PEM Fuel Cell Metallic Bipolar Plates: Technical Status and Nitridation Surface Modification for Improved Performance

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Outline

- Considerations for Metallic Bipolar Plates
  - -short commentary on state-of-the-art for protection of metallic bipolar plates addressed
- Metallic Bipolar Plates and the Nitridation Concept
- Exploratory Single-Cell Fuel Cell Evaluation of Nitrided 15 cm^2 FeCrV Stainless Steel Stampings
  - -1000 h test results
  - -rapid cycle quartz/plasma lamp nitriding
- Single-Cell Evaluation of 50 cm^2 Stamped/Laser Welded/Nitrided FeCrV Bipolar Plate Assembles
  - -collaboration with General Motors

Considerations for Protection of Metallic Bipolar Plates

ORNL Viewpoint

Electrically Conductive, Corrosion-Resistant Coating Candidate Materials Long Established

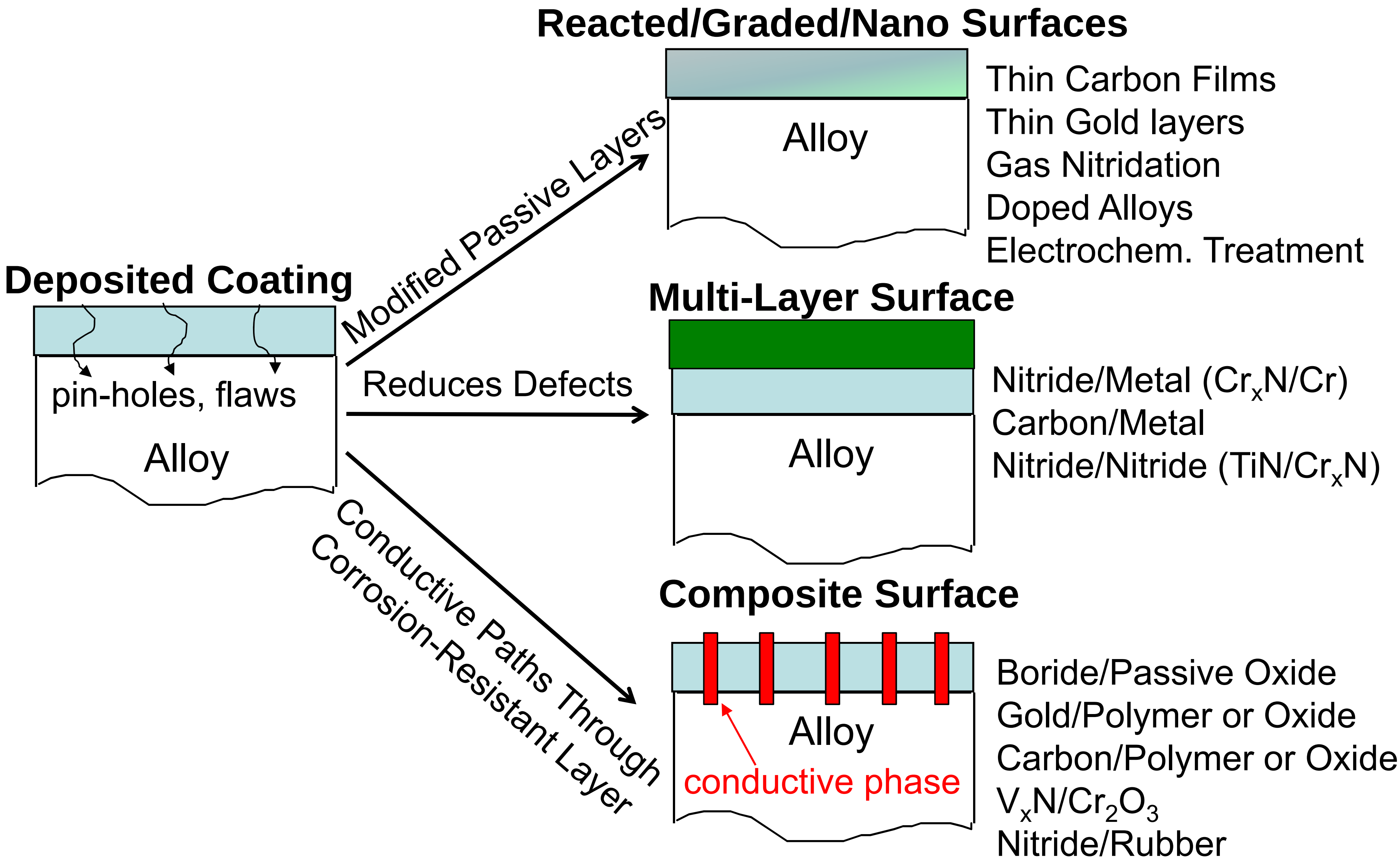
After Borup and Vanderborgh, MRS Proceedings 1995

Carbon-Based	Metallic
Graphite	Inert metals (e.g. Nb)
Conductive Polymer	Metal Nitrides
Diamond, Diamond Like Carbon	Metal Carbides
Organic Self-Assembled Monolayers	Noble Metals (e.g. gold)

*conductive oxides have also been examined in past decade

- Manufacturing considerations of coating approach cost, flow-field coverage, and defect incidence are key to success
- Not clear if can be completely prime reliant on coating for protection
  - -alloy substrates likely need good degree of inherent corrosion resistance (challenge for steel and Al substrates, favors stainless steel)

Evolution of Coating Architectures to Better Protect Metallic Bipolar Plates Surfaces



State-of-the-Art Performance Benchmark is Electroplated Gold on Stainless Steel

What are current literature trends for lower cost coated metal alternatives?

- Nano Gold variations (layers and composites)
  - may be only option if encounter frequent excursions >1V
- Carbon-based surfaces
- Cr-nitrides
- Electrochemical treatments

Very dependent on end use application: some coatings that fail automotive performance or cost targets may be acceptable for stationary or portable applications

How Do We Usually Assess Candidate Bipolar Plate Alloys and Coatings?

•Desired lifetimes of ~5000 h (auto) to 40,000 h^+ (stationary)

•Accelerated single-cell and stack testing protocols available

-manufacturing bipolar plates of exploratory alloys or coatings can be difficult, costly, and complicated

•Early screening typically accomplished with ex-situ flat sheet coupon immersion polarization corrosion tests less than 8 h

-metallurgical surface conditions of flat plates may be significantly different than cold work stamped foils

-flat coupons far easier to coat than stamped plates

Corrosion and Interfacial Contact Resistance (ICR) are Key for Metallic Bipolar Plates

- Electrochemical screening by immersion in hot sulfuric acid with high levels of F^- may now be overly aggressive
  - -better membrane-electrode assemblies (MEAs) and improved water management reduce corrosivity of bipolar plate operating environment

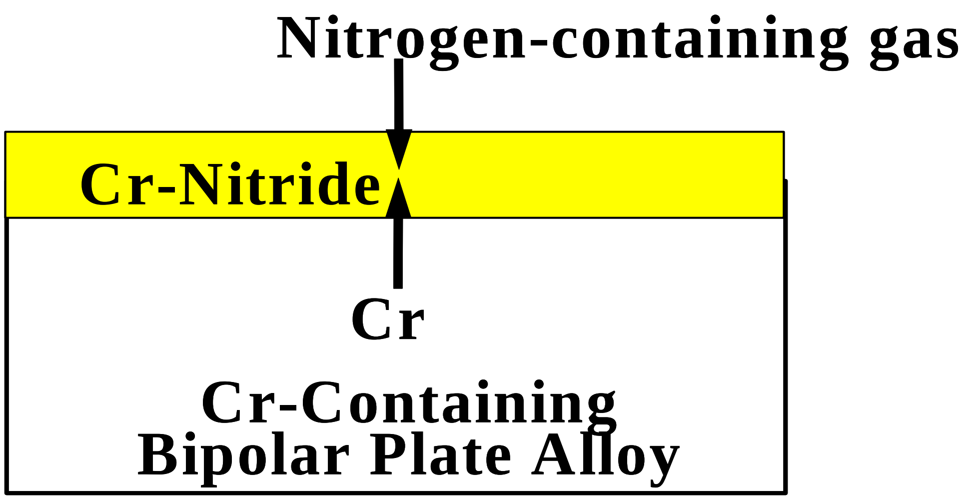
- Oxide layer formation and increased ICR may be bigger issue than metal corrosion/dissolution and MEA contamination

- Current density target numbers from hot sulfuric acid polarization corrosion tests are of limited use
  - -how current density reflects ICR increase or metal ion dissolution material dependent (e.g. different coating materials may need different targets)

