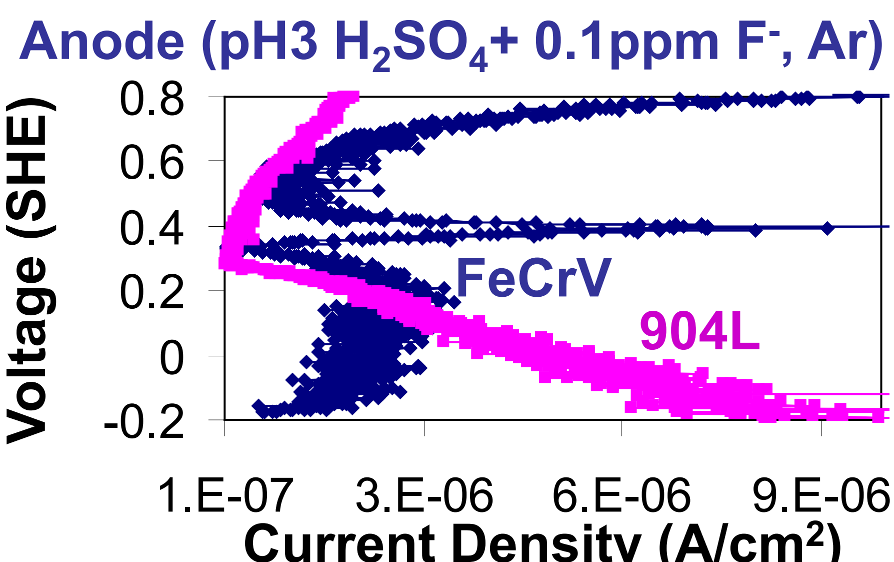


- Automated, step-continuous conventional nitriding system at 500,000 systems per year, mark up not included
  - -keys are short nitriding cycle and high furnace plate stacking density
- Nitriding by pulsed plasma arc lamp in range of 16-44 cents/kW
  - -feasibility to nitride Ti in “seconds” previously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

