Engineered Glass Seals for SOFCs

Edgar Lara-Curzio
Materials Science & Technology Division
Oak Ridge National Laboratory
Acknowledgments

• Valerie Garcia-Negron, Dan McClurg, Rosa Trejo, Amit Shyam, Hannah Stokes, Beth Armstrong, John Henry

• This research was sponsored by the US Department of Energy, Office of Fossil Energy, SECA Core Technology Program at ORNL under Contract DEAC05-00OR22725 with UT-Battelle, LLC.

• Rin Burke and Briggs White of NETL for guidance and support.
Outline

• Background
• Alfred University
• Mo-Sci
• Engineered Seals with SCN and G6 glasses
  • Characterization
  • Routes to low-cost manufacturing
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.

Objective

• To develop viscous glass seals for SOFCs
Viscous Glass Sealants for Solid Oxide Fuel Cells
DE-NT-5177

Executive Summary of 3 Candidate Viscous Glasses

May 2014

Scott Misture and James Shelby, co-PIs
Mark Naylor, Ph.D. student
Tongan Jin, Postdoctoral researcher

Alfred University
Alfred, NY
Three glasses identified as strong candidates

- All glasses contain Ga$_2$O$_3$ up to 15 mole percent to modify the alkaline earth borosilicate base compositions.
- Testing out to 1000 hours in air, dry 4% H$_2$ in N$_2$, and wet 100% H$_2$ show that all three crystallize extensively but retain some amorphous phase to provide viscous behavior.
- Excellent compatibility with alumina and YSZ, but not with spinel.

(see publications and compositions in *Int. J. Hydrogen Energy*, 2013)
Viscous Sealing Glasses for Solid Oxide Fuel Cells

Summary for SECA Industry Teams

Cheol-Woon (CW) Kim
MO-SCI Corporation, Rolla, MO
ckim@mo-sci.com  Tel: 573-364-2338

Richard K. Brow
Department of Materials Science and Engineering
and the Graduate Center for Materials Research
Missouri University of Science and Technology, Rolla, MO
brow@mst.edu  Tel: 573-341-6812
Promising compositions were identified

- Alkali-free barium borosilicate
- Preferred compositions exhibit promising sealing behavior
- Prepared a total of 105 compositions and measured properties ($T_g$, $T_s$, $T_{Liq}$, and CTE) of all of the compositions

<table>
<thead>
<tr>
<th>Phase II</th>
<th>Glass 73</th>
<th>Glass 75</th>
<th>Glass 77</th>
<th>Glass 102</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass system</td>
<td>BaO-RO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_g$ (°C) measured from CTE curve</td>
<td>624</td>
<td>623</td>
<td>625</td>
<td>604</td>
</tr>
<tr>
<td>Dilatometric $T_s$ (°C)</td>
<td>640</td>
<td>650</td>
<td>656</td>
<td>639</td>
</tr>
<tr>
<td>CTE 40-500°C (/°C)</td>
<td>8.48x10^{-6}</td>
<td>8.17x10^{-6}</td>
<td>9.25x10^{-6}</td>
<td>7.25x10^{-6}</td>
</tr>
<tr>
<td>Liquidus T (°C)</td>
<td>800</td>
<td>810</td>
<td>810</td>
<td>Non-Crystallizing</td>
</tr>
</tbody>
</table>
Most promising viscous glass: G102 (alkali-free barium borosilicate)

- G102 seal has survived 148 thermal cycles (800°C to RT; cooling rate ~5°C/min, heating rate ~13°C/min) in dry air and wet forming gas at a differential pressure of 0.5 psi (26 torr) over the course of >5,000 hours without failure and the test was deliberately terminated for analysis.
G102 seals after thermal cycles

- Excellent wetting and bonding to both aluminized metal and YSZ
- Glass is homogeneous
- No crystals in glass
- No significant elements from metal or ceramics diffusing into glass
- \( \text{BaAl}_2\text{Si}_2\text{O}_8 \) layer at glass/metal interface

