Nitrided Metallic Bipolar Foils in PEM Fuel cells

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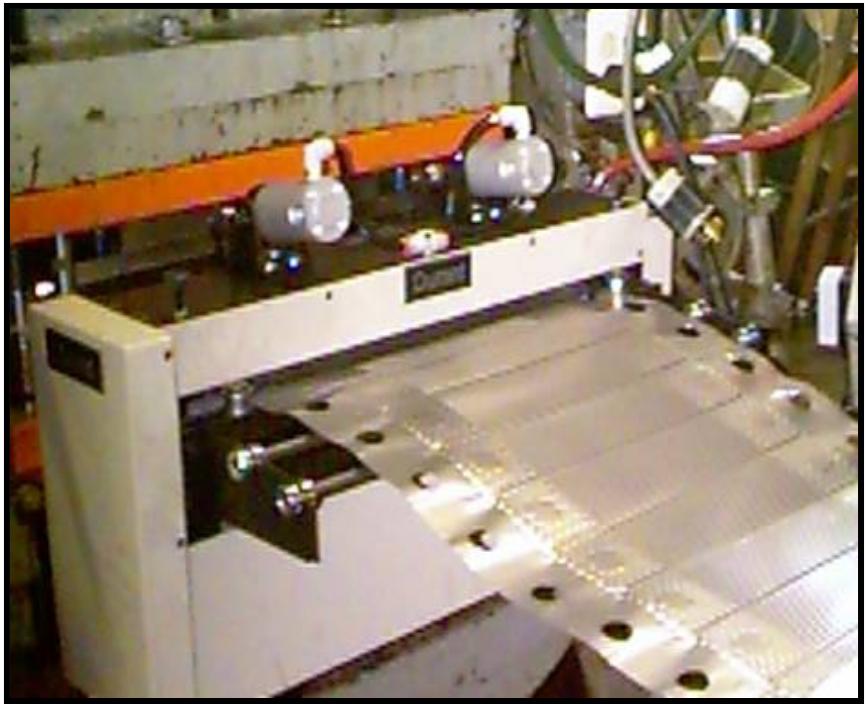
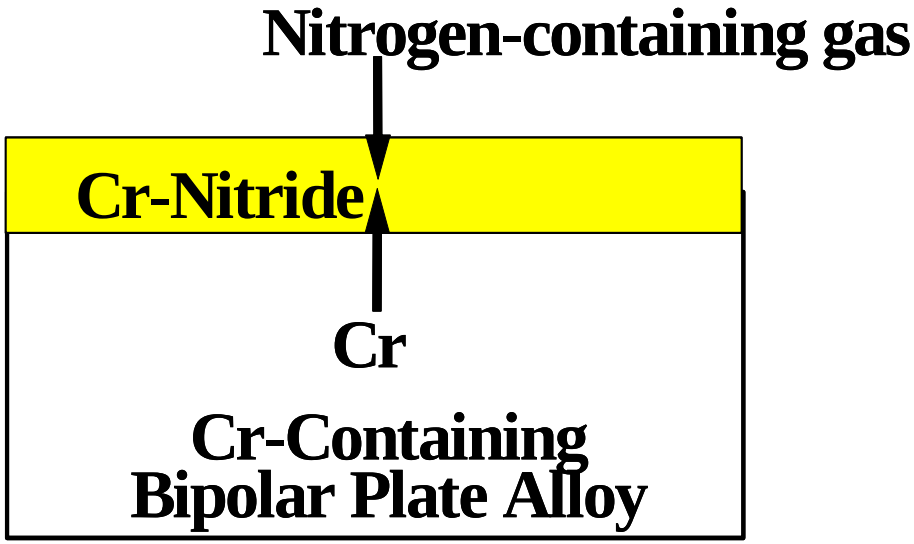
Thin Stamped Metallic Bipolar Plates for Low-Cost & High-Volume Manufacturing

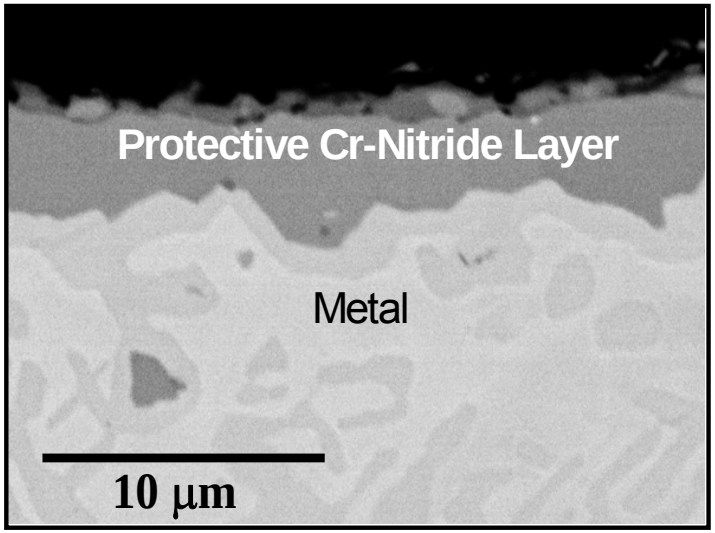
- Metal bipolar plates attractive due to their thinness and stampability
  - As thin as 50 microns
- Metals limited by high interfacial contact resistance and corrosion resistance
  - coating or surface modification needed



(Courtesy AGNI GenCell Inc)

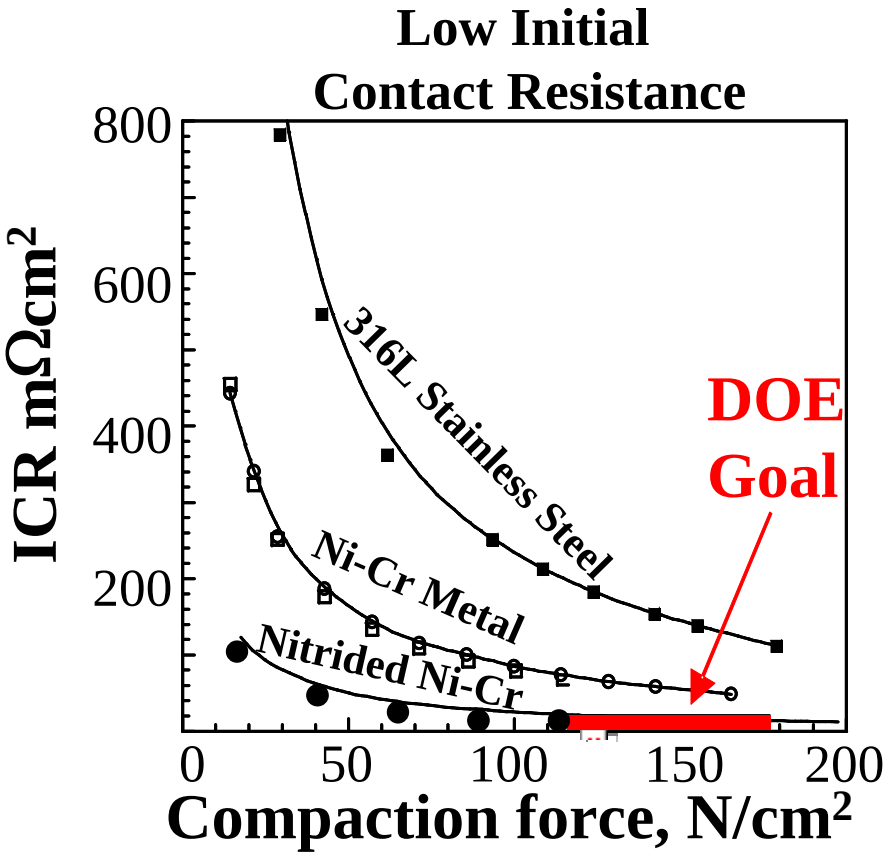
Thermally Grown Cr-Nitride Enables Corrosion Protection and Low Contact Resistance

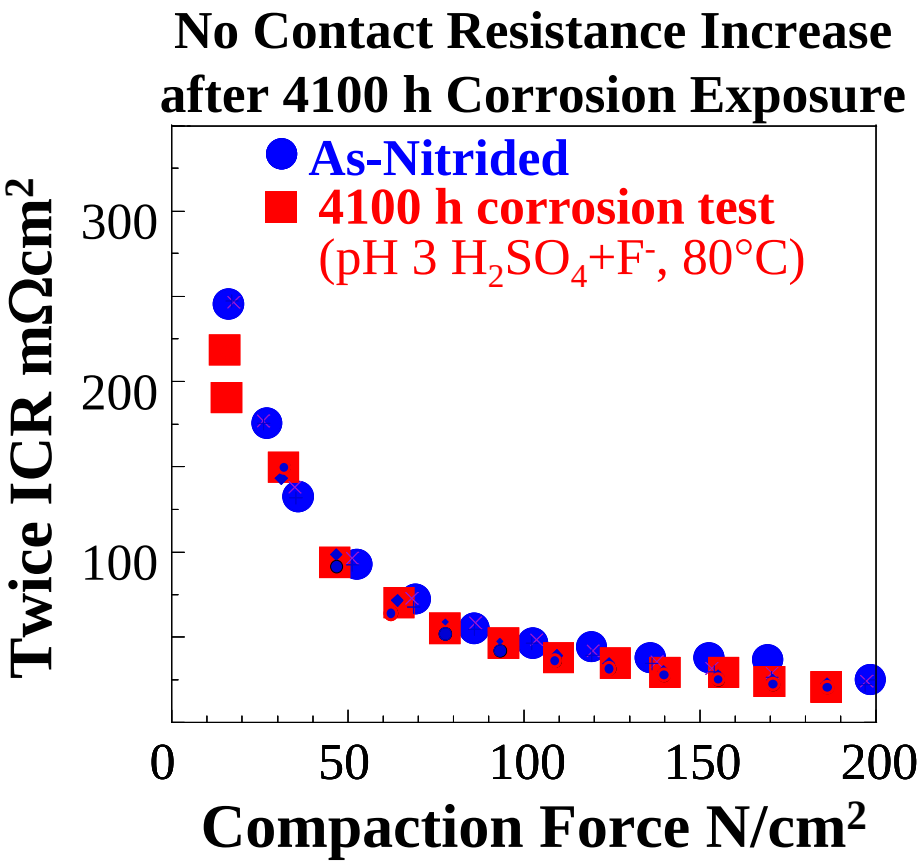




- Nitrides are corrosion resistant with low surface contact resistance
- Chemical reaction at the metal surface, not a deposited coating
  - High temperature favors reaction of all exposed metal surfaces
  - No pin-hole defects
  - Amenable to complex geometries
- Stamp then nitride
  - Industrially established and inexpensive

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



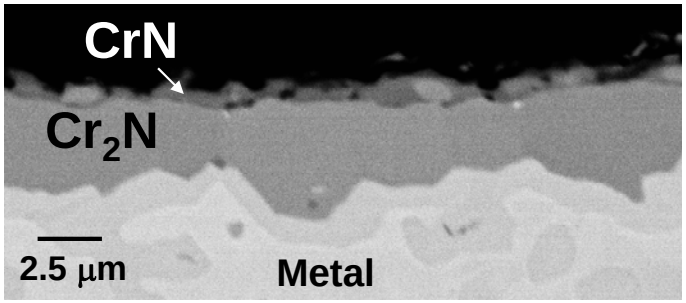


- 4100h in LANL bipolar corrosion test cell (Air/H_2 pH 3 H_2SO_4 + F- 80°C)
- No attack of Cr_xN and minimal metal ion dissolution

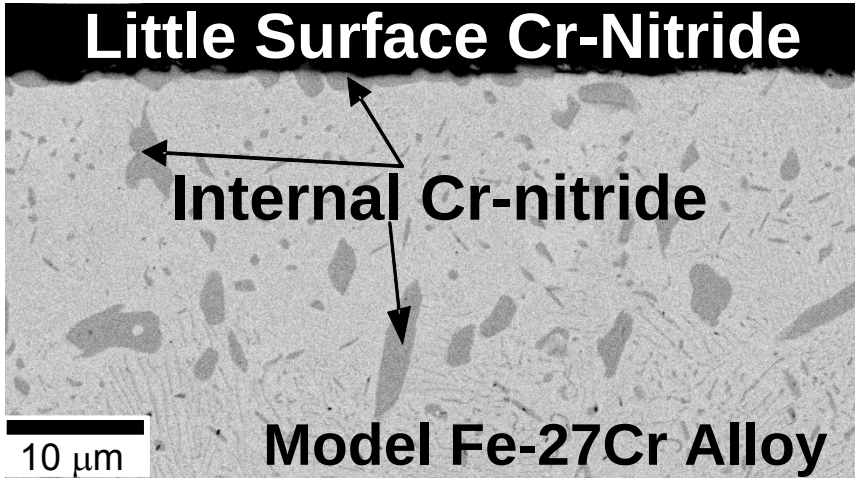
Need Fe-Base Stainless Steel to Meet $5/kW Cost Goals for Auto Applications

- Commercial Ni-Cr Alloys in range of ~$15-25/lb
  - Far too expensive for automotive use, and DOE target of $5/kW
- Focus on Fe-based stainless steels (SS): ~$2-8/lb
- However, simple Fe-Cr does not allow for a nitride surface layer
  - High N_2 permeability leads to internal Cr-nitride

