Engineered Glass Seals for SOFCs

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• Matt Chou, Jeff Stevenson (PNNL).

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Outline

• Background
• Engineered Glass Seals
  • Characterization
  • Routes to low-cost manufacturing
• Summary
Background

Requirements for SOFC seals

• Simultaneous fulfillment of thermal, physical, chemical, mechanical and electrical property requirements.

• Phase stability and chemical compatibility without substantial property degradation for 40,000 hours in oxidizing and wet reducing environments.

• Address potential lack of flatness and/or parallelism of cells with large active area

Objective

• To develop engineered glass seals for SOFCs.

• Identify low-cost manufacturing processes
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Engineered Glass Seals

ceramic second phases

Multicomponent silicate glass matrix
### Composition SCN Glass

#### As sintered

<table>
<thead>
<tr>
<th>Element</th>
<th>at %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>57.13</td>
</tr>
<tr>
<td>Si</td>
<td>25.64</td>
</tr>
<tr>
<td>K</td>
<td>2.85</td>
</tr>
<tr>
<td>Ba*</td>
<td>2.00</td>
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<tr>
<td>Na</td>
<td>3.84</td>
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<tr>
<td>Ca</td>
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<td>Al</td>
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<tr>
<td>Mg</td>
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<tr>
<td>Ti</td>
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</tr>
<tr>
<td>B</td>
<td>0.04</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Atom Probe Tomography  Lara-Curzio et al. 2012 SECA Workshop
Microstructural Evolution of multicomponent silicate glasses

Ongoing exposure tests have surpassed 25,000 hrs

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Viscosity of SCN Glass

- Viscosity decreases with temperature and increases with time of exposure.
- Increase in viscosity could be explained by precipitation of crystalline phases.

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Engineered Glass Seals

Frangible ceramic particles

Multicomponent silicate glass matrix

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Wetting Behavior of Engineered Glass Seals

1:1  
1:2  
1:3  

ZHB  

Agsco  

SCN glass  

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Viscosity of SCN glass containing zirconia hollow spheres

The viscosity of the seal can be tailored to accommodate the large temperature gradients in SOFCs during transients and steady state operation.
Engineered Glass Seals

zirconia fibers
Zirconia Tube with Machined Sinusoidal Pattern
Zirconia tubes have been bonded to zirconia plates using engineered glass seal. This is the specimen configuration for testing in dual environments.

Zirconia tube is cut and ground to enable imaging of bonded area using IR imaging.
NDE of engineered glass seals

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Routes to low-cost manufacturing

- Tape casting
- Screen printing
- Fused deposition (3D Printing)
Routes to low-cost manufacturing

• Tape casting
Tape Casting

- SCN glass
- Hollow zirconia spheres
- Organic binder

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Post-mortem analysis of SCN-1 glass with 15V% ZrO₂ fibers after 12 thermal cycles

- No iso-propanol penetration along sealing edges or through bilayer
- No micro-cracks on sealing glass

Matt Chou and Jeff Stevenson (PNNL)
Thermal cycling of SCN-1 glass with ZrO$_2$ fibers

- ~40°C to 800°C in 3h, held for 3h at 800°C then furnace cooled to ~40°C in ambient air, 1 cycle/day.
- Constant leak rates suggested hermetic seal (observed leakage was from perimeter mica seal)
- Post-mortem check with iso-propanol showed no penetration

![Graph showing leak rate over thermal cycles](image)
Routes to low-cost manufacturing

- Tape casting
- Screen printing
Screen-printed engineered glass seals

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Screen-printed engineered glass seals
Screen-printed engineered glass seals
Screen-printed engineered glass seals

**Cross-sectional view**

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The viscosity of the seal can be tailored to accommodate large temperature gradients in SOFCs during operation.
Screen-printed engineered glass seals

- SCN glass or G6 glass
- Hollow zirconia spheres

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After Sintering

Sintering Process:
Up to 600 °C in 6 hrs, then up to 850 °C to 2 hrs.
een-printed engineered glass seals

Left Edge

SCN-ZHB-3:1-5:1 (sandwich)

1.5KX

100X

500X
Printed engineered glass seals

Middle Side

SCN-ZHB-3:1-5:1 (sandwich)
utes to low-cost manufacturing

Tape casting
Screen printing
Fused deposition (3D Printing)
Dissed Deposition (3D Printing)

[Diagram showing X-Y-Z Stage, Extrusion Nozzle, Plastic Filament Supply Coil, and Table.]


Composite mixture of glass, ceramic 2\textsuperscript{nd} phase and binder
Fused Deposition (3D Printing)
We are using a 3-D printer to manufacture engineered glass seals with predetermined concentration values of glass and ceramic particles/ceramic fibers.

The concentration of second phases and distribution of sizes would depend on topographic features of the cell and maximum local temperature.
Viscosity of SCN glass containing zirconia particles

The viscosity of the seal is tailored to accommodate the large temperature gradients experienced during initial starts and steady operation.

- Low viscosity
- High viscosity
We are using a 3-D printer to manufacture engineered glass seals with predetermined concentration values of glass and ceramic particles/ceramic fibers.

The concentration of second phases and distribution of sizes would depend on topographic features of the cell and maximum local temperature.
Engineered glass seals are being developed for SOFCs. Designs consist of a multi-component silicate glass matrix and a ceramic second phase (hollow spheres, fibers, particles). The effectiveness and durability of these seals are being investigated. Low-cost manufacturing processes are being developed.