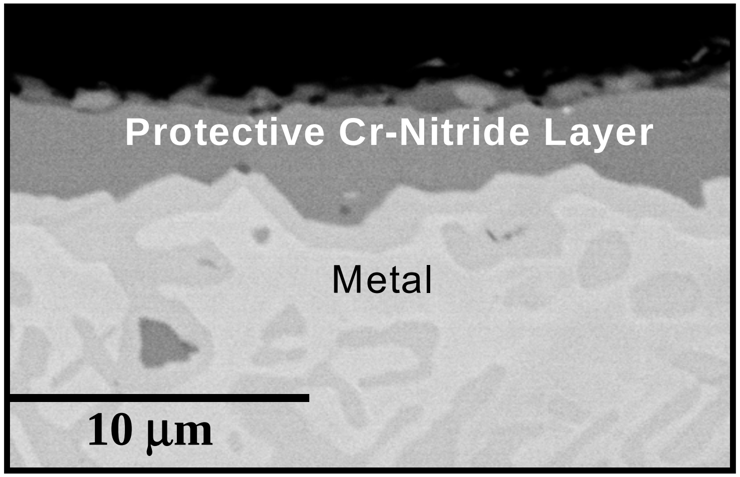
- Strong need for more open literature studies that relate ex-situ corrosion and ICR assessment to in-situ fuel cell test results

Nitridation Approach

Gas Nitridation: Thermally Grown Cr-Nitride to Protect Metallic Bipolar Plates

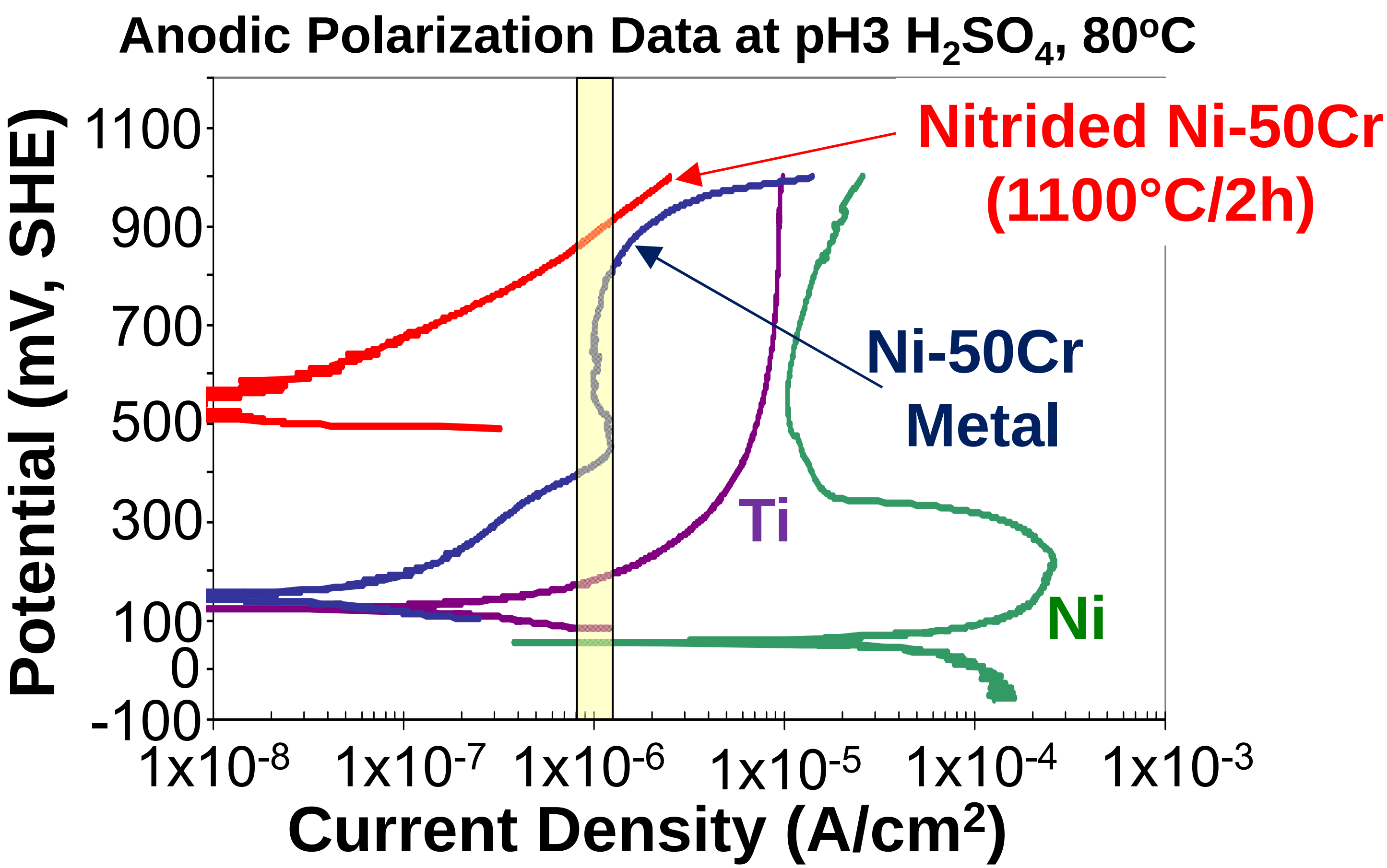


Model Ni-50Cr Alloy
(SEM Cross-Section)

