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 cm² FeCrV Stainless Steel Stampings
  - 1000 h test results
  - rapid cycle quartz/plasma lamp nitriding

• Single-Cell Evaluation of 50 cm² Stamped/Laser Welded/Nitrided FeCrV Bipolar Plate Assemblies
  - 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

<table>
<thead>
<tr>
<th>Carbon-Based</th>
<th>Metallic</th>
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<tbody>
<tr>
<td>Graphite</td>
<td>Inert metals (e.g. Nb)</td>
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<tr>
<td>Conductive Polymer</td>
<td>Metal Nitrides</td>
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<tr>
<td>Diamond, Diamond Like Carbon</td>
<td>Metal Carbides</td>
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<tr>
<td>Organic Self-Assembled Monolayers</td>
<td>Noble Metals (e.g. gold)</td>
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*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

- **Deposited Coating**
  - pin-holes, flaws

- **Reacted/Graded/Nano Surfaces**
  - Thin Carbon Films
  - Thin Gold layers
  - Gas Nitridation
  - Doped Alloys
  - Electrochem. Treatment

- **Multi-Layer Surface**
  - Nitride/Metal (Cr$_x$N/Cr)
  - Carbon/Metal
  - Nitride/Nitride (TiN/Cr$_x$N)

- **Composite Surface**
  - Boride/Passive Oxide
  - Gold/Polymer or Oxide
  - Carbon/Polymer or Oxide
  - V$_x$N/Cr$_2$O$_3$
  - Nitride/Rubber

- **Conductive Phase**
- Reduces Defects
- Modified Passive Layers
- Conductive Paths Through Corrosion-Resistant Layer
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

- 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$_x$N surface layer
- Stamp then nitride: Industrially established and low cost
Cr$_x$N Formed on Nitrided Model Ni-50Cr Alloy Exhibits Good Corrosion Resistance

Anodic Polarization Data at pH3 H$_2$SO$_4$, 80°C
Cr$_x$N Surface on Model Nitrided Ni-50Cr Exhibits and Maintains Low ICR

- 4100h in LANL bipolar corrosion test cell (Air/H$_2$, pH 3 H$_2$SO$_4$ + F$^-$, 80°C)- No attack of Cr$_x$N 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 $\text{Cr}_x\text{N}$ Surface on Stainless Steels

- Stainless steels internally nitride: corrosion
- Form $\text{Cr}_2\text{O}_3$ by preoxidation to keep $\text{N}_2$ at surface
  - convert surface $\text{Cr}_2\text{O}_3$ to surface $\text{Cr}_x\text{N}$ 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, N₂-4H₂-0.5O₂; Nitridation: 1000°C, 1-3 h, N₂-4H₂ (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 \((V, Cr)_x N\) in \((Cr, V)_2 O_3\)

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

Lower alloy Cr, V content and shorter nitriding cycles (1-2 h at 1000°C) to reduce cost result in \( V_xN \) in \( \text{Cr}_2\text{O}_3 \) surface rather than continuous \( \text{Cr}_x\text{N} \)

Better Corrosion Resistance
Low ICR and Good Corrosion Resistance Achieved with Nitrided FeCrV Foils

- Polarization in 1M H₂SO₄ + 2 wppm F⁻ for 7 h at 0.14V (H₂, 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 Benchmark to Stainless Steels and Graphite

Fuel Cell Test Cycle (1000-1200 total h)

- 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 cm² 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

- Initial Nitrided Fe20Cr4V
- Aged (1114h)
- Initial Graphite
- Aged (1175h)
- Initial Untreated 904L-SS
- Aged (1122h)
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 μg/cm²) level of metal ion contamination with 904 L
- 321 tested for 120 h showed regions of 1-70 μg/cm² metal contamination
Robustness/Repeatability Concern for Fe-20Cr4V and Short 1-2 h Nitridation Cycles (Multiple Tests)

- Performance decline in test
- Significantly higher V-O signal in flow-field (no Fe oxidation)
- Oxidation of VxN
- Likely inadequately nitrided (needed longer cycle this run)

Oxidation seen in 1.5h Nitrided Stamping
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 1000°C/10 min Treated Fe-20Cr-4V

- Surface consistent with V(Cr)ₓN dispersed in (Cr,V)₂O₃
- Virtually no Fe in treated region (usually correlates w/ good corrosion resist.)
- 900-1000°C; 5 to 15 min peak temperature holds

Driver is Lower-Cost Processing, Better Surface
Quartz-Lamp-Treated Stampings Show Promising Single-Cell Fuel Cell Behavior

Initial V-I Curves Using N212 MEA

1000°C: 5,10 Min Quartz Lamp Treated

- 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 Assessments

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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