SECA Core Technology Program
R&D at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

July 24, 2012
13th Annual SECA Workshop
Pittsburgh, PA
Objective

- Provide R&D support to SECA program
  - 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
Technology Transfer Process

► **First step:** Testing and characterization at sub-stack level
  - Materials Characterization
    - XRD, SEM, EDS, TEM, XPS, TGA, DSC, PSA, dilatometry, electrical conductivity, single & dual atmosphere oxidation
  - Multiple Component Tests
    - Button cell testing
    - ASR testing of interconnect/cathode contact/cathode structures
    - Electrical testing and leak testing of seal/interconnect and cell/seal/interconnect structures

► **Second step:** Testing under realistic “stack-like” conditions to bridge the gap between small-scale tests (e.g., button cells) and SECA industry team stacks
Technology Transfer Process

► SECA CTP Stack Test Fixture

■ Advantages:
  ● Can evaluate/validate new materials and fabrication processes under more realistic conditions
  ● Larger cell size than button cells (50mm x 50mm)
  ● Complete stack functionality (cell, cell frame, seals, interconnects, electrical contact materials)

■ Challenges:
  ● Increased complexity (and cost) of assembly, co-fabrication of seals and electrical contact materials
  ● Multiple components & phenomena, so results can be more difficult to interpret

■ Note: PNNL has transferred fixture design and test protocols to other SECA CTP participants (NETL, U. Conn.)

► Final step:
  ■ Delivery of topical reports
  ■ Delivery of materials to SECA industry teams for in-house evaluation
Scope of Work

- Determined through consultation with NETL program management and SECA industry teams
  - Increased communication with industry teams in past year

- Current areas of emphasis
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC, Ceramic interconnects
  - Seals for SOFC stacks
    - Devitrifying glass seals, Compliant glass seals
  - Cathode materials and interactions
    - In-situ XRD characterization, Effects of humidity
  - Anode materials and interactions
    - Effects of high fuel utilization, Mitigation of sulfur poisoning
  - Modeling
    - 2D and 3D modeling tools to assist in cell/stack design
    - Modeling of cell/stack degradation processes
Seal Development

- **Devitrifying Glass Seals**
  - A series of devitrifying glass seals with sealing temperatures between 825 and 1000°C have been developed.
    - Good CTE match to other components
    - Rapid stabilization of dimensions and microstructure due to devitrification
    - Good bonding to YSZ and interconnects (with aluminization of steel surface)
      - Reactive air aluminization process developed at PNNL
  - Current work focused on improved wetting/flow behavior at sealing temperatures ≥ 950°C

- “Compliant” glass seals also under development
  - Collaboration with ORNL
  - Potential advantages: reduction of thermal stresses, self-healing behavior
  - Potential challenges: crystallization, reactivity, and containment

- Poster Presentation
  - Glass Seal Development at Pacific Northwest National Laboratory
Cathodes

■ Current Priorities:
  ● Investigating degradation mechanisms
    ◆ In-situ high temperature XRD of operating LSCF cathodes
    ◆ 700, 750, and 800ºC
  ● Effects of air humidity on cell performance
    ◆ LSCF and LSM/YSZ cathodes
    ◆ Dry air vs. 3%H₂O

■ Poster Presentations
  ● Effects of Humidity in Cathode Air on LSM-YSZ Cathodes
  ● Extended Duration (1000 h) In-situ XRD of Operating LSCF Cathodes
Anodes

**Effects of high steam content (high fuel utilization) on Ni-YSZ anodes**
- Test anode-supported button cells with Ni/YSZ anodes and LSM/YSZ cathodes
- Test conditions
  - 700°C, 800°C, 900°C
  - Constant current corresponding to 0.7 or 0.8 V
  - Fuel is a simulated coal gas
  - Fuel humidity corresponding to various fuel utilizations achieved by adding oxygen
  - Include “control” cells held at low fuel utilization
- Ac and dc electrochemical measurements of each cell
- Monitor temperature of each individual cell
- Post-test characterization using SEM/EDS, TEM, and EBSD

**Poster Presentation**
- Durability of Nickel/Zirconia Anodes in SOFCs at High Fuel Utilization
Alloy Interconnects and Protective Coatings

- Primary emphasis is on AISI 441 w/ Ce-modified MnCo spinel (MC) protective coating. Current activities:
  - Long-term evaluation of oxidation resistance and electrical performance
  - Effects of alloy surface treatments on oxidation behavior, spallation resistance are under investigation (collaboration with Allegheny Ludlum)
  - Optimization of ultrasonic spray fabrication process: coating uniformity and thickness
    - **Poster presentation**
      - The Effect of Spinel Coating Thickness on SOFC Interconnect Resistance