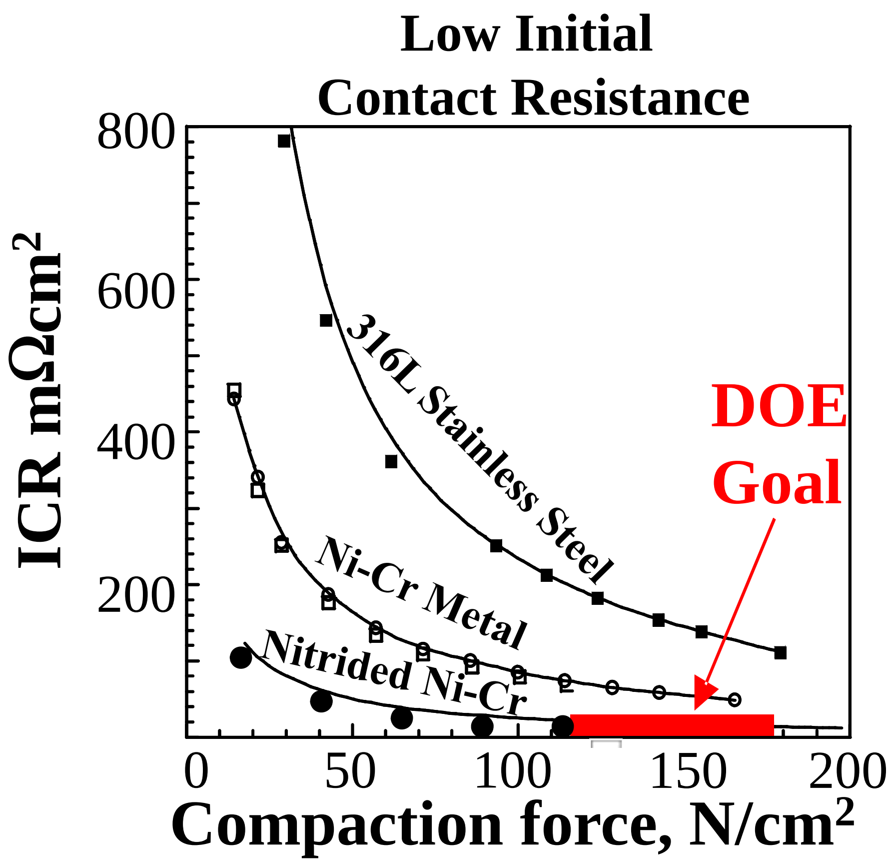


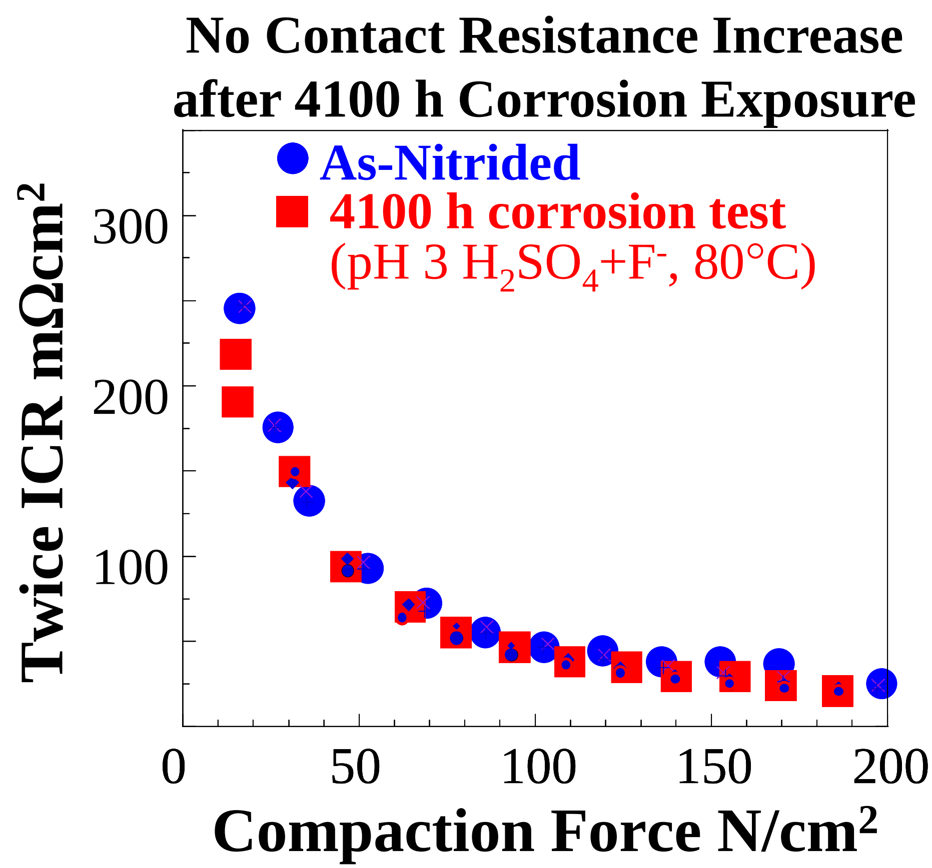
- Surface conversion not a deposited coating
- High temperature favors reaction of all exposed metal surfaces
  - -few, if any, pin-hole defects
  - -not line of sight limited, amenable to complex geometries e.g. flow fields
  - -drawback: very substrate alloy dependent, most compositions won't form continuous Cr_xN surface layer
- Stamp then nitride: Industrially established and low cost

Cr_xN Formed on Nitrided Model Ni-50Cr Alloy Exhibits Good Corrosion Resistance



Cr_xN Surface on Model Nitrided Ni-50Cr Exhibits and Maintains Low ICR





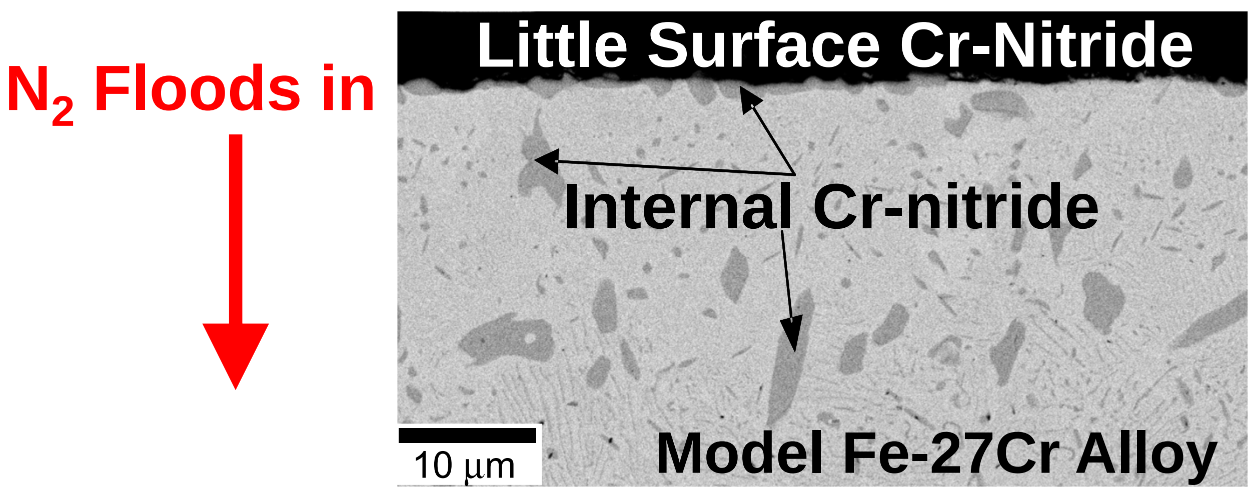
•4100h in LANL bipolar corrosion test cell (Air/H_2 pH 3 H_2SO_4 + F- 80°C)- No attack of Cr_xN and minimal metal ion dissolution (K. Weisbrod test cell)

•Good single-cell fuel cell test behavior also observed

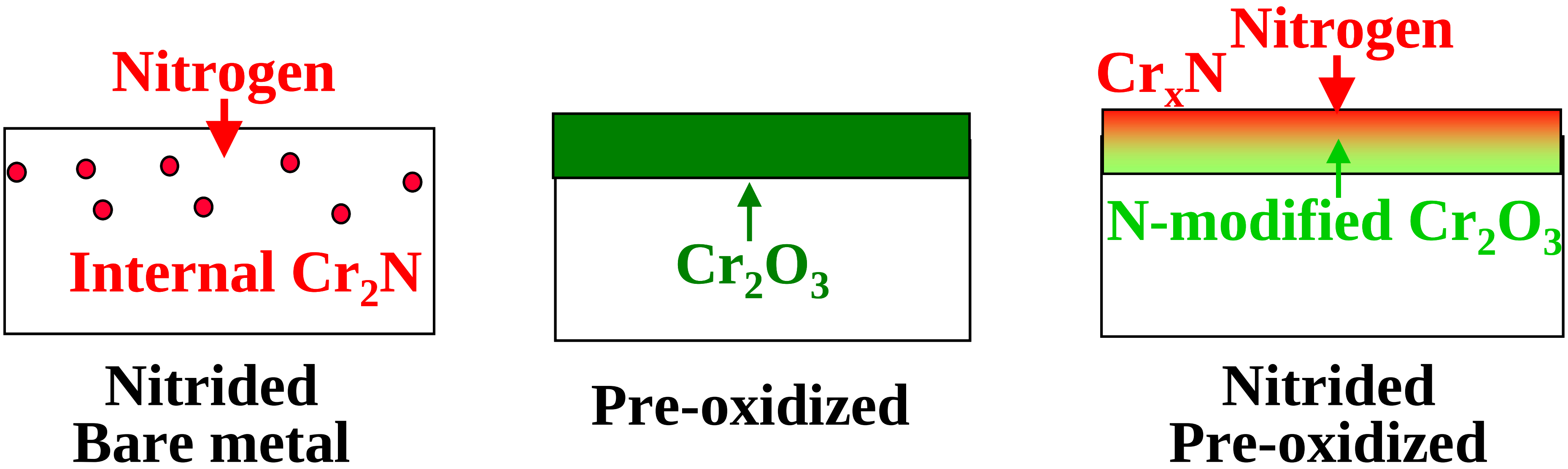
Need Fe-Base Stainless Steel to Meet $3-5/kW Cost Goals for Auto Applications

- Commercial Ni-Cr Alloys in Range of ~$15-25/lb
  - -far too expensive for automotive use
- Focus on Fe-Base Stainless Steels: ~$2-8/lb

- High N_2 Permeability Makes Surface Cr-Nitride Formation Difficult on Fe-Cr: poor corrosion resistance

