Alkali-Free Barium Borosilicate Viscous Sealing Glasses for Solid Oxide Fuel Cells

Cheol-Woon (CW) Kim and Joe Szabo

MO-SCI Corporation, Rolla, MO; ckim@mo-sci.com

Richard K. Brow and Jen Hsien Hsu

Department of Materials Science and Engineering and the Graduate Center for Materials Research

Missouri University of Science and Technology, Rolla, MO; brow@mst.edu

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Why Consider a Viscous Glass Seal for an SOFC?

- Potential for lower thermal stresses through viscous relaxation at operational temperatures
  - Less critical that seal has CTE mismatch to dissimilar materials
- Potential for 're-sealing' at operational temperatures through viscous flow
- Potential solution for the flatness and/or parallelism issue of (planar) cells for large scale SOFCs

Objectives

- Develop glass compositions that exhibit stable thermomechanical/ thermochemical properties, including viscosity, for use as seals for SOFCs
  - Requisite Thermal and Physical Properties
    - a) Long-term stability in viscosity (650-850°C)
    - b) T_g: <650°C: thermal stress will be relieved
    - c) T_{soft}: <650°C: requisite flow for re-sealing behavior
    - d) T_{Liq}: <800°C (as low as possible): a small volume fraction of crystals
    - e) CTE(RT-subT_g): 10-12.5×10^{-6}/°C (YSZ-SS441)
- Conduct hermetic sealing tests
- Characterize thermochemical reactions

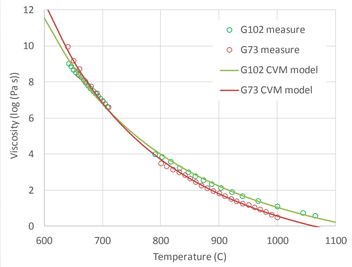
Promising Compositions Were Identified

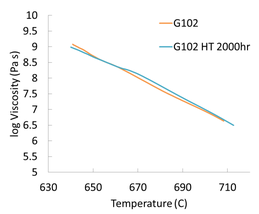
- Preferred compositions exhibit promising sealing behavior

	Phase II			
	Glass 73	**Glass 75**	**Glass 77**	**Glass 102**
Glass system	BaO-RO-Al_2O_3-B_2O_3-SiO_2			
T_g (°C) measured from CTE curve	624	623	625	604
Dilatometric T_s (°C)	640	650	656	639
CTE 40-500°C (/°C)	8.48x10^{-6}	8.17x10^{-6}	9.25x10^{-6}	7.25x10^{-6}
Liquidus T (°C)	800	810	810	Non-Crystallizing

Stable Viscosity

- Viscosity measurements provide valuable performance information

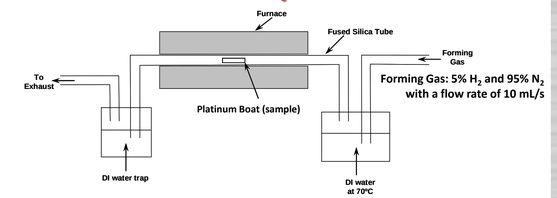




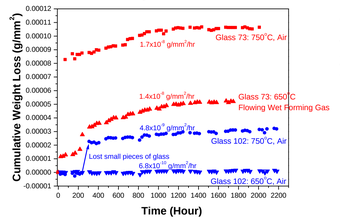
- Stable viscosity of Glass 102 after 2000 hr heat treatment at 800°C

Glass	**CVM Fitting Parameters**			**T_g(°C)**	**Isokom T(°C), log (η) (Pa-s)**				
	m	**T_g(°C)**	**log η∞**	**Dilatometer**	**11**	**9**	**6.6**	**4**	**2**
G73	64.13	606	-3.5	624	621	654	706	788	887
G102	57.18	593	-3.3	604	610	647	706	800	916

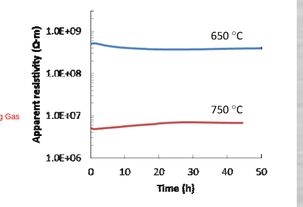
Volatility



Volatility of Glasses

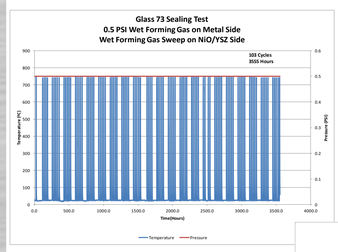


Electrical Resistivity (G102) in Air

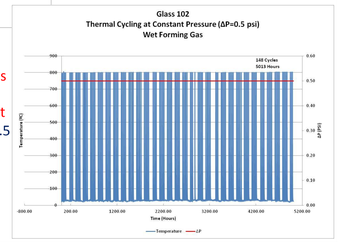


Methods from Chou et al., *International Journal of Hydrogen Energy* 37 (2012) 18372–18380

