Engineered Glass Seals for SOFCs

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Lara-Curzio et al. 2014 SECA Workshop. July 22, 2014

Acknowledgments

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- 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

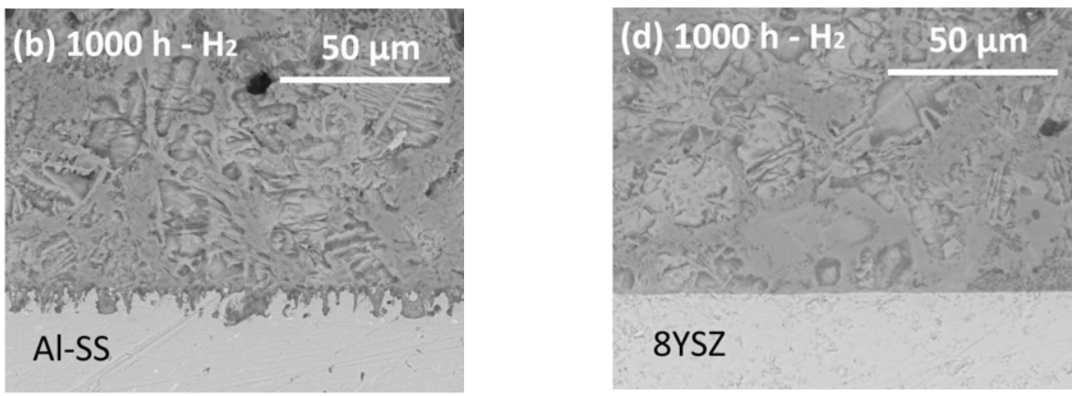
Scott Misture and James Shelby, co-PIs
Mark Naylor, Ph.D. student
Tongan Jin, Postdoctoral researcher

Alfred University
Alfred, NY

Three glasses identified as strong candidates

- All glasses contain Ga_2O_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.

1000 hours under wet H_2



(see publications and compositions in *Int. J. Hydrogen Energy*, 2013)

Viscous Sealing Glasses for Solid Oxide Fuel Cells

Summary for SECA Industry Teams

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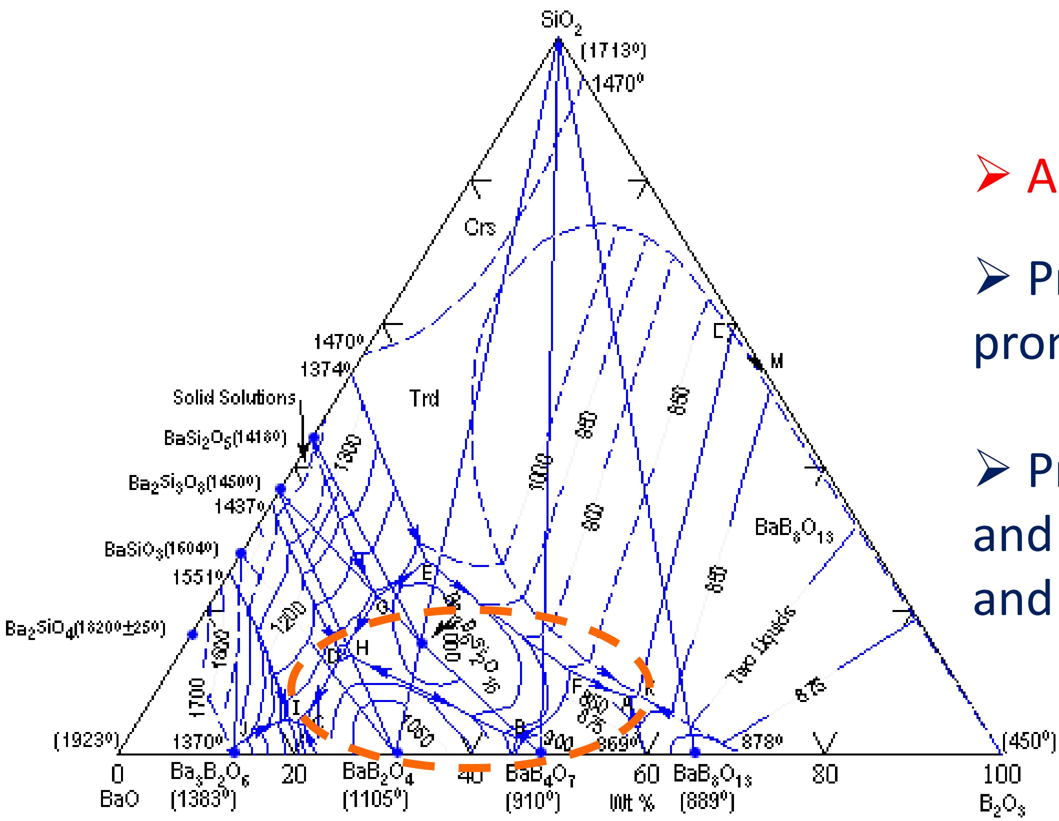
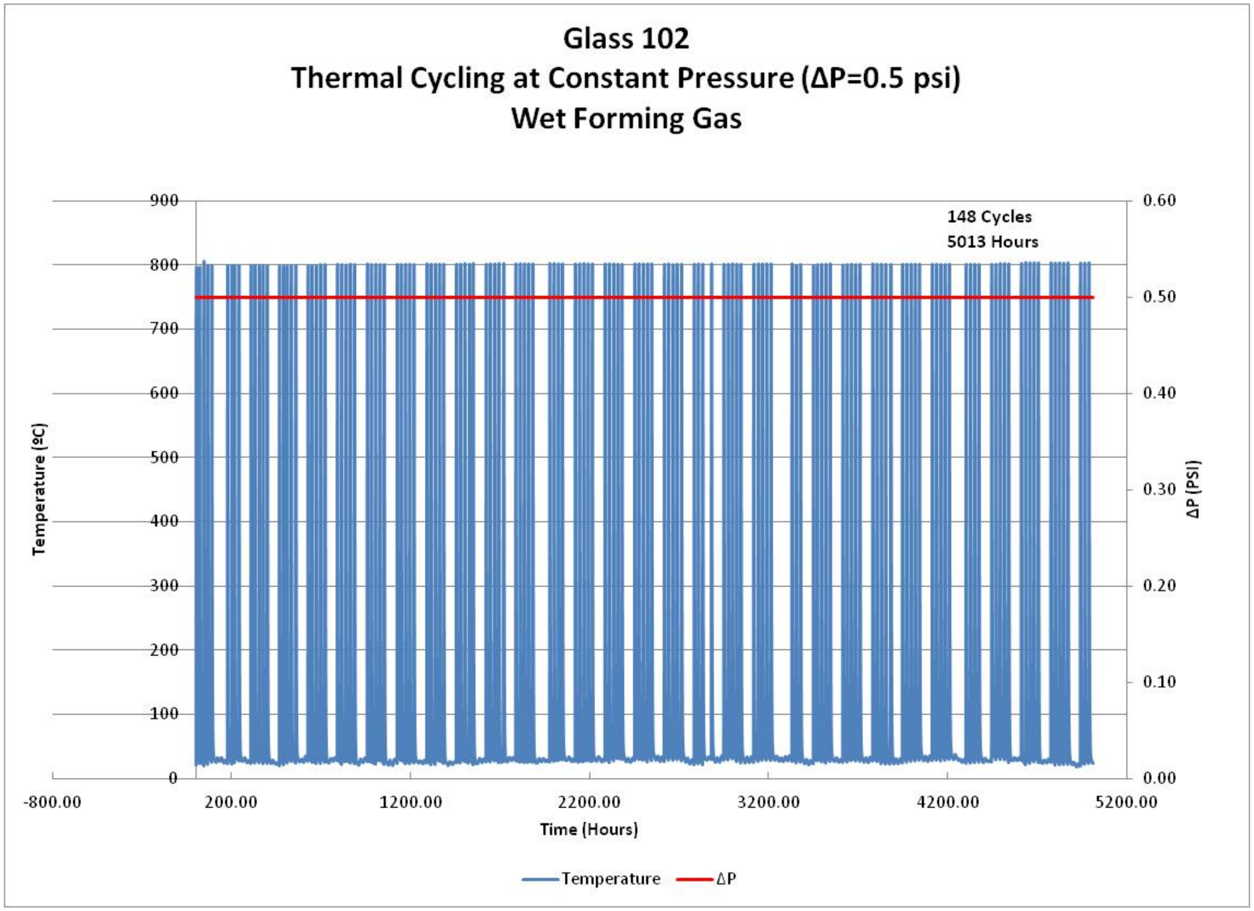
Promising compositions were identified



- 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

	Phase II			
	Glass 73	**Glass 75**	**Glass 77**	**Glass 102**
Glass system	$BaO\text{-}RO\text{-}Al_2O_3\text{-}B_2O_3\text{-}SiO_2$			
T_g (°C) measured from CTE curve	624	623	625	604
Dilatometric T_s (°C)	640	650	656	639
CTE 40-500°C (/°C)	8.48×10^{-6}	8.17×10^{-6}	9.25×10^{-6}	7.25×10^{-6}
Liquidus T (°C)	800	810	810	Non-Crystallizing

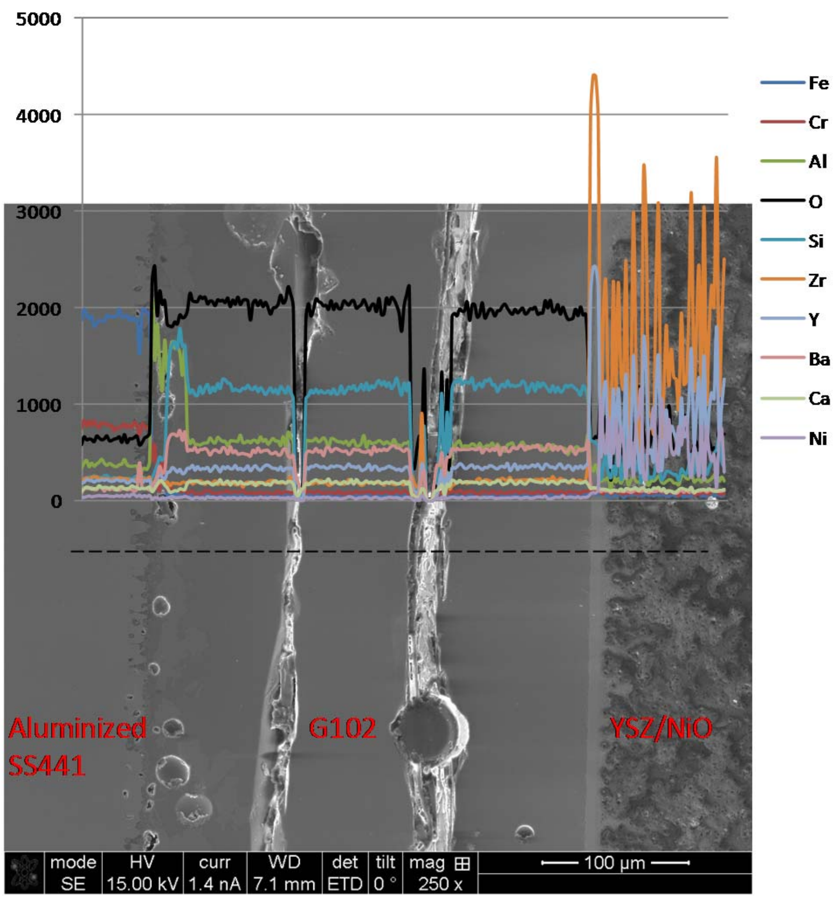
Most promising viscous glass: G102
(alkali-free barium borosilicate)



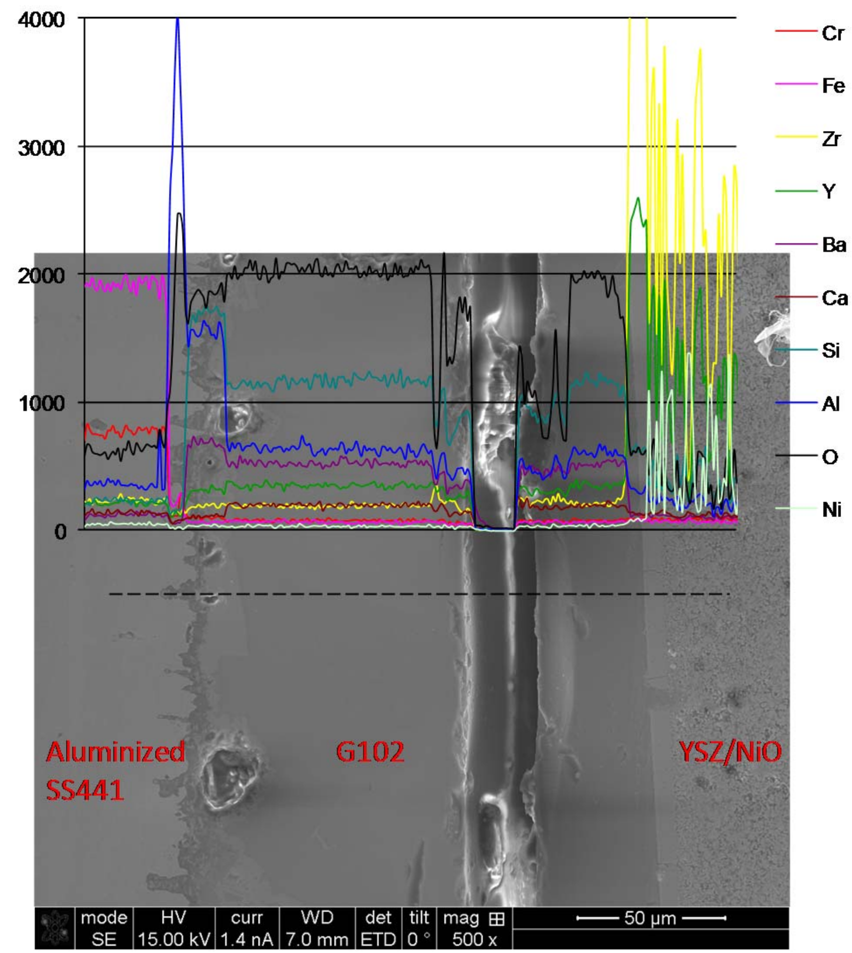
- G102 seal has survived 148 thermal cycles (800°C to RT; cooling rate ~5°C/min, heating rate ~13°C/min) in dry air and wet forming gas at a differential pressure of 0.5 psi (26 torr) over the course of >5,000 hours without failure and the test was deliberately terminated for analysis

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
- $BaAl_2Si_2O_8$ layer at glass/metal interface



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

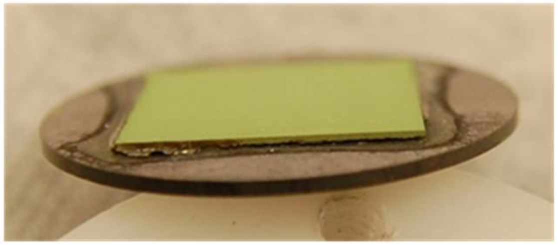


148 Thermal Cycles (>5,000 hrs) in Wet Forming Gas

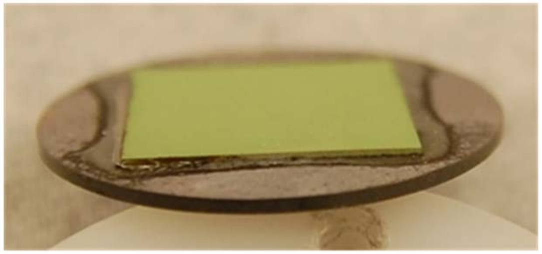
Re-sealing behavior of G102

➢ 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

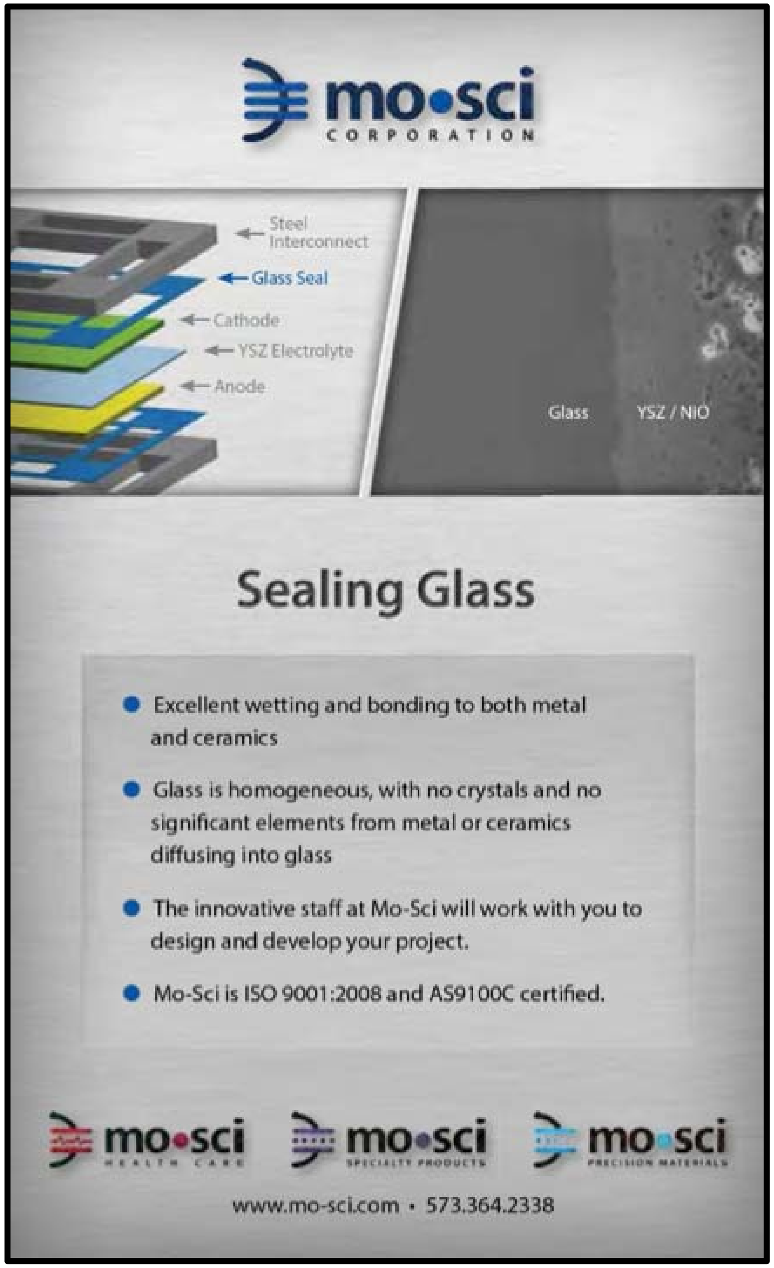


G102 cracked by thermal quenching



G102 crack healed after re-heating to >744°C for 2 hrs mo•sci CORPORATION

MISSOURI S&T University of Science & Technology



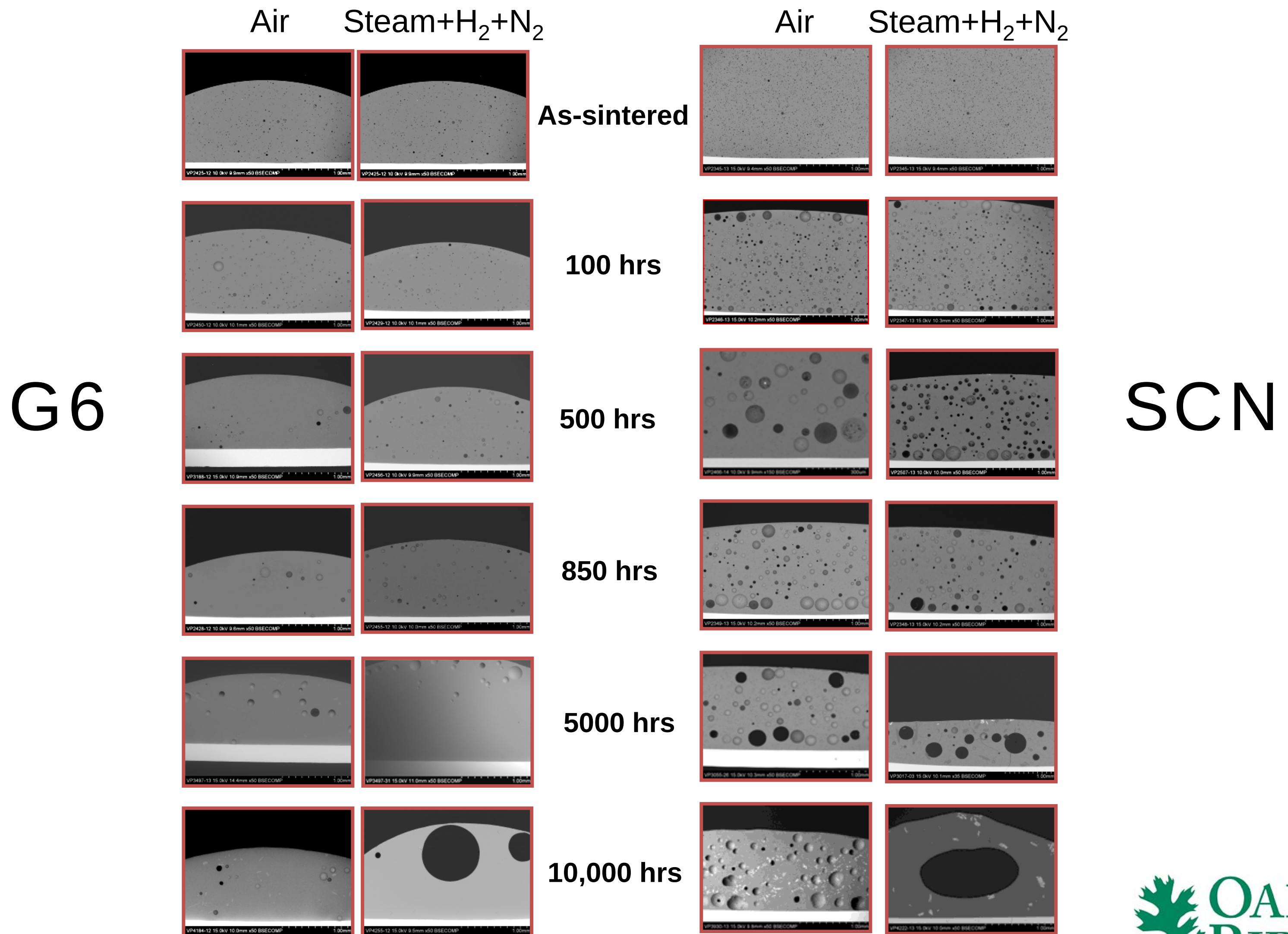
Composition of G6 and SCN Glasses

As sintered

Table I. Chemical Composition of SCN-1 Glass; G6 Glass

	Weight%	
Element	**ICP-MS**	**ICP-AES**
SCN−1		
Si	51.9	54.8
K	15.0	13.4
Ba	14.0	12.9
Na	9.8	8.3
Ca	3.9	5.0
Al	3.4	3.4
Mg	1.2	1.3
Ti	0.5	0.6
B	0.1	0.1
Zn	0.1	0.0
G6		
Si	50.5	53.4
Na	15.5	12.6
Ba	7.7	7.2
B	6.3	6.0
Zn	5.8	5.8
Al	5.2	5.1
Ca	4.1	5.0
K	3.2	3.2
Mg	1.5	1.6
Fe	0.2	0.1

Microstructural Evolution of multicomponent silicate glasses



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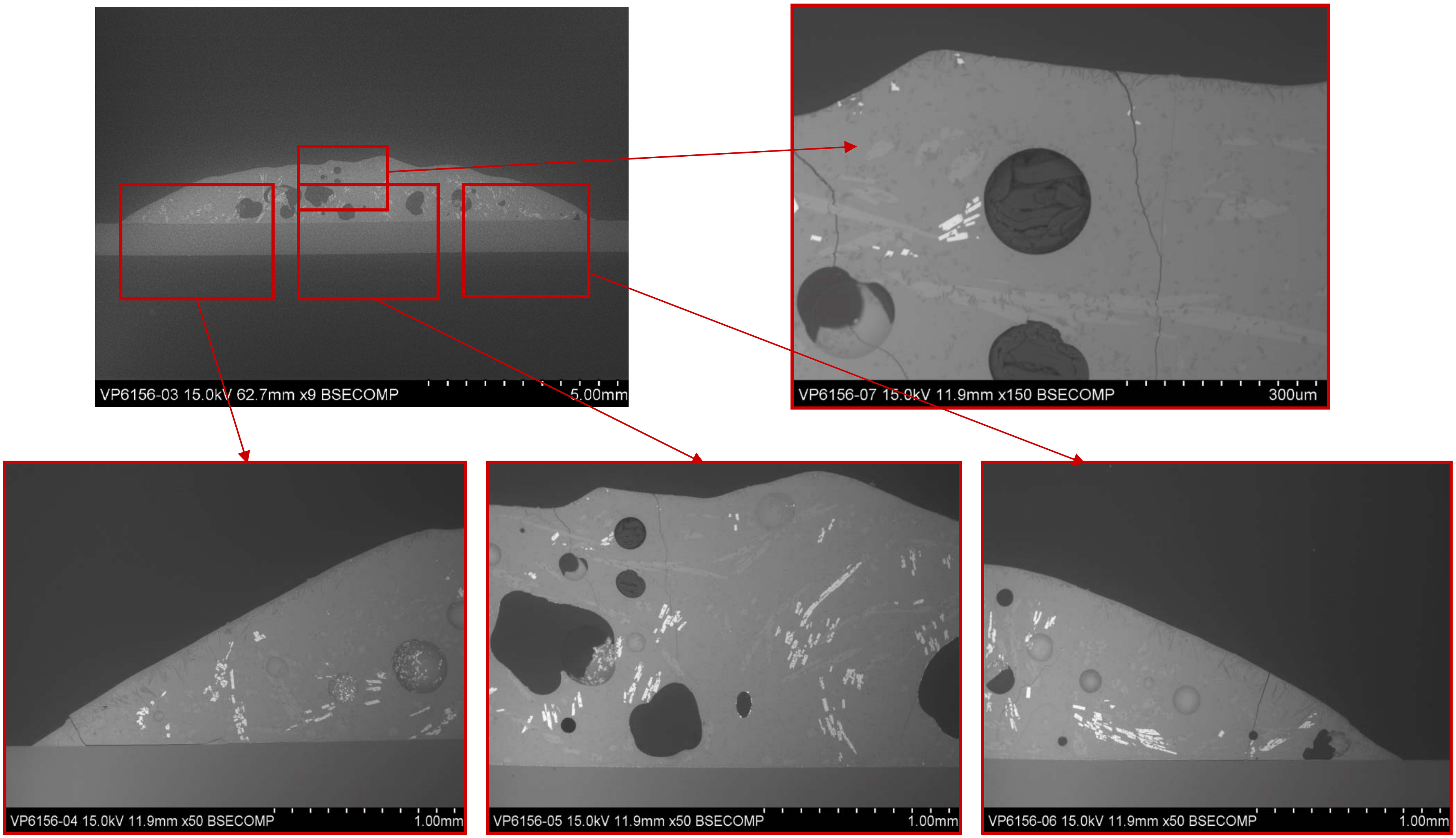
SCN glass on Al_2O_3 Substrate



25,000 hrs in air

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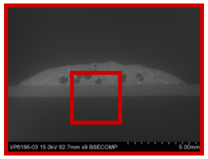

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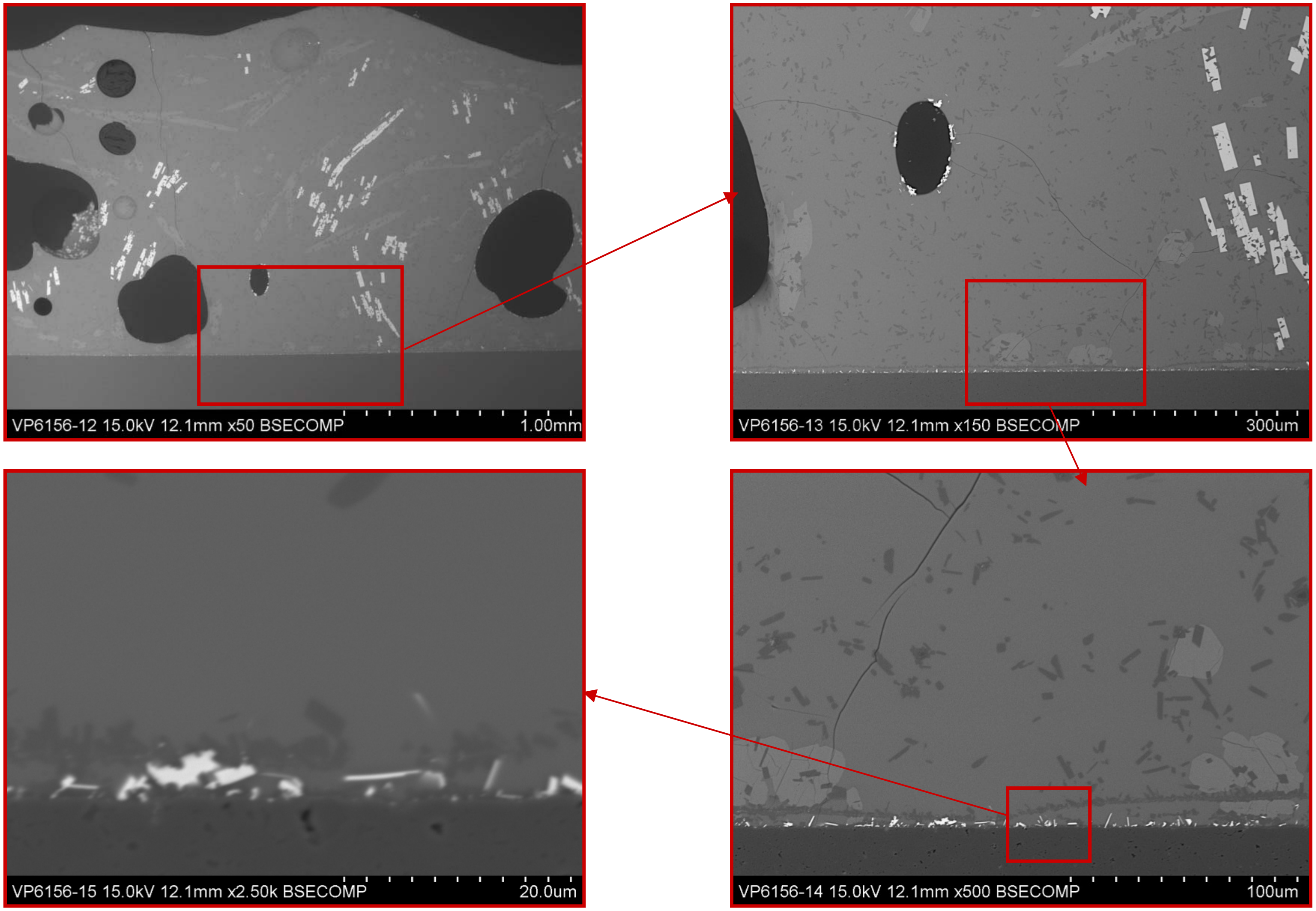

25,000 hrs in air

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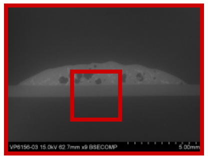
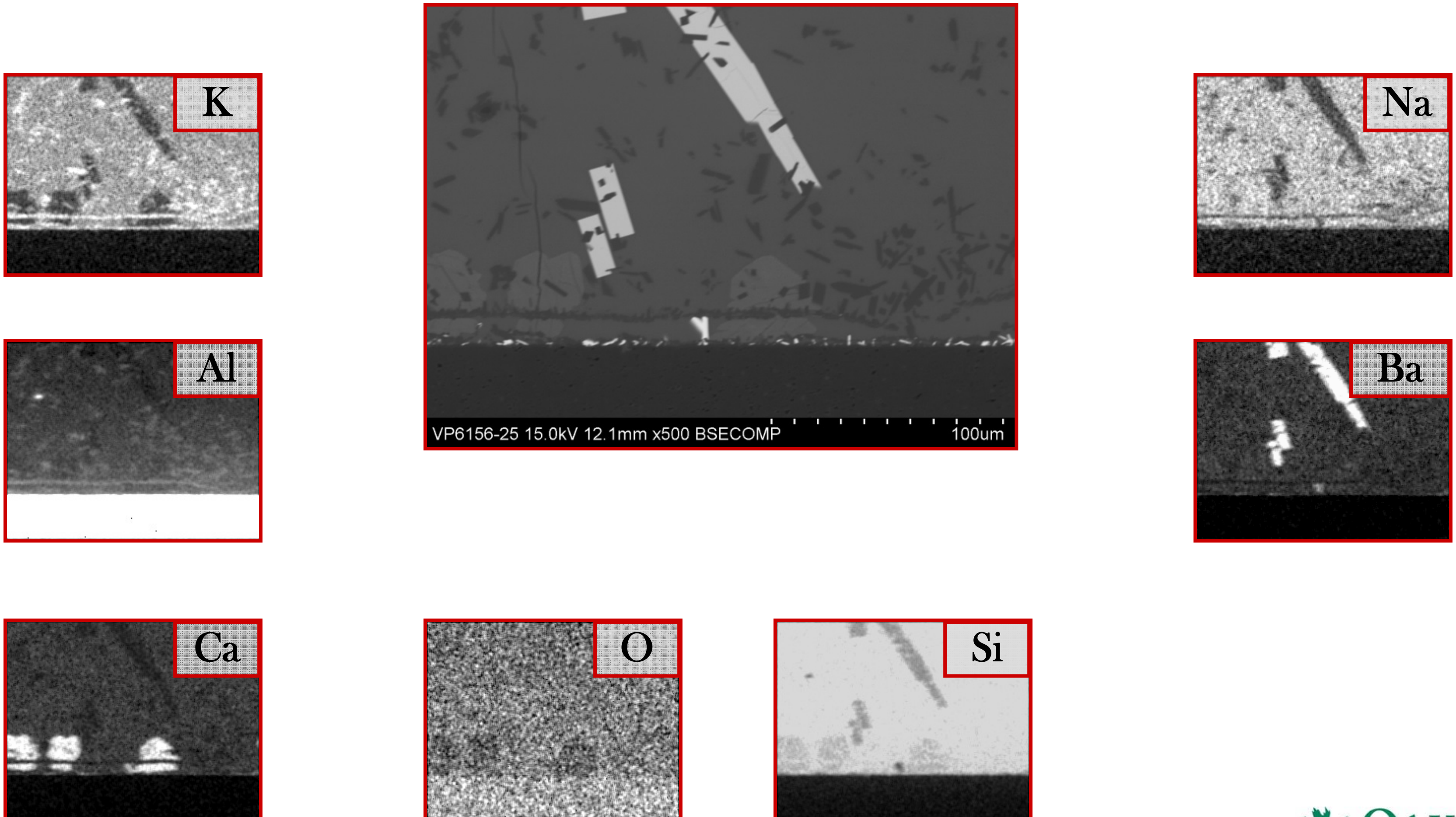


SCN glass on Al_2O_3 Substrate



25,000 hrs in air

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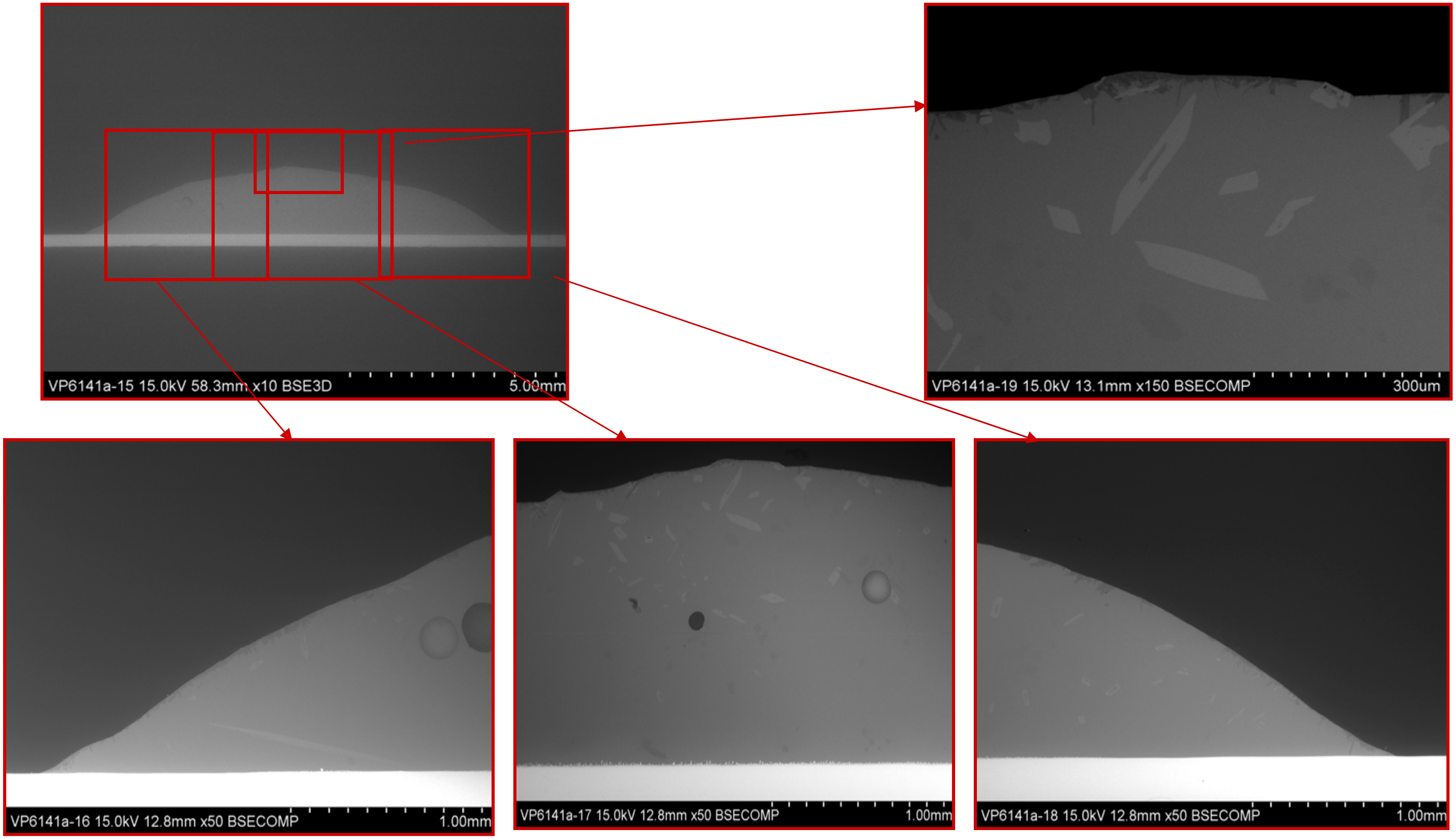
G6-YSZ-68

After 25,000 Hours in Air



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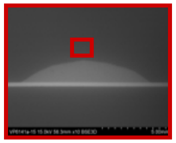
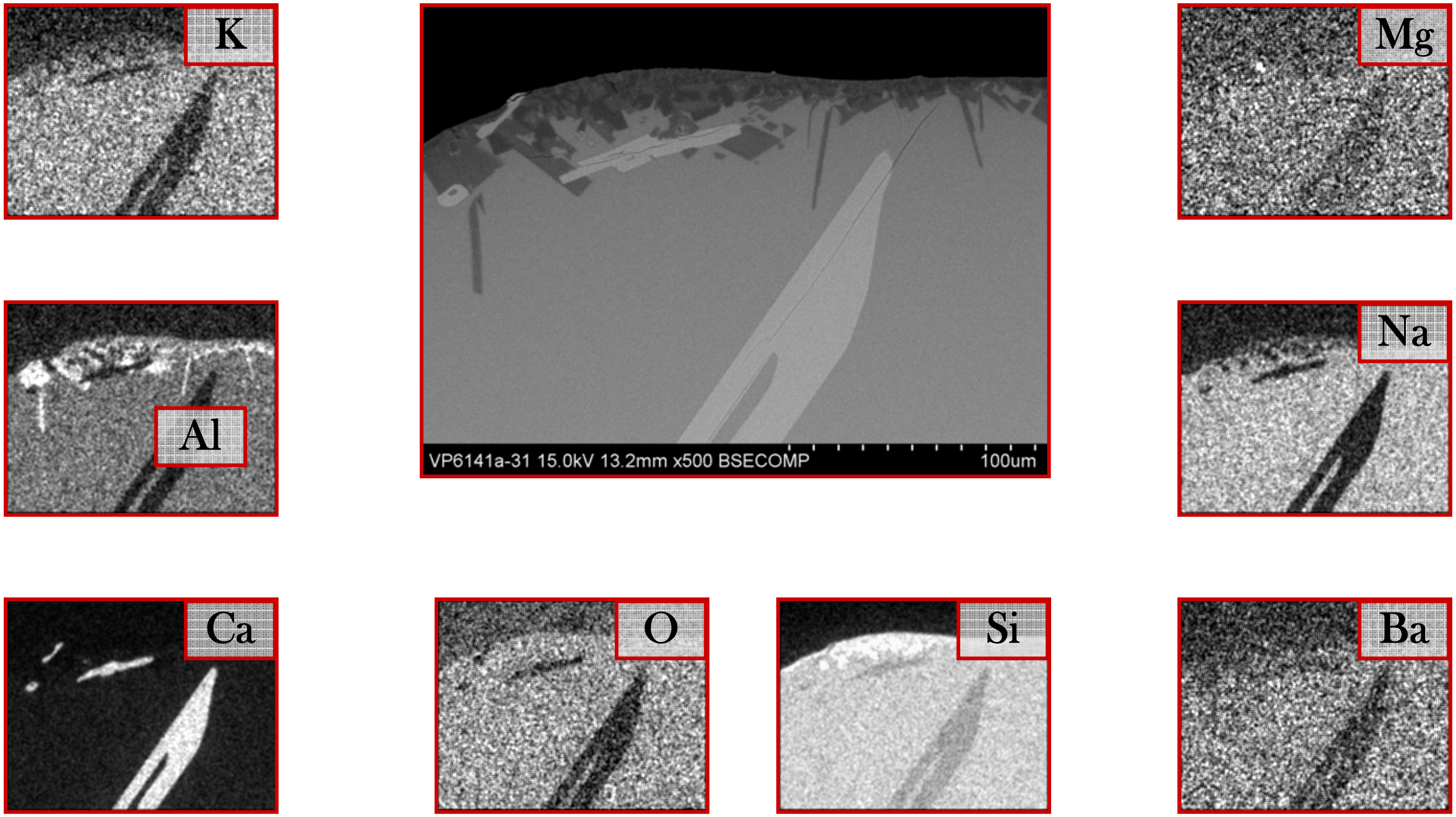


G6-YSZ-68

After 25,000 Hours in Air



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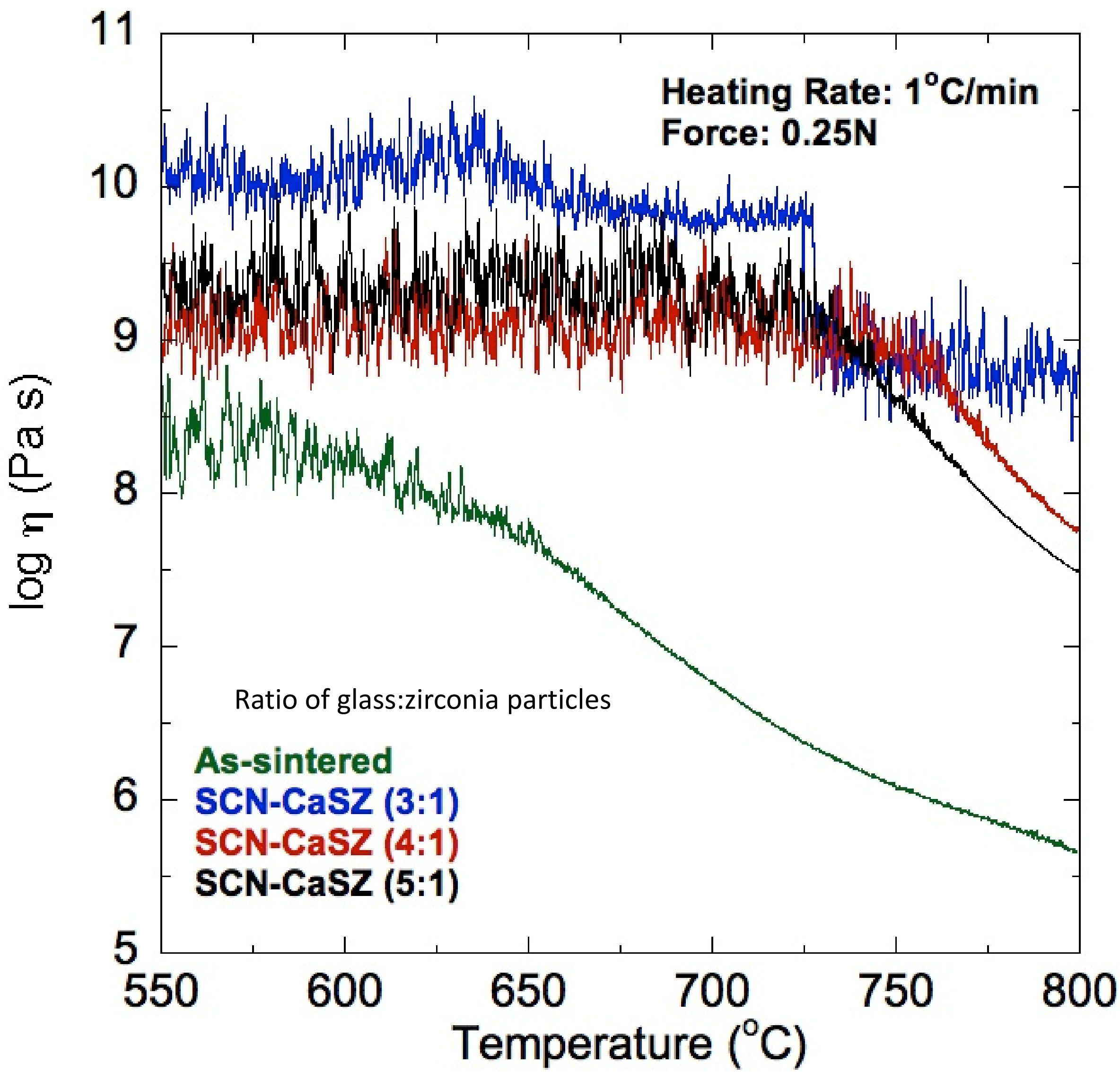
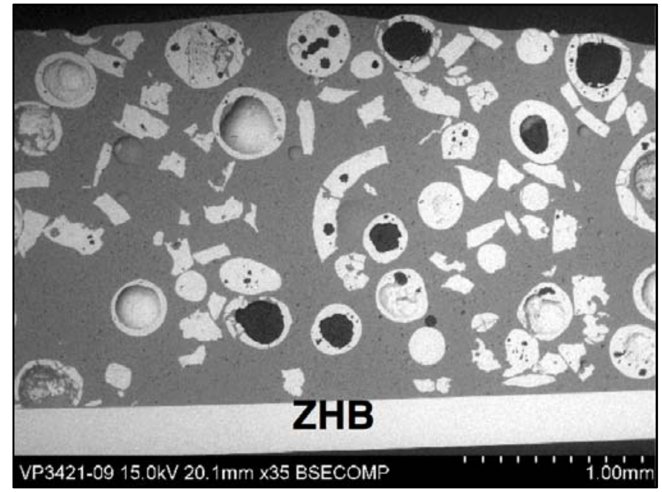
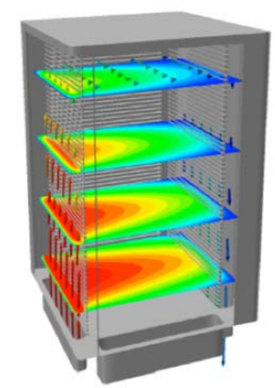
Viscosity of SCN glass containing zirconia hollow spheres





Frangible calcia-stabilized zirconia particles in SCN glass matrix

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



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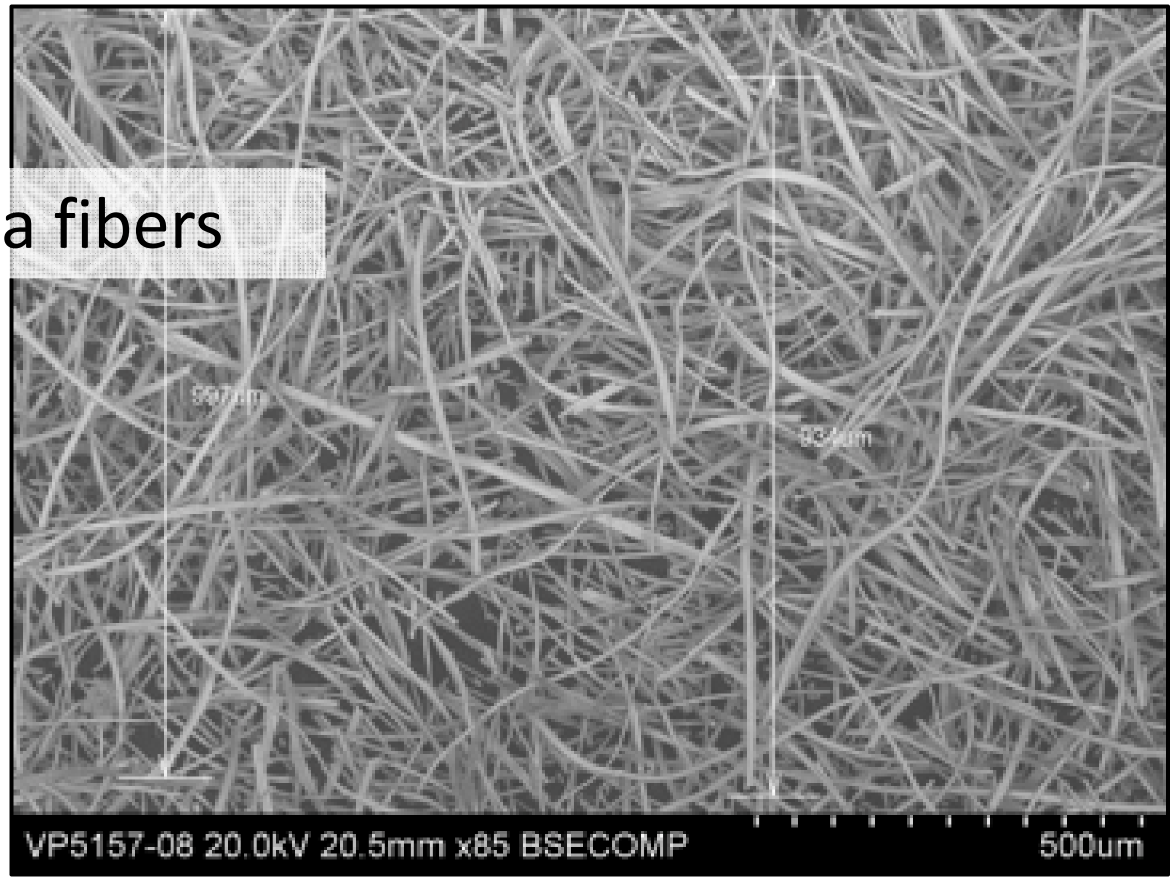
Engineered Glass Seals



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Routes to low-cost manufacturing

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

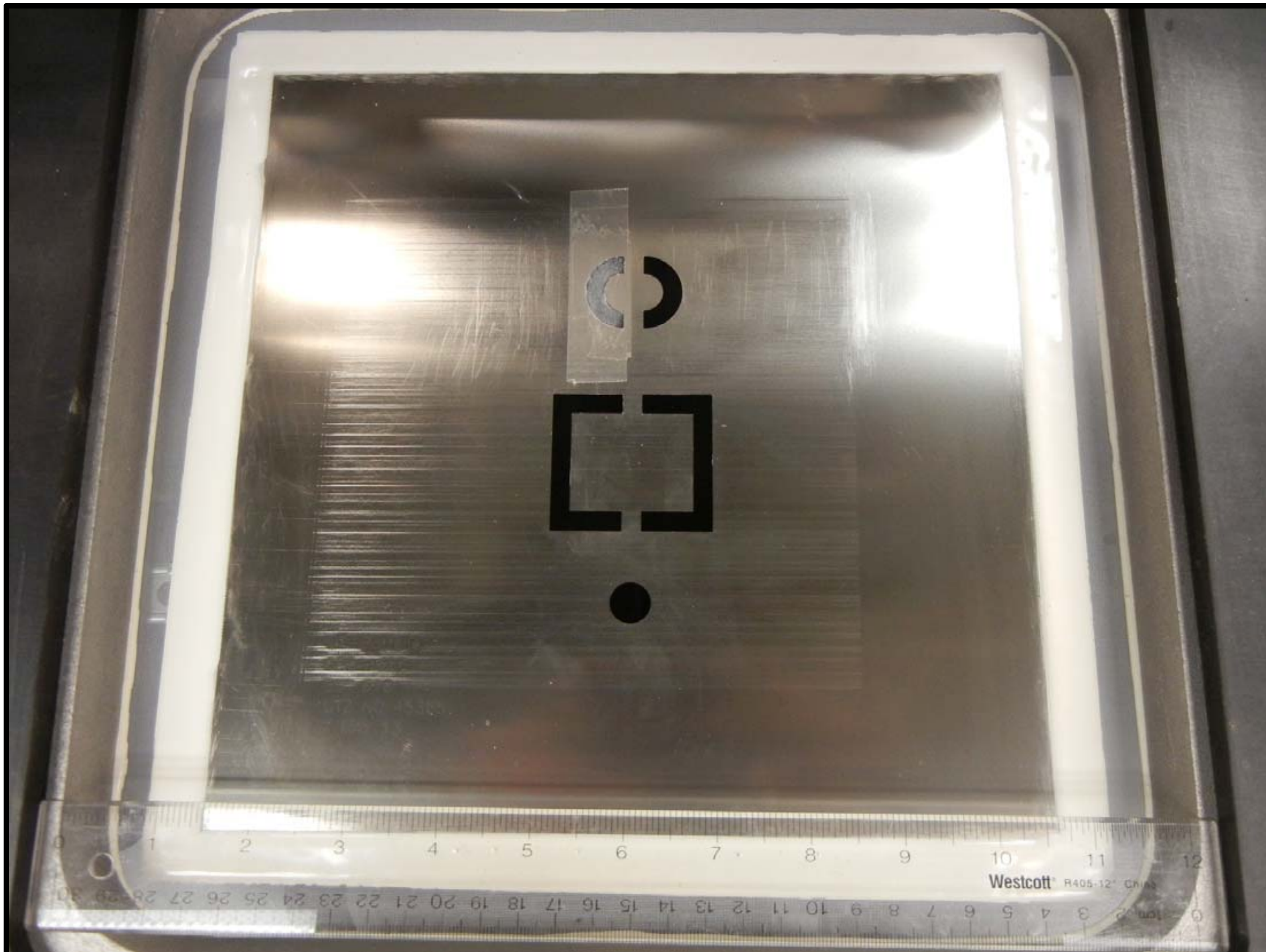
Tape Casting

- SCN glass
- Hollow zirconia spheres
- Organic binder

Routes to low-cost manufacturing

- Tape casting
- Screen printing

Screen-printed engineered glass seals



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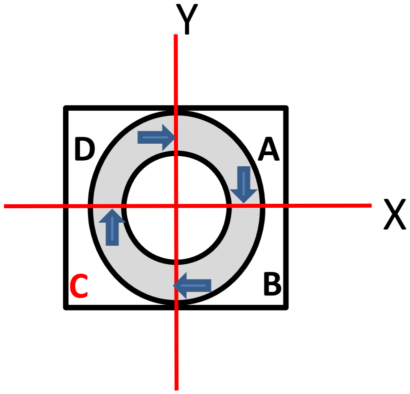
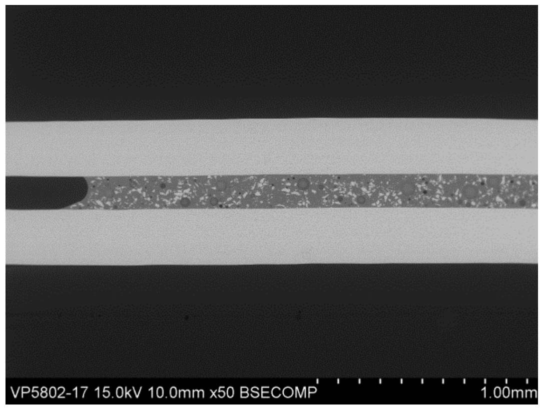
Screen-printed engineered glass seals

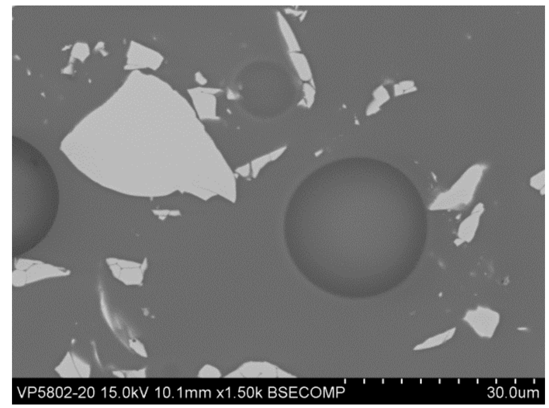
SCN-ZHB-3:1-5:1 (sandwich)



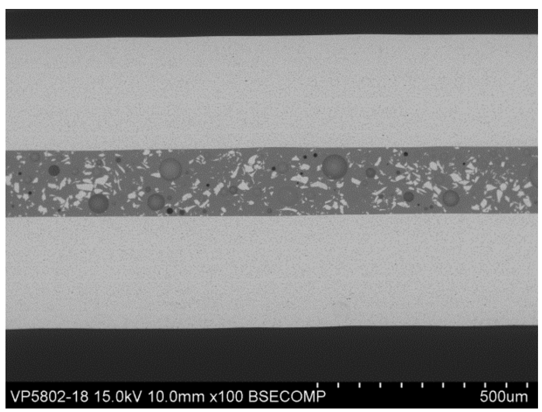
Left Edge



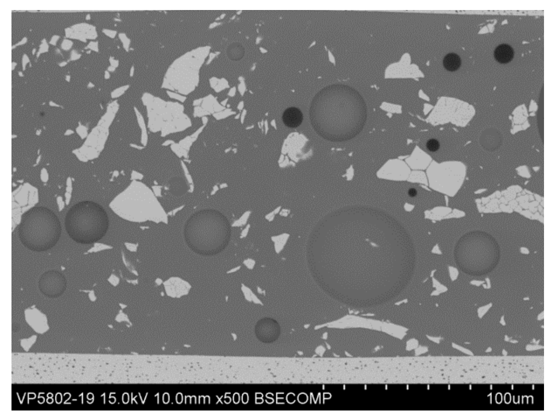
50X



1.5KX



100X



500X

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Routes to low-cost manufacturing

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- Screen printing
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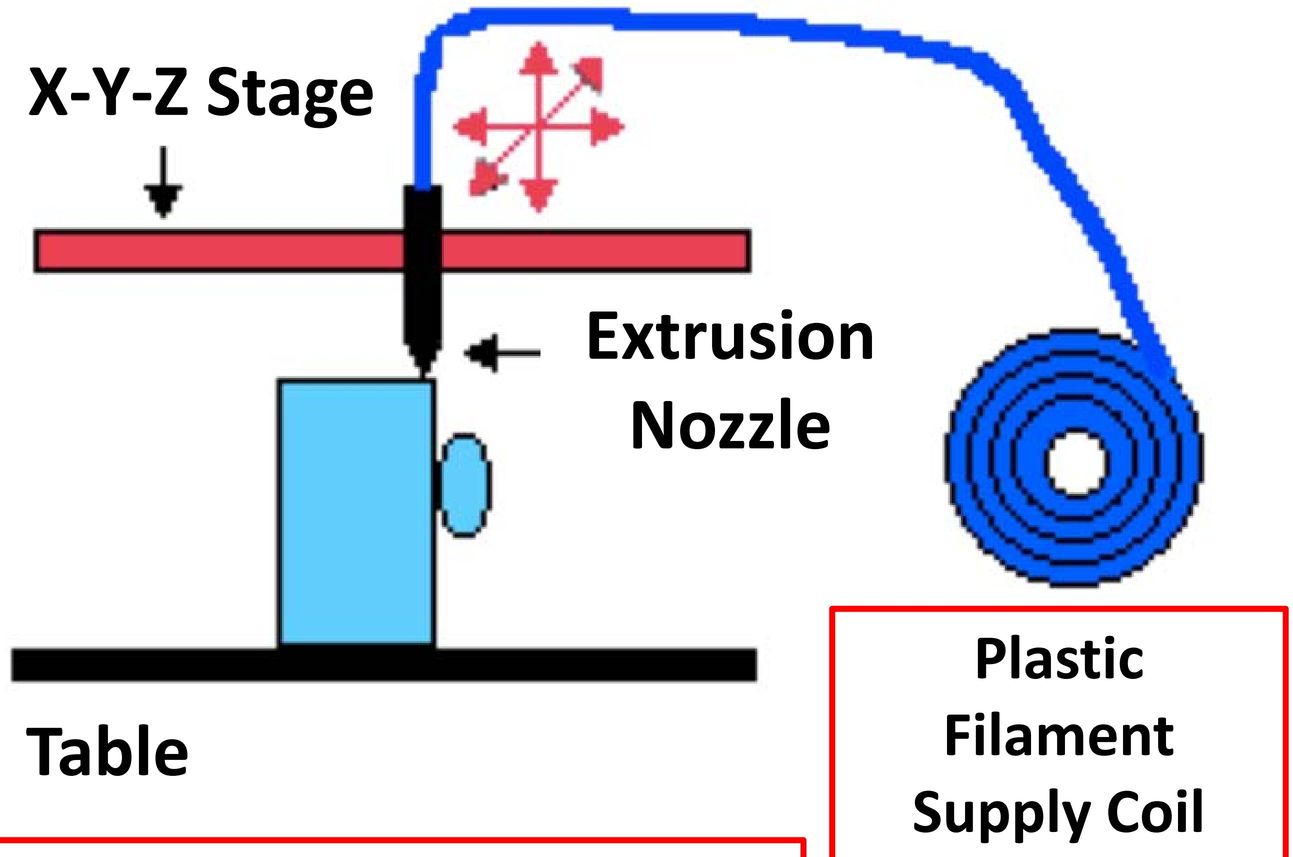
Fused Deposition (3D Printing)



Composite mixture of glass, ceramic 2nd phase and binder

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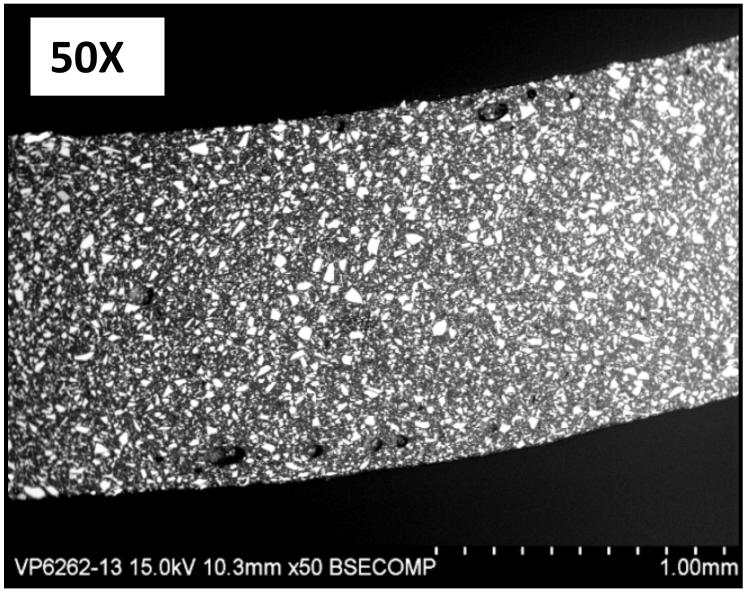
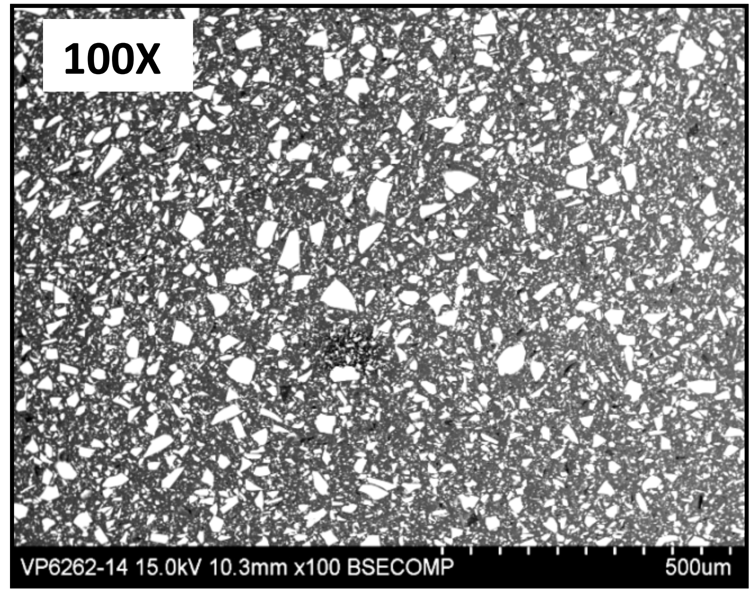
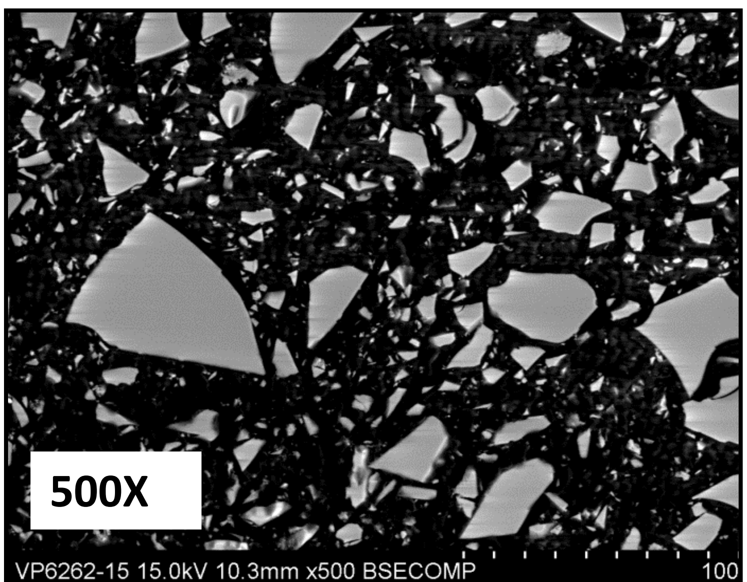
PLA/SCN: 70/30







Extruded Wire

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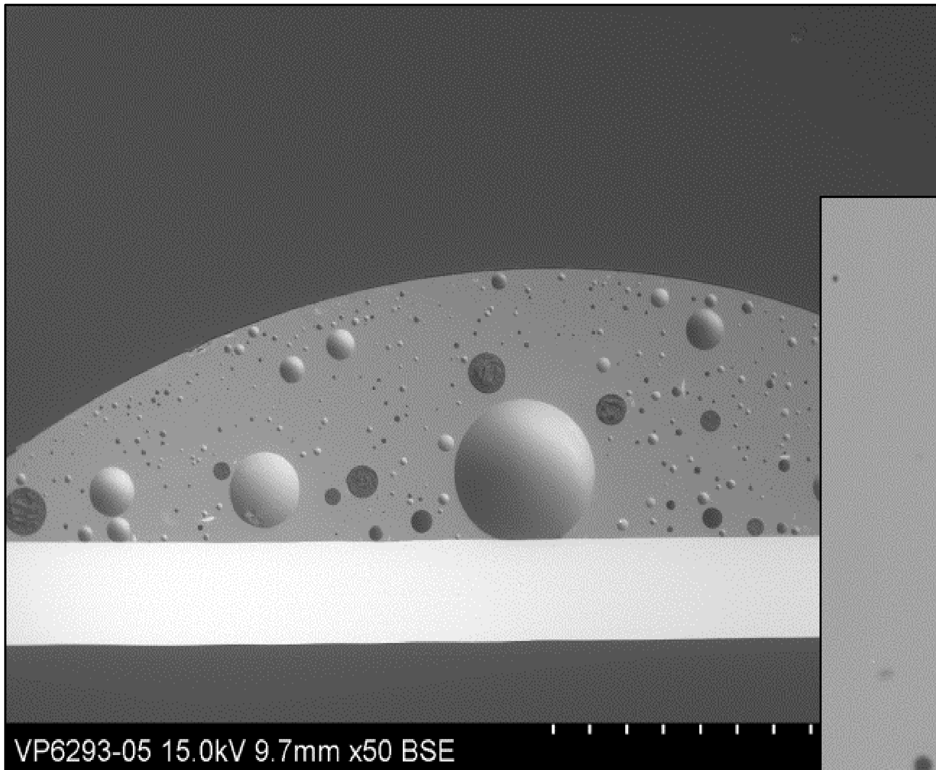
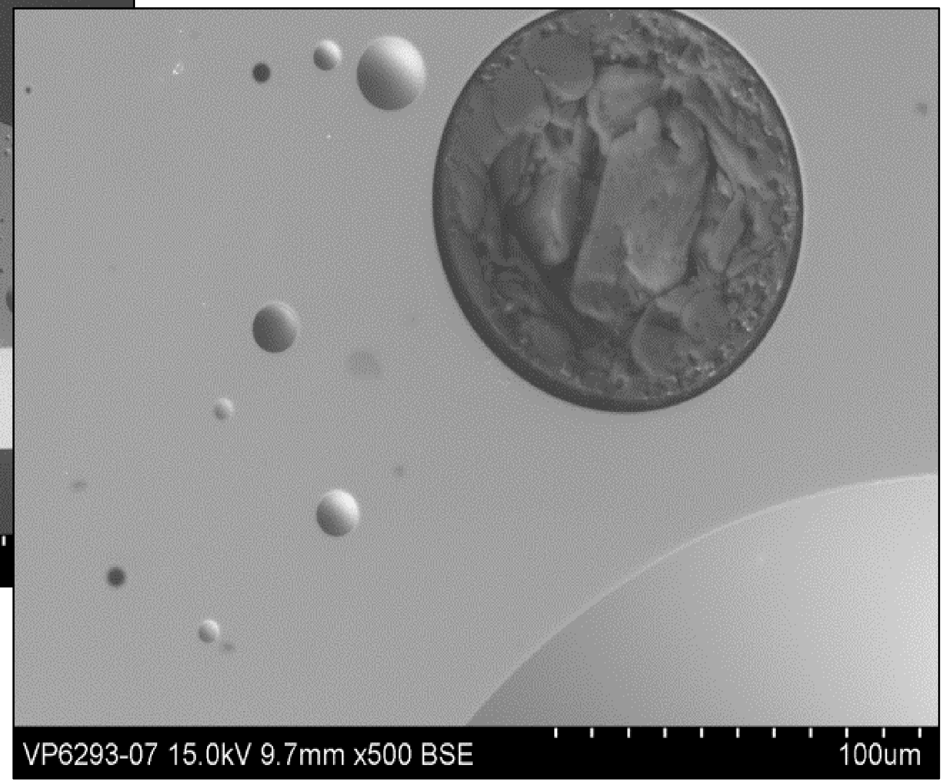
PLA/SCN: 70/30

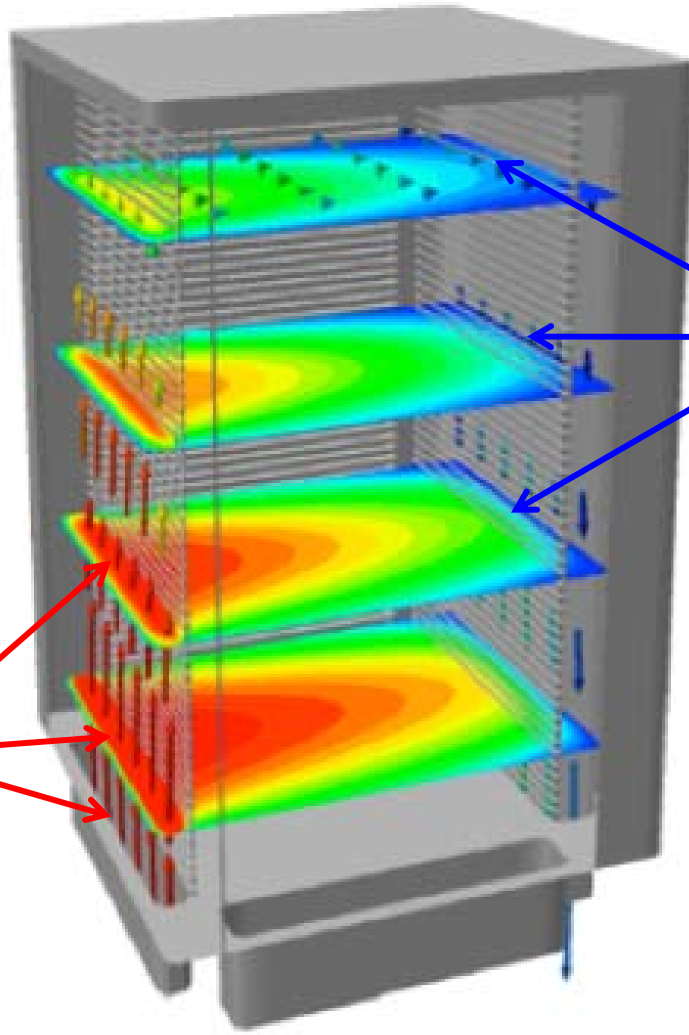


Sintered Wire:



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.



Low viscosity

high viscosity

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