PROGRESS IN SEALS FOR SOLID OXIDE FUEL CELLS

C.A. Lewinsohn
S. Elangovan
Ceramatec Incorporated
Salt Lake City, Utah

Acknowledgments
K. Cameron – fabrication, characterization and testing
D. Larsen - fabrication, characterization and testing
S. Quist – FEA modeling
M. Timper – cell testing

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**Seal Requirements**

- Low leak rate: good adhesion, high density.
- Ability to withstand thermal cycling/CTE match with cell components.
- Compatible with cell materials.
- Environmental stability in oxidizing and reducing conditions.
- No negative effect on cell performance.
- Acceptable cost.
Seal Strategies

- Compressive
  - Mica + compression
  - Ceramic felt + compression
  - Metallic seals + compression

- Adhesive
  - Cement
  - Glass
  - Glass-ceramic
  - Composite
  - Non-reactive metals (gold, hastelloy, etc.)
  - Reactive metals (silver, titanium, brazes, etc.)
Ceramatec experience: Cement Seal

- Adequate for new materials (Lanthanum Gallate)
- Porous - Stable OCV, but low fuel utilization
- Thermal cycle not possible
Ceramatec experience: Glass-Ceramic

- Sealed LSGM button cell
Ceramatec experience: Glass Seal

Joining Similar Materials

- Zirconia Electrolyte
- Zirconia Tube
Ceramatec experience: Glass Seal

Joining Dissimilar Materials

- Tailored CTE allows joining metal-YSZ
- Thermal cycle effect - to be determined
Ceramatec experience: YSZ Button Cell Thermal Cycle Effect
Ceramatec experience:

Electrochemical oxygen generation devices

- Ceramic stack
  - front - inlet air
  - left - insulated air baffle
  - top - O₂ gas port

- Cells electrically in series

- Layered components
  - interconnect
  - cell
  - insulator

- Gas flow
  - air - cross flow
  - O₂ - radial flow
    - central port out

O₂ containing gas in

O₂ flow

O₂ depleted gas out

O₂ product

Ceramatec experience: Electrochemical oxygen generation devices
Ceramatec experience:
Electrochemical oxygen generation devices

Process control and monitoring affects performance and reliability
Ceramatec experience: Electrochemical oxygen generation devices

- Cells cycled between RT and 700C, 100 times
- Stacks cycles > 90 times
Mechanical behavior of seals – FEA analysis

- 10 x 10 cm stack
- ¼ stack model
- Symmetric boundary conditions on cut planes
- Bottom surface fixed in vertical direction
- Upper surface unconstrained
FEA model

- Stress free temperature: 1000°C
- Seal dimensions: 50 microns thick, 1 cm wide

### Material Properties

<table>
<thead>
<tr>
<th>Component</th>
<th>E (GPa)</th>
<th>ν</th>
<th>CTE (ppm °C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interconnect</td>
<td>200</td>
<td>0.29</td>
<td>12</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>185</td>
<td>0.31</td>
<td>11</td>
</tr>
<tr>
<td>Seal</td>
<td>20, 100, 200</td>
<td>0.20</td>
<td>11</td>
</tr>
</tbody>
</table>
Seal Stresses – FEA analysis

Maximum shear stress occurs near corner

\[ E_{\text{seal}} = 20 \text{ GPa} \quad E_{\text{seal}} = 200 \text{ GPa} \]
Electrolyte Stresses – FEA analysis

Maximum shear stress occurs near corner

\[ E_{\text{seal}} = 20 \text{ GPa} \quad \text{and} \quad E_{\text{seal}} = 200 \text{ GPa} \]
Electrolyte Stresses – FEA analysis

Seal compliance doesn’t significantly affect electrolyte stresses

![Graph showing electrolyte stresses vs. seal modulus]
Seal Stresses – FEA analysis

- Elastic modulus of silicate glass
- Elastic Modulus of SiCN glass
- Tensile strength of SiCN glass