New Protocol Ex-Situ Corrosion and ICR of Foils



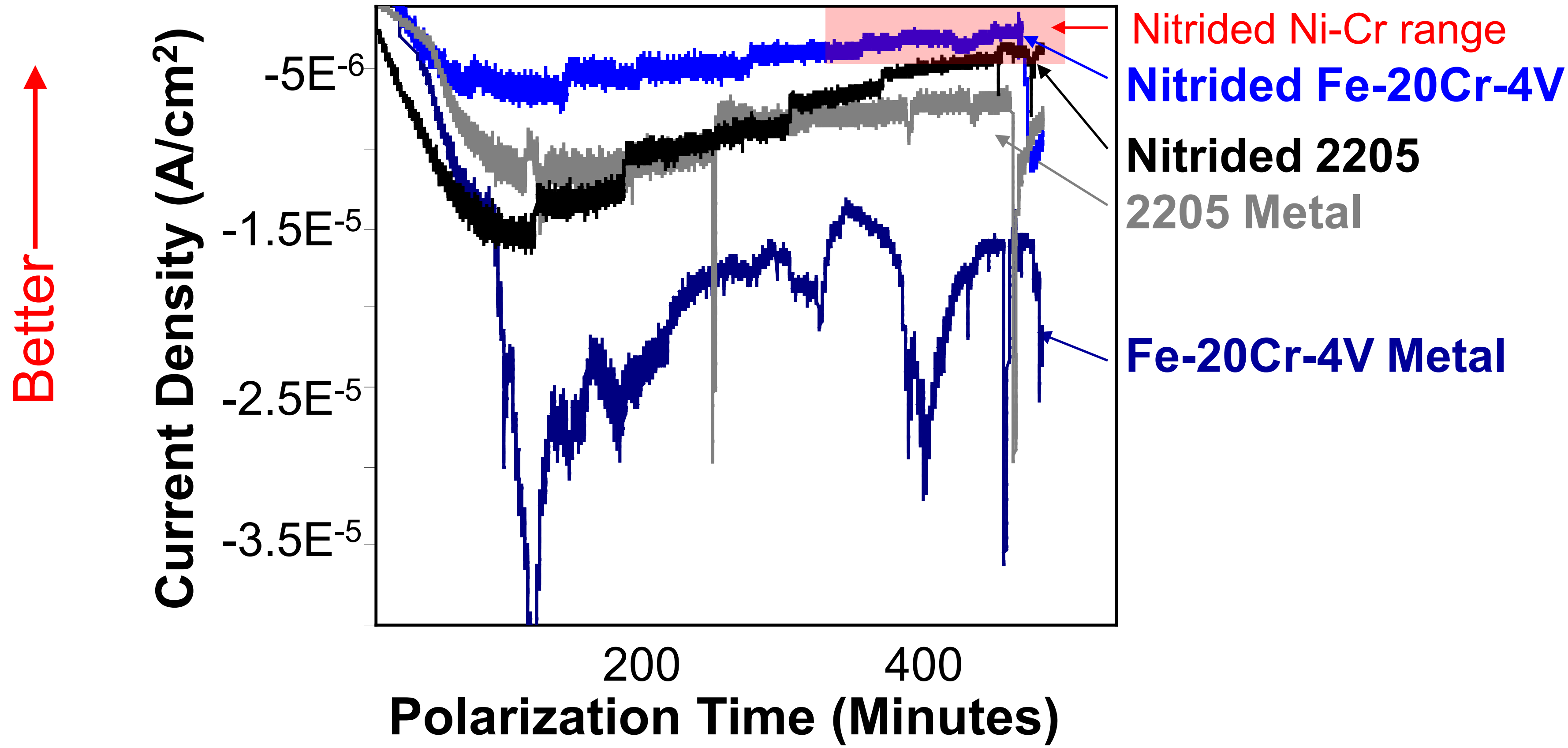




- 904L and archival nitrided FeCrV tested under new DOE protocols
- Neither material meets new 10^{-6} to 10^{-8} A/cm^2 corrosion targets
  - -low conductivity test solution, numbers dependent on test cell setup?
  - -cathode test not run to 24-100 h target due to NREL lab test safety rules
- Nitrided FeCrV significant ICR benefit

Nitrided Foils Exhibit Good Corrosion Resistance Under Simulated Aggressive Anode Conditions

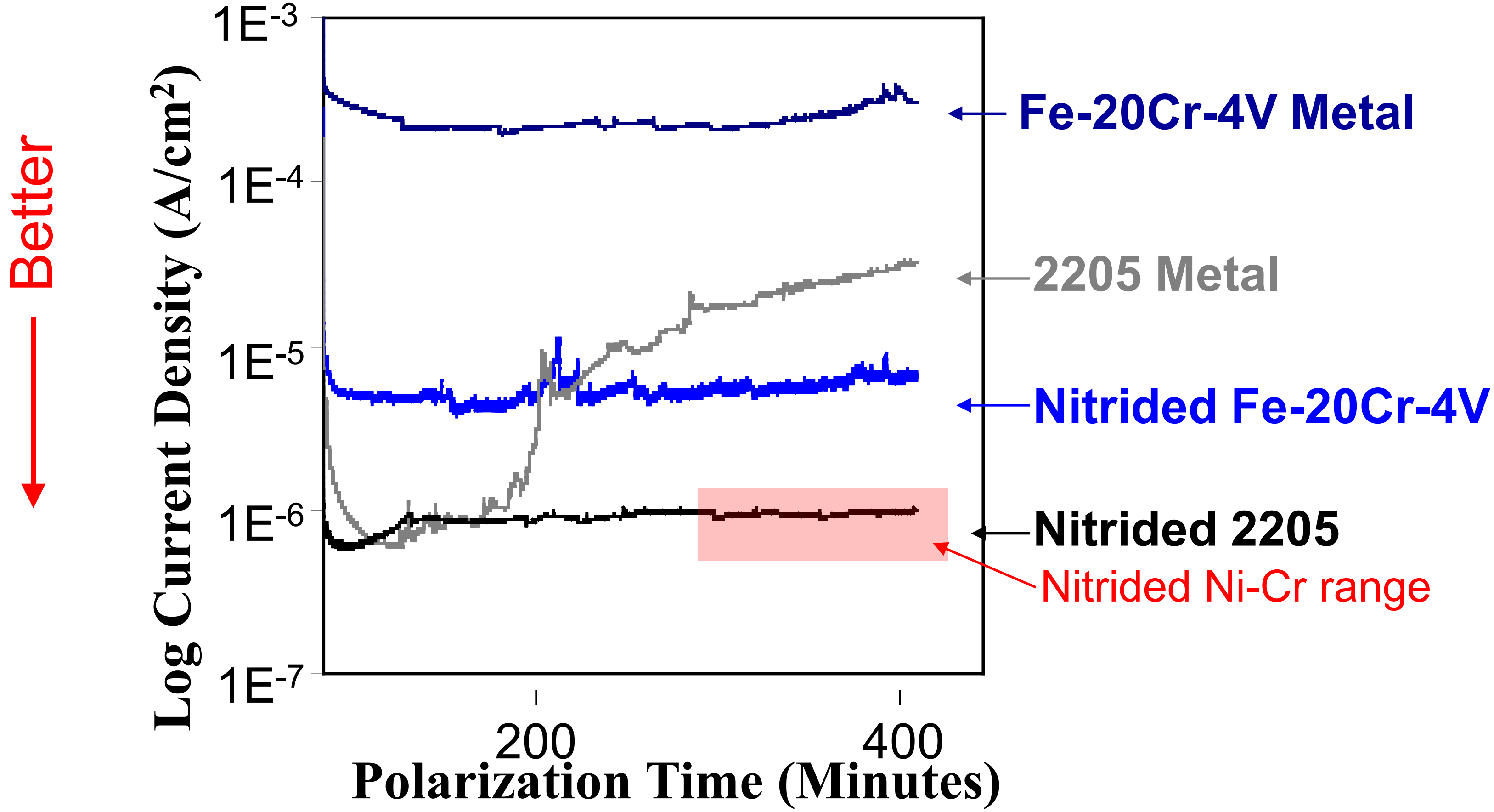
Polarization Evaluation at 70°C in 1M H_2SO_4+ 2 ppm F^- held at +0.14V vs SHE, H_2 purged



