Reliability and Durability of Materials & Components for SOFCs

Edgar Lara-Curzio
Metals & Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6069

SECA Core Technology Program Review
February 20, 2002
Acknowledgments

Work sponsored by the US Department of Energy, Office of Fossil Energy, SECA Core Technology Program at ORNL under Contract DE-AC05-00OR22725 with UT-Battelle, LLC.

M. Radovic, B. Armstrong, Claudia Walls, Michael Lance
Metals & Ceramics Division
Oak Ridge National Laboratory
Outline

- Objectives
- Predicting Reliability
  - Infancy Failures
  - Wear/Degradation-induced Failure
- Evaluation of Material Properties
- Implications of Results for Manufacturing
- Future Work
  - Phase Identification and Micromechanical Stress Calculations
Objectives

In collaboration with industrial teams and other Core Technology Program participants,

- To develop/adapt/recommend test techniques to evaluate the properties and behavior of materials and components for SOFC.

- To identify and understand the mechanism responsible for the failure of materials and components for SOFCs.

- To develop methodologies for predicting the durability and reliability of materials and components for SOFCs.
A bathtub curve describes the evolution of the failure rate for most complex systems.
What information is needed to predict infancy failures of SOFCs?

- Stress distribution
- Distribution of strengths

Stress (MPa)
What information is needed to predict infancy failures of SOFCs?

**Stress Distribution**
- Geometry
- Temperature Distribution
- Mechanical Loads
- Boundary Conditions
- Elastic Constants
- Volumetric Changes
- Thermal Expansion

**Elastic Constants as a function of:**
- porosity
- temperature

**Volumetric Changes due to reduction**

**Distribution of Strengths**
Strength as a function of:
- porosity
- temperature
- size

**Toughness**
- interfacial

**Reliability/Probability of Failure**
Characterized Materials

8YSZ - Zirconia stabilized with 8mol% Yttria
NiO/YSZ - 75mol%NiO/25mol%YSZ, a precursor to Ni/YSZ anode

<table>
<thead>
<tr>
<th></th>
<th>8YSZ</th>
<th>NiO/YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td># of laminated layers</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Nominal Thickness, mm</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Pore former, vol%</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sintering conditions</td>
<td>1400 °C for 2 h</td>
<td>1400 °C for 2 h</td>
</tr>
<tr>
<td>Measured porosity, %</td>
<td>6.2 ±1.0</td>
<td>6.3 ±1.5</td>
</tr>
<tr>
<td></td>
<td>5.7 ±1.2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>22.8 ±1.1</td>
</tr>
<tr>
<td></td>
<td>19.8 ±0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.8 ±0.3</td>
<td></td>
</tr>
</tbody>
</table>
Young’s and Shear Moduli

Impulse Excitation Technique (ASTM C1259-98)

\[ E_{t,f} = \frac{37.699 f_{t,f}^2 D^2 m \left(1 - \mu^2\right)}{K_{t,f}^2 h^3} \]

- \( E_{t,f} \): Young's modulus as measured by torsional/flexural resonance
- \( m \): mass of the disc
- \( t \): height of the disc
- \( D \): diameter of the disc
- \( F_{t,f} \): fundamental torsional/flexural resonant frequency of the disc
- \( K_{t,f} \): a correction factor (ASTM C1259-98)
- \( \mu \): Poisson's ratio

Oak Ridge National Laboratory
U. S. Department of Energy
Young’s and Shear Moduli

8mol% YSZ as a function of porosity

This work:

\[ E = 229.85 \left(1 - 3.80p\right) \]
\[ G = 88.24 \left(1 - 3.69p\right) \]
\[ E = 234.54 \exp(-4.35p) \]
\[ G = 90.20 \exp(-4.51p) \]

Literature*:

\[ E = 219.53 \left(1 - 2.50p\right) \]
\[ G = 83.22 \left(1 - 2.39p\right) \]
\[ E = 220.27 \exp(-2.76p) \]
\[ G = 83.47 \exp(-2.63p) \]


OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY
Young’s and Shear Moduli
75mol%NiO/YSZ as a function of porosity

This work:
E = 195.49 (1 – 1.96 p)
G = 75.15 (1 – 1.93 p)
E = 204.47 exp(-2.76 p)
G = 78.09 exp(-2.65 p)