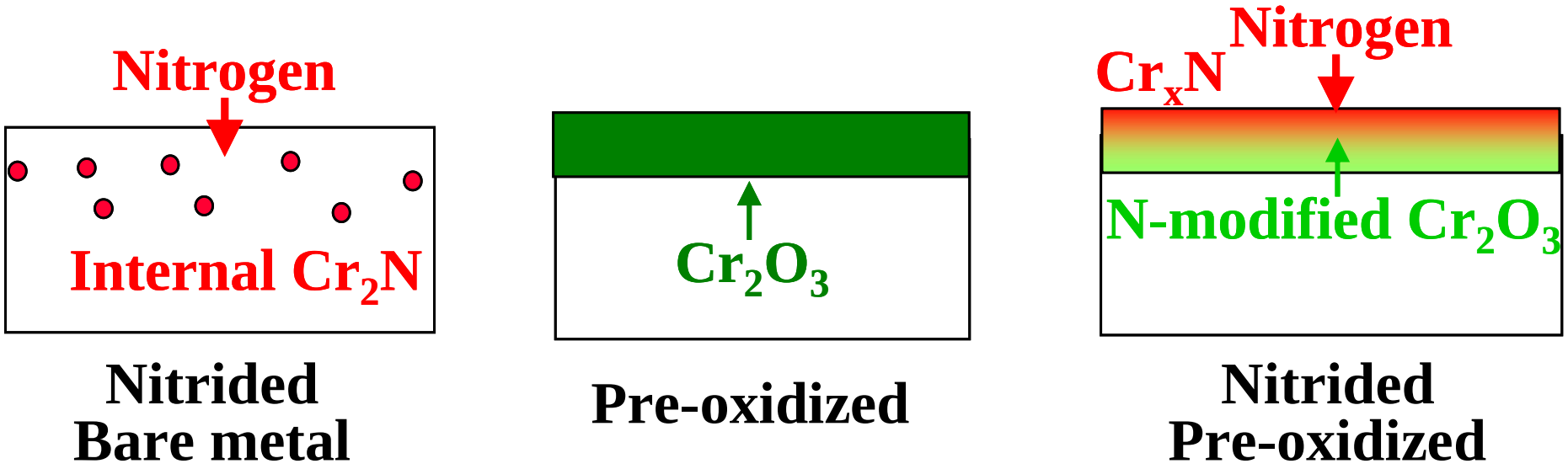
Nitrided Ni-50Cr



N_2 Floods in



Pre-Oxidation followed by nitridation to form Cr_xN surface on stainless steels



- Pre-oxidation method developed to facilitate nitride layer
  - form Cr_2O_3 by preoxidation to keep N_2 at surface
  - convert surface Cr_2O_3 to surface Cr_xN by nitridation

- V addition to stainless steel assists conversion to nitride

Goal is to Balance Stampability / Cost / Nitride Formation in 100μm Alloy Foils

Down Select to
Fe-20Cr-4V
(20% Cr, 4%V, bal Fe)
and
Commercial 2205
(Fe-22Cr-5Ni-0.2V)

Protective Nitride
↑Cr ↑V ↓Ni

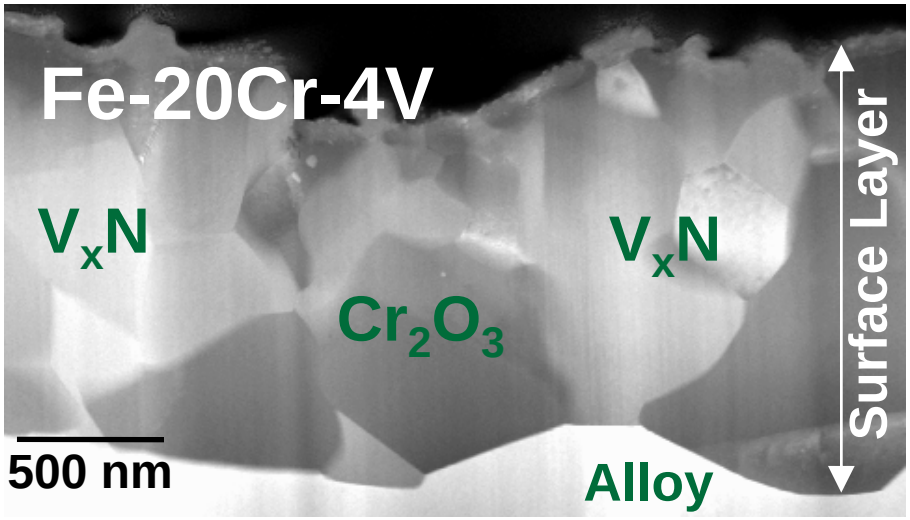
Overlap Yields Successful Alloy

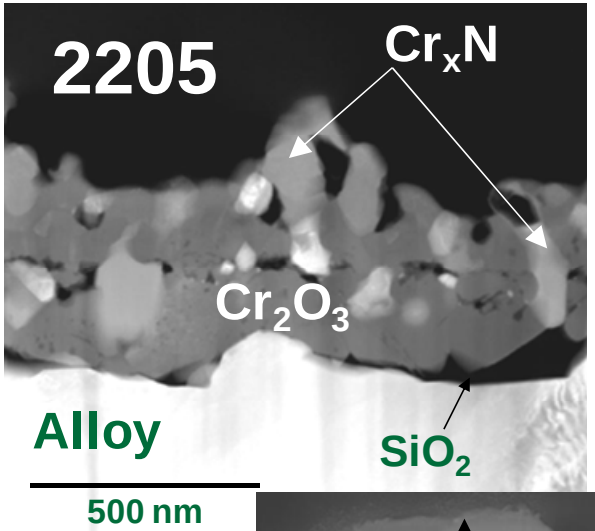
Stampability
↓Cr ↑Ni

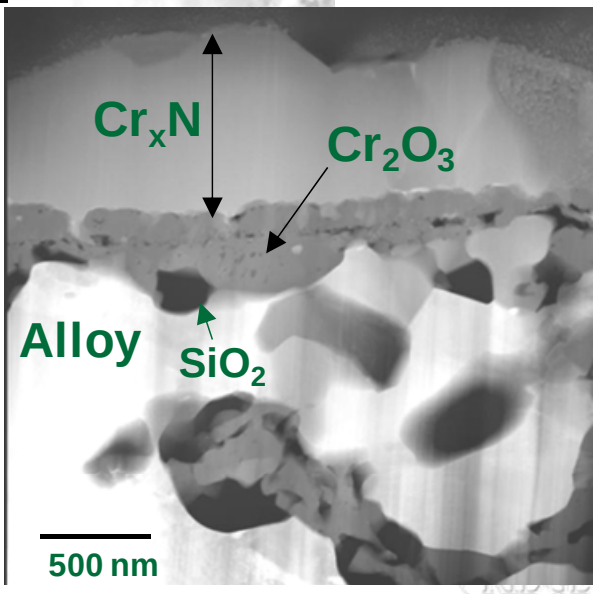
Cost
↓V ↓Ni

Mixed Oxide/Nitride Structures formed on Fe-20Cr-4V and 2205 Foils

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



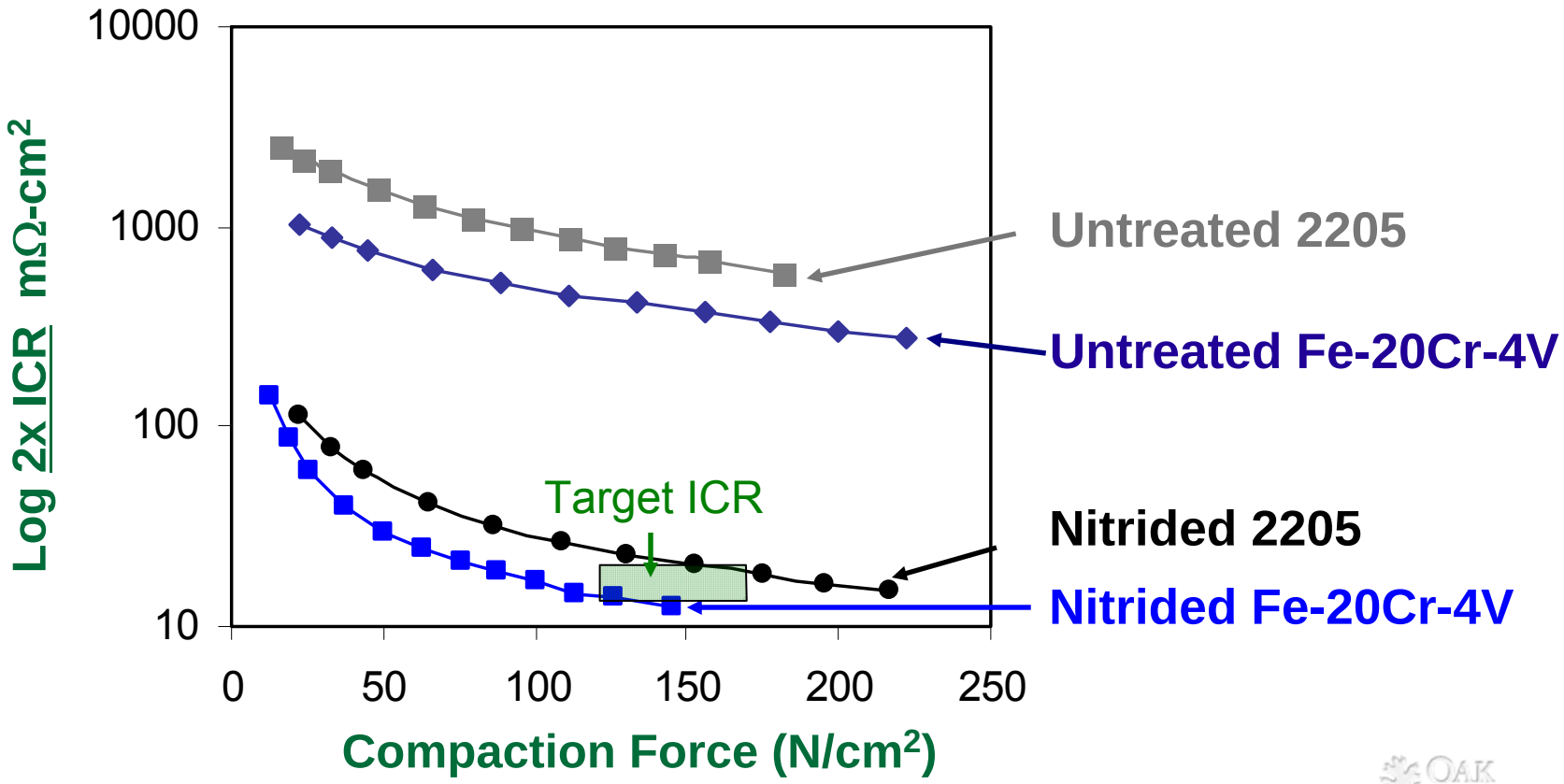




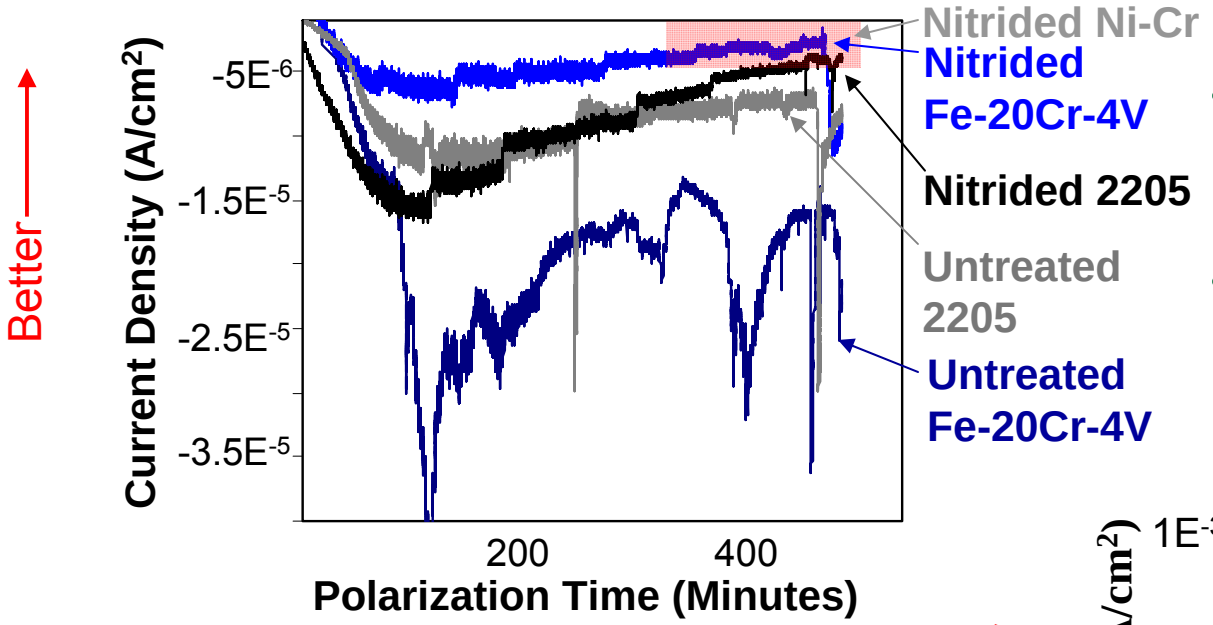
- Continuous Cr-nitride not observed as with model NiCr/FeCr material
  - Due to short pre-oxidation/nitriding cycle
  - lower Cr, V content to lower cost
- Through-thickness V_xN for Fe-20Cr-4V
  - better conductivity path

Nitridation Significantly Reduces Foil Interfacial Contact Resistance (ICR)

- ICR one of the main concerns with metallic bipolar plates
- Nitriding alloy at surface significantly lowers ICR

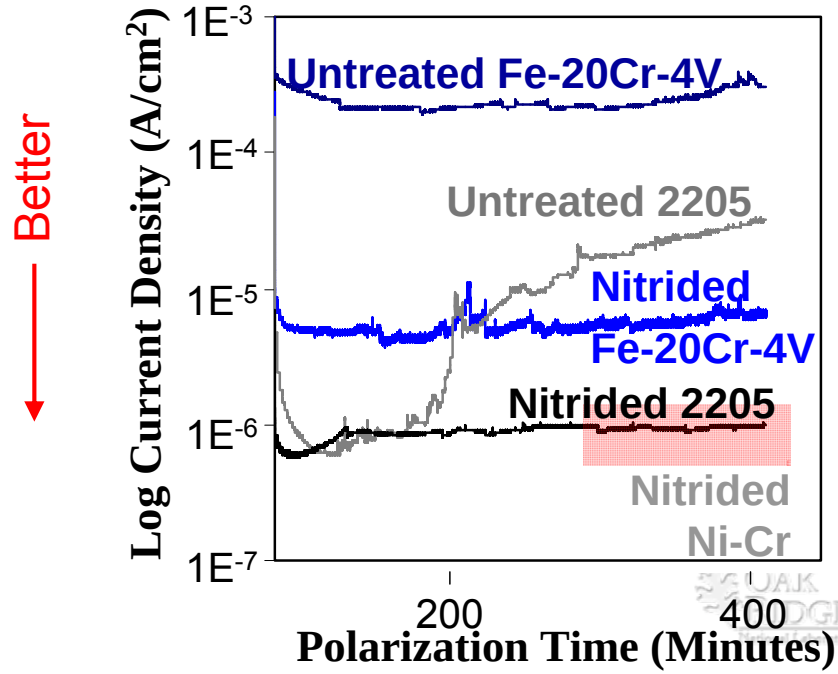


Nitrided Foils Corrosion Resistant Under Simulated Aggressive Conditions



Anode conditions

- 70°C in 1M H_2SO_4+ 2 ppm F- held at +0.14V vs. SHE, H_2 purged
- Nitrided Fe-Cr-4V and 2205 comparable to Nitrided Ni-Cr