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

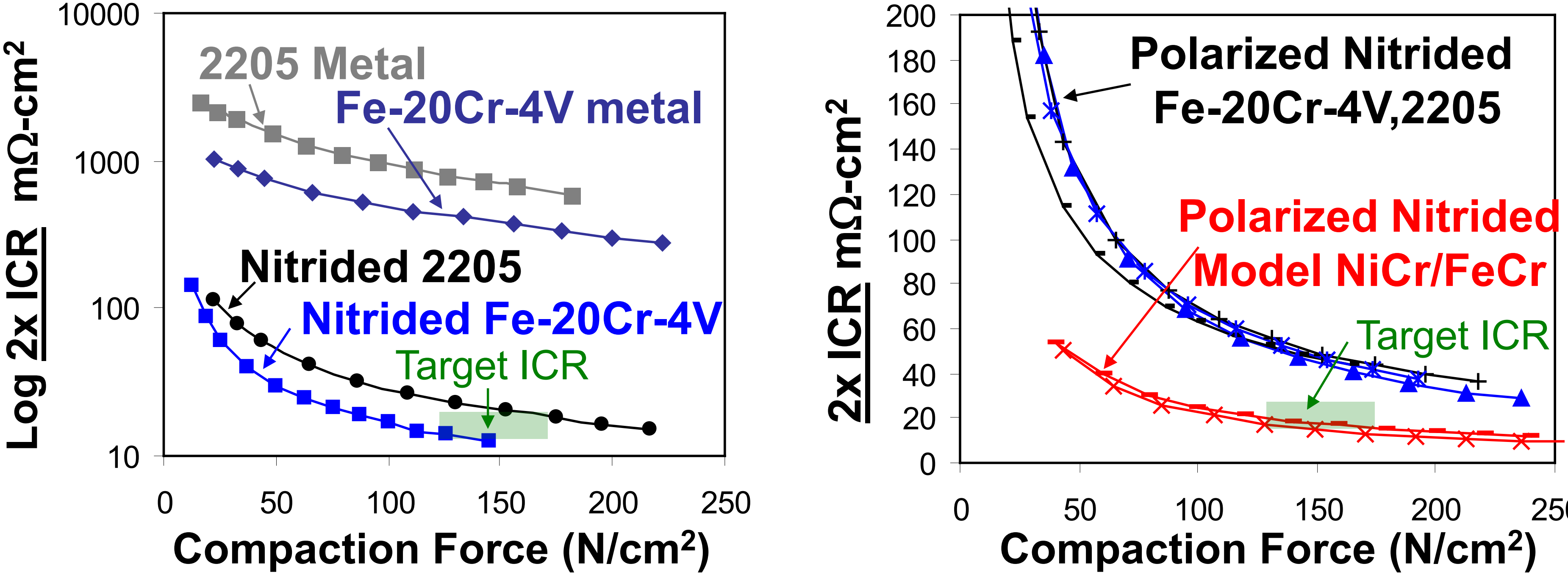
Nitrided Foils Exhibit Good Corrosion Resistance Under Simulated Aggressive Cathode Conditions

