FUNDAMENTAL STUDIES OF THE DURABILITY OF MATERIALS FOR INTERCONNECTS IN SOLID OXIDE FUEL CELLS
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J. Hammer, S. Laney, F. Pettit, & G. Meier
Department of Materials Science & Engineering
University of Pittsburgh

N. Dhanaraj & J. Beuth
Department of Mechanical Engineering
Carnegie Mellon University

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PROJECT STRUCTURE

NETL
Dr. Lane Wilson  Technical Monitor
Dr. Chris Johnson  NETL Fellowship Mentor

University of Pittsburgh
Prof. Frederick. S. Pettit  Co-principal Investigator
Prof. Gerald. H. Meier  Co-principal Investigator
Ms. Julie Hammer  Graduate Student
Mr. Scot Laney  NETL Partnership Fellow
Ms. Mary Birch  Senior Project Student

Carnegie Mellon University
Prof. Jack L. Beuth  Co-principal Investigator
Ms. Nandhini Dhanaraj  Graduate Student

Completed
Ms. Kelly Coyne  B.S. Engineering Phys.
Ms. Carrie Davis  B. S. Materials Science
Mr. Wesley Jackson  B. S. Materials Science
PROGRAM FOCUS

TASK I: Mechanism-Based Evaluation Procedures (Chromia-Forming Alloys)

• Characterization of Exposed Fuel Cell Interfaces
• Growth Rates of Chromia Scales on Cr and Ferritic Alloys
• Adhesion of Chromia Scales
• Oxide Evaporation
• Complex Atmosphere Testing

Note: An important theme which cuts across Tasks I and II is the establishment of accelerated testing protocols.
PROGRAM FOCUS;
TASK II: FUNDAMENTAL ASPECTS OF THERMOMECHANICAL BEHAVIOR

- XRD Stress Measurements (Chromia Films)
- Indentation Testing of Interface Adhesion
- Indentation Test Fracture Mechanics Analysis

Key Issues: What leads to spallation: scale thickening, stress changes or changes at the interface?
Can we quickly evaluate alloy systems without testing to the time for spontaneous spallation?
PROGRAM FOCUS
TASK III: Alternative Material Choices

This Task involves theoretical analysis of possible alternative metallic interconnect schemes including:

• Control of Growth Rate and Conductivity of Simple Oxides (e.g. CoO, NiO)
• Ni and dispersion-strengthened Ni
• Low CTE Alloys Based on Fe-Ni (Invar)
• Bi-layer Alloys

The most promising systems will be evaluated experimentally with regard to durability and oxide conductivity
TASK I: RESULTS
Oxidation of Ferritic Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Exposure Conditions</th>
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</thead>
<tbody>
<tr>
<td>E-BRITE (26 Cr-1 Mo)</td>
<td>T = 700°C, 900°C</td>
</tr>
<tr>
<td>AL 453 (22 Cr + Ce/La)</td>
<td>One-Hour Cycles</td>
</tr>
<tr>
<td>Crofer (22 Cr + La)</td>
<td>Atmospheres</td>
</tr>
<tr>
<td>ZMG232 (22 Cr + La/Zr)</td>
<td>- Dry Air (SCG)</td>
</tr>
</tbody>
</table>

- Air + 0.1 atm H₂O
- Ar/H₂/H₂O (SAG)
  
(p₀₂ = 10⁻²⁰ atm at 700°C and 10⁻¹⁷ atm at 900°C)
TASK I: RESULTS
Diagram of Apparatus
Previous Results

- Oxidation in wet air produced the most severe degradation at 900°C (accelerated chromia growth on Crofer and AL453 and increased spallation from E-brite).
- ASR correlated with oxide thickness.
- Thin specimens deform under oxidation-induced stresses.
TASK I: RESULTS
Dry Air Exposures – 700°C

Time vs. Mass Change / Area (700°C, dry air)
TASK I: RESULTS
Simulated Anode Gas (Ar-4%H₂, H₂O) Exposures – 700ºC

Time vs. Mass Change / Area for Crofer, E-brite, AL453, & Ni (700ºC, Ar/H₂/H₂O)
TASK I: RESULTS
Wet Air (0.1 atm H₂O) Exposures - 700°C

Time vs. Mass Change / Area (700°C, wet air)
TASK I: RESULTS
Microstructural and Phase Identification
Crofer 700°C