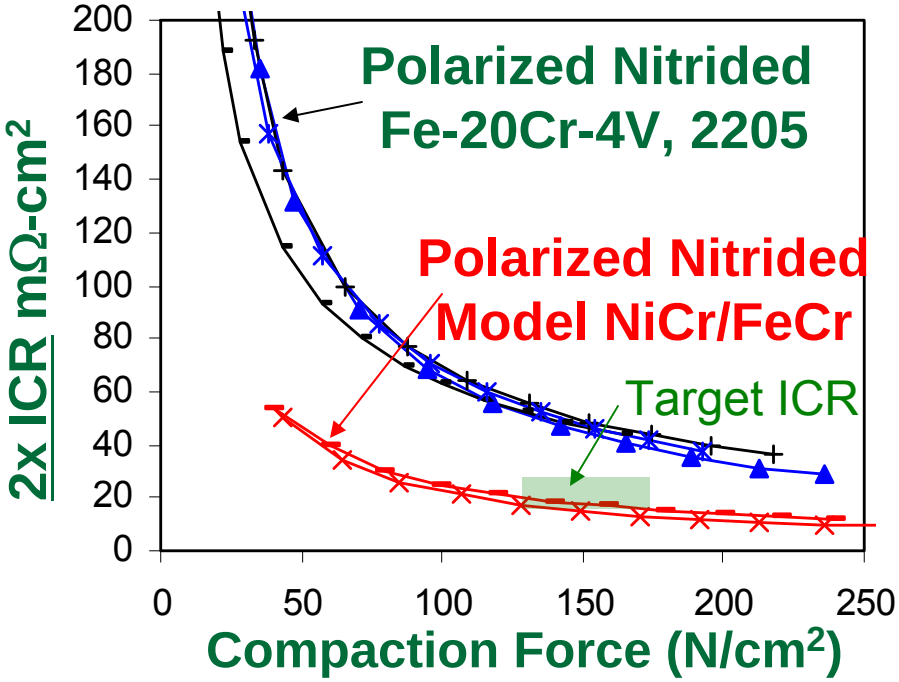


Cathode conditions

- 70°C in 1M H_2SO_4+ 2 ppm F- held at +0.84V vs. SHE, aerated
- Nitrided 2205 comparable to model Ni-Cr, Nitrided Fe-20Cr-4V moderately higher

Nitrided Foils Exhibited Moderate Increase in ICR on Polarization

- 7h polarization of nitrided foils under simulated aggressive anode and cathode conditions raised ICR beyond target value
  - remains still order of magnitude lower than untreated metal
  - test condition may be overly aggressive
  - 7h polarized nitrided model NiCr/FeCr alloys showed only small ICR increases

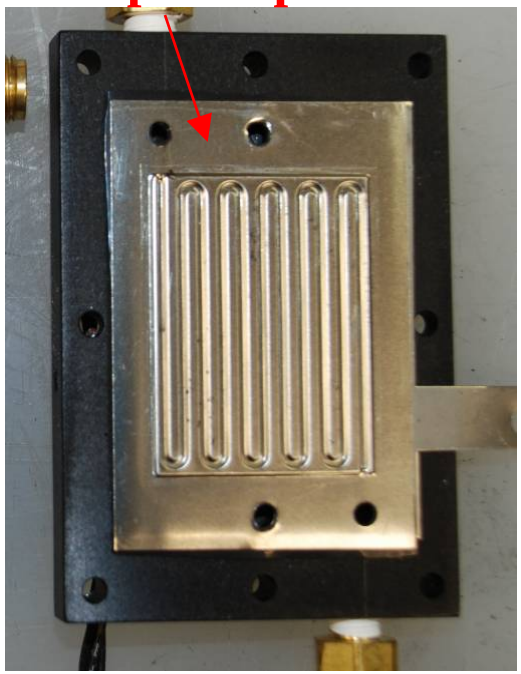


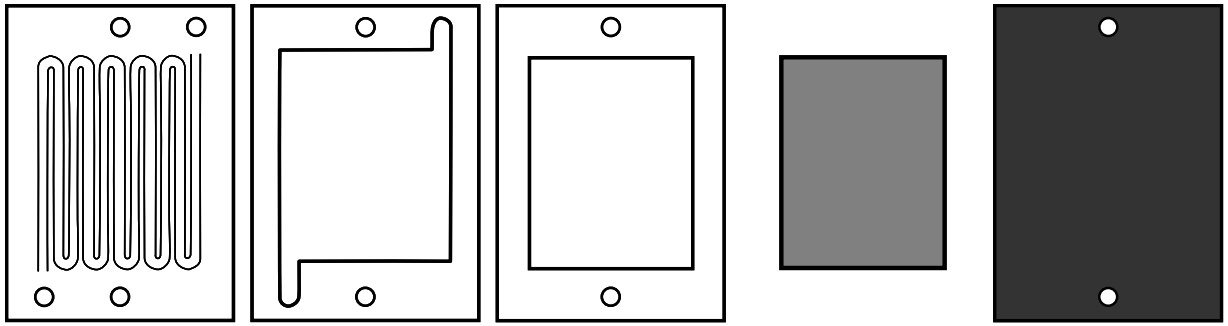
PEM Fuel Cell Evaluation and Durability

Single-Cell PEM Fuel Cell Testing of Stamped Foils

- Incompatibility of foils with commercially available fuel cells required new fuel cell design
  - 16 cm^2 active area, serpentine flow path
- Design enables use of either metal foils or graphite plates
- Evaluate performance and durability
  - V-containing alloys: 2205 and Fe-20Cr-4V
    - Untreated and nitrided
  - Untreated 904L-SS (Fe-25Ni-20Cr-5Mo)
  - Baseline comparison against graphite plate

Stamped Bipolar Plate





1 – Metal foil or graphite plate

2 – 250 micron Viton gasket with channel

3 – 50 micron FEP gasket

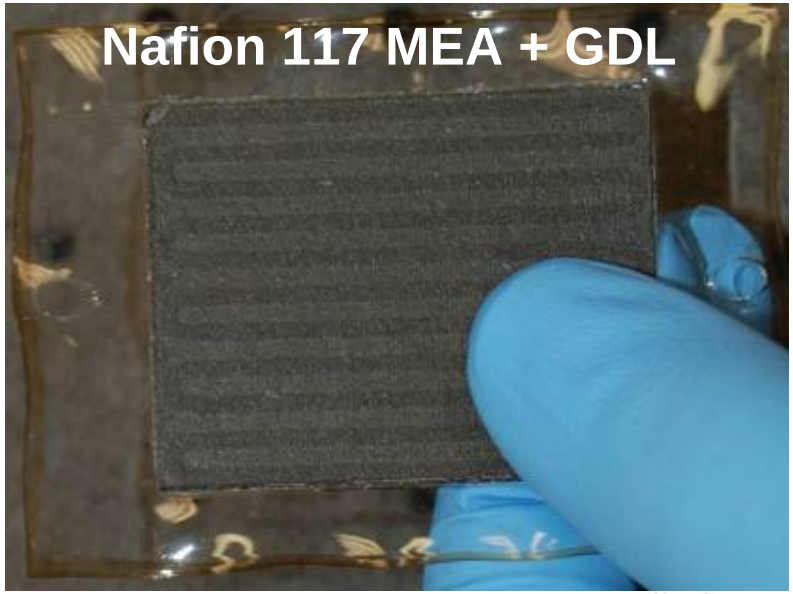
4 – 380 micron Gas diffusion layer (GDL)

5 – 35 micron Gore MEA with Pt/C layer everywhere

Evaluation of Performance and Durability

- Initial performance using thin Gore PRIMEA membranes
  - Membrane is 35 microns
  - Total MEA is 50 microns (2 mils)
  - Cut from center of large MEA
  - GDL is separate piece

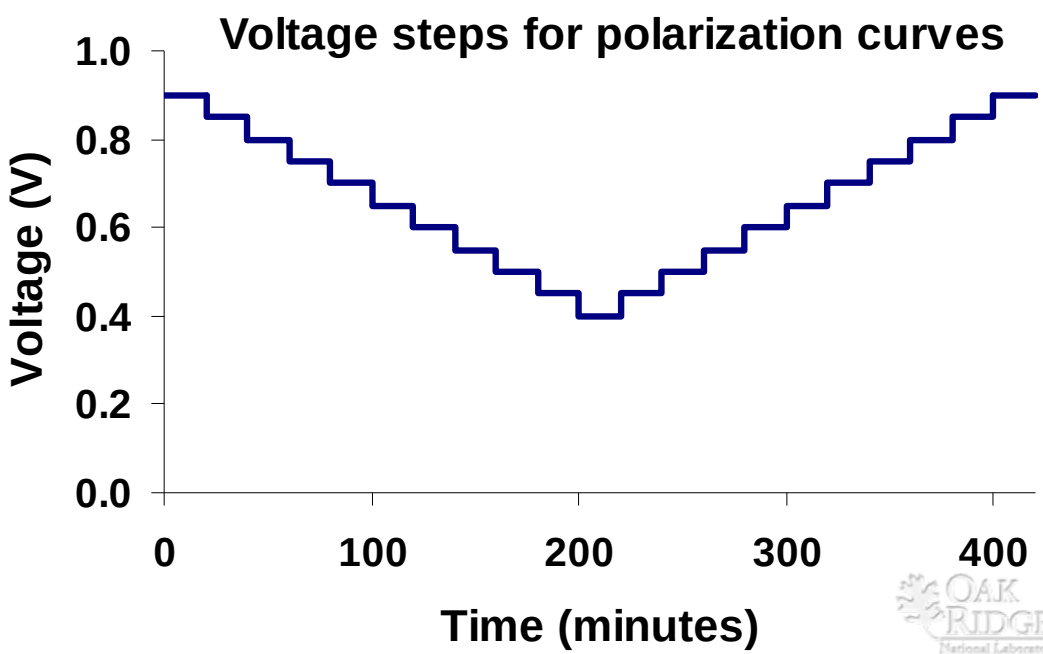
- 1000 h durability of plates using thicker Nafion 117 MEAs
  - Membrane is 175 microns (7 mils)
  - Electrode and GDL integrated into membrane layer
  - Specifically designed for implementation in GenCell/ORNL PEMFC



- Re-evaluate plates with fresh Gore MEA after 1000h durability testing

Polarization curve evaluation conditions

- Operating Conditions
  - Temperatures: 78°C dew point, 79°C inlet, and 80°C cell
  - Air: 25.5 psig, 2.5 x stoichiometric O_2 flow, minimum 100 sccm
  - H_2: 25 psig, 1.2 x stoichiometric H_2 flow, minimum 50 sccm
- Break-in
  - Gore: 8 cycles of 30 min @ 0.6 V, 30 min @ 0.4V, and 1 min @ open circuit
  - Nafion: 16 cycles of 30 min @ 0.6 V, 30 min @ 0.4V, and 1 min @ open circuit
- Performance Curves (V-I)
  - Constant voltage
  - Hold 20 minutes at each voltage
  - 0.05V steps
  - Decreasing then increasing
    - average reported
  - Repeat three times



Performance and Durability Evaluation

Initial Performance Assessment Using 35 micron Gore PRIMEA Membrane (5510)

↓

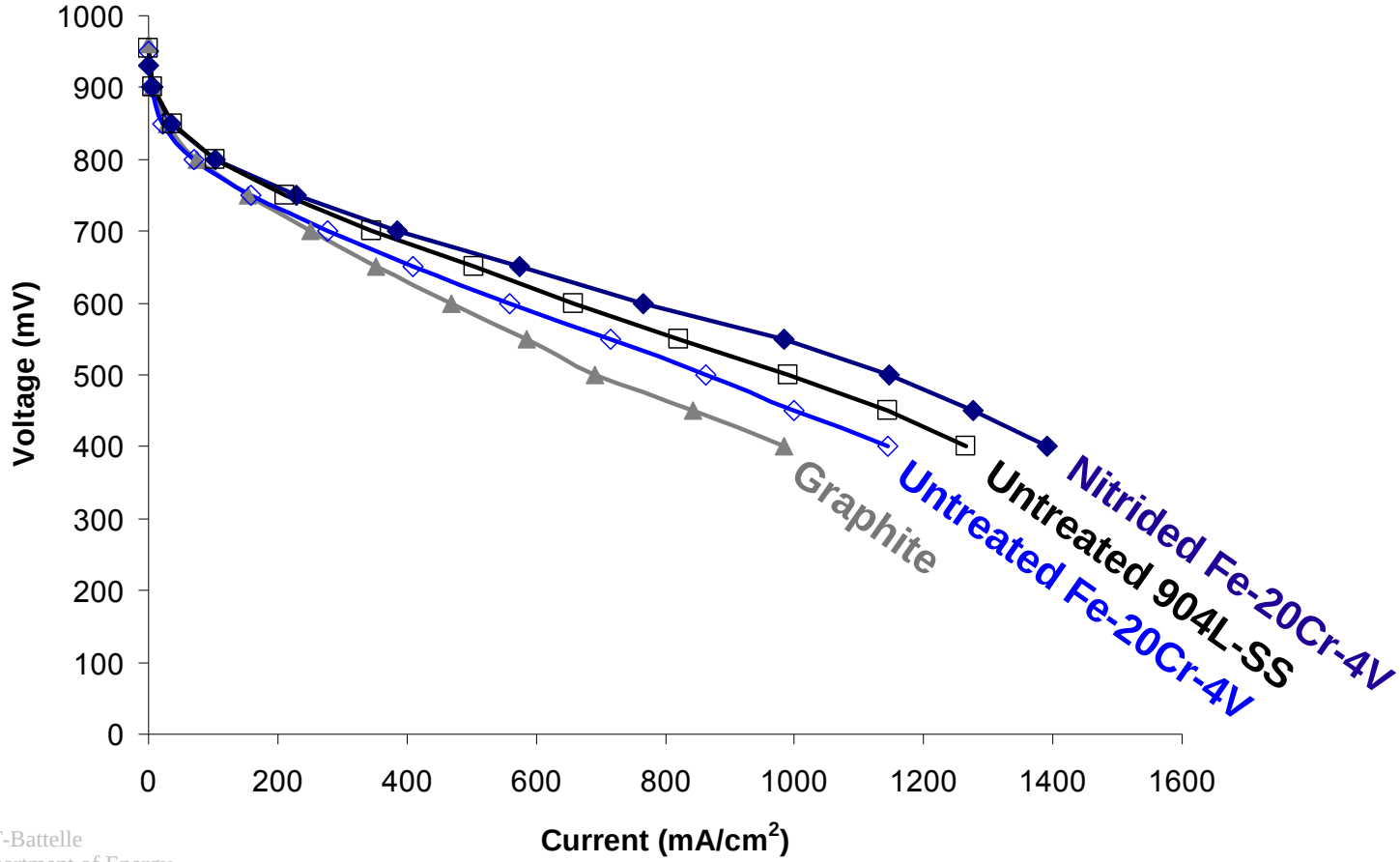
1000+ h Durability Evaluation Using 175 micron Nafion 117 MEA while voltage cycling