- Investigation of alternative coating compositions (e.g., oxides with reduced Co content, aluminization)
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 SiO$_2$ 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 (Mn$_{0.5}$Co$_{0.5}$)$_3$O$_4$ 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>
<thead>
<tr>
<th>$k_p$ (g$^2$/cm$^4$-s)</th>
<th>800ºC</th>
<th>850ºC</th>
</tr>
</thead>
<tbody>
<tr>
<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>
</tbody>
</table>
Area Specific Resistance (ASR) Measurements

\[ \text{ASR}_{\text{cathode-interconnect}} = \Phi \left( \text{scale, contactmaterial, coatings} \right) \]

Simulated cathode with dense body and porous surface layers

Contact Layers

Interconnect (coated)

Current Density: 0.5A.cm\(^{-2}\)

ASR Stack (3 sets)
Long-Term ASR measurements: 800°C
Long-term testing of Ce-MC spinel-coated AISI 441

- 6,000 hour test under stack-like conditions (SECA CTP stack test fixture)
- 800°C; air vs. moist H₂/N₂

Poster Presentation: “Recent Progress in SOFC Stack Test Fixture Development and Materials Validation at PNNL”
Spinel-coated cathode IC and LSM contact interface
Spinel-coated cathode IC and LSM contact interface
Spinel-coated cathode IC and LSM contact interface
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)

- 0.020” thick coupons coated with Ce-MnCo spinel, heat-treated in air at 800 or 850°C; 16 coupons for each condition
# 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>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
</tr>
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<tbody>
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<td>4000</td>
<td>X</td>
<td></td>
<td></td>
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</tr>
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<td>XX</td>
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<td></td>
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<tr>
<td>12000</td>
<td>XX</td>
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<td>X</td>
<td>L</td>
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<tr>
<td>18000</td>
<td>XX</td>
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</table>

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
18000 h, 800°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 18,000 hours, 800°C, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ce</th>
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</table>
Surface Treated AISI 441 w/ Ce-modified MnCo spinel coating; 800°C
ASR Results for Surface Treated AISI441
(LSCF cathode and contact, Ce-MC 441)
### 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>
<th>Surface Grind</th>
<th>Surface Blast</th>
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<td>12000</td>
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<td>X</td>
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</tbody>
</table>

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
10000 h, 850°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
- Mill Reference (1200 grit)
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 10,000 hours, 850°C, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ce</th>
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Max.       | 64.99 | 1.01 | 0.78 | 33.58 | 19.48 | 2.27 | 14.95 | 0.50 |   |
Min.       | 58.86 | 0.49 | 0.22 | 3.49  | 7.61  | 0.16 | 9.77  | 0.24 |   |
Reactive Air Aluminization (RAA)

- Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., SrCrO$_4$), which degrade interfacial strength
- Cr volatility from alloys can poison cathodes
- Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects and BOP components

Report on RAA distributed to industry teams in October, 2011

Samples aluminized and delivered to industry teams for evaluation
Reactive Air Aluminizing

- Aluminum powder slurry-based process
- Heat treatment in air
  - 3ºC/min to 1000ºC
  - 1 hour dwell at 1000ºC
  - 3ºC/min cooldown

1. Application & Drying
2. Heat treatment in Air
3. Removal of loose material (leaving behind an adherent, protective coating)

Brush off
Perovskite Interconnects

★ Candidate Compositions

- Yttrium chromite
  - More stable towards water and YSZ than lanthanum chromite
  - \( Y_{0.8}Ca_{0.2}Cr_{0.9}Ni_{0.1}O_3 \)
    - CTE = 11 ppm/K
    - Conductivity in reducing atm: ~5 S/cm
    - Low chemical expansion: 0.06 at 900°C

- Lanthanum chromite
  - \( La_{0.78}Sr_{0.2}CrO_3 \)
    - CTE = 11.1 ppm/K
    - Low chemical expansion: 0.07 at 900°C
    - More stable towards reduction (no Ni, Co, or Cu)?

★ Previously demonstrated densification under constrained conditions

- Multiple liquid infiltrations/heat treatments required

★ Two current approaches to enhance sintering under constrained conditions

- Both involve formation of final perovskite phase during sintering process
  - Reaction sintering approach (enthalpy of reaction)
  - Sintering aid approach (liquid phase assistance + enthalpy of reaction)
Summary

- AISI 441 w/ Ce-modified MnCo spinel coatings exhibits low, stable ASR in long-term testing
  - Less than 20 mΩ-cm² after 25,000 hours at 800°C in air

- Surface-modified AISI 441 w/ Ce-modified MnCo spinel coatings exhibits improved long-term spallation resistance
  - 18,000 hours at 800°C (tests in progress)
  - 12,000 hours at 850°C (tests in progress)

- Future work:
  - Continue long-term testing of surface-modified AISI 441
  - Quantify relationship between surface morphology and oxidation resistance/scale adhesion
    - Prediction/Extension of IC lifetime
Acknowledgements

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