Dry Air
2000 cycles

MnCr$_2$O$_4$
Cr$_2$O$_3$
Si rich oxide
Internal Al$_2$O$_3$

Wet Air
1017 cycles

MnCr$_2$O$_4$
Si rich oxide
Internal Al$_2$O$_3$

SAG
2000 cycles

MnCr$_2$O$_4$
Cr$_2$O$_3$
Internal Al$_2$O$_3$
Si rich oxide
TASK I: RESULTS

Microstructural and Phase Identification

AL453 700°C

Micrographs show the effect of dry and wet air on the microstructure of AL453 at 700°C. The metal layer is protected by an oxide layer, with internal Al₂O₃ visible. In dry air, a Cr₂O₃ layer forms after 2000 cycles. In wet air, Cr₂O₃ with ~7% Fe is observed after 1017 cycles, and Cr₂O₃ with ~11.5% Fe is observed in SAG after 2000 cycles.
TASK I: RESULTS
Microstructural and Phase Identification
ZMG232 700°C

Dry Air
1019 cycles

Wet Air
1017 cycles
TASK I: RESULTS
Microstructural and Phase Identification
E-brite 900ºC

Dry Air
2000-cycles

Wet Air
2005 cycles

SAG
2000 cycles

Cr$_2$O$_3$

Si rich oxides

Internal Al$_2$O$_3$

MnCr$_2$O$_4$

Cr$_2$O$_3$

Si rich oxides

Internal Al$_2$O$_3$
TASK I: RESULTS
Microstructural and Phase Identification
E-brite 700°C

Dry Air
2000 cycles

Sigma Phase

Internal Al₂O₃

Cr₂O₃

Wet Air
1017 cycles

Sigma Phase

Internal Al₂O₃

Cr₂O₃

SAG
2000 cycles
TASK I: RESULTS
Sigma Phase in E-brite at 700°C

Dry Air
2000 cycles
Sigma Phase
(37% Cr, 63% Fe)

SAG
2000 cycles
Sigma Phase
(36.6% Cr, 63.4% Fe)

Wet Air
1017 cycles
Sigma Phase
(36.6% Cr, 63.4% Fe)
Cracks
**Chromia Evaporation**

\[ Cr_2O_3 (s) + \frac{3}{2}O_2 (g) = 2CrO_3 (g) \]

\[ p_{CrO_3} = K^{\frac{1}{2}} a^{\frac{1}{2}}_{cr_2O_3} p^{\frac{3}{4}}_{O_2} \]

\[ MnO (s) + Cr_2O_3 (s) = MnCr_2O_4 (s) \]

\[ \Delta G^0_{1100^\circ K} \approx -89 KJ / mole \]

Chromia Saturation

\[ a_{cr_2O_3} = 1 \quad p_{CrO_3} = 4 \times 10^{-11} \text{ atm} \]

MnO Saturation

\[ a_{cr_2O_3} = 6 \times 10^{-5} \quad p_{CrO_3} = 3 \times 10^{-13} \text{ atm} \]

LaCrO_3 (Activity data from Hilpert et al)

\[ a_{cr_3O_3} = 10^{-7} \quad p_{CrO_3} = 1 \times 10^{-14} \text{ atm} \]
Partial pressures of CrO$_3$ in Equilibrium with Cr$_2$O$_3$, MnO-saturated MnCr$_2$O$_4$, and LaCrO$_3$

Note: similar reductions would be achieved in the pressure of CrO$_2$(OH)$_2$
Crofer oxidized in contact with LaSrMnO$_4$ (cathode) for 88hrs at 900$^\circ$C in air + 0.1atm H$_2$O

Cr$_2$O$_3$ with ~2% Sr, ~4% La, and ~4.7% Mn

MnCr$_2$O$_4$ with ~1.5% Sr and ~2.6% La

MnCr$_2$O$_4$

Crofer (side in contact with cathode)

~74.9% Fe
~20% Cr
~2.2% La
~2% Mn
~0.9% Sr

Crofer (side opposite cathode)

After exposure, the cathode contained ~0.9% Cr and ~1.8% Al
La$_{0.8}$Sr$_{0.2}$CrO$_3$ Coated E-Brite (~5µm thick)

Coating is porous due to a phase transformation during devitrification.
La$_{0.8}$Sr$_{0.2}$FeO$_3$ Coated E-Brite (~5 µm thick)

As Coated Surface

800°C 2 hrs in Ar-H$_2$ (p$_{O_2}$ ~ 10$^{-8}$)

Cracks
La$_{0.8}$Sr$_{0.2}$FeO$_3$ Coated E-Brite (~5µm thick)

La$_{0.8}$Sr$_{0.2}$CrO$_3$ Coated Al 29-4C (~5µm thick)

Chromite coating cracked as well after same exposure conditions.