- Shear strength of SiCN glass
- Shear strength of silicate glass
Thermal Shock

\[ R' = k \sigma_{\text{max}} (1-\nu)/(E\alpha) \]

<table>
<thead>
<tr>
<th>composition</th>
<th>k (W/m-K)</th>
<th>E (GPa)</th>
<th>( \alpha ) (ppm-C(^{-1}))</th>
<th>( \nu )</th>
<th>( \sigma_{\text{max}} ) (MPa)</th>
<th>R’</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicate</td>
<td>1</td>
<td>75</td>
<td>10</td>
<td>0.2</td>
<td>60-100</td>
<td>85.3</td>
</tr>
<tr>
<td>SiCN</td>
<td>10</td>
<td>120</td>
<td>10</td>
<td>0.2</td>
<td>160-200</td>
<td>1200</td>
</tr>
</tbody>
</table>
Preceramic polymer precursor derived seals - rationale

- Leads to formation of amorphous, non-oxide materials with enhanced mechanical properties compared to alternative materials.
- Allows liquid and polymeric processing methods – dip coating, spray coating, molding, injection, etc.
- Allows for introduction of a variety of fillers and additives.
- Precursors wet and adhere to a variety of substrates.
- Relatively lower processing temperature (900 - 1000°C).
Stress due to constrained densification

\[ \sigma_p = 3\eta_f \left[ \frac{\rho}{(3-2\rho)} \right] \dot{\varepsilon} \left/ \left[ 1 - \frac{1}{2} \left[ \frac{\rho}{(3-2\rho)} \right]^{1/2} \right] \right. \]

Critical parameters:
- material viscosity
- shrinkage rate
**TGA/DTA – heating schedule**

- **polycarbosilane**
  - Rate of change greatest between 200 - 600°C
  - Slow heating rate must be used prior to 600°C.

- **polycarbosilazane**
Mitigating shrinkage stresses

- Inert and active fillers:
  - Inert fillers can be used to reduce overall shrinkage
  - Inert fillers reduce initial polymer volume
  - Inert fillers can also be used to modify properties: CTE, compliance
  - Certain active fillers can also be used to reduce overall shrinkage

- Pre-cure, or Partially-pyrolyse precursor to reduce the amount of shrinkage (“quasi-inert filler”):
  - Example - A 24% reduction in stress can be obtained by partial pyrolysis of polycarbosilane to reduce the shrinkage during joint processing by 40%.
Crack-free parts fabricated by controlled processing

- Higher partial pyrolysis temperature decreases overall shrinkage
- Partially pyrolysed material ground into powder and blended with fresh polymer.
- Blended mixture pyrolysed to dense material.
Seal Fabrication

Process Flowchart

- Partially pyrolysed polymer
- Preceramic polymer
- Fillers
- Solvents

Flow:
- grind
- mix
- apply
- pyrolyse
Test seals - fabrication
Test seals - pyrolysed
High thermal expansion, inert fillers used to control CTE

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature Range (°C)</th>
<th>CTE (ppm °C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 mol% yttria-doped zirconia</td>
<td>25-1000</td>
<td>10.6-11.1</td>
</tr>
<tr>
<td>polycarbosilane/Metal 1</td>
<td>200-700</td>
<td>10.0</td>
</tr>
<tr>
<td>polycarbosilane/Metal 2</td>
<td>200-700</td>
<td>7.0</td>
</tr>
<tr>
<td>polycarbosilane/Metal 3</td>
<td>200-700</td>
<td>9.0</td>
</tr>
<tr>
<td>polycarbosilane/Ceramic 1</td>
<td>200-700</td>
<td>7.0</td>
</tr>
<tr>
<td>polycarbosilane/Glass 1</td>
<td>200-600</td>
<td>7.0</td>
</tr>
<tr>
<td>polycarbosilazane/Metal 1</td>
<td>200-600</td>
<td>10.0</td>
</tr>
<tr>
<td>polycarbosilazane/Metal 2</td>
<td>200-700</td>
<td>5.0</td>
</tr>
<tr>
<td>polycarbosilazane/Metal 3</td>
<td>200-700</td>
<td>10.0</td>
</tr>
<tr>
<td>polycarbosilazane/Ceramic 1</td>
<td>200-700</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Preliminary results indicate cell performance is not affected by the presence of seal material in the fuel stream.
## Leak rate

