Compliant glass seal development at PNNL

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- Introduction and objectives
- Experimental: materials and test fixture
- Q1: chemical compatibility study with YSZ coating
- Q2: electrical stability under 0.8V loading
- Q3: volatility evaluation in dual environment
- Q4: validation in stack test fixture

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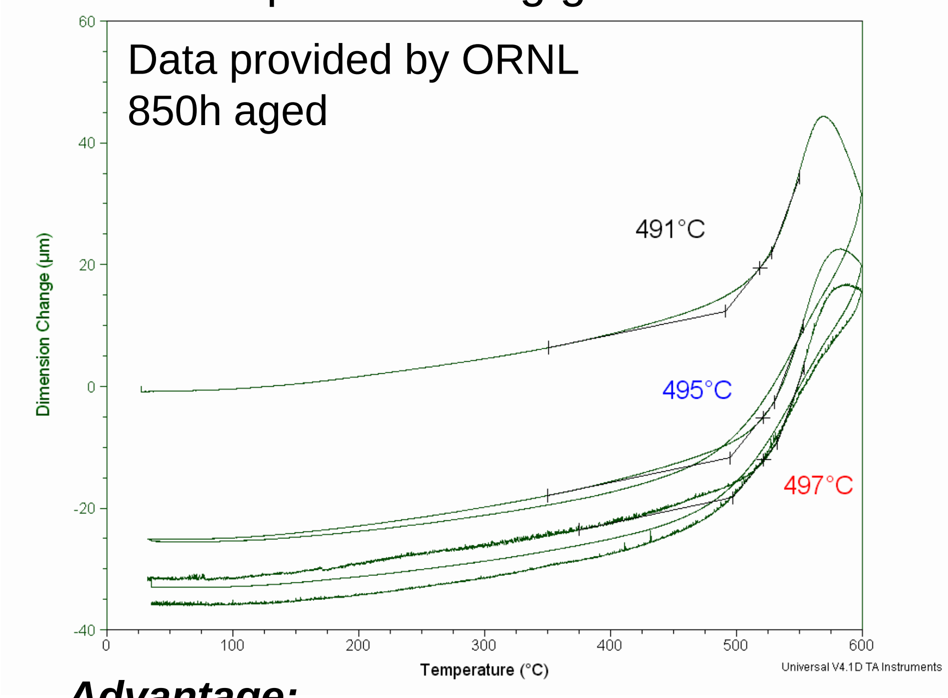
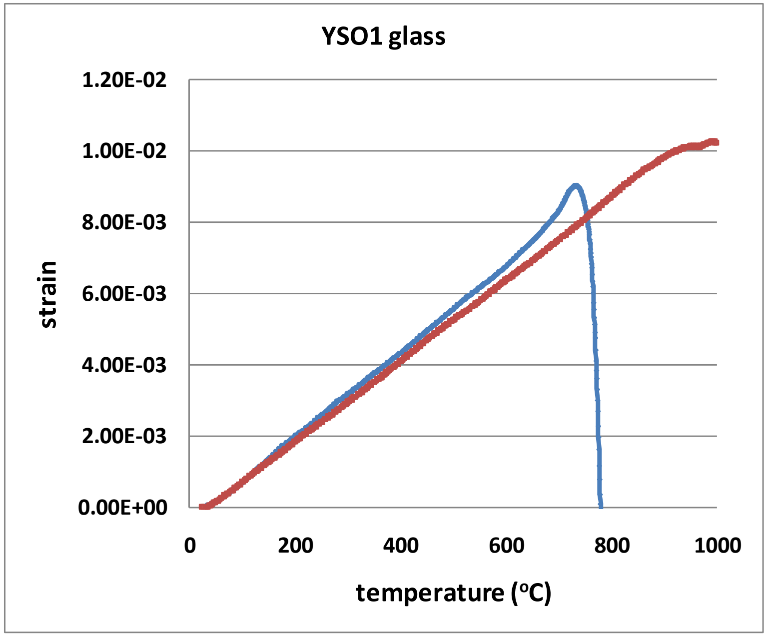
Compliant versus refractory sealing glass

$$\sigma = E \, \Delta\alpha \, \Delta T$$

Compliant sealing glass



Refractory sealing glass



Advantage:

Low stress or relaxation, healing?