↓

Re-Evaluate Performance of 1000+ h Durability Tested Plates with Fresh Gore MEA

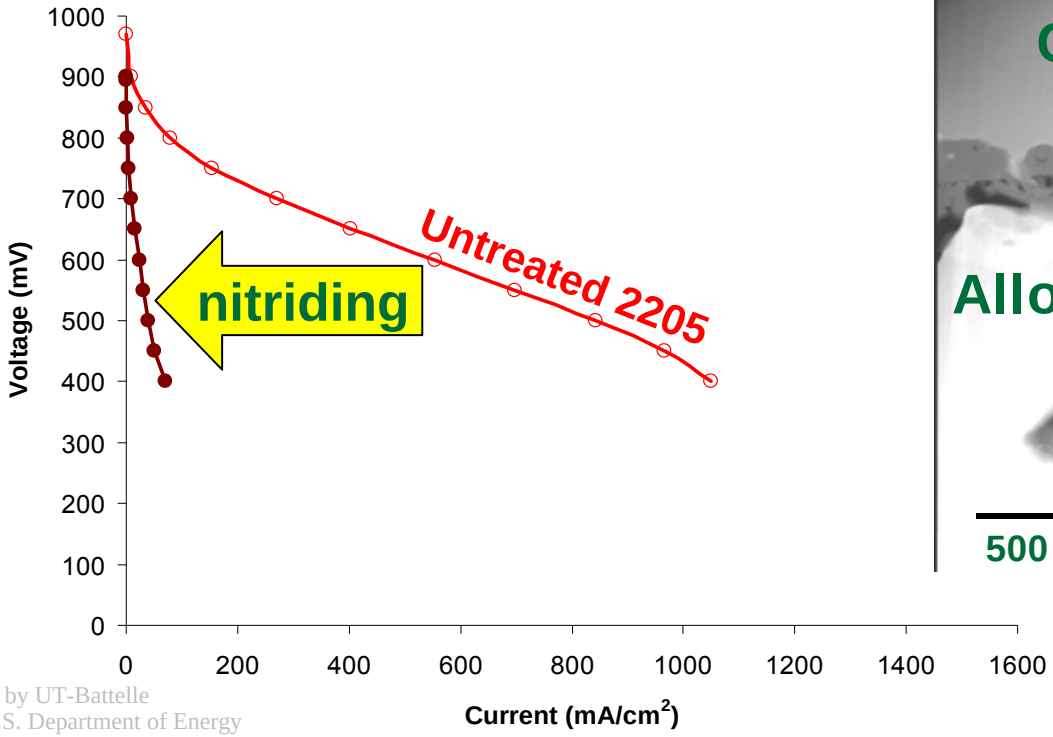
Initial performance evaluation illustrates potential of nitrided foils

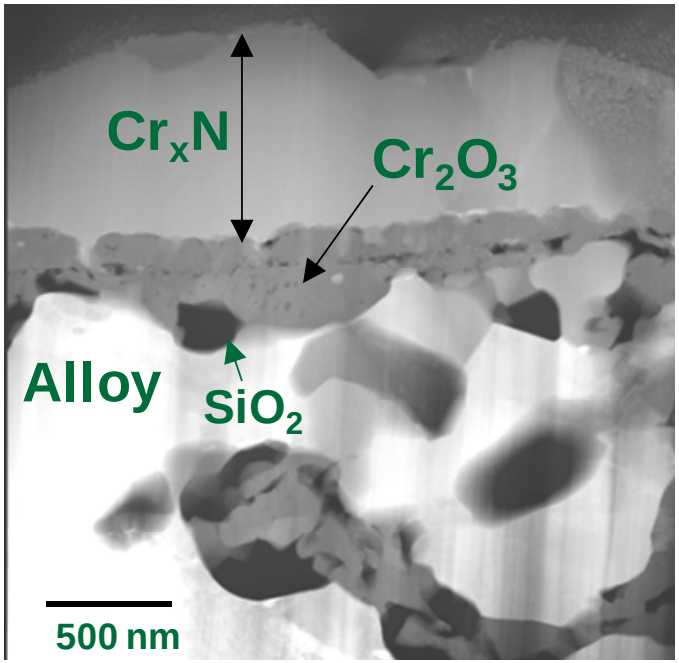
- Third polarization curve shown
- Nitrided Fe-20Cr-4V exhibited best initial behavior
- Low initial graphite performance most likely due to slight differences in machined flow channels/lands versus stamped flow channels



2205-SS performance illustrates the effects of continuous oxide layer

- Initial coupon testing showed good ICR
  - Some scatter observed in ICR values; continuous oxide layer observed
- Pre-oxidation/nitridation process negatively affects performance
- Illustrates importance of having right alloy for starting point
  - 2205: Fe-22Cr-5Ni-0.2V; perhaps not enough Vanadium
- No durability tests performed





Performance and Durability Evaluation

Initial Performance Assessment Using 35 micron Gore PRIMEA Membrane (5510)

↓

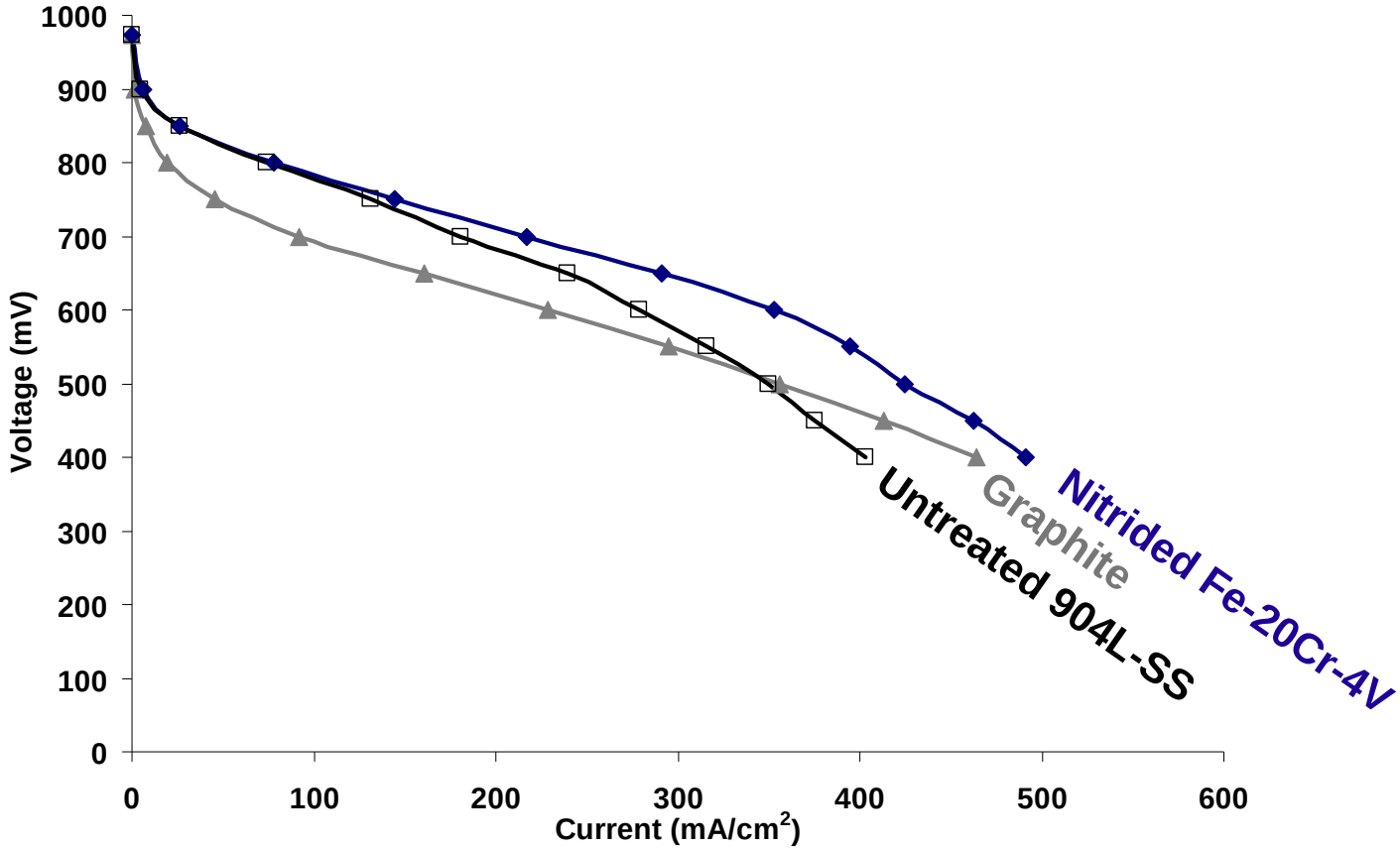
1000+ h Durability Evaluation Using 175 micron Nafion 117 MEA while voltage cycling

↓

Re-Evaluate Performance of 1000+ h Durability Tested Plates with Fresh Gore MEA

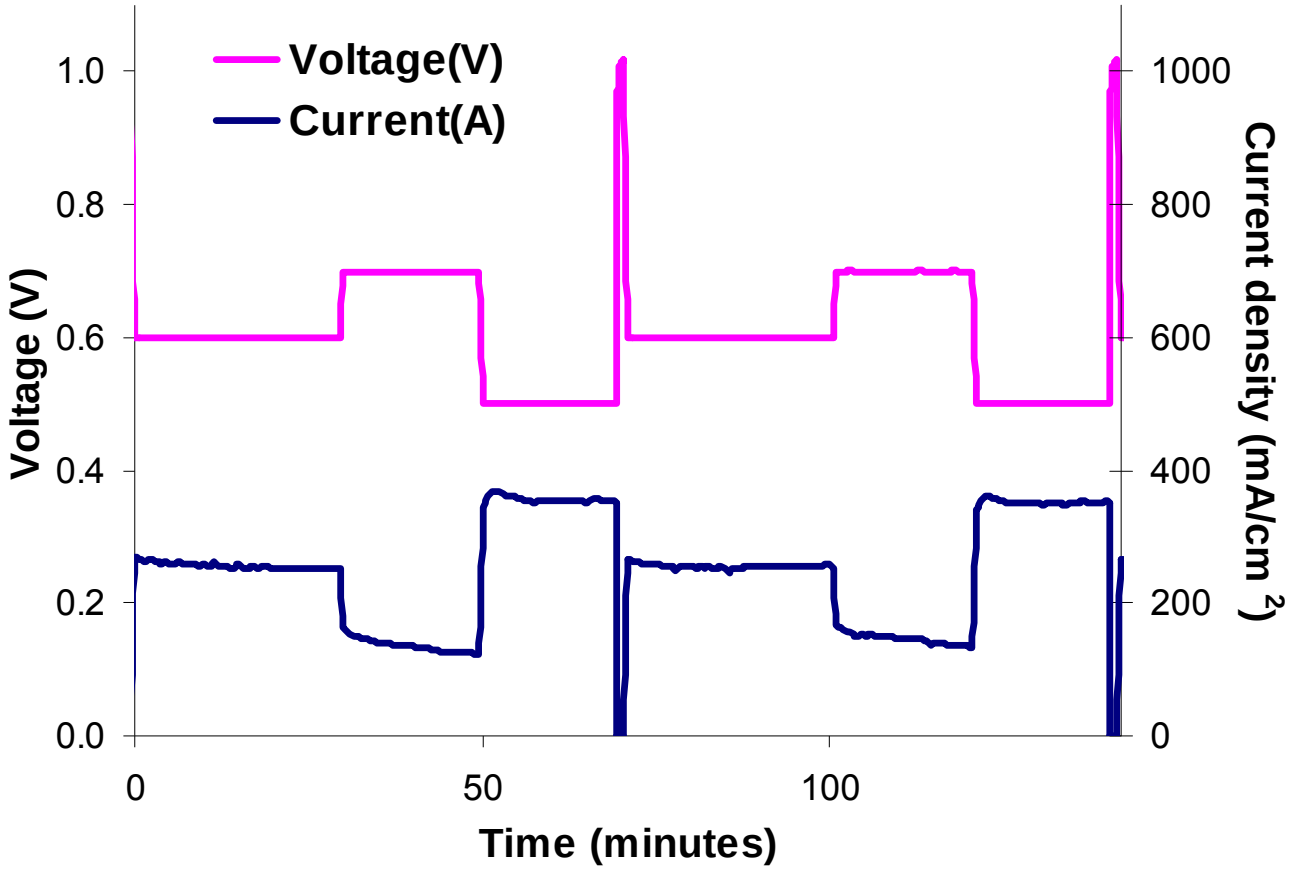
Initial performance with Nafion-117

- Similar relative performance trends observed with Nafion-117
  - However, 904L-SS performance declines relative to other materials at higher loads