Literature*:
E = 205.46 (1 – 2.10 p)
G = 77.04 (1 – 2.03 p)
E = 207.13 exp(-2.48 p)
G = 78.04 exp(-2.38 p)

Thermogravimetric Analysis (TGA) of NiO/YSZ Reduction

Reduction of NiO measured for different samples. Samples were reduced for a different period of time at 800°C in 4%H2-96%Ar gas mixture.
Young’s and Shear Moduli vs. wt% of Reduced NiO in Anode

![Graph showing Young’s and Shear Moduli vs. wt% of Reduced NiO](image)

- Young’s Modulus (E) in GPa
- Shear Modulus (G) in GPa

Reduced NiO, wt%
What information is needed to predict infancy failures of SOFCs?

**Stress Distribution**
- Geometry
- Temperature Distribution
- Mechanical Loads
- Boundary Conditions
- Elastic Constants
- Volumetric Changes
- Thermal Expansion

**Elastic Constants** as a function of:
- porosity
- temperature

**Volumetric Changes** due to reduction

**Distribution of Strengths**
- Strength as a function of:
  - porosity
  - temperature
  - size

**Reliability/Probability of Failure**
- Toughness
  - interfacial
Thermal Expansion of NiO/8YSZ

expansion (%) = -0.049 + 1.181 \times 10^{-3} T + 4.526 \times 10^{-8} T^2

Dilatometry (air)
8YSZ/NiO-8YSZ

250 C antiferromagnetic - paramagnetic phase transition
Thermal Expansion of 8YSZ

\[
\text{expansion (\%)} = -0.045 + 8.277 \times 10^{-4} T + 1.8312 \times 10^{-7} T^2
\]
What information is needed to predict infancy failures of SOFCs?

Stress Distribution
- Geometry
- Temperature Distribution
- Mechanical Loads
- Boundary Conditions
- Elastic Constants
- Volumetric Changes
- Thermal Expansion

Elastic Constants as a function of:
- porosity
- temperature

Volumetric Changes due to reduction

Distribution of Strengths
Strength as a function of:
- porosity
- temperature
- size

Toughness
- interfacial

Reliability/Probability of Failure
Biaxial Strength
Ring-on-ring Testing (ASTM C1499-01)

\[ \sigma_f = \frac{3F}{2\pi h^2} \left[ (1-\nu) \left( \frac{D_s^2 - D_l^2}{2D^2} \right) + (1+\nu) \ln \frac{D_s}{D_l} \right] \]

where \( F \) is breaking load, \( h \) sample thickness, \( \nu \) is Poisson’s ratio and \( D, D_s \) and \( D_l \) are diameter of sample, supporting ring and loading ring, respectively.
Biaxial Strength
NiO/8YSZ – Weibull plots

\[ \text{Strength, MPa} \]

\[ \text{Probability of Failure, \%} \]

Not reduced
Fully reduced
NiO/YSZ
30% Pore Former
Room Temperature
4-layers

\[ b_2 = 18.8243, h_2 = 44.7583 \]

Oak Ridge National Laboratory
U.S. Department of Energy
Biaxial Strength
NiO/YSZ – Weibull plots

NiO/YSZ
Room Temperature
Porosity, %
7
20
23
## Biaxial Strength

### NiO/YSZ – Summary of Weibull statistics

<table>
<thead>
<tr>
<th>Characteristic strength (MPa) / Weibull modulus</th>
<th>Average strength ± Standard Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO/YSZ</td>
</tr>
<tr>
<td># layers -Pore former/Porosity, %</td>
<td>2 - 30/23</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>105.9 / 3.5</td>
</tr>
<tr>
<td></td>
<td>95.3 ± 27.2</td>
</tr>
<tr>
<td># layers -Pore former/Porosity, %</td>
<td>4 - 30/23</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>111.3 / 16.5</td>
</tr>
<tr>
<td></td>
<td>107.3 ± 10.8</td>
</tr>
<tr>
<td># layers -Pore former/Porosity, %</td>
<td>6 - 30/23</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>90.6 / 3.3</td>
</tr>
<tr>
<td></td>
<td>80.8 ± 32.1</td>
</tr>
</tbody>
</table>

| Ni/YSZ (Fully reduced NiO/YSZ)                |
| # layers -Pore former/Porosity, %             | 4 - 30/41                                   |
| Room Temperature                              | 44.7 / 18.7                                 |
|                                               | 43.5 ± 2.9                                  |