148 Thermal Cycles (>5,000 hrs) in Air

148 Thermal Cycles (>5,000 hrs) in Wet Forming Gas
## Re-sealing behavior of G102

### Summary of re-sealing tests (ex-situ)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Viscosity, log η (Pa-s)</th>
<th>Observation (# of experiments)</th>
<th>Viscosity, log η (Pa-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G73</td>
<td>800</td>
<td>2</td>
<td>3.6</td>
<td>Healed (6 tests) 3.6</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2</td>
<td>5.0</td>
<td>Healed (2 tests) 5.0</td>
</tr>
<tr>
<td></td>
<td><strong>725</strong></td>
<td>2</td>
<td>5.8</td>
<td><strong>Healed (3 tests)</strong> 5.8</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2</td>
<td>6.8</td>
<td>Healed once, but not a second time 6.8</td>
</tr>
<tr>
<td>G102</td>
<td>850</td>
<td>2</td>
<td>3.0</td>
<td>Healed (1 test) 3.0</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2</td>
<td>4.0</td>
<td>Healed (1 test) 4.0</td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>2</td>
<td>4.6</td>
<td>Healed (1 test) 4.6</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>2</td>
<td>4.6</td>
<td>Healed (1 test) 4.6</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2</td>
<td>5.2</td>
<td>Healed (1 test) 5.2</td>
</tr>
<tr>
<td></td>
<td><strong>744</strong></td>
<td>2</td>
<td>5.4</td>
<td><strong>Healed (2 tests)</strong> 5.4</td>
</tr>
<tr>
<td></td>
<td>740</td>
<td>2</td>
<td>5.5</td>
<td>Not healed (2 tests) 5.5</td>
</tr>
<tr>
<td></td>
<td>736</td>
<td>2</td>
<td>5.6</td>
<td>Not healed (1 test) 5.6</td>
</tr>
<tr>
<td></td>
<td>730</td>
<td>2</td>
<td>5.8</td>
<td>Not healed (1 test) 5.8</td>
</tr>
</tbody>
</table>

- G102 cracked by thermal quenching
- G102 crack healed after re-heating to >744°C for 2 hrs
Sealing Glass

- Excellent wetting and bonding to both metal and ceramics
- Glass is homogeneous, with no crystals and no significant elements from metal or ceramics diffusing into glass
- The innovative staff at Mo-Sci will work with you to design and develop your project.

www.mo-sci.com • 573.364.2338
### Composition of G6 and SCN Glasses

As sintered

<table>
<thead>
<tr>
<th>Element</th>
<th>SCN-1 ICP-MS</th>
<th>SCN-1 ICP-AES</th>
<th>G6 ICP-MS</th>
<th>G6 ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>51.9</td>
<td>54.8</td>
<td>50.5</td>
<td>53.4</td>
</tr>
<tr>
<td>K</td>
<td>15.0</td>
<td>13.4</td>
<td>15.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Ba</td>
<td>14.0</td>
<td>12.9</td>
<td>7.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Na</td>
<td>9.8</td>
<td>8.3</td>
<td>6.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Ca</td>
<td>3.9</td>
<td>5.0</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Al</td>
<td>3.4</td>
<td>3.4</td>
<td>5.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2</td>
<td>1.3</td>
<td>4.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Ti</td>
<td>0.5</td>
<td>0.6</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.1</td>
<td>0.0</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Microstructural Evolution of multicomponent silicate glasses

G6

SCN

Air      Steam+H2+N2

As-sintered

100 hrs

500 hrs

850 hrs

5000 hrs

10,000 hrs
SCN glass on Al$_2$O$_3$ Substrate

25,000 hrs in air
SCN glass on Al₂O₃ Substrate

25,000 hrs in air
SCN glass on Al$_2$O$_3$ Substrate

25,000 hrs in air
G6-YSZ-68

After 25,000 Hours in Air
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
Routes to low-cost manufacturing

- Tape casting
- Screen printing
- Fused deposition (3D Printing)
Tape Casting

- SCN glass
- Hollow zirconia spheres
- Organic binder
Routes to low-cost manufacturing

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

Left Edge

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

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

Table

X-Y-Z Stage

Extrusion Nozzle

Plastic Filament Supply Coil

Composite mixture of glass, ceramic 2\textsuperscript{nd} phase and binder

http://www.additive3d.com
PLA/SCN: 70/30

Extruded Wire
PLA/SCN: 70/30

Sintered Wire:
Viscosity of SCN glass containing zirconia particles

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