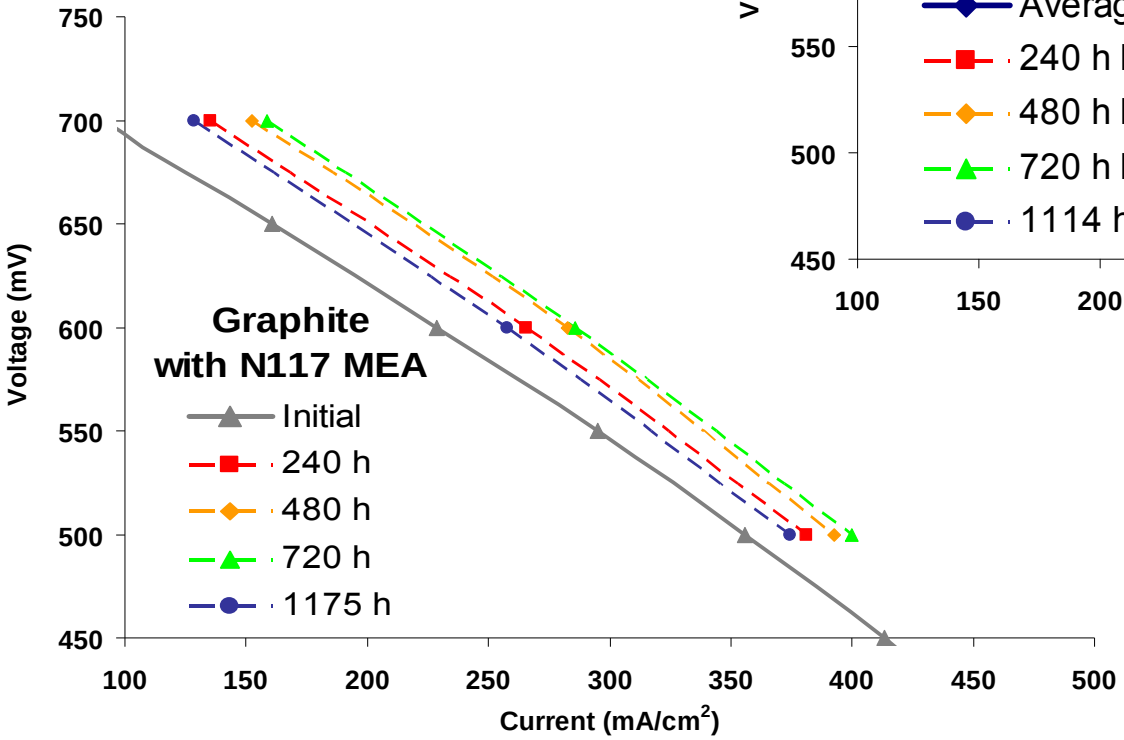
Voltage cycling implemented for 1000h durability evaluation

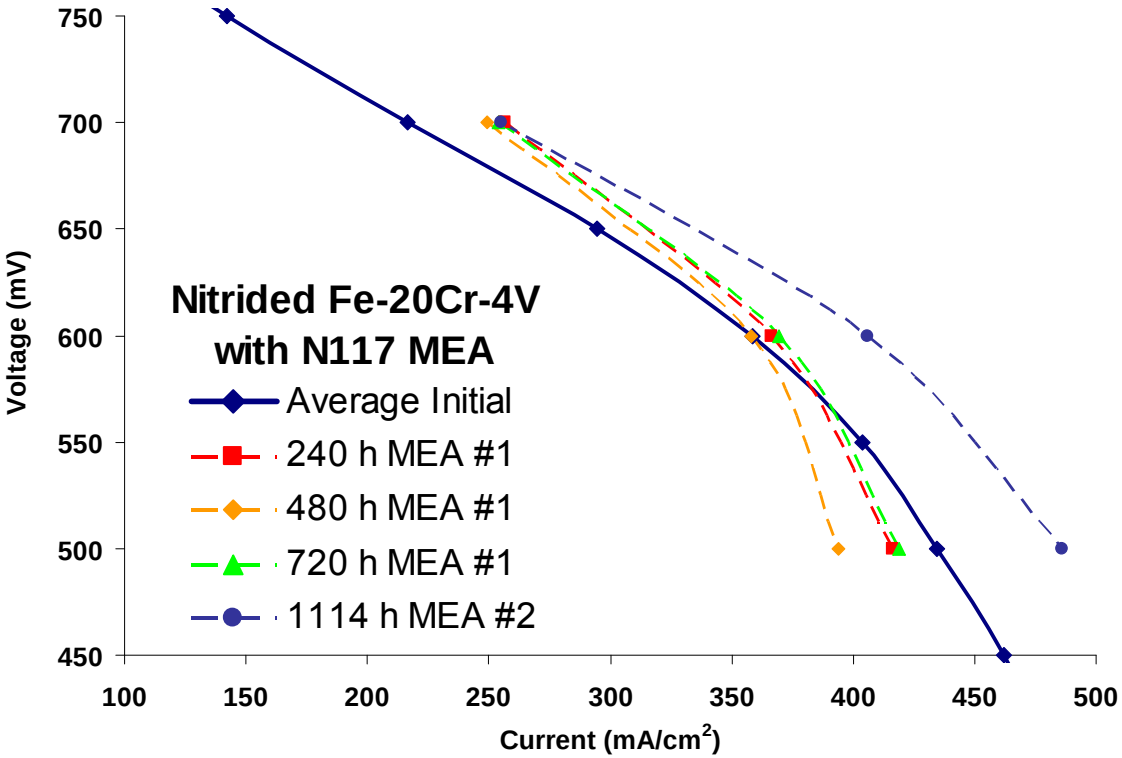
- Voltage cycling for >1000 hours
  - 30 min @ 0.6 V
  - 20 min @ 0.7V
  - 20 min @ 0.5V
  - 1 min @ OCV
- Operating Conditions
  - 78°C dew point, 79°C inlet, and 80°C cell
  - Air: 25.5 psig, 2.5 x stoich O_2 flow, 100 sccm min
  - H_2: 25 psig, 1.2 x stoich H_2 flow, 50 sccm min



Performance maintained during voltage cycling

- Performance generally improves during voltage cycling with Nafion-117
  - graphite and Fe-20Cr-4V





Voltage cycle

1. 0.6V for 30 minutes
2. 0.5V for 20 minutes
3. 0.7V for 20 minutes
4. OCV for 1 minute

Performance and Durability Evaluation

Initial Performance Assessment Using 35 micron Gore PRIMEA Membrane (5510)

↓

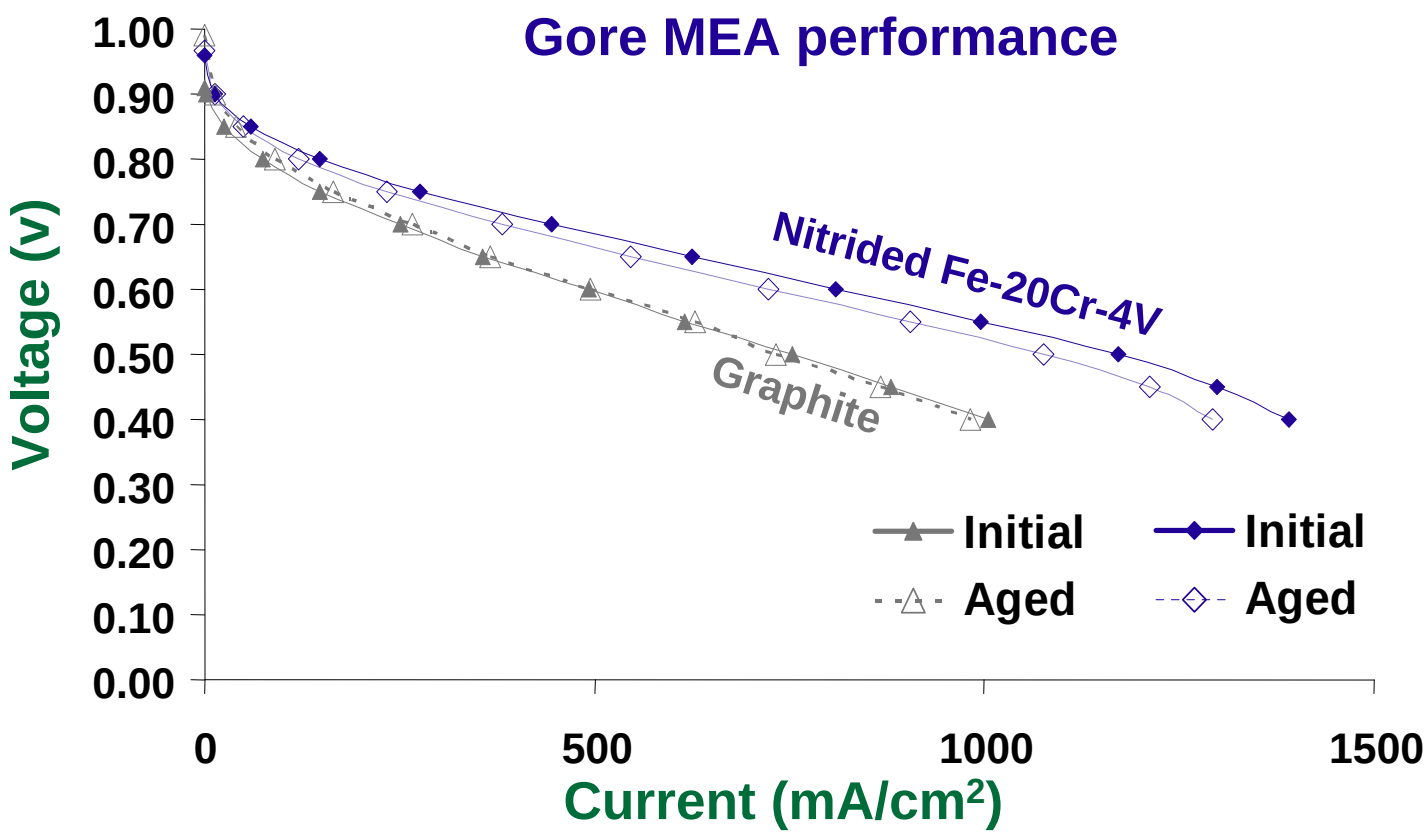
1000+ h Durability Evaluation Using 175 micron Nafion 117 MEA while voltage cycling

↓

Re-Evaluate Performance of 1000+ h Durability Tested Plates with Fresh Gore MEA

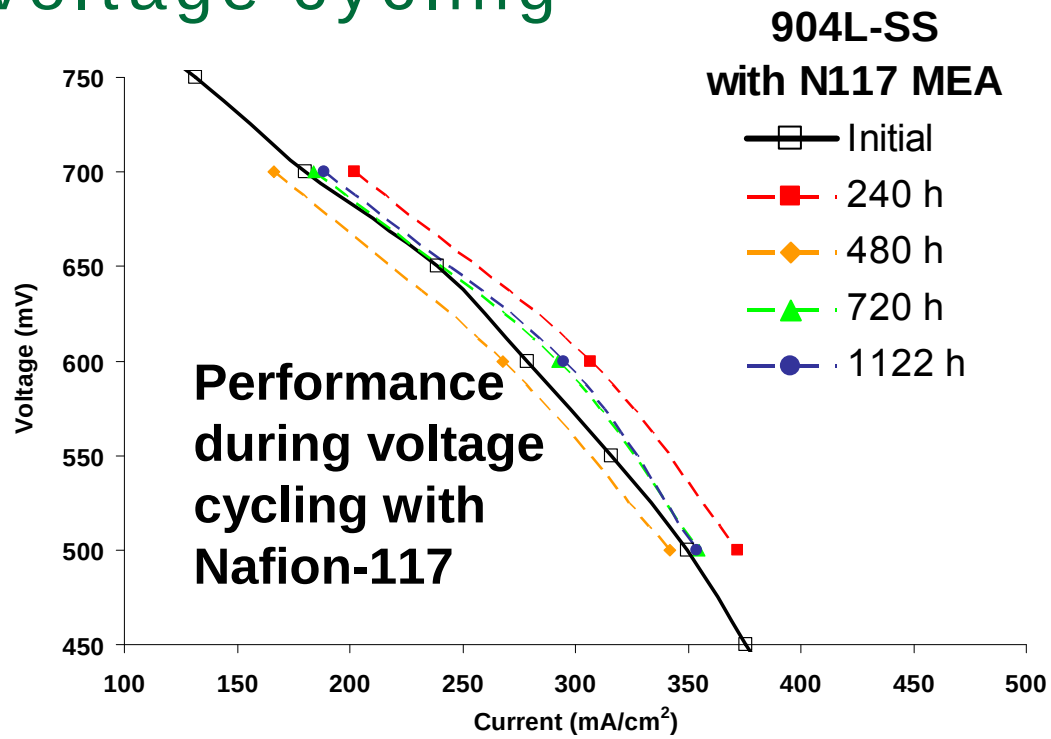
Nitrided Fe-20Cr-4V: Performance maintained after 1000+ hours of voltage cycling

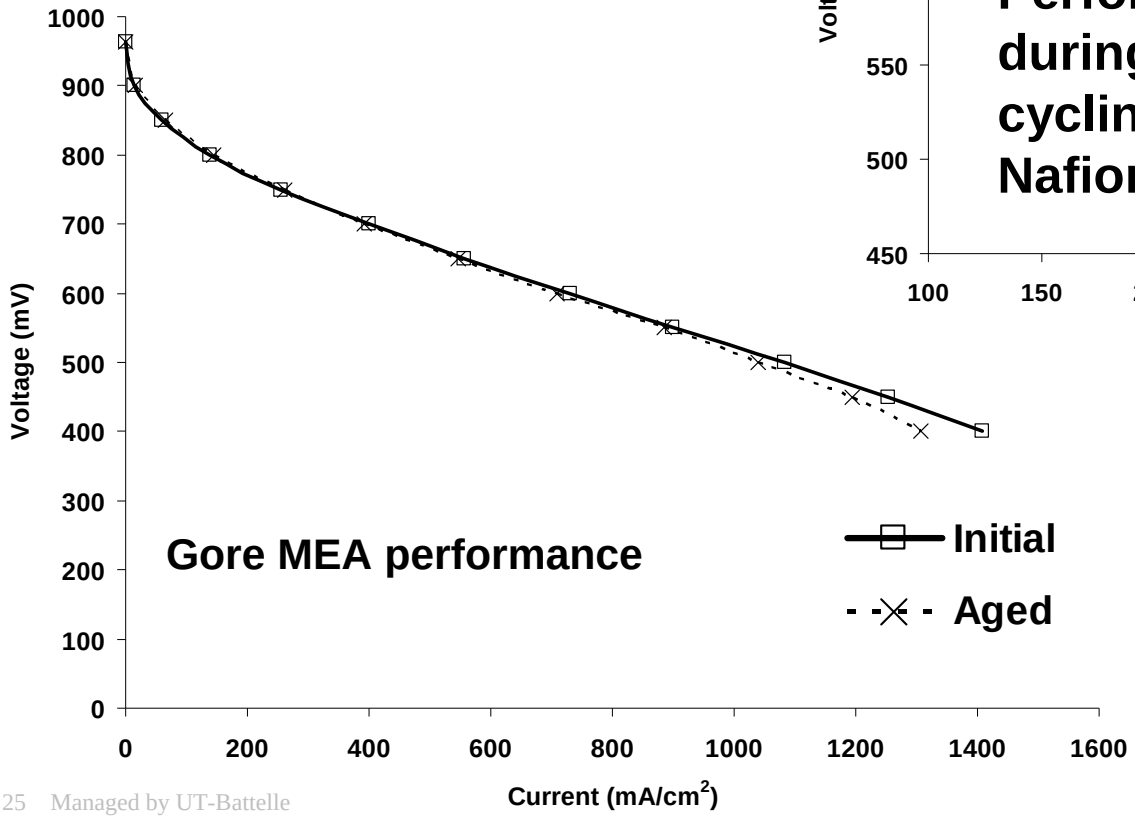
- "Before and after" performance with Gore MEA shows <10% decrease
  - Most likely due to build-to-build variations