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Leak rate (sccm/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia electrolyte/zirconia electrolyte</td>
<td>1.3 x 10^{-3} *</td>
</tr>
<tr>
<td>Zirconia electrolyte/metal interconnect</td>
<td>1.9 x 10^{-3}</td>
</tr>
<tr>
<td>Metal interconnect/metal interconnect</td>
<td>2.7 x 10^{-2}</td>
</tr>
<tr>
<td>Alumina/inconel sealed w/compressive, hybrid mica seal (PNNL data measured at 800ºC)</td>
<td>1.6 x 10^{-4}</td>
</tr>
</tbody>
</table>

* Same as for a proprietary glass seal w/matched thermal expansion but higher reactivity with ceramic SOFC components.
Leak rate – effect of thermal cycling

RT – 800°C in 8 h
800°C – RT in 8h 10 cycles

➢ Very little degradation in leak rate due to thermal cycling
## Seal performance

### 4 cm diameter SOFC tests

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>polycarbosilane + metal filler</th>
<th>polycarbosilane + ceramic filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1.038 V</td>
<td>1.065 V</td>
</tr>
<tr>
<td>850</td>
<td>1.030 V</td>
<td>1.052 V</td>
</tr>
<tr>
<td>900</td>
<td>1.008 V</td>
<td>1.042 V</td>
</tr>
</tbody>
</table>

Cooled to 50°C

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1.031</td>
<td>1.073</td>
</tr>
<tr>
<td>850</td>
<td>0.992</td>
<td>1.062</td>
</tr>
<tr>
<td>900</td>
<td>0.949</td>
<td>1.050</td>
</tr>
</tbody>
</table>
Seal and SOFC Standards

- Standards allow for comparison among various seal materials
- Standards facilitate design evaluation and modeling
  - Seal leak rate
  - Seal material shear strength

ASTM C28: Advanced Ceramics
Committee chairs: Michael Jenkins, Steve Gonzcy
Applications - SOFCs
Task Leader: C. Lewinsohn, Ceramatec Inc.
Opportunities for Graded Seals

- It is well established that proper design of graded interlayers in joints:
  - Reduces magnitude of peak residual stresses compared with monolithic interlayer
  - Allows positioning of the location of peak stresses away from brittle regions
  - Reduces edge stress singularities
- Recent research has found:
  - Crack trajectories may be manipulated by control of geometry and interlayer properties


Approach for Seal Design

- Discrete layers of different compositions
  Ceramic and metal fillers used to vary thermal expansion coefficient of seal
  Individual layers applied by spin coating
  Effects of joint architecture and microstructure to be examined

- Objectives
  Establish optimum conditions for strength
  Find relationship between strength and geometry, microstructure and composition of seal

Professor Ivar Reimanis is currently funded for graded materials research by: DOE/Office of Basic Energy Sciences and U.S. Army Research Office
Reducing Peak Stresses

FEA Results

- Stresses depend on
  - joint thickness
  - architecture

R. Torres, G. W. Mustoe, I. E. Reimanis, and J. J. Moore,
Summary

- Several candidate materials and methods exist for sealing SOFCs.
- These materials and methods must be tailored to the devices and applications.
- A balance of material properties is required for an effective seal.
- Device design can be used to influence seal requirements.
- Pyrolysis of preceramic polymer precursors offers a promising method for sealing SOFCs, further study is required.
- Further modeling, materials testing, design evaluation, and adoption of standards are strongly recommended.