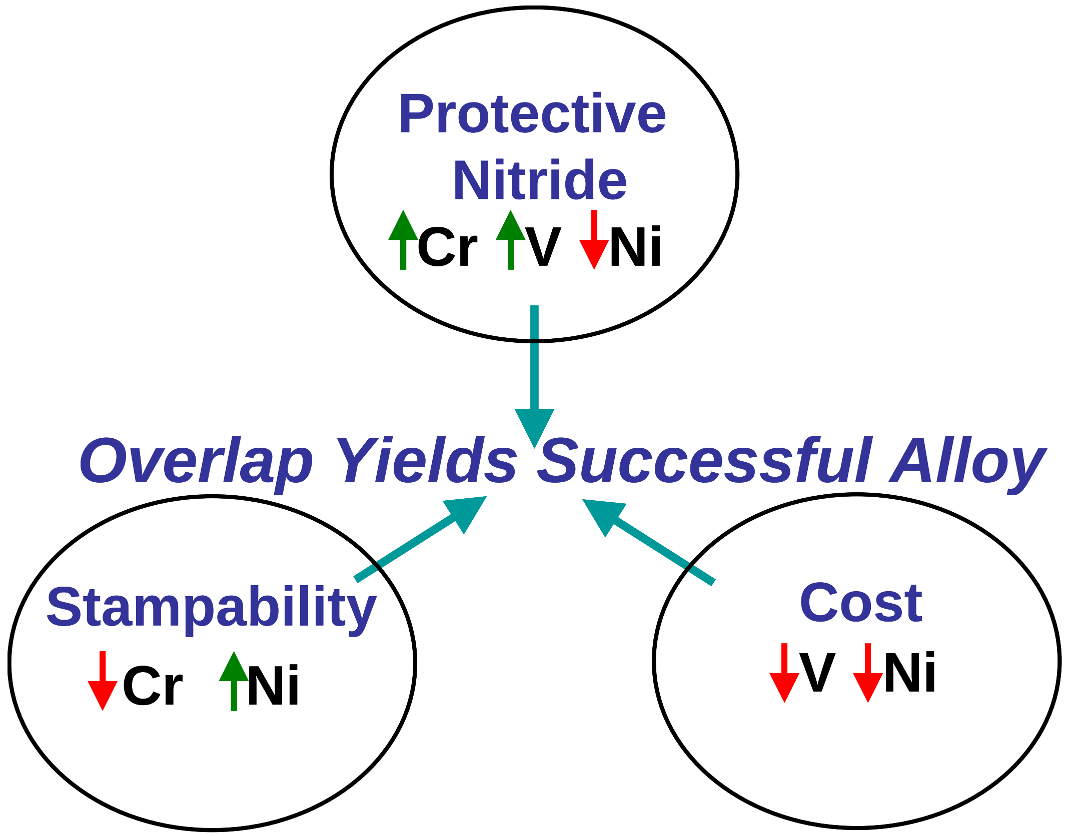


Pre-Oxidation Followed by Nitridation to Form Cr_xN Surface on Stainless Steels



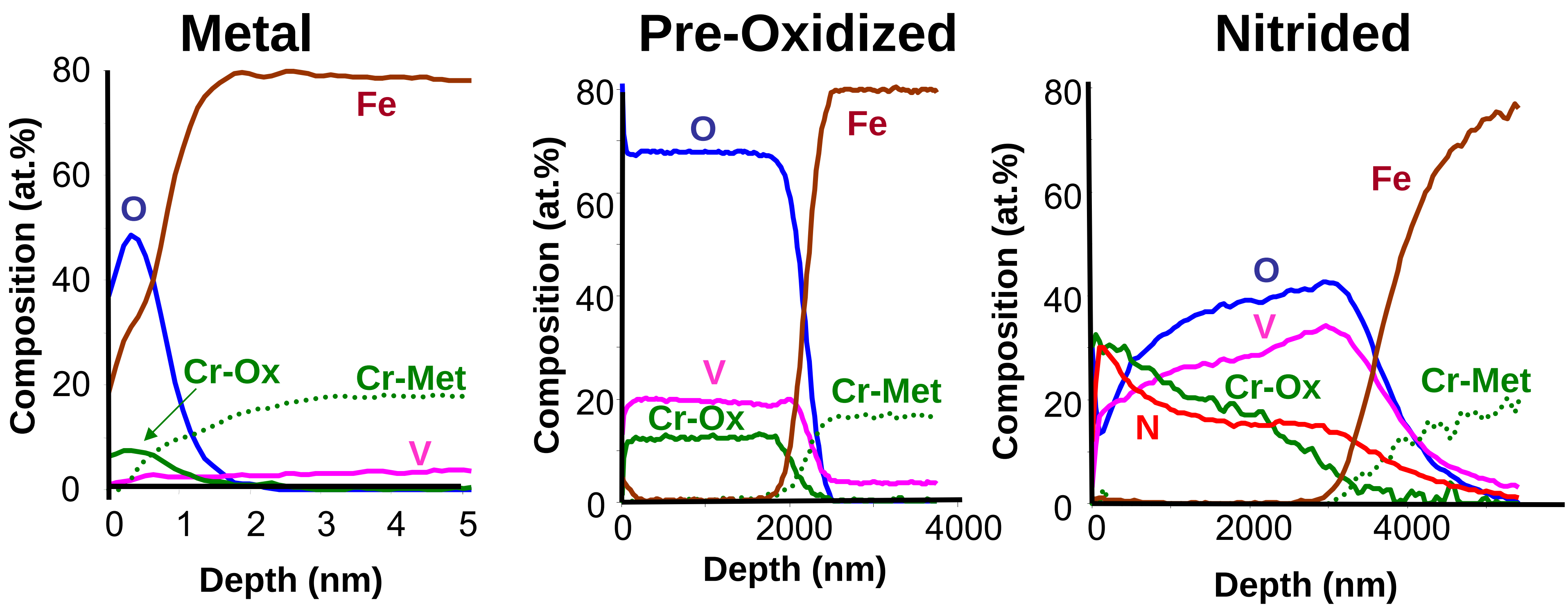
- Stainless steels internally nitride: corrosion
- Form Cr_2O_3 by preoxidation to keep N_2 at surface
  - -convert surface Cr_2O_3 to surface Cr_xN by nitridation
- V added to stainless steel assists conversion to nitride
  - -good ICR and corrosion results with model Fe-27Cr-6V alloy

ORNL Developed Fe-(20-23)Cr-4V Wt.% Alloy Foils



- Co-optimize ductility (for stamping) and low alloy cost with protective nitride surface formation
- Pre-oxidation: 900°C, 5 min to 1 h, N_2-$4H_2$-$0.5O_2$; Nitridation: 1000°C, 1-3 h, N_2-$4H_2$ (separate steps here, can be combined in single step)

Surface Chemistry Changes for Fe-20Cr-4V On Pre-Oxidation and Nitriding

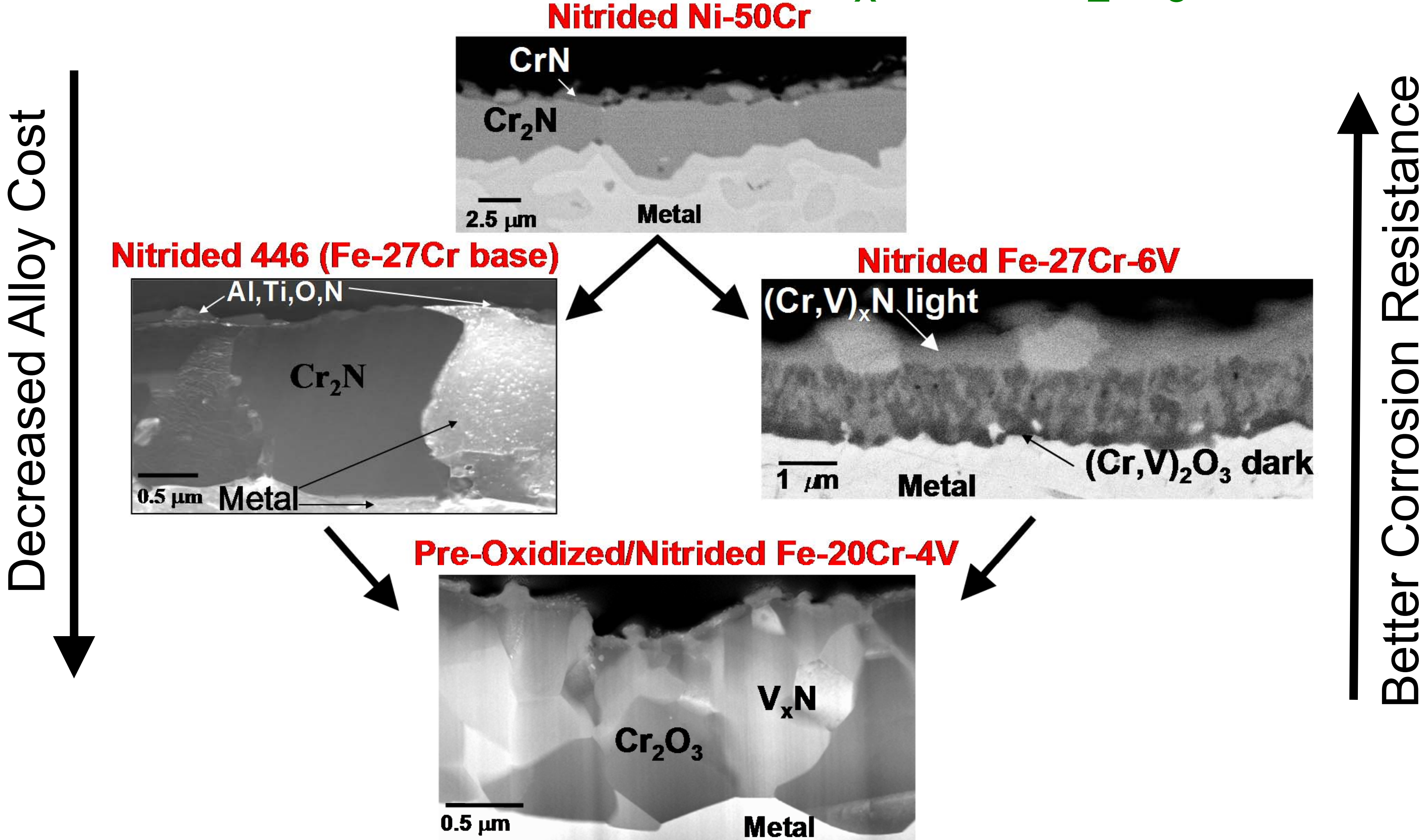


- Under ideal circumstances Fe completely eliminated from surface by pre-oxidation and nitridation