Untreated 904L: Performance also maintained after 1000+ hours of voltage cycling

- Same trends observed during voltage cycling with Nafion-117
- "Before and after" performance with Gore MEA shows <7% decrease



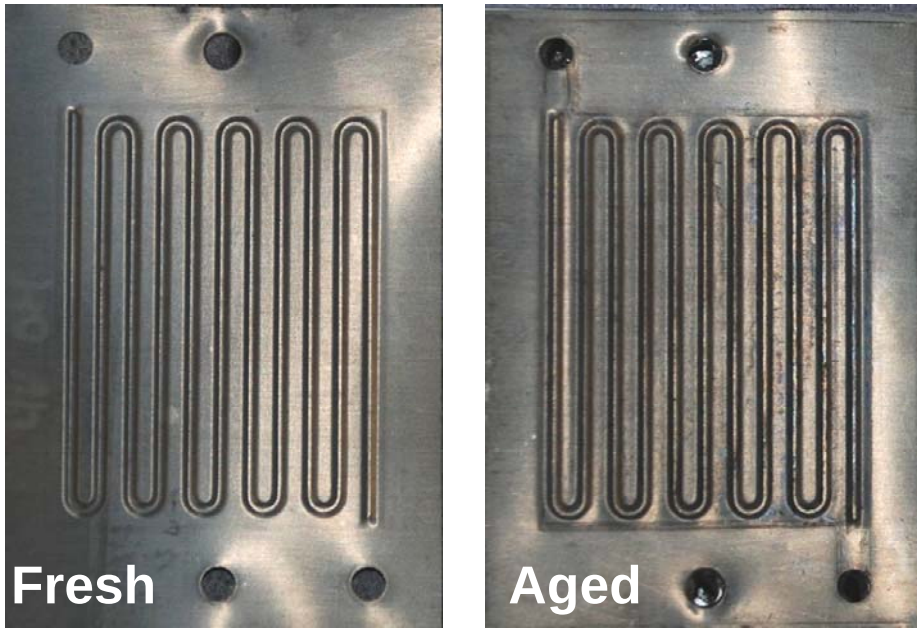


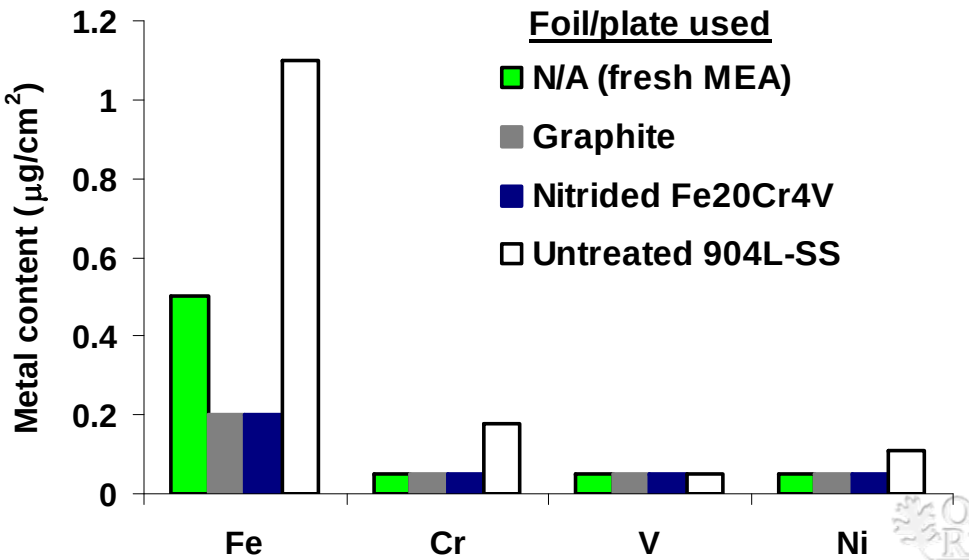
Voltage cycle

1. 0.6V for 30 minutes
2. 0.5V for 20 minutes
3. 0.7V for 20 minutes
4. OCV for 1 minute

Nitride layer protects MEA from metal contamination

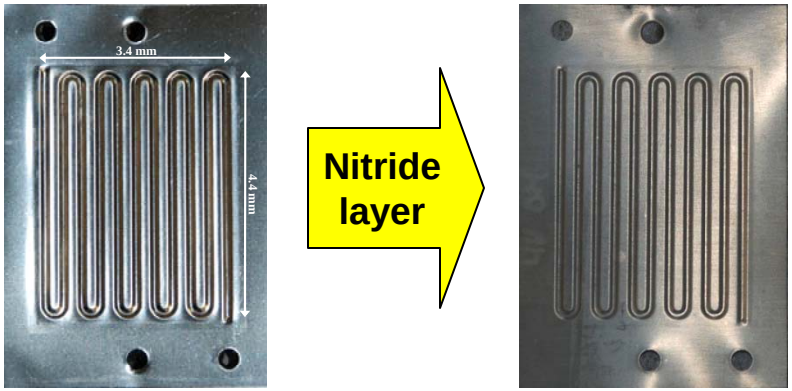
- No visible pitting or corrosion
- XRF analysis implemented to quantify metals in MEA
- Graphite and Nitrided Fe-20Cr-4V MEAs are clean
  - Fe, Cr, V levels are all near detection limits
- 904L-SS MEA much greater Fe than other samples
  - Although performance was not affected, suggests longer tests may have durability issues



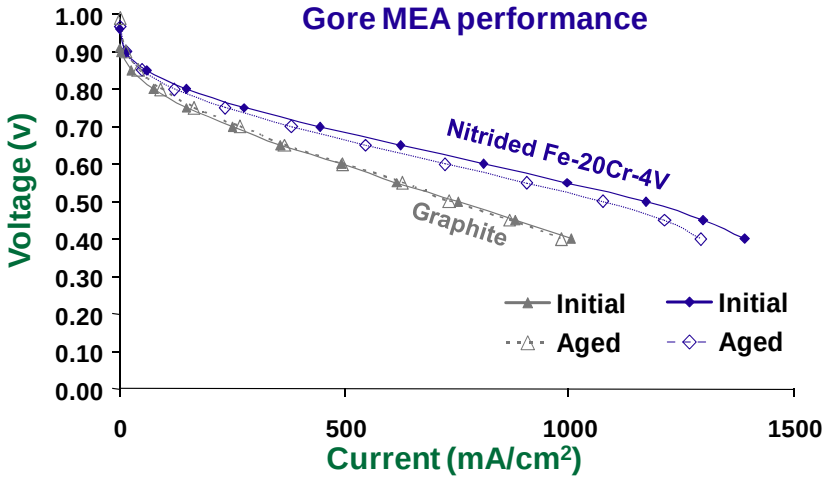


Summary

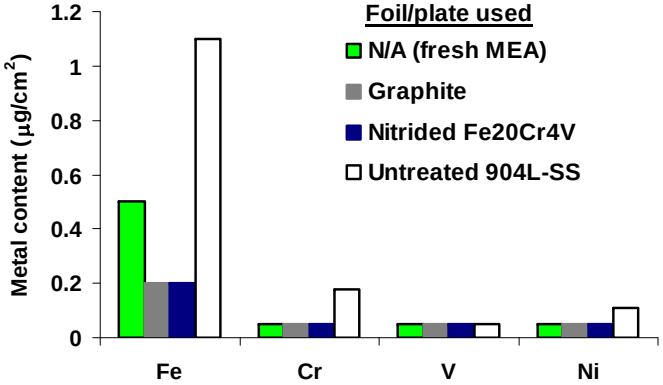
- Thin stamped metallic plates can be nitrided and result in low ICR
  - Minimal warping



- Nitride layer is durable under aggressive durability tests
  - Sulfuric acid submersion
  - PEMFC voltage cycling



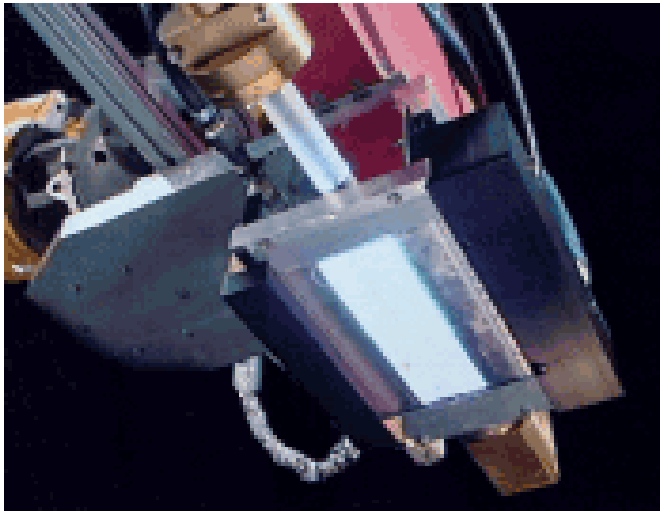
- Nitrided layer minimizes metal contamination in MEA
  - Fe levels near background levels with graphite and nitrided metals



Future directions and new partnership

- Lower-Cost Nitriding with Plasma Arc/Quartz Lamps
  - Plasma arc and quartz lamps for rapid nitriding heating/cooling
    - potential nitriding in seconds to minutes instead of hours
  - Rapid heating may favor more nitride-rich surface
  - Single-cell testing planned for stamped and lamp-nitrided foils
- Advanced single cell evaluation with new OEM
  - Include joining/welding considerations

Quartz Lamp Furnace Modified for Nitriding



ORNL Plasma Arc Lamp

Acknowledgements

- G.W. Garner for performing the pre-oxidation nitridation exposures

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Additional Slides

Teaming and Primary Responsibilities

- Oak Ridge National Laboratory:
  Alloy design, nitridation optimization, characterization, single-cell fuel cell design and testing

- Arizona State University:
  Single-cell fuel cell design and testing

- ATI Allegheny Ludlum:
  Alloy foil manufacture

- AGNI-GenCell:
  Design and stamping of bipolar plate flow-field features

- Los Alamos National Laboratory:
  Stack testing/performance assessment, characterization, single-cell fuel cell design and test protocol

- National Renewable Energy Laboratory:
  Corrosion/contact resistance evaluation

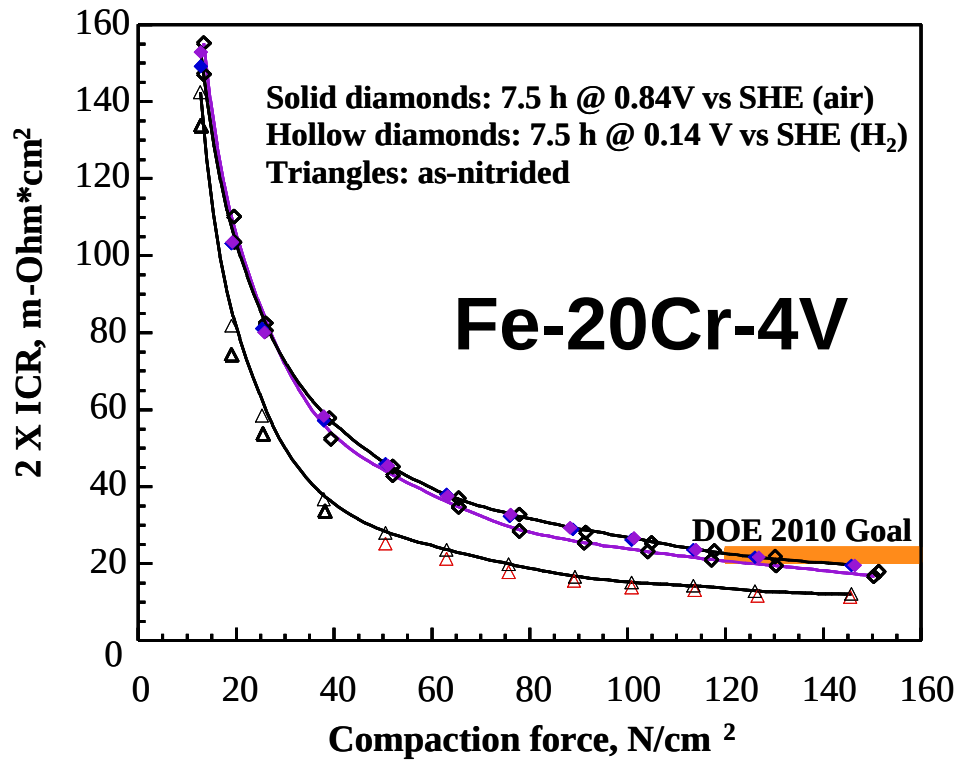
Cr Ferritics show good ductility and are amenable to stamping