Wetting,

Disadvantage:

metal-stable, narrow T window,

volatile, reactive/corrosive?

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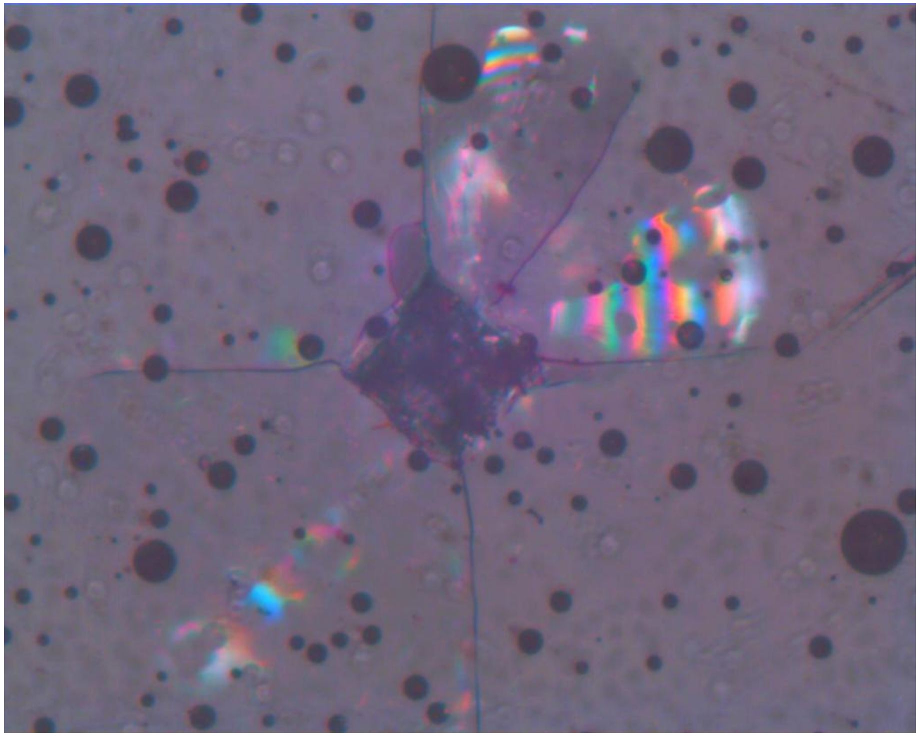
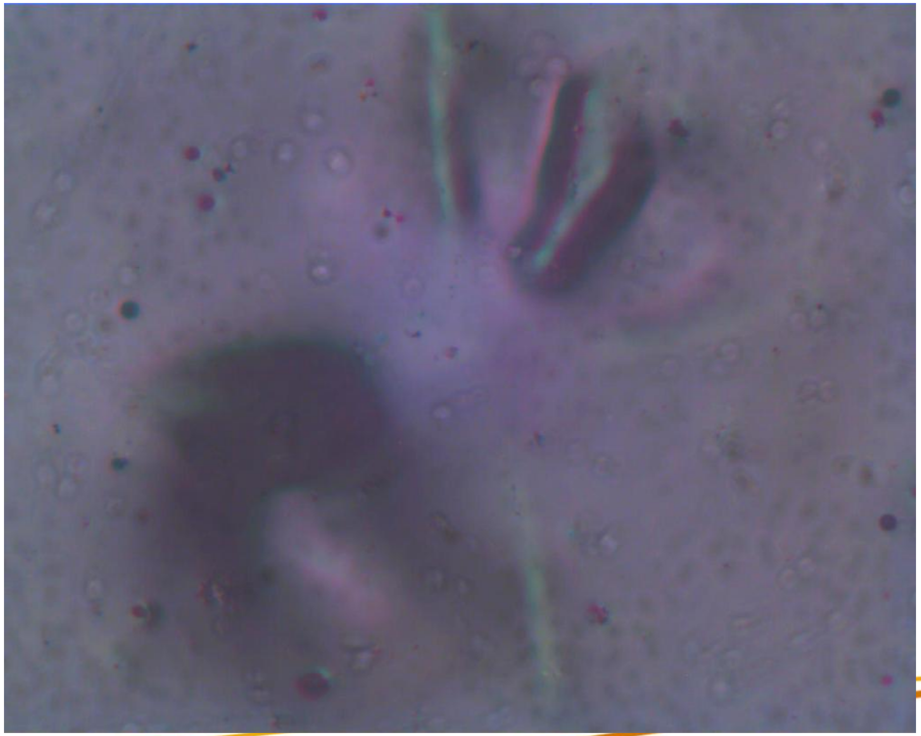
Crack healing

- Commonly observed in glass at elevated temperatures.
- 3 mechanisms proposed: diffusion-driven thermal healing, adhesion from intermolecular forces, and chemical reaction at crack-tip



SCN-1 indented @ 2 kg



Fired to 700ºC held for 6min

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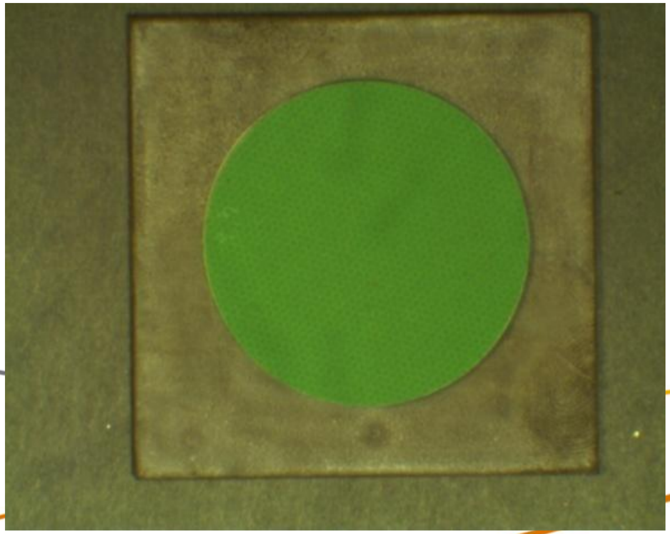
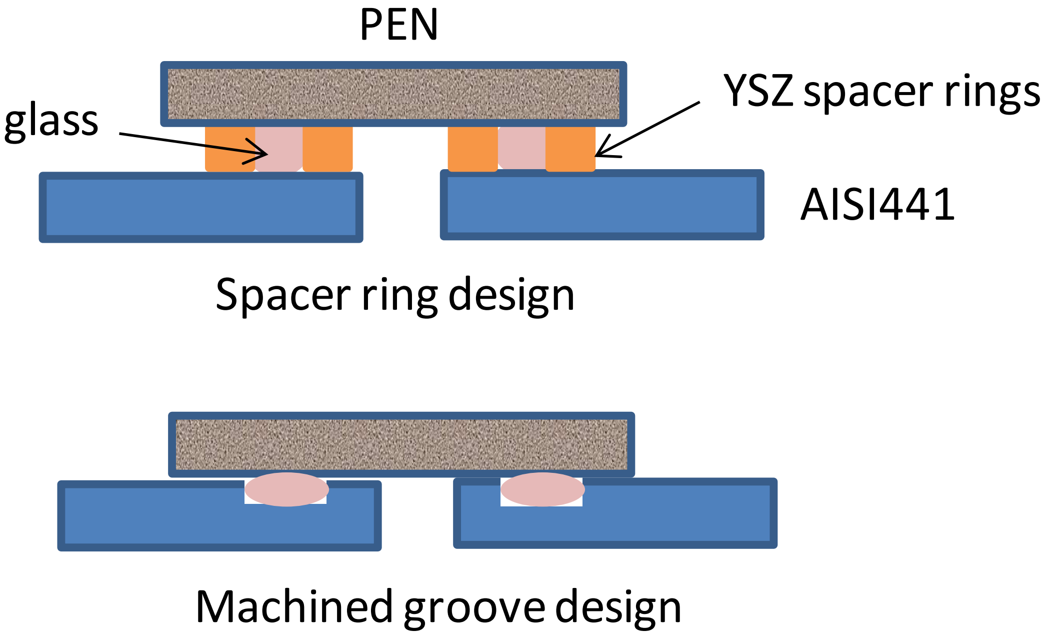
Objectives

- To conduct a comprehensive study of a commercial compliant sealing glass in terms of *thermal, chemical*, *electrical*, physical, and mechanical stability in SOFC environments.
- To apply compliant glass in stack test fixture for validation.

Experimental: sample preparation

1. Thickness of spacer rings ~220 μm
2. SCN-1 glass mixed with ESL450 binder to form paste





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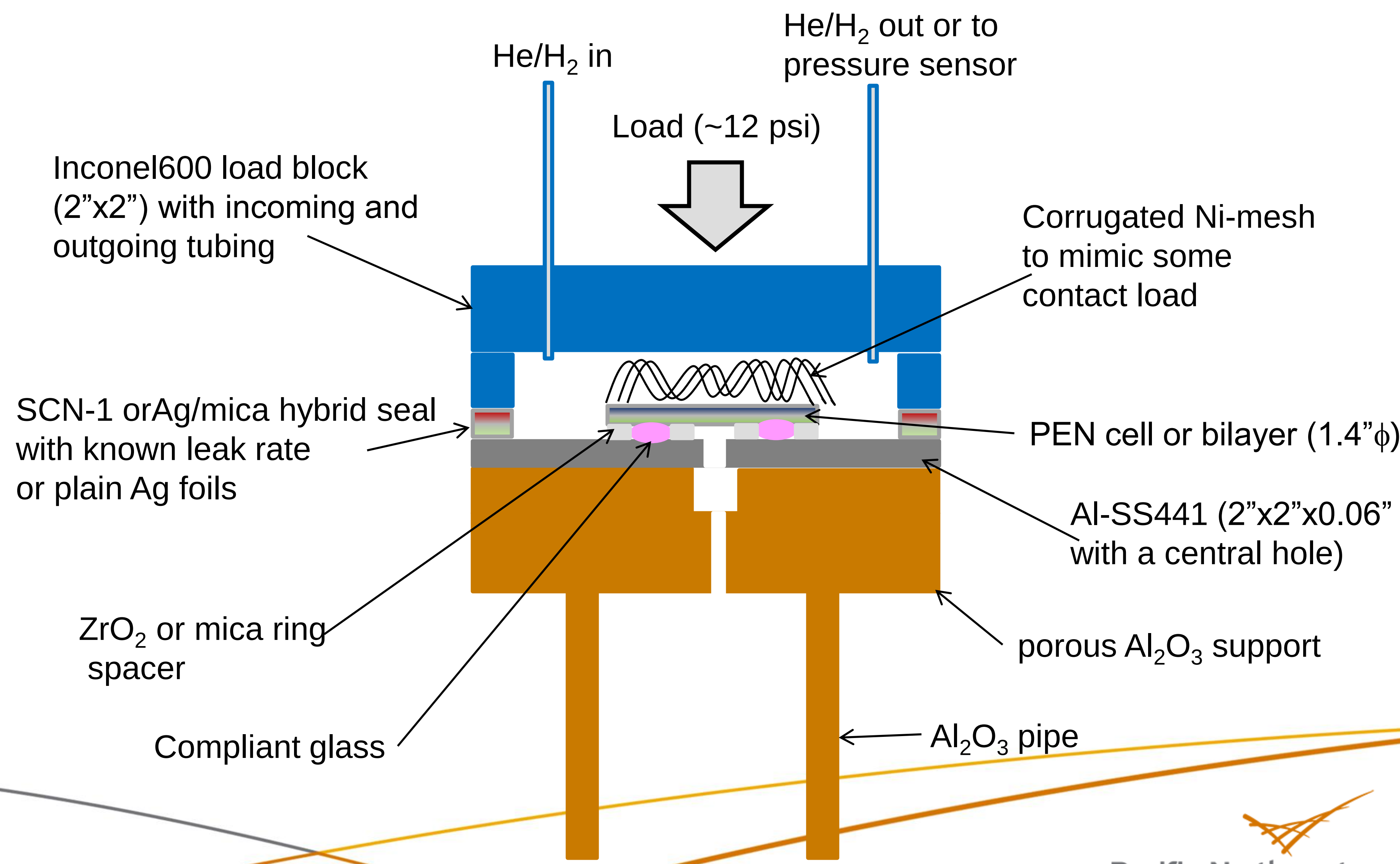
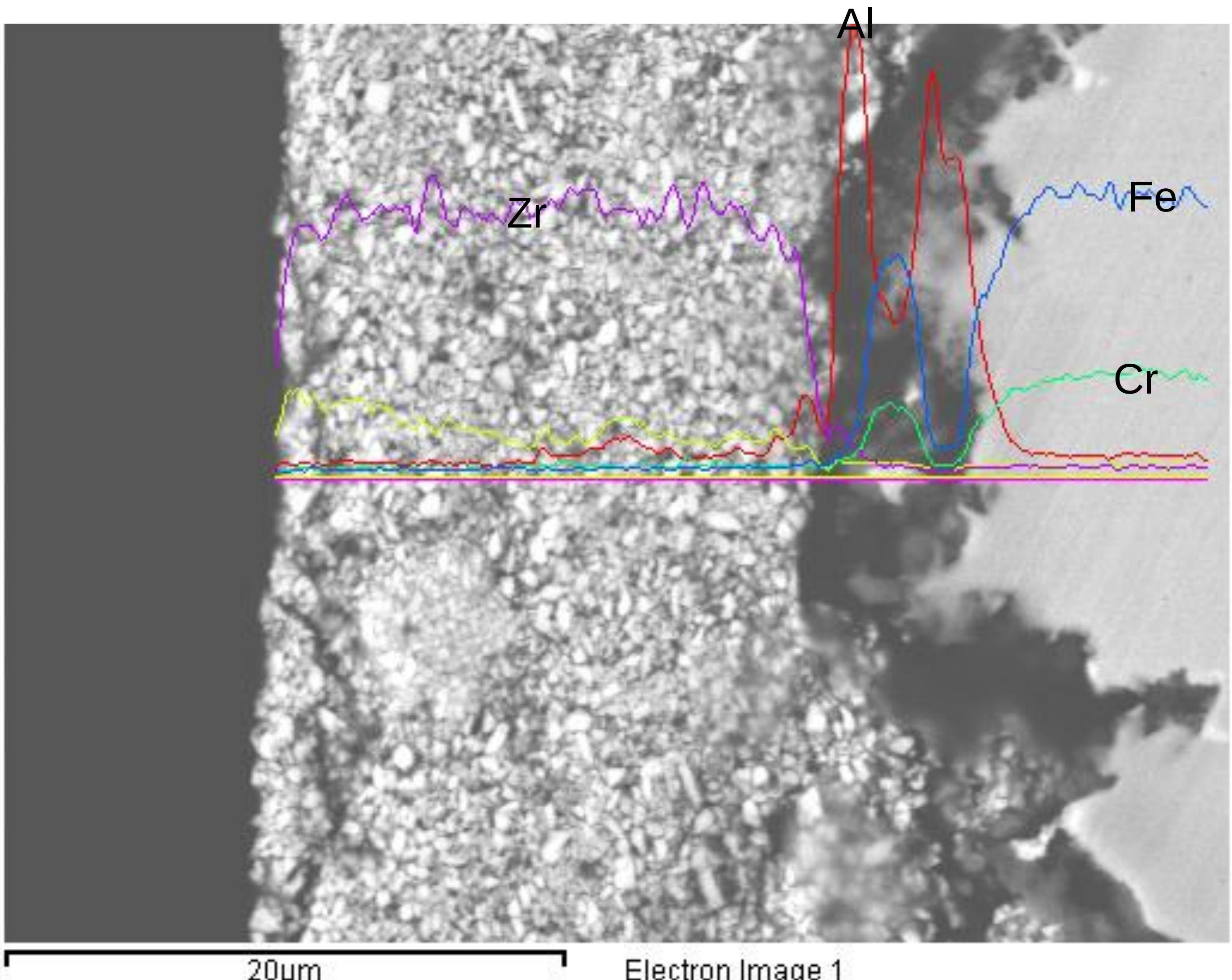
Experimental: stability and high-temp leak test



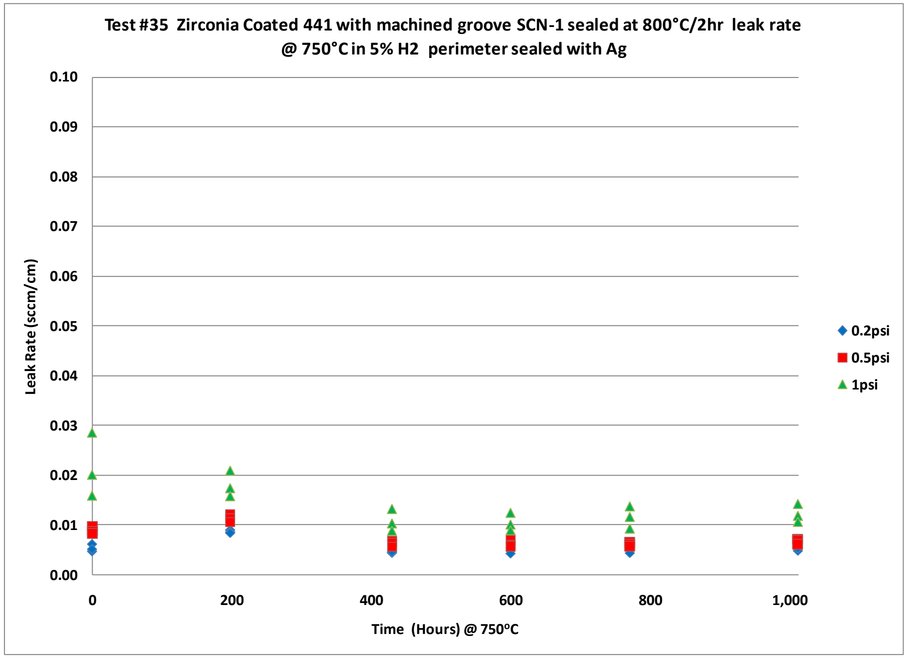
Microstructure of YSZ and Al_2O_3 coated SS441



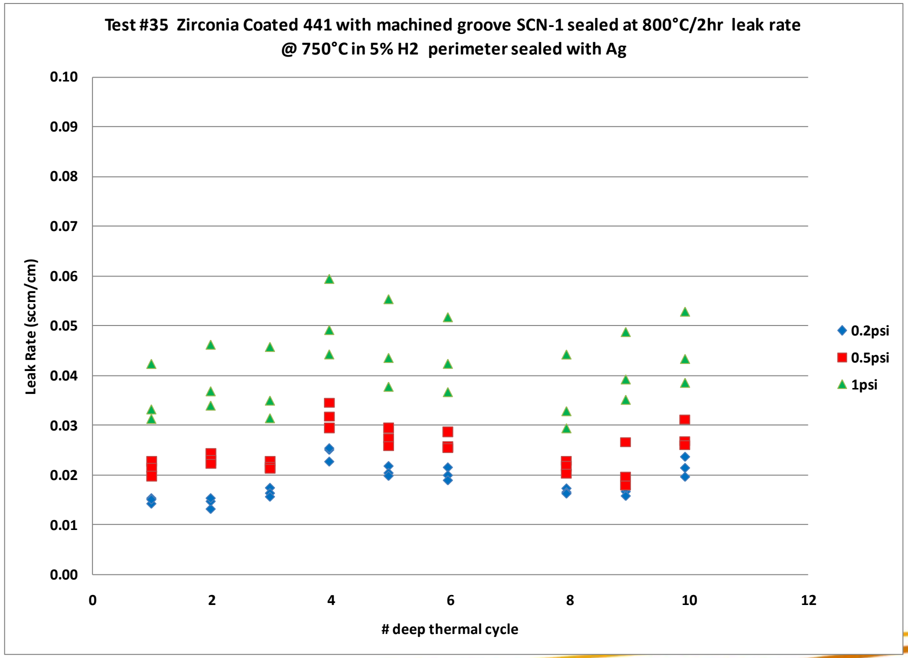
Q1: chemical compatibility with YSZ and Al_2O_3 coated SS441 in dual environment at 750ºC