  -yields $(V,Cr)_xN$ in $(Cr,V)_2O_3$

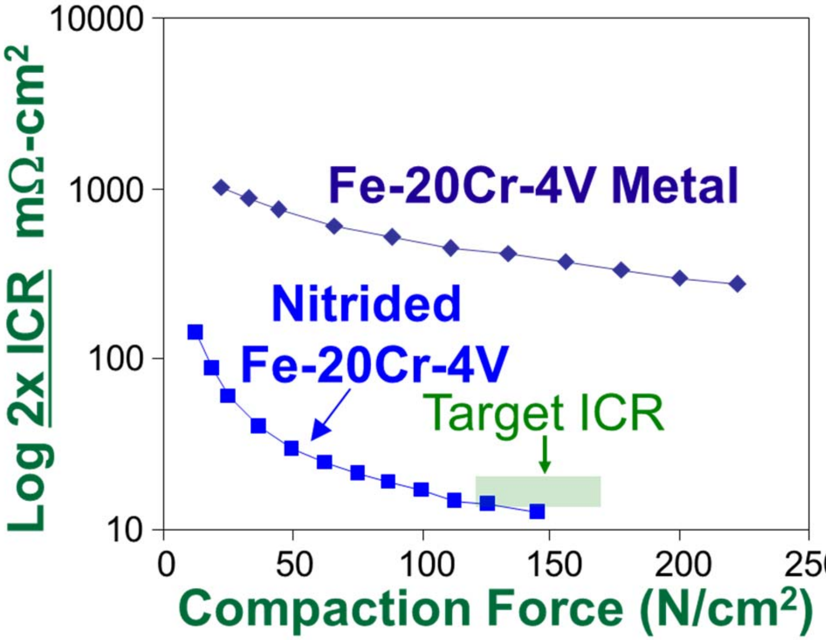
- Above for prepped laboratory sheet coupon, foil tends to retain a few % Fe in surface (900-1000°C: 1-2 h peak temperature hold)

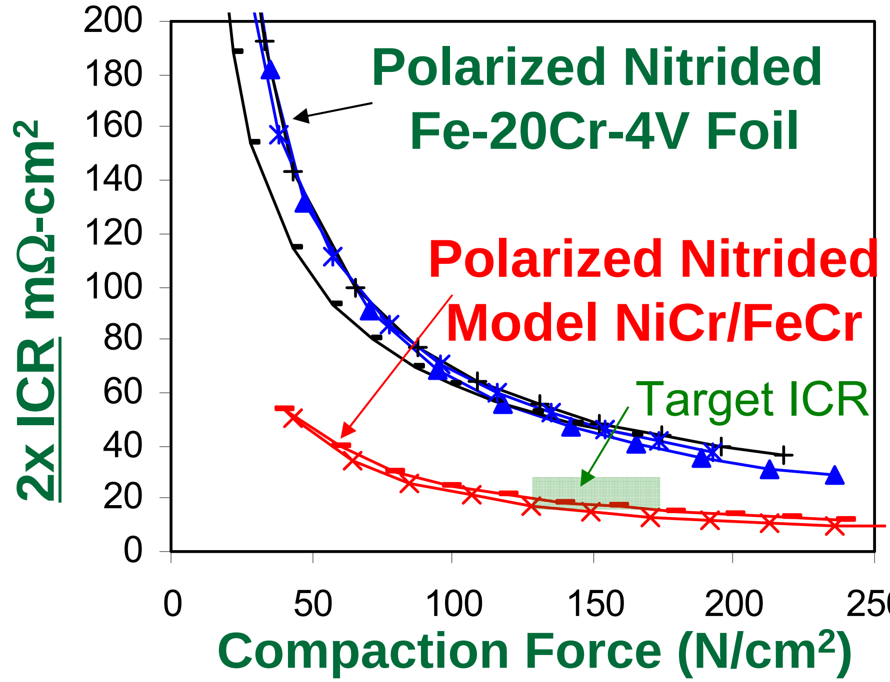
Continuous Cr_xN to Cr_xN+Oxide to Through-Thickness V_xN in Cr_2O_3



Lower alloy Cr, V content and shorter nitriding cycles (1-2 h at 1000°C) to reduce cost result in V_xN in Cr_2O_3 surface rather than continuous Cr_xN