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

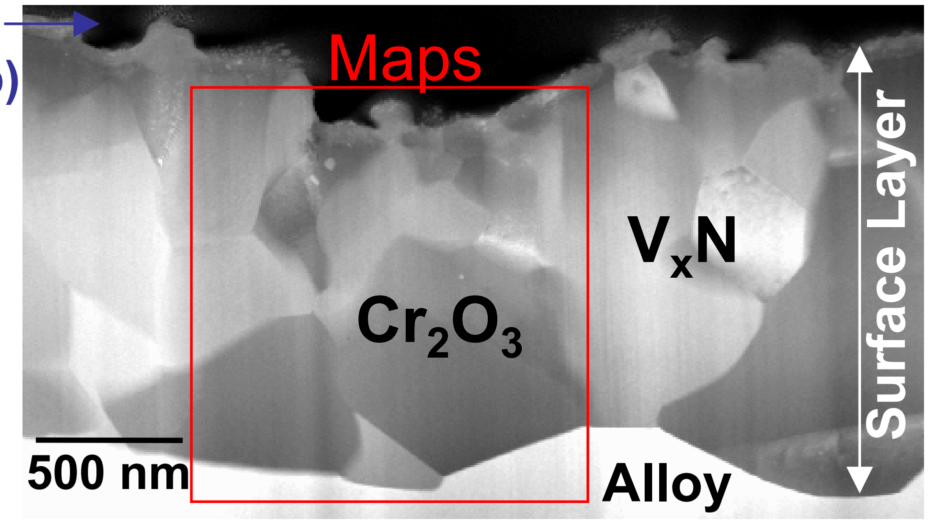
Nitridation Significantly Reduces Foil Interfacial Contact Resistance (ICR)

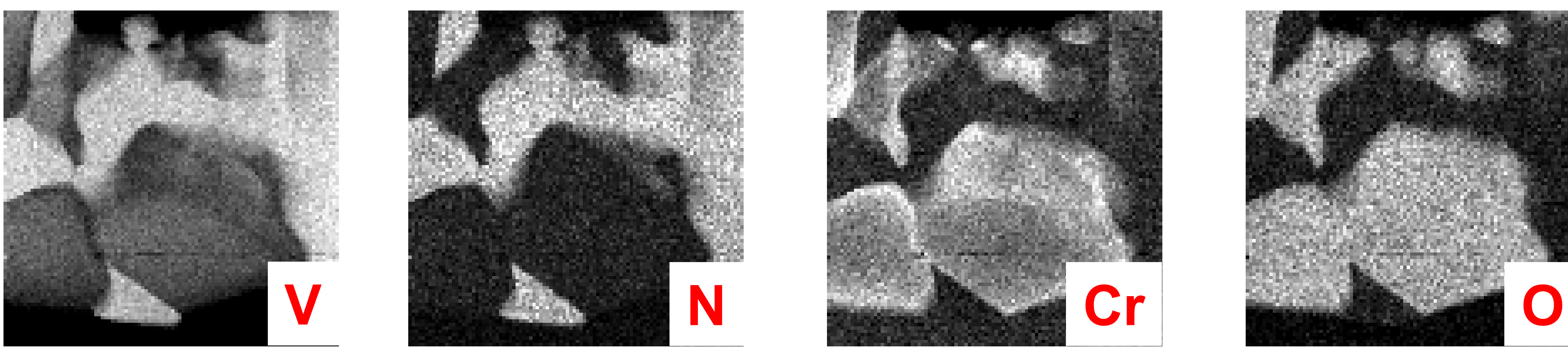


- 7h polarization of nitrided foils under simulated aggressive anode and cathode conditions raised ICR beyond target value
  - -remains order of magnitude lower than untreated metal
- 7h polarized nitrided model NiCr/FeCr alloys and nitrided Fe-20Cr-4V <u>sheet</u> material showed only small ICR increases

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