Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

Richard K. Brow

Materials Science & Engineering Department - The Graduate Center for Materials Research
University of Missouri-Rolla
Rolla, MO  65409

6th Annual SECA Workshop
Pacific Grove, CA
April 20, 2005
Acknowledgements

This research was primarily done by

- Dr. Signo Reis and Mr. Teng Zhang (UMR)
- Ron Loehman, Sandia National Labs

Thanks to Xiao Dong Zhou, Piotr Jasinski, Harlan Anderson, Clarissa Vierrether (UMR)

The financial support of the Department of Energy (SECA project NT42221/Travis Schultz program manager) is gratefully acknowledged.
Designing glasses for SOFC seals is a significant challenge

Function:
- Prevent mixing of fuel/oxidant within stack
- Prevent leaking of fuel/oxidant from stack
- Electrically isolate cells in stack
- Provide mechanical bonding of components

Challenges:
- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures (>700°C)
  - Long lifetimes (>10000’s hrs)
  - Maintain stability over range of $P_{O_2}$, $P_{H_2O}$
- Relatively low sealing temperatures (<900°C)
  - Avoid altering other SOFC materials

For some designs, glass-ceramics may be suitable
Ba-silicate glass-ceramics have shown promise

Meinhardt, et al., USP 6,532,769  
Mar. 18, 2003

Excellent CTE match to zirconiа

Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases; e.g., BaO⋅2SiO₂, 2BaO⋅3SiO₂
The problem, as seen by 'a glass guy'

1. **Challenging compositional design problem**
   - Uncommon combination of properties
   - Investigate uncommon families of glasses

2. **Glass-ceramics are a likely option**
   - Crystallization studies- seal processing and long-term material stability

3. **Interfacial chemistry**
   - Glass-metal reactions
   - Material stability/volatility
   - Thermochemical stability
Our compositional design is based on unusual glass structures

"Invert Glasses": discontinuous silicate anions tied-together through modifying cations.

• Greater CTE’s
• More fragile viscosity behavior
  • ‘shorter’ glasses
• More ‘basic’ reaction chemistries

• Metasilicates (chains): [O]/[Si]~3.0
• Polysilicates (short chains): [O]/[Si]>3.0

• Greater CTEs from polysilicate crystalline phases
UMR glass-ceramics under development

- ZnO-modified alkaline earth invert silicates
  - Mixed CaO, SrO, ZnO (45-55 mole%)
  - \([\text{O}] / [\text{Si}] > 3.3, \text{SiO}_2 < 45 \text{ mole\%}\)
  - Minor oxides include Al\(_2\)O\(_3\), B\(_2\)O\(_3\), TiO\(_2\)

Property design targets:
- Seal/crystallized <\(850^\circ\text{C}\)
- CTE-match to YSZ/other cell materials
- Thermomechanically stable at >\(700^\circ\text{C}\)
- Thermochemically stable in oxidizing/reducing conditions
- Stable interfaces with a variety of materials

System G#27

After \(850^\circ\text{C}\) for 2hrs in argon with TiO\(_2\) without TiO\(_2\)
RO-silicate compositions with desirable thermal properties

$\text{B}_2\text{O}_3$ reduces sealing temperatures and increases residual glass in crystallized samples
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio.

"As made glasses"

- G36: $C T E_{RT-600} = 11.4 \times 10^{-6}/^\circ C$
- G27: $C T E_{RT-600} = 8.4 \times 10^{-6}/^\circ C$

Glasses with different ZnO/(SrO+CaO) ratios:
- ZnO/(SrO+CaO) = 0.00
- ZnO/(SrO+CaO) = 0.35
- ZnO/(SrO+CaO) = 1.00
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio

% Linear Change

Temperature (°C)

ZnO/(SrO+CaO)=0.00
ZnO/(SrO+CaO)=0.35
ZnO/(SrO+CaO)=1.00

G36
CTE_{RT-600}=12.4\times 10^{-6}/°C

G27
CTE_{RT-600}=10.0\times 10^{-6}/°C

LG38
CTE_{RT-600}=5.5\times 10^{-6}/°C

"As sealed glasses"
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio.

- ZnO/(SrO+CaO)=0.00, CTE=12.4 ppm/°C
- ZnO/(SrO+CaO)=0.35, CTE=10.0 ppm/°C
- ZnO/(SrO+CaO)=1.00, CTE=5.5 ppm/°C

As-sealed G27
- (1) - Ca₂ZnSi₂O₇
- (2) - CaSrAl₂Si₂O₇

As-sealed G36, 750°C for 10 days

As-sealed LG38
Representative crystalline phases in the UMR glass-ceramics

- **Pyrosilicates**
  - CaSrAl$_2$SiO$_7$, Ca$_2$ZnSi$_2$O$_7$
- **Orthosilicates**
  - Sr$_2$SiO$_4$, Zn$_2$SiO$_4$
- **Composition** is most important parameter for final phase distribution.