Low ICR and Good Corrosion Resistance Achieved with Nitrided FeCrV Foils

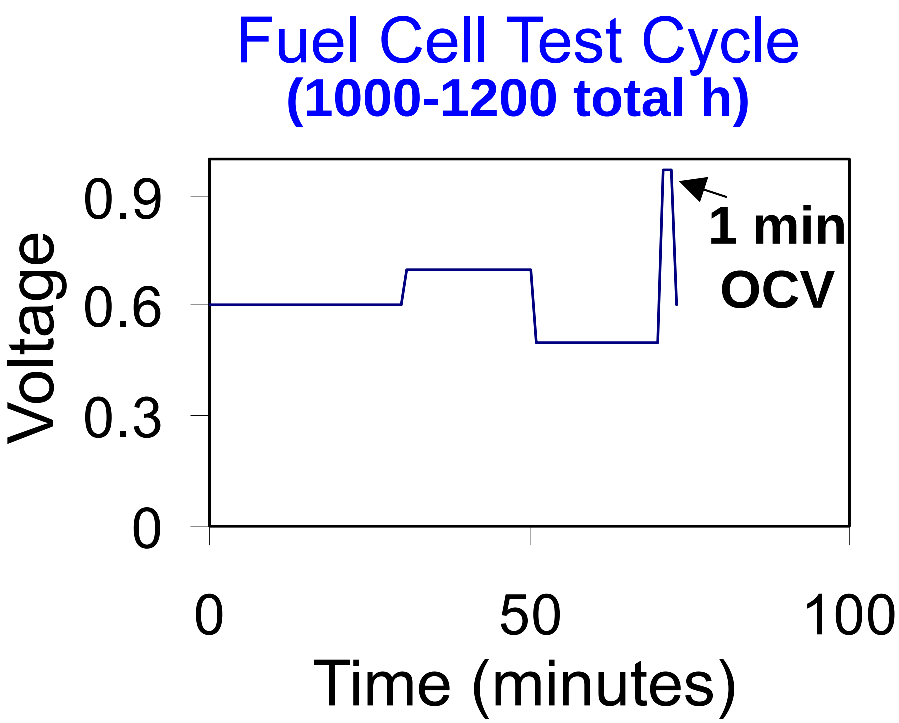


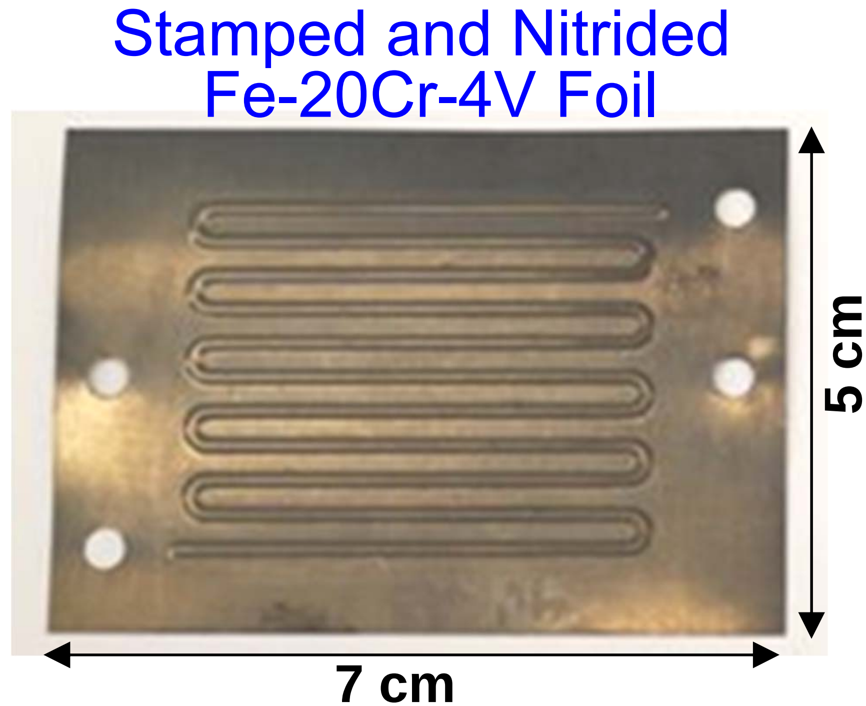


- Polarization in 1M H_2SO_4 + 2 wppm F^- for 7 h at 0.14V (H_2, anode simulation) or 0.84 V (aerated, cathode simulation) vs SHE
- Corrosion resistance of nitrided FeCrV foils (3 to 5 μm A/cm²) not quite as good as FeCrV sheet coupons or model NiCr/FeCr sheet alloy coupons
- Moderate ICR increase for nitrided FeCrV foils after polarization

Single-Cell Fuel Cell Testing of 15 cm^2 Active Area Stampings

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

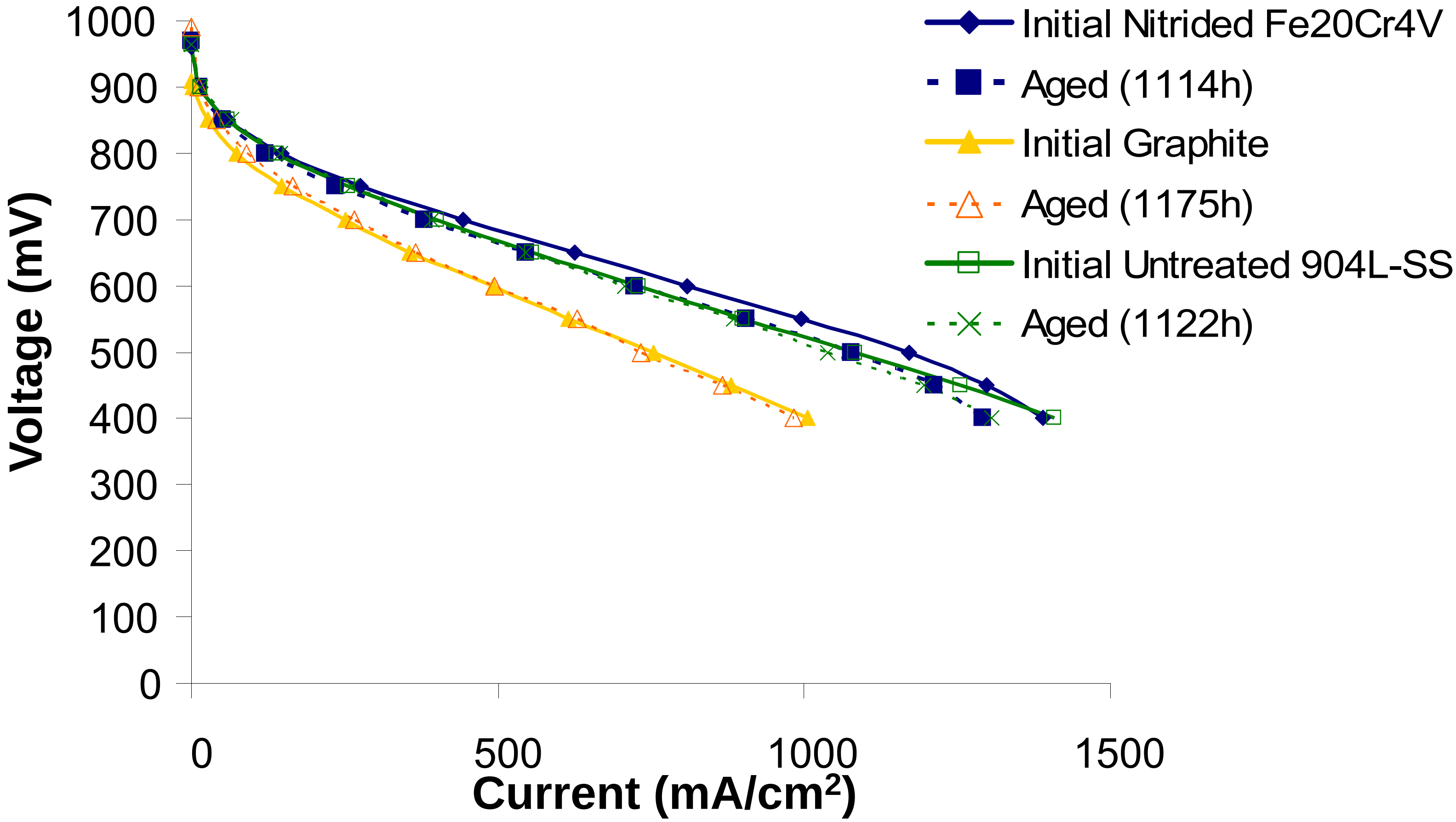




- Operating conditions: 80°C, 25 psig
  performance curves (V-I):0.9-0.4V, 0.05V steps, 20 min./step, repeat 3x
- Simple serpentine ~15 cm^2 active area stamped foils for metals, machined graphite block of similar flow-field design

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

V-I Curves of Aged Plates Using Fresh Gore PRIMEA MEA

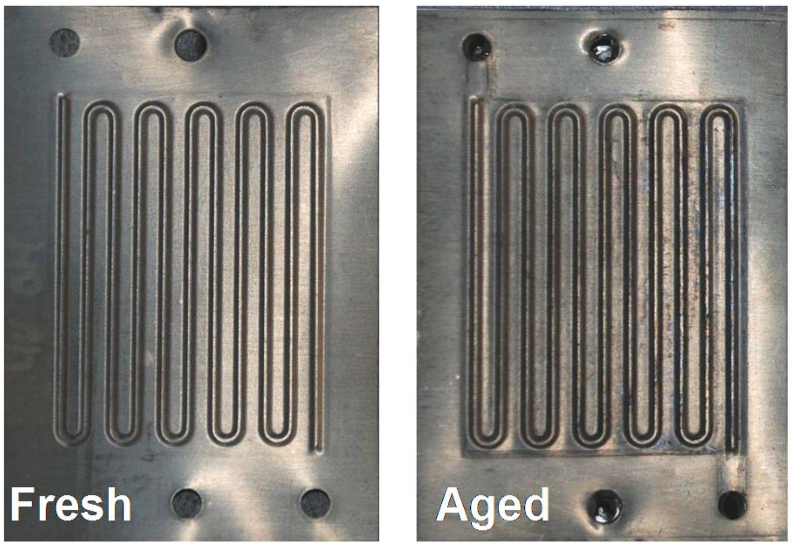


•Slight decline in nitrided Fe-20Cr-4V data within fuel cell build-to-build variation (< 5-10% variation of peak power output)

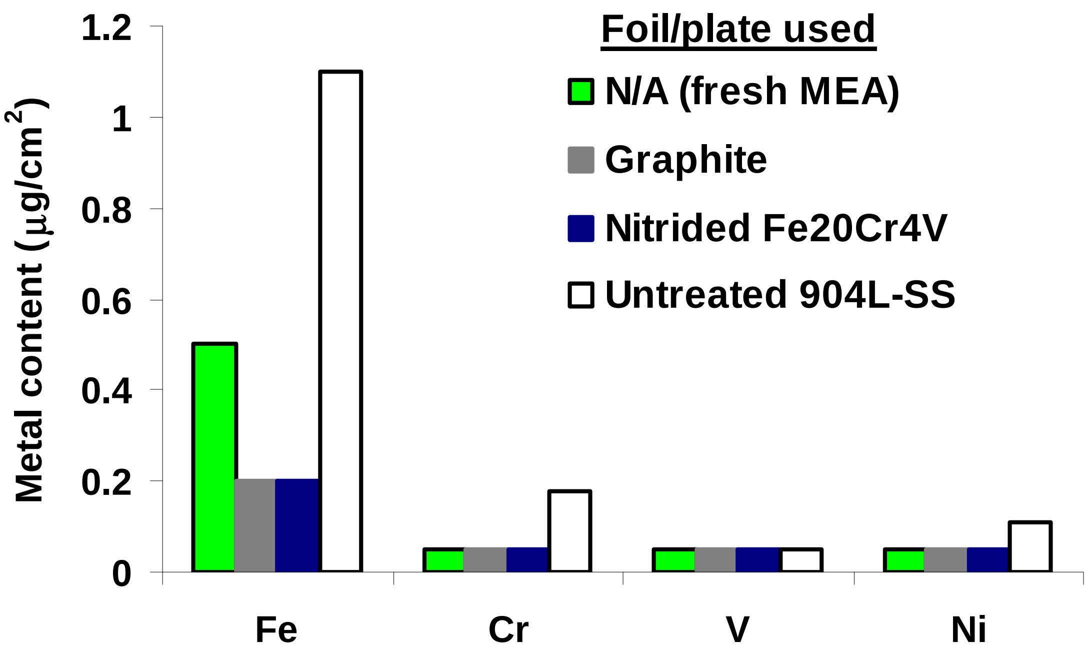
•Lower performance of graphite attributed to flow-field differences w/stampings