Hermetic Sealing Tests



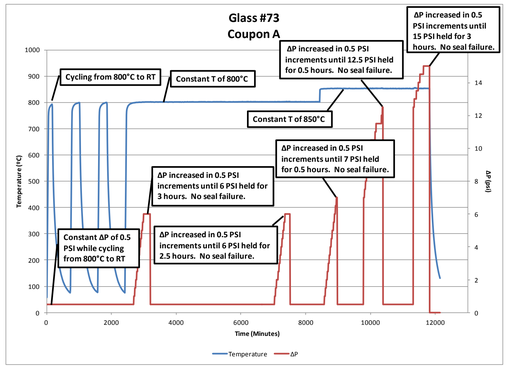
- Glass 73 seal has survived 103 thermal cycles (750°C to RT; cooling rate ~5°C/min, heating rate ~13°C/min) in dry air and wet forming gas at a differential pressure of 0.5 psi (26 torr) over the course of >3,500 hours without failure and the test was deliberately terminated for analysis



- 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

Re-Sealing Tests

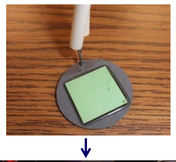
- Tried to break a seal by fast cooling as possible in the furnace, but no seal failure
- Glass 73-Coupon: No seal failure up to 15 psi, 850°C



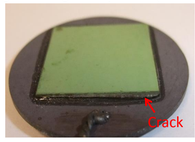
Re-Sealing Tests (ex-situ)

- Glass 73-Coupon: Thermally cracked and healed

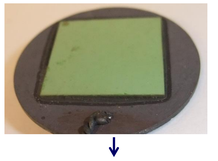
Seal originally found to be hermetic



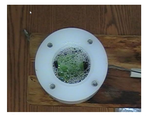
Glass seal deliberately cracked by high cooling rate quench (>25°C/s)



Crack healed after re-healing to 725°C for 2 hrs



Foaming in soapy water

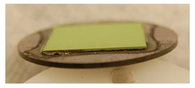


No foaming in soapy water

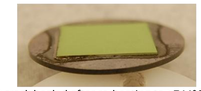
Re-Sealing Tests-cont. (ex-situ)

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

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



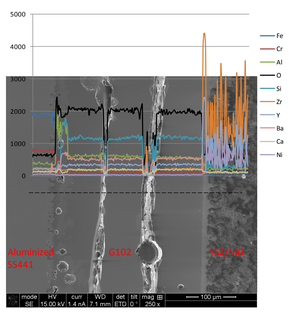
G102 cracked by thermal quenching



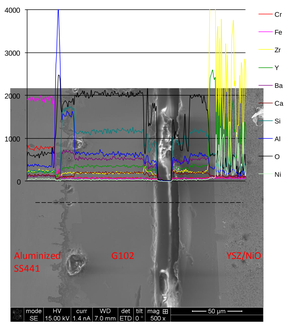
G102 crack healed after re-heating to >744°C for 2 hrs

Long-Term Reactivity Characterization-thermally cycled

- 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
- $BaAl_2Si_2O_8$ layer at glass/metal interface

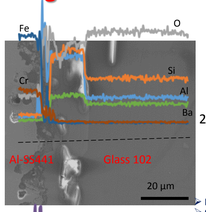


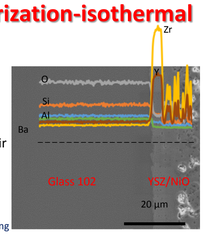
148 Thermal Cycles (>5,000 hrs) in Air



148 Thermal Cycles (>5,000 hrs) in Wet Forming Gas

Long-Term Reactivity Characterization-isothermal





2280 hrs at 800°C in air

- Excellent wetting and bonding
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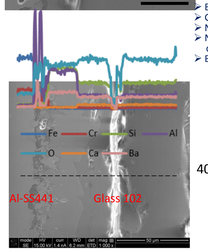
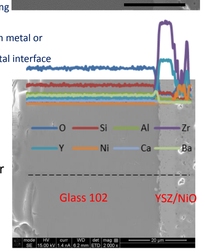
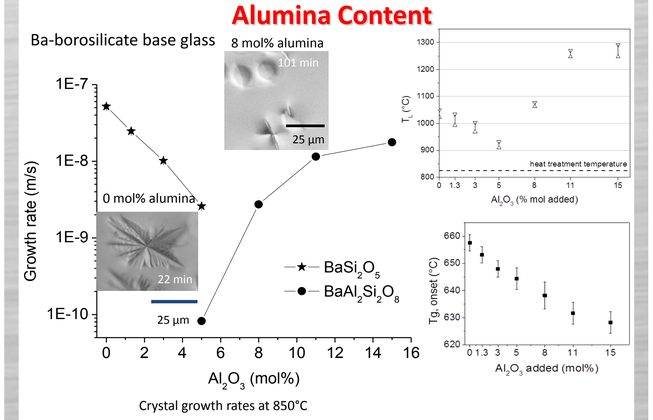
- $BaAl_2Si_2O_8$ layer at glass/metal interface





4000 hrs at 800°C in air

Crystal Growth Kinetics Depend on Alumina Content



Crystal growth rates at 850°C

Summary

- We have developed an alkali-free Ba-borosilicate glass that resists crystallization under SOFC operational conditions
- We have produced hermetic seals with SOFC components
  - survive thermal cycling
  - reseal when thermally shocked
- These glasses can react with aluminized stainless steel and celsian ($BaAl_2Si_2O_8$) will form under SOFC operational conditions

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