Cross sections show the coating to be much more dense, but also confirms the cracks seen from the surface.
Task I Summary

- Oxidation morphologies were similar at 700 and 900°C.
- MnCr$_2$O$_4$ is more stable than other transition metal chromates.
- Measurable interaction between Crofer and cathode material.
- Sigma-phase was observed to form in the higher Cr content alloys at 700°C.
- Chromia growth reduced under chromite coating.
- Chromite and ferrite coatings cracked during devitrification.
TASK I: FUTURE WORK
Work Planned for Next Twelve Months

• Continue Conductivity Measurements on Scales
• Continue Study of Effect of Contact with Anode and Cathode Materials
• Experiments to Decrease Chromia Growth Rate (Reactive Elements, Elimination of Grain Boundaries in Chromia)
• Study the kinetics of sigma-phase formation.
• Investigate Effects of Simultaneous Exposure to Cathode and Anode Gases
• Continue Study of Effects of Coatings (Chromite) on Chromia Growth and Evaporation
TASK II SUMMARY

- Indentation Has Been Used to Induce Spallation in Vapor- and SAG-Exposed E-BRITE and in Coated Specimens
- Initial Observations and Fracture Calculations are Consistent with Observations
- Ability to Predict Spallation Behavior at Early Times is Key as Testing Temperatures are Reduced

TASK II: FUTURE WORK

Work Planned for Next Twelve Months

- Extend Modeling of Indentation of E-BRITE to Other Substrate Systems
- Incorporate Oxide Thickness and XRD Stress Measurements into Models: Identify Mechanisms Leading to Spallation
- Indentation Tests on E-BRITE for Longer Exposures at 900° C in Wet Air and Simulated Anode Gas
- Indentation Tests on Specimens Exposed at 700° C
- Study of Adherence of Exposed Coated Specimens
TASK III: RESULTS
Comparison of oxide thickness for NiO and Cr$_2$O$_3$ -700°C

Estimated ASR is approximately the same for Ni and Crofer after oxidation
Task III: TYPICAL RESULTS
Co-8 wt% Cu - 900ºC Dry Air - 28 hours

Pt markers observed above scale/alloy interface
Copper Concentrations 125 hr exposure

Note significant “uphill diffusion” of Cu in CoO.
Parabolic Rate Constants at 900ºC

Summary: Cu was successfully doped into CoO but growth rate was not decreased.
TASK III: PRELIMINARY RESULTS
Alternative Material Choices
• This Task involves a theoretical evaluation of alternate metallic materials which have properties superior to the ferritic alloys.

• CoO scales have been successfully doped with Cu from an alloy but growth rate was not decreased

TASK II: FUTURE WORK
Work Planned for Next Twelve Months
• Work on doping of CoO and NiO by alloying will continue focusing on growth rate and conductivity.

• The most promising materials will be fabricated and tested.
SUMMARY AND CONCLUSIONS

The aim of this project is to evaluate the chemical and thermomechanical stability of ferritic alloys in the fuel cell environment.

The understanding gained will be used to attempt to optimize the properties of the ferritic alloys.

A parallel study is evaluating the potential use of alternate metallic materials as interconnects.
Collaboration, advice, and support from the following organizations is gratefully acknowledged:

- PNNL (P. Singh, G. Yang)
- NETL Morgantown (C. Johnson, L. Wilson, G. Richards)

We would welcome the opportunity to collaborate with other branches of the National Laboratories and Industry.
TASK I: RESULTS
Wet Air (0.1 atm H₂O) Exposures (for Ni) - 700°C

Time vs. Mass Change / Area for Ni (700°C, wet air)
TASK I: RESULTS
Dual Atmosphere Conditions
800ºC, 3 cycles, 100 hours per cycle
TYPICAL RESULTS

TASK II: THERMOMECHANICAL BEHAVIOR
Stress Measurements with 220 Lattice Plane – 900°C, Dry Air

Crofer Stress Measurement Using the 220 Lattice Plane (900°C, Dry Air, 100 Cycles)

\[ y = -0.0107x + 1.2458 \]

\[ y = -0.0107x + 1.2458 \]

Stress = -2.19 ± 0.03 GPa

\[ y = -0.0107x + 1.2458 \]
TASK II: THERMOMECHANICAL BEHAVIOR

USE OF TINTING TO VIEW SAG SPECIMEN DEBONDS

- Two Indents after 464 Hours at 900°C
- 60kg Indent, 10min at 700°C (tint), 150kg Indent (Mechanics Analysis Shows Increased Load Only Increases the Size Scale of the Damage)
- Tinting allows Clear Visualization of Debond Size at 60kg
- Visual Extent of Debonding Roughly Equals Actual Extent of Debonding
TASK II: THERMOMECHANICAL BEHAVIOR
SAG SPECIMEN INDENT FRACTURE MODELING

• Finite Element Model of the Indent Problem: Substrate Strains Transferred to the Chromia Scale
• Fracture Mechanics Formulas Estimate $G_c$ vs. Normalized Debond Radius (Residual Stress of -2.22 GPa in Chromia Scale)
• $R/a = 2.5$ and $t_{oxide} = 2 \mu m$ Yields: $G_c = 34$ J/m²