Nitrided Surface on Fe-20Cr-4V Protected MEA from Metal Contamination

Nitrided Fe-20Cr-4V Plates



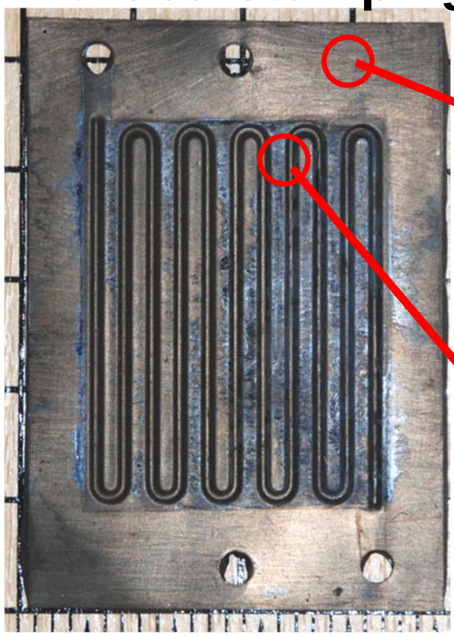
X-ray Fluorescence (XRF) of MEAs

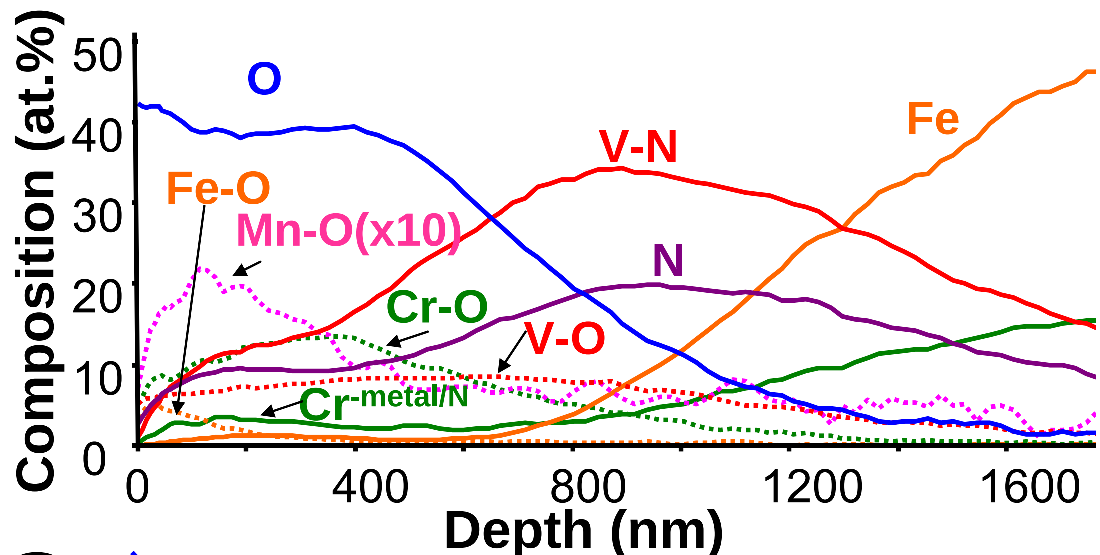


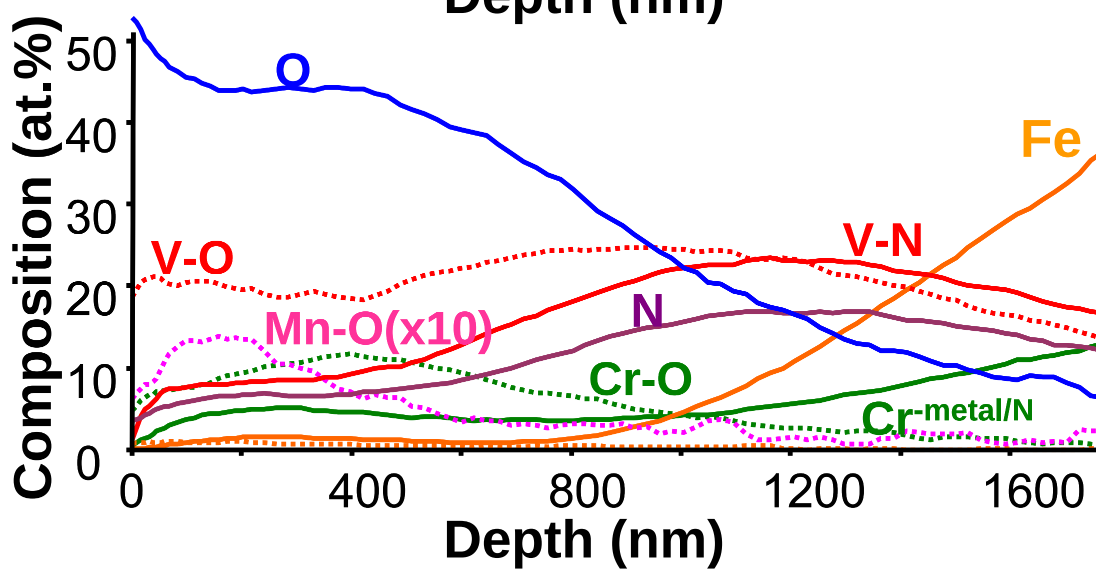
- No visible attack of nitrided Fe-20Cr-4V plates (slight staining-GDL contact)
- XRF found MEAs from graphite and nitrided Fe-20Cr-4V plates “clean”
- Small (~1 $\mu g/cm^2$) level of metal ion contamination with 904 L
- 321 tested for 120 h showed regions of 1-70 $\mu g/cm^2$ metal contamination

Robustness/Repeatability Concern for Fe-20Cr4V and Short 1-2 h Nitridation Cycles (Multiple Tests)

Oxidation seen in 1.5h Nitrided Stamping







-Performance decline in test

-Significantly higher V-O signal in flow-field (no Fe oxidation)

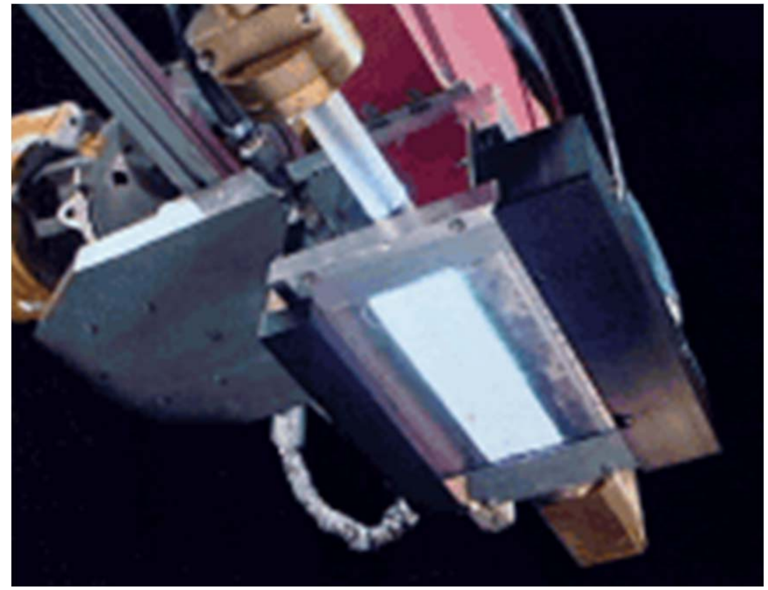
-Oxidation of V_xN

-Likely inadequately nitrided (needed longer cycle this run)

Rapid/More Robust Nitriding with Quartz Lamps?