**Graphs**
- As-sealed (850°C/4 hrs)
  
  CaSrAl$_2$SiO$_7$
  Ca$_2$ZnSi$_2$O$_7$

- 28 days/750°C

---

SECA Workshop, 4/20/05 (12)  
R.K. Brow, brow@umr.edu  
University of Missouri-Rolla
Dilatometry indicates good CTE-match with YSZ

- Breaks indicate residual glass in crystallized samples

\[ \alpha_{\text{RT to 750}} \approx 100 \times 10^{-7}/^\circ \text{C} \]

\[ \alpha_{\text{RT to 600}} \approx 95 \times 10^{-7}/^\circ \text{C} \]
Dilatometry indicates good CTE-match with YSZ

Expansion of residual glass

CTE match below 650ºC

Glass #27

-0.04 0.00 0.04 0.08 0.12

Temperature(ºC)

As sealed
3 days/750ºC
7 days/750ºC
14 days/750ºC
28 days/750ºC

∆CTE(glass-YSZ)
Glass-ceramic microstructure evolves with time

Residual glass crystallizes with time
DTA provides information about sealing glasses

- Glass transition
- Glass crystallization
- 2 mole% B$_2$O$_3$
- 5 mole% B$_2$O$_3$
DTA provides information about the nature of the residual glass

Heat-treated at 750°C

As sealed

1 day

4 days

28 days

As melted

\( T_g \)

\( T_x \)

Less intense crystallization peaks, less residual glass
DTA results are used for crystallization kinetic studies

G#27 sealing glass treated in air

Avrami equation: 
\( (1-x) = \exp(-Kt^n) \);

n=1: surface crystallization

% of residual glasses

0 20 40 60 80 100

0 4 8 12 16

time (hours)

"as made glass"

- at 775°C, \( \tau = 8.5 \)
- at 800°C, \( \tau = 4.1 \)
- at 825°C, \( \tau = 0.6 \)
- at 850°C, \( \tau = 0.2 \)
DTA results are used for crystallization kinetic studies

$k = \nu_0 \exp\left(-\frac{E}{RT}\right)$

Studies are presently underway to:

1. Characterize the effects of nucleating agents on crystallization kinetics

2. Develop compositions less prone to crystallization

$E = 496 \text{ kJ/mol}$, $\nu = 1.37 \times 10^{20} \text{ /sec}$
Glass #36 is less prone to crystallization at 750°C

Potential materials for composite seals

$T_D \sim 750°C$
Glass stability in wet forming gas has been evaluated

- Higher B$_2$O$_3$ contents make the glasses less stable
- No correlation between ZnO contents and glass stability in reducing environments

![Graph showing weight at 750°C (g/cm²) with time (hrs) for different B$_2$O$_3$ contents.](image)
Glass-ceramics are more stable in forming gas than glasses.

The diagram shows the weight loss of glass-ceramics at 750°C using forming gas, with data points for Amorphous samples and Crystallized samples. The graph compares samples G#B27 and G#27 treated at different temperatures (800°C and 850°C) for 2 hours.
Test seals have been prepared with SOFC coupon materials

- Glass pastes
  - Glass powders, ~45mm & <5mm
  - PVB binders
  - Binder burn out: 500°C/air; glass
    sealed: 850°C/argon
  - Glass thickness: 20-400mm
- Interconnect alloy: E-bright
  - Cr-ferritic steel (26% Cr)
  - CTE ~ 11.7 ppm/°C
- YSZ coupons (8%Y₂O₃)
  - CTE ~ 10 ppm/°C

“As sealed” Glass 25 paste with YSZ and E-bright substrates (850°C/4hrs, Ar)
Test seals have been prepared with SOFC coupon materials

- Glass pastes
  - Glass powders, ~25µm
  - Interconnect alloy: Crofer
  - Cr-ferritic steel
  - CTE ~ 11.9 ppm/°C
After sealing:
  - Glass-ceramic thickness: 100-200µm

EDS shows little Cr-diffusion into the glass-ceramic
distance from the interface (µm)

Glass 27 with Crofer APU22 after four days at 750°C in air
Cr-rich interfacial reaction products are found at the glass/E-bright interfaces.

Glass#25/E-brite; 750°C for 14 days.
Glass #27 reacts with E-brite alloy at 950°C

Precipitates contain Zn, Cr, Al, and O

E-brite

After sealing cycle of 10 min @ 950°C

From Ron Loehman, Sandia

Sandia National Labs - Advanced Materials Laboratory

No detection of Cr in the glass matrix
The glasses do not appear to react with anode materials.

G#27/Anode interface after 11 cycles in Ar/H₂ atmosphere

From Ron Loehman, Sandia
**Glass-metal adhesion strength measured by pin-pull test**

---

**Romulus adhesion testing machine- Quad Group Inc.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Failure Stress (MPa)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>G#27/Crofer APU 22</td>
<td>39.5 ± 4.2</td>
<td>Glass failure</td>
</tr>
<tr>
<td>G#27/430SS</td>
<td>44.7 ± 1.9</td>
<td>Glass failure</td>
</tr>
<tr>
<td>G#36/Crofer APU 22</td>
<td>10.0 ± 0.8</td>
<td>Interface failure</td>
</tr>
<tr>
<td>G#36/430 SS</td>
<td>19.2 ± 0.7</td>
<td>Interface failure</td>
</tr>
</tbody>
</table>
Research Plans

Compositional development
• Crystallizing and non-crystallizing compositions
  • Viscosity and crystallization kinetics
• Design guidance for desirable properties

Seal studies
• Glass-metal reaction chemistry
• Hermeticity and cell tests
  • Univ. Cincinnati
  • Univ. Connecticut
  • NexTech, et al.
SOFC Seal Summary

- SOFC seals offer an interesting materials challenge
- 'Invert' polysilicate compositions have promising combinations of properties
  - 'Invert' glass-ceramics can be designed with thermal and chemical properties desired for some SOFC seal designs.
  - Thermo-chemical and thermo-mechanical stabilities are critical for long-term applications.
- Vaporization
- Interfacial reactions

Thank you for your attention!