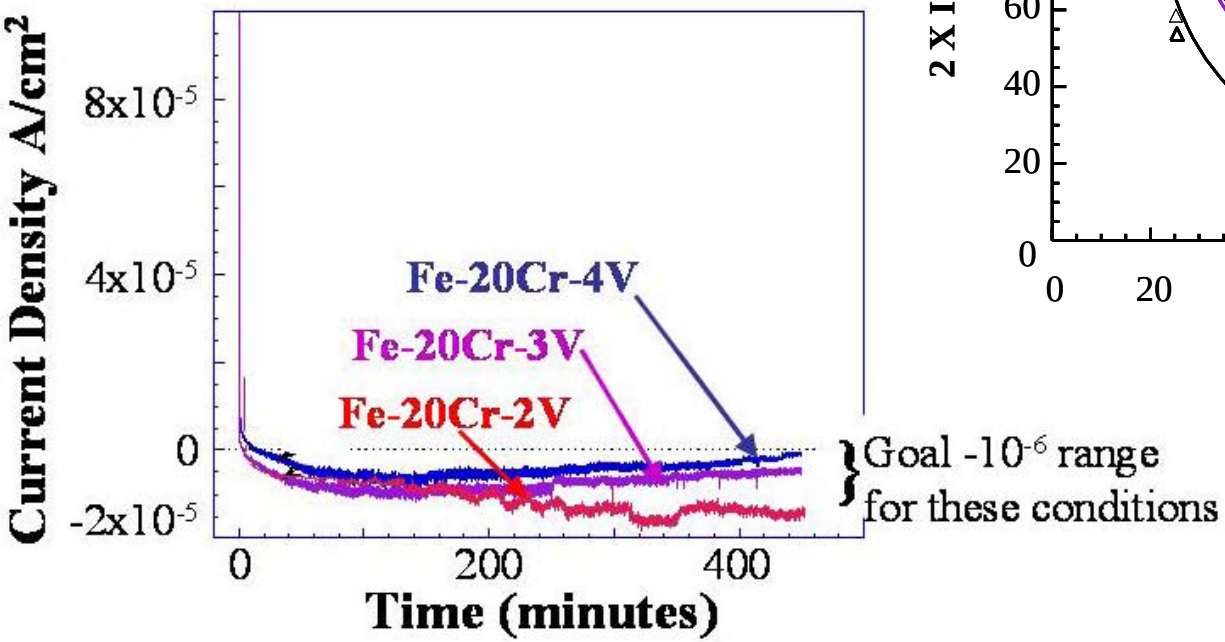
Alloy	Description	Flow-Field Stampability (channel depth/foil thick)
444	Fe-18Cr-2Mo Ferritic	**6.0**
316L	Fe-18Cr-12Ni Austenitic	**5.3**
904L	Fe-20Cr-25Ni-5Mo Aust.	**5.3**
Fe-15Cr-10Ni-3V	**Near-Austenitic**	**5.3**
Fe-20Cr-4V	**Ferritic**	**4.4**
Fe-20Cr-2V-5Ni	**Duplex**	**4.3**
Fe-20Cr-2V	**Ferritic**	**4.1**
2205	Fe-22Cr-5Ni-3Mo Duplx.	**3.8**
E-brite	Fe-26Cr-1Mo Ferritic	**2.5**

Better Flow-Field Stamping

Fe-Cr-V alloys show excellent corrosion resistance and low contact resistance

- Fe-20Cr-4V meets DOE target for interfacial contact resistance (ICR)
- Series of Fe-Cr-V alloys demonstrate excellent corrosion resistance
  - Highly-aggressive simulation for anode-side environment





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

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

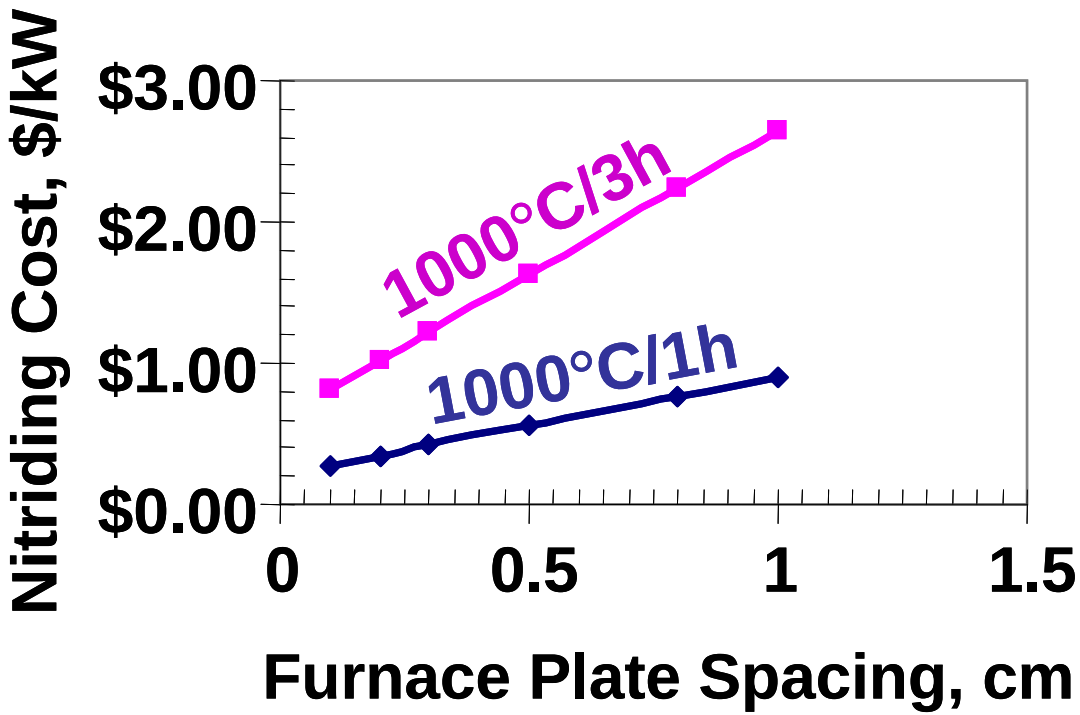
Foil Thickness	Density kg/kW	Bipolar Plate Cost ($/kW)		
		$3/lb Alloy	$5/lb Alloy	$7/lb Alloy
50 μm	0.26	$2.31	$3.47	$4.58
100 μm	0.38	$3.15	$4.26	$6.57
200 μm	0.64	$4.86	$7.69	$10.51

- 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 < $0.75/kW for nitriding costs

Nitriding Costs Feasible at $0.75/kW

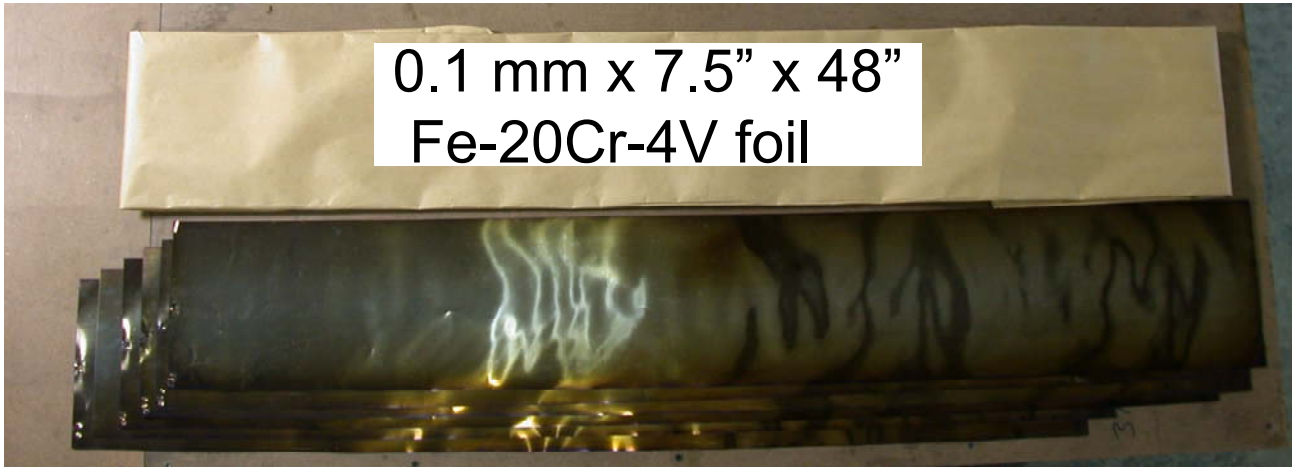
Preliminary Cost Analysis by B. James, Directed Technologies



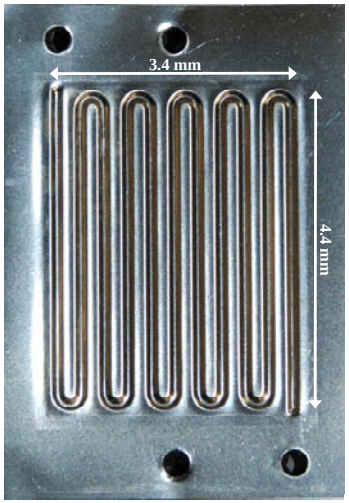
- Automated, step-continuous conventional nitriding system at 500,000 systems per year, mark up not included
  - keys are short nitriding cycle and high furnace plate stacking density

- Nitriding by pulsed plasma arc lamp in range of $0.16-0.44/kW

Developmental foils synthesized, stamped with flow path and then nitrided



Produced at Allegheny Ludlum



Stamped at AGNI-GenCell

Pre-oxidation 900°C/15 min

Nitridation 1000°C/1h

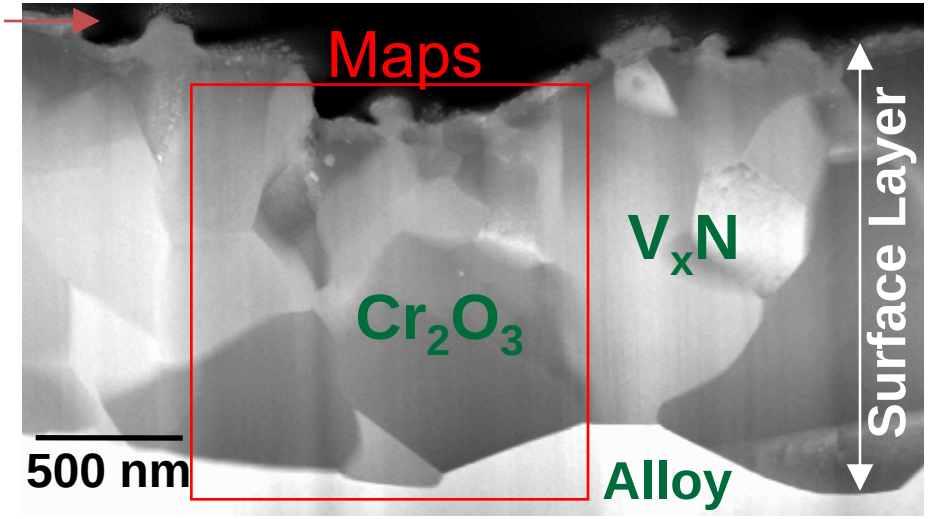
Nitrided at ORNL

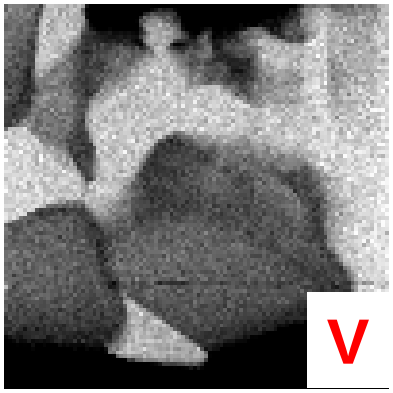
- Developmental duplex and austenitic foils also manufactured
- Commercially available 2205-SS also nitrided
  - more accessible to developers
  - selected due to availability and Cr level

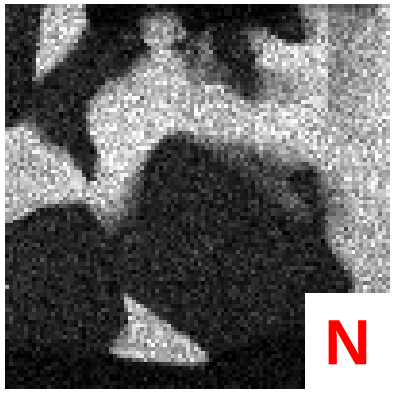
Fe-20Cr-4V: V_xN dispersed in Cr_2O_3 layer

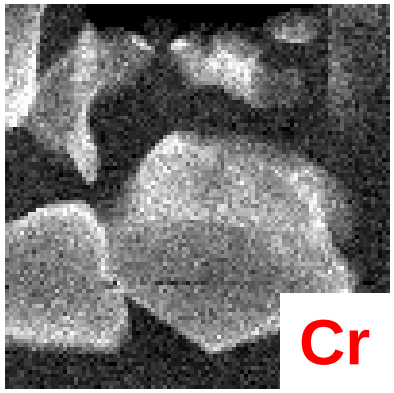
Cross-Section TEM Analysis of Pre-Oxidized/Nitrided Fe-20Cr-4V

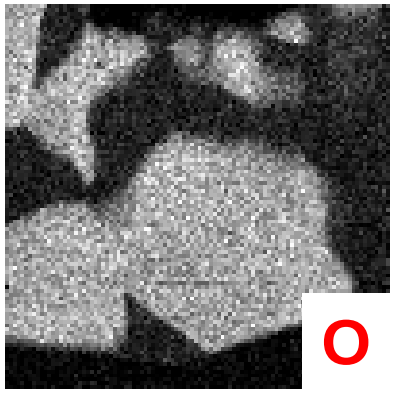
- Cr_xN particles at surface
  - not retained in TEM prep
- Through thickness V_xN paths but no continuous Cr_xN as with model alloys
- Consequence of pre-oxidation/nitridation cycle to meet cost goals