Quartz Lamp Furnace

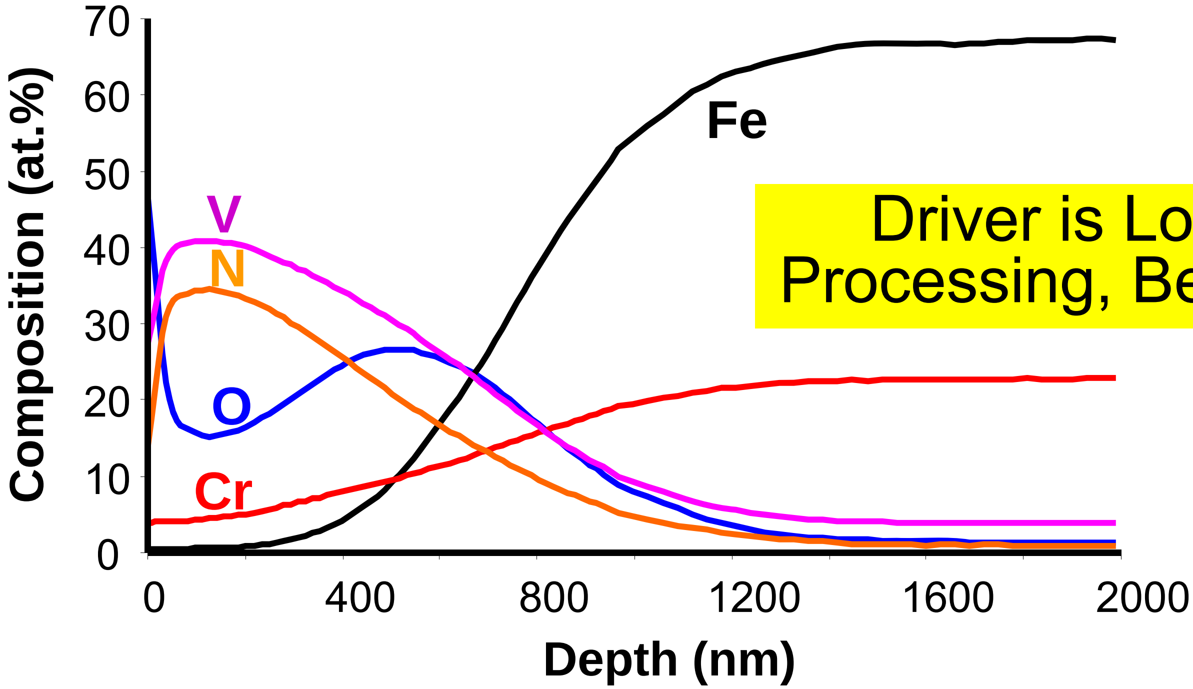
Plasma Arc Lamp



- Plasma arc and quartz lamps for rapid nitriding heating/cooling
  - -potential nitriding in minutes instead of hours (faster cycle, lower cost!)
- Rapid heating may favor more nitride-rich surface
  - -less transient oxidation, less Fe at surface
  - -potential for more robust surfaces?
- Minimizes brittle σ phase formation permitting higher-Cr stainless steel alloys (if can be stamped)

Desired Surface Formed by Rapid Nitriding Using Quartz Lamp Heating Technology

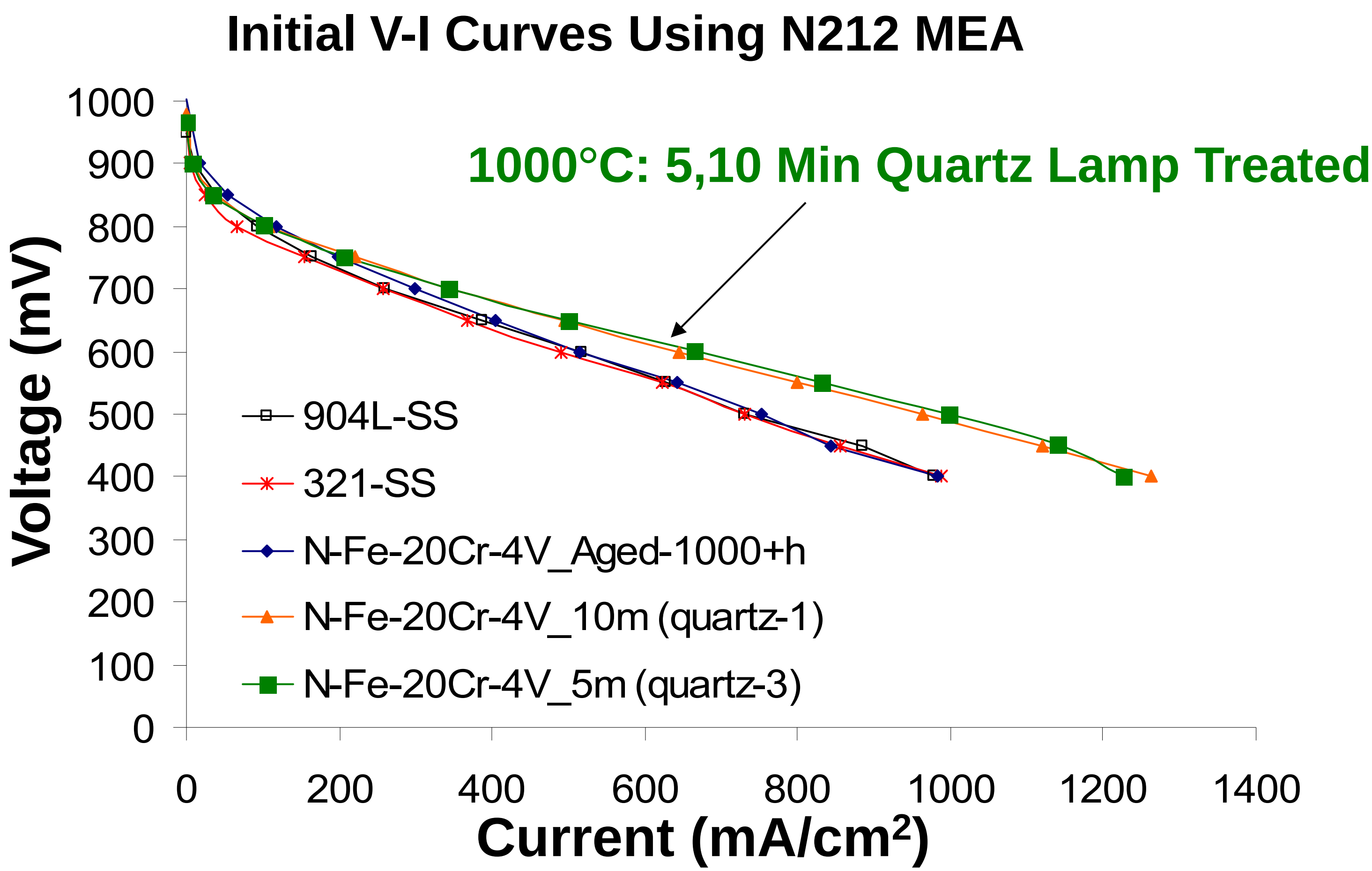
XPS Surface Chemistry of <u>1000°C/10 min</u> Treated Fe-20Cr-4V



Driver is Lower-Cost Processing, Better Surface

- Surface consistent with $V(Cr)_xN$ dispersed in $(Cr,V)_2O_3$
- Virtually no Fe in treated region (usually correlates w/ good corrosion resist.)
- 900-1000°C; 5 to 15 min peak temperature holds

Quartz-Lamp-Treated Stampings Show Promising Single-Cell Fuel Cell Behavior



- Better V-I behavior than standard nitriding procedure
  - -reasons why not understood (ex-situ ICR coupons showed similar values)
- Durability testing yielded generally positive results

General Motors (GM) Interaction: Manufacturability and Single-Cell Assesments

Details to be published soon. Presented slides in this section not yet available for release

Summary

- Promising manufacturability and single-cell fuel cell results obtained for stamped, laser welded, gas nitrided Fe-(20-23)Cr-4V alloy foils

- Quartz lamp nitriding shows promise for low cost, robust surfaces

- May be able to extend approach to existing commercial SS foils
  - -favor ≥ 20 wt.% Cr ferritic (nitride forming additions Ti, V, etc)
  - -best chance with quartz lamp (grow passive oxide layer with nitride particles)

- Concern for nitrided surfaces if frequent operation excursions > 1V

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