| NiO/YSZ                                      |
| # layers -Pore former/Porosity, %             | 4 - 0/7                                     |
| Room Temperature                              | 134.6 / 8.6                                 |
|                                               | 127.4 ± 17.3                                |
| # layers -Pore former/Porosity, %             | 4 - 25/20                                   |
| Room Temperature                              | 93.3 / 9.4                                  |
|                                               | 88.5 ± 11.4                                 |
| # layers -Pore former/Porosity, %             | 2, 4 and 6 - 30/23                          |
| Room Temperature                              | 79.6 / 3.4 - 115.4 / 17.4                   |
|                                               | 65.4 ± 25.3 - 111.6 ± 7.6                   |
| Room Temperature                              | 152.3 / 5.8                                 |
|                                               | 140.9 ± 28.6                                |
| Room Temperature                              | 98.9 / 7.0                                  |
|                                               | 92.6 ± 15.1                                 |
| Room Temperature                              | -                                          |

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY
Biaxial Strength

8YSZ – Weibull plots

Strength, MPa

Probability of Failure, %

Strength, MPa

Probability of Failure, %

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY
# Biaxial Strength

## 8YSZ – Summary Weibull Statistics

<table>
<thead>
<tr>
<th>8mol%YSZ</th>
<th>Characteristic strength (MPa) / Weibull modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average strength ± Standard Deviation (MPa)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Room Temperature</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>345.3 / 4.2</td>
<td>313.7 ± 84.8</td>
<td>182.4 / 4.8</td>
<td>222.2 / 3.7</td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td></td>
<td>131.5 / 4.4</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>127.10 ± 29.4</td>
<td></td>
</tr>
<tr>
<td>800°C</td>
<td>208.9 / 5.9</td>
<td>175.4 / 8.2</td>
<td>160.5 / 4.3</td>
</tr>
<tr>
<td>193.9 ± 38.8</td>
<td>166.2 ± 25.6</td>
<td>145.5 ± 41.1</td>
<td></td>
</tr>
</tbody>
</table>
Fracture Toughness
Double Torsion Testing

\[ K_I = PW_m \left( \frac{3(1+\nu)}{Wt^4 \xi} \right)^{1/2}, \xi = 1 - 1.26(t/W) + 2.4(t/W)\exp\left[-\pi W/(2t)\right] \]

Precracked @ 0.02 mm/min and tested @ 1 mm/min

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>8YSZ</th>
<th>NiO/YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{IC}), MPa m(^{1/2})</td>
<td>1.65 ± 0.02</td>
<td>1.04 ± 0.13</td>
</tr>
</tbody>
</table>
Implications of stochastic nature of strength
Implications of stochastic nature of strength

If a specimen of size $V_o$ has average strength $\sigma_o$, then

Bigger samples are weaker than smaller samples

$\frac{\sigma}{\sigma_o}$ is plotted against $V/V_o$ for different volume ratios.
Impact of Stochastic Strength on Manufacturing Decisions

Instead of building large cells, which are weaker than smaller cells, why not using a larger number of smaller cells to cover the same surface area?
Impact of Stochastic Strength on Manufacturing Decisions

![Graph showing the relationship between Weibull Modulus and Coefficient of Variation (γ/V/V0)](image)

- Weibull Modulus: 0, 5, 10, 15, 20, 25, 30
- Coefficient of Variation (γ): 0, 4, 6, 8, 10
- Strength Ratio: (γ/γ₀) changes accordingly

- V/V₀ = 9

**Equation:**

\( \sigma = \frac{\gamma}{\gamma_0} \)
Future Work

• Complete implementation of methodology to predict reliability of model system (geometry, materials).
• Verification of stress predictions using Raman spectroscopy.
• Determination of fracture toughness and adhesion strength of thin coatings.
• Effect of thermal cycling on reliability and durability
• Long-term reliability
• Compositional Analysis and Micromechanical Modeling
Compositional Analysis and Micromechanical Modeling

Ni, O, Zr
white – maximum
blue – ZrO
Red – Ni
Yellow – NiO

Ni
white – maximum
Black -minimum

Zr
white – maximum
Black -minimum

O
white – maximum
Black -minimum
Compositional Analysis and Micromechanical Stress Modeling

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY