SECA Core Technology Program
R&D at PNNL: Overview


Pacific Northwest National Laboratory
Richland, WA 99354

July 23, 2013
14th Annual SECA Workshop
Pittsburgh, PA
Objective

► Provide R&D support to SECA program
- From SECA Program Mission statement: “Increase reliability, robustness, and durability of cell and stack technology”
- Development/evaluation of improved materials and fabrication processes for SOFC cells and stacks
- Improved understanding of performance degradation mechanisms
- Development/implementation of modeling tools to facilitate cell and stack design and optimization
- Technology transfer to industry teams
  - Stack test fixture validation
  - Topical reports, journal articles
  - Semi-annual one-on-one reviews, SECA Workshop
  - Provide materials, software for evaluation/implementation by industry teams
Scope of Work

- Determined through consultation with NETL program management and SECA industry teams
  - Increased communication with industry teams in recent years

- Current areas of emphasis (combined experimental/modeling approach)
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC interconnects
  - Seals for SOFC stacks
    - Compliant glass-based seals
  - Cathode materials and interactions
    - Effects of humidity; In-situ XRD characterization
  - Anode materials and interactions
    - Effects of high fuel utilization; Mitigation of sulfur poisoning
  - Cell/stack design
    - 2D and 3D modeling tools to assist in cell/stack design
    - Poster Presentation: ROM Tool for SOFC Modeling (Brian Koeppel)
    - Oral Presentation: Modeling Tools for SOFC Design and Analysis (Brian Koeppel)
Seals for SOFC Stacks

- **Primary Challenge**
  - Reliability during thermal cycling (high residual stresses)

- **Approach (collaboration with ORNL)**
  - “Compliant glass” based seals: Glass exhibits low Tg and relatively low viscosity at operating temperature, resulting in mitigation of mechanical stresses during operation and thermal cycling. Potential for self-healing of cycling-related damage.

  ORNL is primarily responsible for materials properties characterization, while PNNL has primary responsibility for modeling and seal test activities.

  - Evaluate thermal, mechanical, and chemical sealing glass properties (including glass-based composites).
  - Design and test compliant glass-based seals to evaluate seal performance in terms of leakage, mechanical stability, and reactivity (e.g., interactions with adjacent materials, electrode poisoning due to volatilization and deposition of glass constituents).
  - Develop compliant glass constitutive models to simulate thermal stresses, seal damage evolution, and healing behavior during stack operation.
Compliant Glass-based Seals

► Status (completed work)

■ Measurement of thermo-physical and mechanical properties (viscosity, CTE, elastic constants, crystallization rate; 15,000 hours)

■ Assessment of electrical, microstructural, and chemical stability
  ● High electrical resistance maintained with aluminized steel components
  ● Some de-vitrification observed; controlled by limited amount of Ba and Al in glass
  ● Minimal volatilization over stack lifetime
  ● Potential issues associated with pore coarsening/void formation

Glass only

15 vol% Zirconia fiber

Aged 800ºC, 250 hours
Compliant Glass-based Seals

- Ongoing/Future work
  - Inclusion of fillers (zirconia fibers, particles) to modify viscosity, control porosity and displacement
  - Optimization of seal design and fabrication techniques
  - Long-term evaluation of seals in seal test fixture and stack test fixture
  - Modeling of microstructural, thermophysical, and mechanical behavior
    - Self-healing behavior
    - Simulation of seal performance in stacks
- Preliminary assessment in seal test fixture:

12 deep thermal cycles (RT to 800°C)
Preliminary evaluation of compliant glass seal: ~1300h, 800°C, 3 thermal cycles

- No cross-bubbling at room temperature
- No discoloration on either cathode and anode side
- No iso-propanol penetration along sealing edges or through cell

- Long-term evaluation in stack test fixture is in progress

  • Poster: Compliant Glass Seal Development at Pacific Northwest National Laboratory (Matt Chou; collaboration with ORNL)
Cathodes

- **Primary Challenges**
  - Long-term stability
  - Effects of contaminants

- **Approach**
  - Emphasis on effects of humidity in cathode air stream on cell performance
    - Button cell tests (including high temperature XRD) at varying temperatures and humidity levels
    - Modeling to develop improved understanding of cathode reactions and degradation mechanisms
  - Leveraging activities/results with other SECA Core Program cathode researchers

- **Status**
  - 1000 hour cell tests completed on LSCF and LSM-20/YSZ; performance trends identified

- **Ongoing / Future activities**
  - Tests in progress on LSM-0 (LM) and LSM-5
  - High temperature XRD on working cathodes: Effect of humidity on LSM/YSZ cathodes
  - Modeling of kinetics, thermodynamics, and possible reactions with LSM-20

- **Posters:**
  - LSM-20/YSZ Cathode Response to Elevated Steam Content in 500-1000 h Tests (John Hardy; collaboration with NETL)
  - In-Operando XRD of Anode-Supported LSCF Cathodes at 700 – 800°C for 1000 h (John Hardy)
Anodes

Primary Challenges
- Long-term microstructural stability in high water environments
- Effects of contaminants

Approach
- Emphasis on effects of high fuel utilization (high water content) on Ni-YSZ anode performance
  - Cell and coupon tests at varying temperatures and water levels
  - Fuel is simulated clean coal gas
- Mitigation of sulfur poisoning

Ongoing / Future activities
- Microstructural changes (Ni coarsening) observed at 900 and 1000°C at high fuel water contents; tests and analysis in progress
- Attempting to correlate anode electrochemical performance with microstructural changes

Poster:
- Stability of Nickel in Ni/Zirconia Electrodes at High Steam Concentrations (Olga Marina)
SOFC Interconnects & Coatings

► Primary Challenges
  ▪ Cr volatility (cathode poisoning)
  ▪ Increasing electrical resistance
  ▪ Scale de-bonding/spallation

► Approach
  ▪ Low cost ferritic stainless steel interconnects with protective coatings (MnCo spinel, aluminization)
  ▪ Experimental: Oxidation testing, ASR testing, stack fixture testing, micro/nano indentation
  ▪ Modeling: Finite element-based modeling tools utilizing experimentally obtained strength data to determine spallation mechanisms and predict interconnect lifetime

► Posters

  ▪ Recent Progress of SOFC Materials Validation in a Generic Stack Fixture at Pacific Northwest National Laboratory (Matt Chou)

  ▪ Novel Interconnect Spinel Coating Process for Planar SOFC Stacks (Jung Pyung Choi)

  ▪ Interconnect Lifetime Prediction from Interfacial Indentation (Brian Koeppel)
Low-cost Alloy-based Interconnects

**Interconnect Alloy: AISI 441**
- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO₂ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

**Interconnect Coating: Ce-modified (Mn₀.₅Co₀.₅)₃O₄ Spinel**
- High electrical conductivity (~60 S/cm), good CTE match (~11 ppm/K)
- Ceria inclusions improve oxide scale adherence
- Coating improves oxidation resistance and mitigates Cr volatility

<table>
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<tr>
<th>k_p (g²/cm⁴-s)</th>
<th>800°C</th>
<th>850°C</th>
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</thead>
<tbody>
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<td>Ce-MC coated 441</td>
<td>2 x 10⁻¹⁴</td>
<td>1 x 10⁻¹³</td>
</tr>
<tr>
<td>Bare 441</td>
<td>5 x 10⁻¹⁴</td>
<td>3 x 10⁻¹³</td>
</tr>
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</table>
Surface Modifications to AISI 441

- Goal: Improve long-term scale adhesion under spinel coating

- Provided by Allegheny Ludlum:
  - 1. Mill reference (as would be provided to a customer without any additional modifications)
  - 2. Desiliconized (treatment to sequester silicon from the near surface of the sheet; an alternative to decreasing Si content of alloy)
  - 3. Surface blasted (abrasion/peening resulting in surface deformation)
  - 4. Surface ground (rough surface abrasion resulting in surface deformation)
  - 5. Temper rolled (cold rolling process resulting in through-thickness deformation)

- Oxidation testing of 0.02” thick, MnCo spinel-coated coupons at 800 and 850°C
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 800°C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Tempered</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
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X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample
# - coupon not removed for analysis due to limited # of coupons remaining
20000 h, 800°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
20000 h, 800ºC in air

Surface Blast

Surface Grind

Desiliconized

Cold Rolled
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 800ºC, air

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<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<td>2.67</td>
<td>12.50</td>
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</tbody>
</table>

Atomic%
Surface Treated 441 w/coating; 800°C

![Graph showing scale thickness over time for different surface treatments.]

- Mill reference
- Temper rolled
- Surface ground
- Surface blast
- Desiliconized
### Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850°C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
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Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850°C

Time (hours) Scale Thickness (microns)

- Mill reference
- Temper rolled
- Surface ground
- Surface blast
- Desiliconized
20000 h, 850°C in Air

- Surface Blast
- Surface Ground
- 50% Cold Rolled
20,000 h; 850°C in air

Surface Blast

Surface Grind

Cold Rolled

Desiliconized
Surface Blast AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 850ºC, air

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<th>Fe</th>
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Atomic%
Spinel composition (metals basis)

Surface blast coupons, except 850°C, 12000 and 14000h are surface grind
Effect of Cr on spinel electrical conductivity and CTE

Optimization of Surface Blast Surface Modification

- 441 samples (0.5 mm) were prepared via surface grit blasting to further quantify and understand the effects of surface morphology on oxidation/spallation behavior.
  - Grit size was varied to evaluate two distinctively different processed surfaces (G80 vs. G40).
  - Long-term oxidation testing in progress.

Grit size: G80 (0.125-0.425 mm)  Grit size: G40 (0.300-1.00 mm)
Summary

- PNNL is using experimental and computational methodologies to support SECA Industry Team SOFC development.

- **Interconnects**
  - Spinel-coated, surface-modified AISI 441 exhibits improved long-term scale spallation resistance compared to coated, unmodified AISI 441.
    - Surface blast appears to be most promising surface treatment
      - 26,000 hours at 800ºC (tests in progress)
      - 22,000 hours at 850ºC (tests in progress)
      - Topical Report delivered to SECA Industry Teams (January 2013)

- **Cathodes**
  - Cell test results indicate that effects of moisture (3% water) on degradation rate become more severe with decreasing temperature for both LSCF and LSM/YSZ cathodes.

- **Anodes**
  - Microstructural changes (Ni coarsening) observed at 900 and 1000ºC at high fuel water contents.

- **Compliant Seals**
  - Preliminary results indicate excellent isothermal performance (>1000 hours) and stability towards thermal cycling
The work summarized in this paper was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- NETL: Shailesh Vora, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz
- ATI Allegheny Ludlum: Matt Bender
- ORNL: Edgar Lara-Curzio
- PNNL: Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn