Compliant Glass Seal Development at Pacific Northwest National Laboratory

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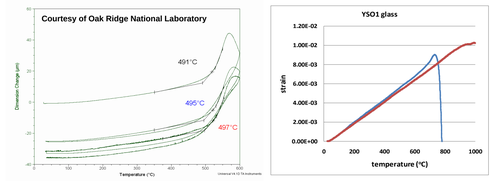
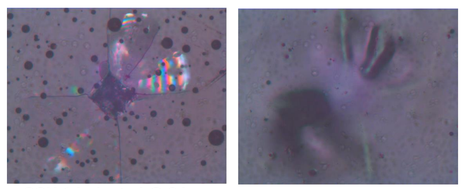
Introduction:

Glass seal is one of the main challenges to advancing SOFC technology, due to stringent requirements in long-term stability of thermal, chemical, mechanical, and electrical property both in bulk and interface. Pacific Northwest National Laboratory has been evaluating a novel compliant glass for potential benefit of low residual stress and self-healing. In previous years alkali-containing silicate compliant glass (SCN-1) showed good thermal cycle stability, chemical compatibility with SOFC parts, and acceptable electrical stability. In FY14 the objectives are:
(A) long-term validation of alkali-containing (17%) compliant silicate glass (SCN-1) with 15% ZrO_2 fibers in stack fixture test
(B) validation of no-alkali containing silicate compliant glass (G102) in stack fixture test

Comparison of compliant and refractory glass



Potential for self-healing of compliant glass



SCN-1 indented @ 2 kg

Fired to 700°C held for 6min

(A) long-term validation of engineered compliant SCN-1 glass in a stack fixture test

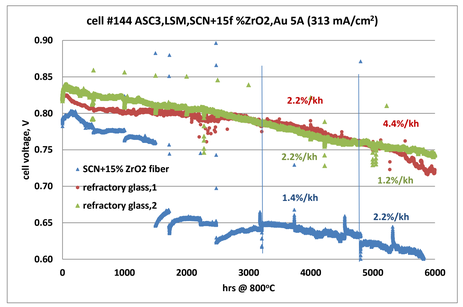
Materials and Processing

1. As-received SCN-1 glass and G102 (MoSci, MO)
2. SCN-1 glass added with 15% ZrO_2 short fibers
3. Ce-(Mn,Co) spinel coating of surface-blasted AISI441
4. Aluminization of as-received AISI441
5. AISI441 interconnect and window frame
6. Glass seal for WF/PEN at 800-850°C/2h
7. LSM20 or LSC20 (FCM) and Ni paste + Ni mesh as contact
8. Final seal at 850°C/2h and tested at 800°C with fuel H_2:N_2=1:1 (3% H_2O) versus air at constant current mode
9. Impedance and IV sweep tests at every 500h
10. Air side heat exchanger made of alumina (99%)
11. Thermal cycling between 800°C and ~50°C at 250°C/h ramp rate.

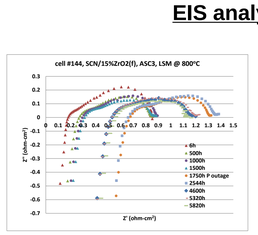
A commercial NiO-YSZ supported YSZ cell (5cm x 5cm) with LSM cathode (16 cm^2) and compressive mica perimeter seal

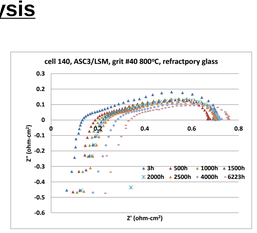
Long-term cell performance

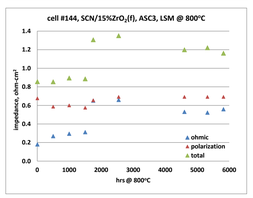
800°C and constant current mode with fuel of H_2:N_2=1:1
One deep thermal cycle per 500h for the first 1500h
Power outage ~1750h where loss of air and compressive loading
Comparable degradation rate to refractory glass (no alkalis)

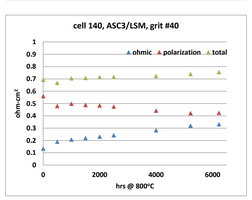


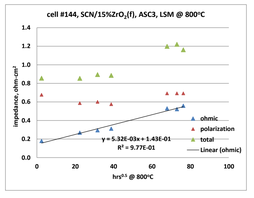
EIS analysis

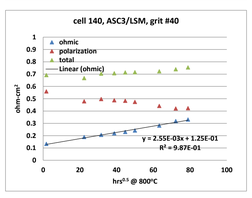


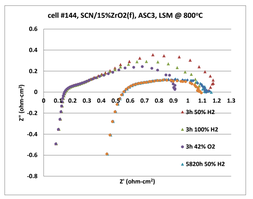




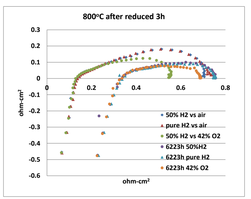






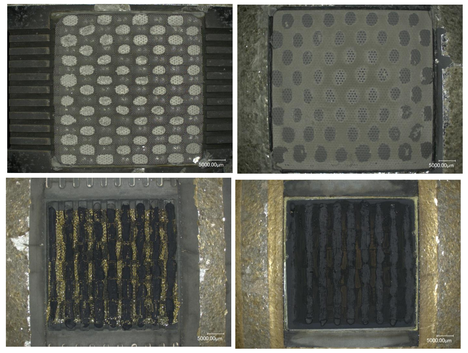


compliant glass



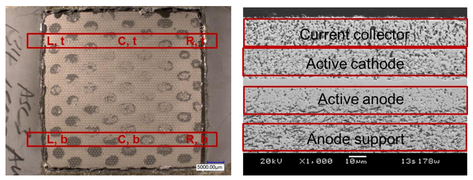
refractory glass

Post-mortem analysis after ~5820h and 3 deep thermal cycles



No discoloration on both cathode and anode, consistent with hermetic check with cross-bubbling and iso-propanol penetration. No substantial glass spreading observed.

Microstructure and interfacial analysis



Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	60.61		0.67	0.31	0.03		18.68	4.80		15.17
#2	67.88		0.36		0.04	0.05	8.81	0.31	0.51	13.49	7.01
#3	46.68					0.03		31.27		22.37	
#4	47.16					0.04		31.04		22.13	

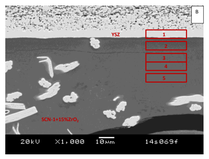
Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	60.60	0.81	0.20	0.03		18.59		4.98		14.96
#2	68.06	0.34			0.33	8.93	0.33	0.28	15.52	6.75
#3	46.01						32.50		21.77	
#4	48.13	0.04					29.54		22.67	

Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	59.48	0.71	0.27	0.02		19.10		4.83		15.44
#2	66.98	0.47		0.04		9.51	0.32	0.82	15.02	7.51
#3	45.03	0.09		0.02	0.01		33.40		21.55	
#4	47.40	0.04			0.01		29.92		22.80	

Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	60.27	0.49	0.24	0.05		18.89		4.65		15.43
#2	67.87	0.17		0.03		9.32	0.31	0.83	15.04	7.12
#3	45.78			0.04	0.05		32.74		21.62	
#4	47.16				0.02		30.84		22.31	

Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	59.51	0.89	0.46	0.04		19.08		4.79		15.40
#2	67.45	0.39		0.01	0.03	9.42	0.29	0.68	15.04	7.19
#3	44.60	0.26			0.02		33.56		21.21	
#4	47.84	0.01			0.02		29.90		22.41	

Area	O	Na	Si	K	Cr	Mn	Ni	Sr	Zr	La
#1	59.69	0.73	0.36	0.02		19.12		4.87		15.39
#2	67.22	0.45			0.16	9.41	0.34	0.69	15.39	7.09
#3	45.34				0.04		33.46		21.44	
#4	47.56	0.04			0.02		30.18		22.57	

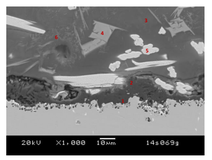


from figure 6A

Area	O	Mg	Al	Si	K	Ca	Ni	Zr	Ba
#1	71.33						0.80	27.87	
#2	66.35	0.53	1.67	27.82	1.59	0.35	0.11	0.85	0.71
#3	65.32	0.69	1.82	29.24	1.56	0.40	0.09		0.88
#4	66.71	0.72	1.71	27.97	1.48	1.41	0.07		0.94
#5	65.29	0.68	1.73	28.07	1.53	1.73	0.06		0.90

from figure 6B

Area	O	Mg	Al	Si	K	Ca	Ni	Zr	Ba
#1	71.01						1.25	27.74	
#2	66.18	0.51	1.81	29.52	1.39		0.10		0.98
#3	65.75	0.72	1.78	28.88	1.17	0.90	0.08		0.98
#4	65.66	0.77	1.77	28.21	1.13	1.52	0.06		0.79
#5	65.74	0.81	1.74	28.12	1.06	1.70			0.83



from figure 7A

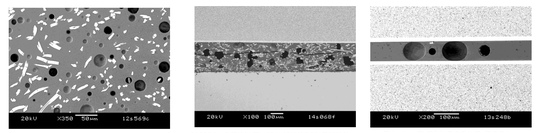
Spot	O	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Zr	Ag	Ba
#1	61.84		36.2	0.35			0.08	0.26	0.84			0.43	
#2	60.69		36.90	1.21		0.28		0.08	0.19		0.40	0.23	
#3	65.17	0.77	1.92	29.1	2.04	0.22	0.22		0.06			0.31	
#4	62.43		0.27	20.9	0.38	10.6						5.33	
#5	70.19									0.25	29.61		

from figure 7B

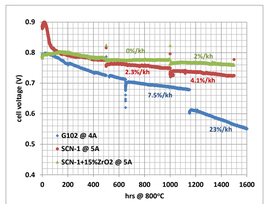
Spot	O	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Zr	Ag	Ba
#1	61.89		37	0.24			0.12	0.50		0.23		0.46	
#2	63.20	0.46	25.2	8.01		0.51	0.85	0.14	1.17	0.14		0.21	
#3	64.11	1.02	1.79	29.3	1.42	1.26							1.18
#4	65.71			20.30	0.13	12.02							1.84
#5	69.80										29.9		
#6	64.71	1.30	1.90	28.2	1.42	0.72							1.76

glass at YSZ and aluminized AISI441 interface

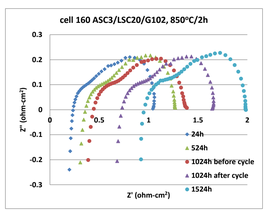
Pore coarsening minimized with fibers



(B) Validation of non-alkali containing Compliant silicate glass G102

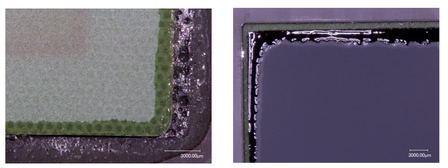


Larger degradation observed for G102 glass than SCN-1 glass



Larger degradation occurred after 2nd thermal cycle at 1024h

Extensive spreading (850°C2h)



Summary and Conclusion

1. **Compliant glass SCN-1 with 15% ZrO_2 fibers was validated in a stack fixture test. It showed good long-term (800°C/5820h) stability and remained hermetic.**
2. **Cell with SCN-1+15% ZrO_2 fibers showed similar degradation (1-2%/1000h) in the last ~3000h over ~6000h test as refractory glass.**
3. **EIS analysis showed the degradation was primarily from increase of ohmic resistance, and showed parabolic.**
4. **Post-mortem EDS/SEM analysis showed minute concentrations (<1%) of Na at cathode side only. K, Cr, and Si were all below detection limit.**
5. **No severe corrosion at YSZ and aluminized AISI441 interfaces.**
6. **Pore coarsening was minimized with inert fibers, and no glass spreading observed, likely due to increased viscosity over time.**
7. **A second compliant silicate without alkalis was also validated in stack fixture test in combined ageing and thermal cycling.**
8. **The cell showed higher degradation as compared to SCN-1 glass. Microstructure analysis remains to be conducted; however, viscosity needs to be tailored from spreading.**

About Pacific Northwest National Laboratory

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The Laboratory employs 4,000 staff members, has a $760 million annual budget, and has been managed by Ohio-based Battelle since 1965.

For more information about the science you see here, please contact:

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