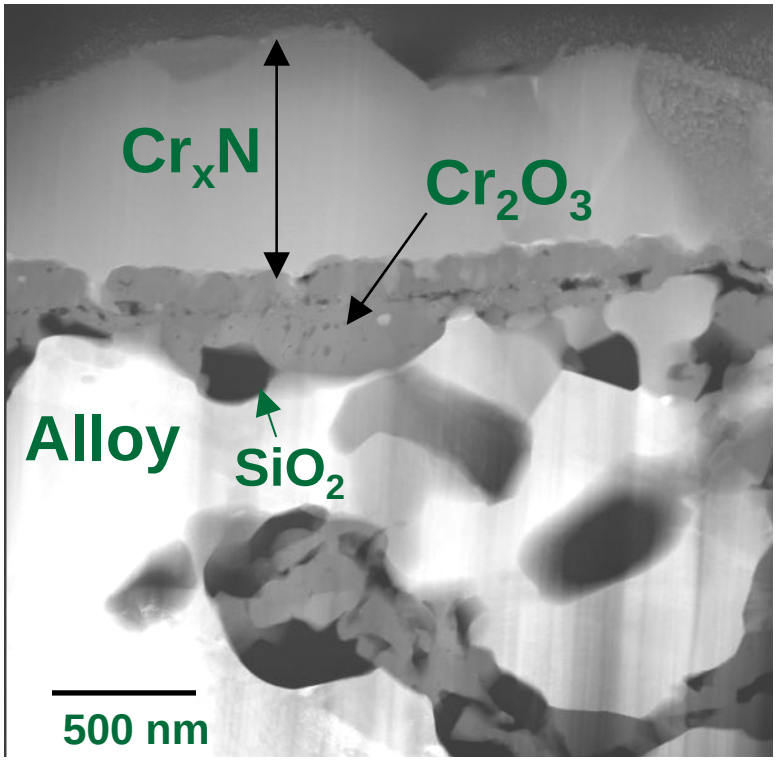


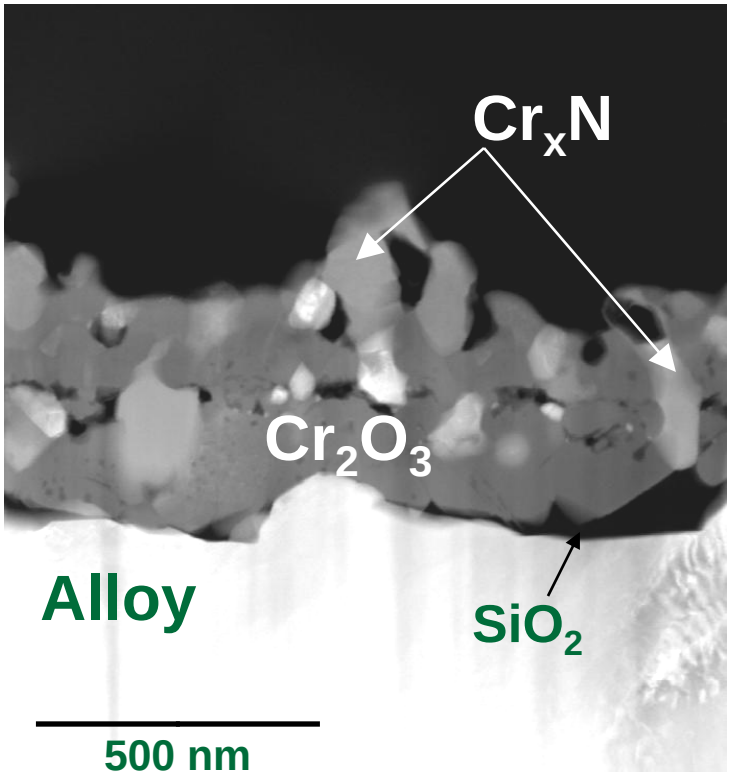




2205: Continuous Cr-Oxide Formed

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

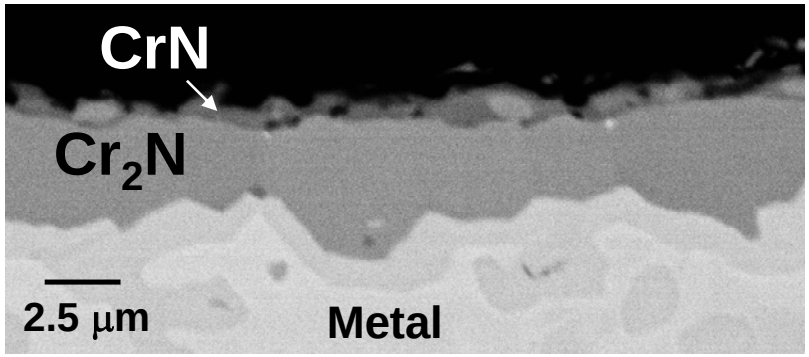




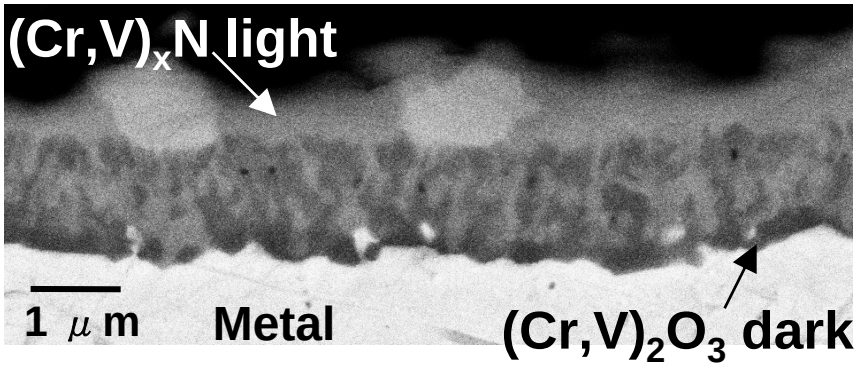
- Significant scatter in run-to-run surface O/N content
  - consequence of lack of strong nitride-forming element in 2205 (only Cr)
- Few through-layer thickness nitride paths
  - continuous inner oxide could compromise electrical conductivity

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

Nitrided Ni-50Cr



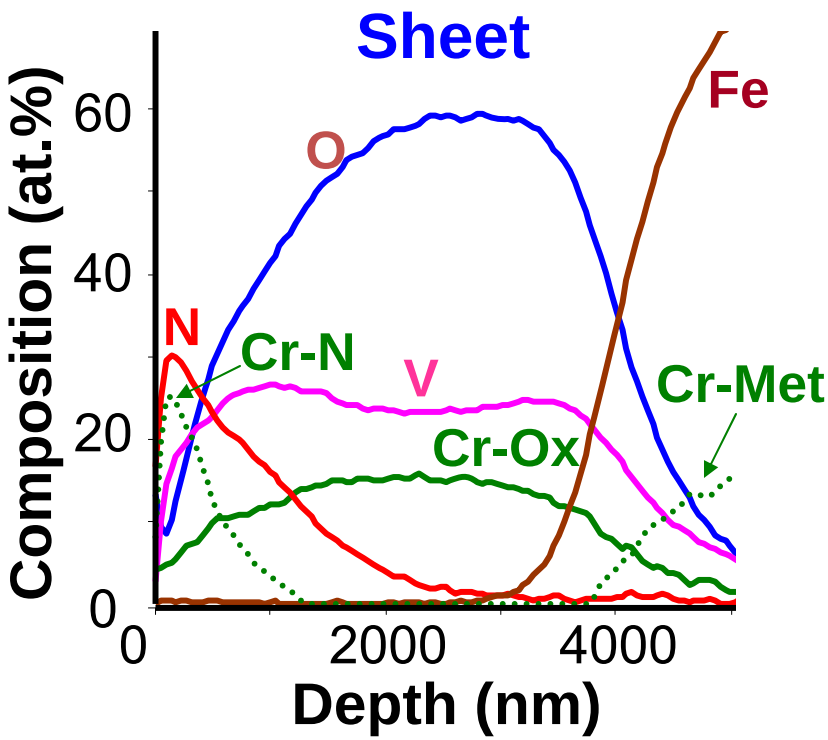
Nitrided Fe-27Cr-6V

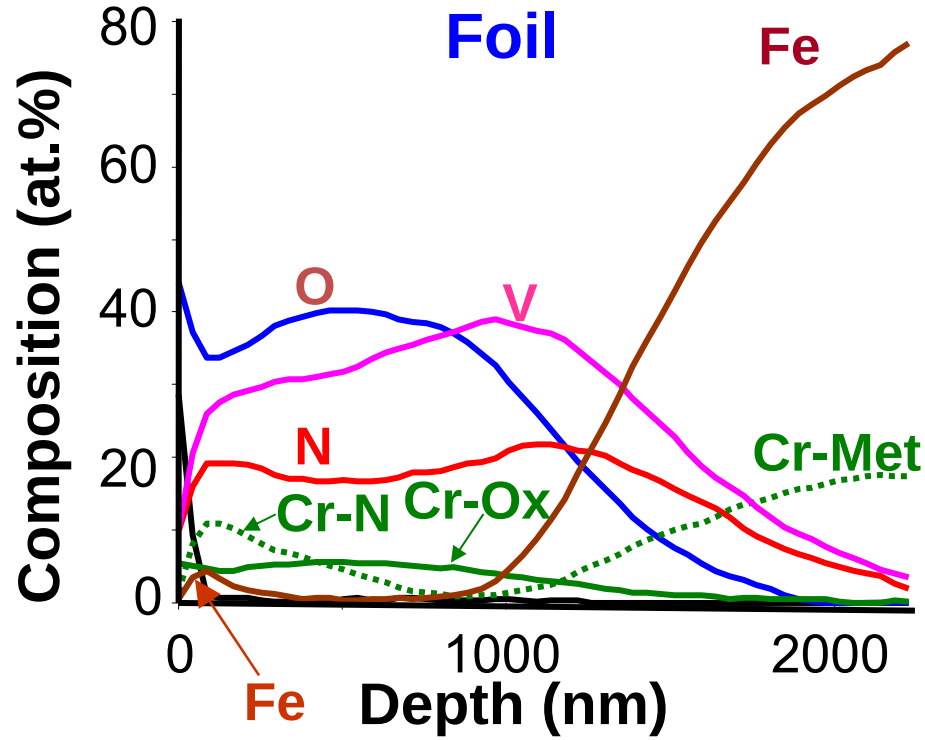


- Nitrided Fe-27Cr-6V Cr-nitride surface formed in mixed nitrogen/oxygen environment over 24 h nitriding cycle
  - -long cycle and mixed N_2/O_2 environment not practical for scale up
  - -used to understand and develop controllable pre-oxidation/nitridation approach with short nitriding cycles to meet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

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

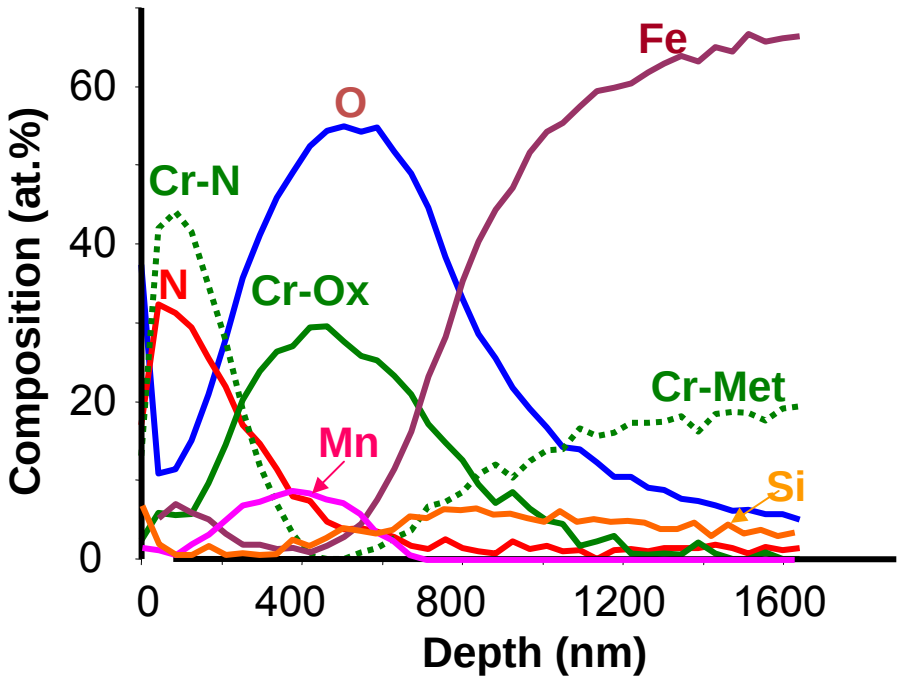
AES Depth Profile of Pre-Oxidized/Nitrided Fe-20Cr-4V

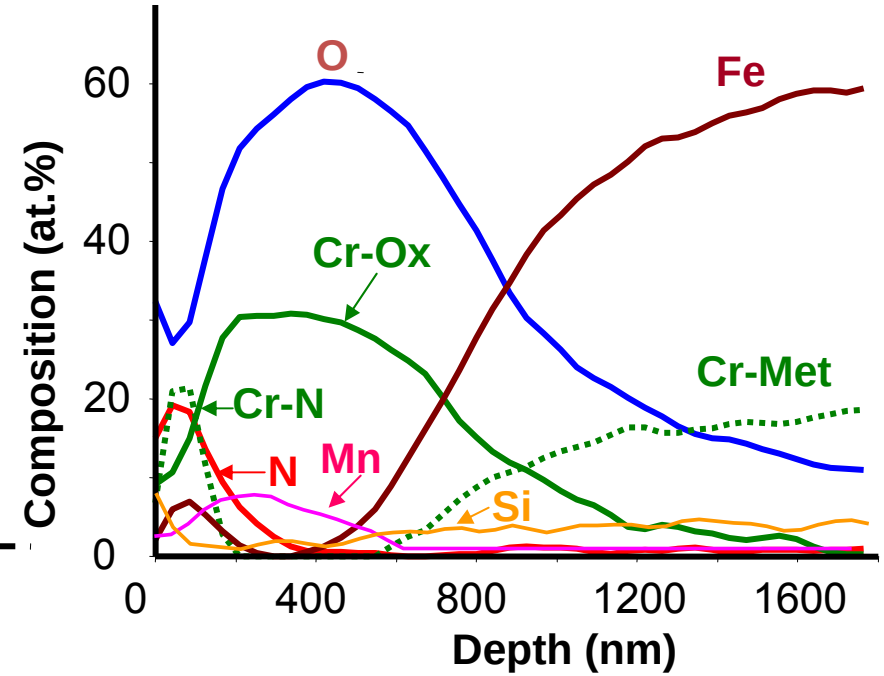




- Foils more sensitive to O_2 impurities in N_2-$4H_2$, more oxide at surface
  - -foil surface finish and microstructure/diffusion effect?
- Foils show small surface Fe peak-not observed in sheet material
  - -may contribute to observed ICR increase on polarization

Run-Run Scatter in O/N at Surface of Pre-Oxidized/Nitrided 2205





- Lack of a strong nitride-forming alloy element (e.g. V) contributes to increased sensitivity to O_2 impurities during nitriding

- Suggests evaluation of commercial alloys with Ti (e.g. 321 stainless)