SCN-1 glass showed good thermal and thermal cycle stability at 700, 750,and 800ºC

Leak test during isothermal ageing



Leak test during thermal cycling



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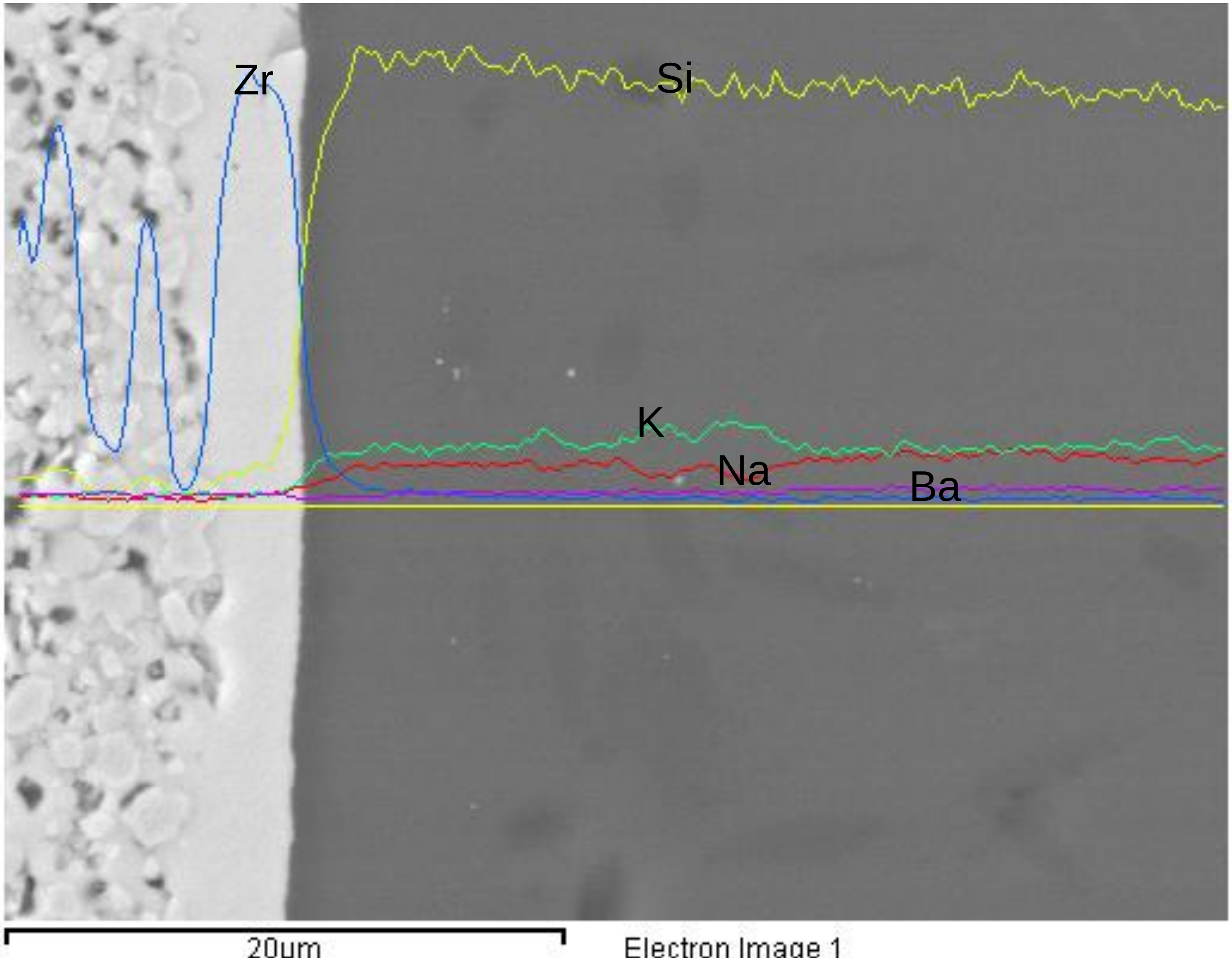
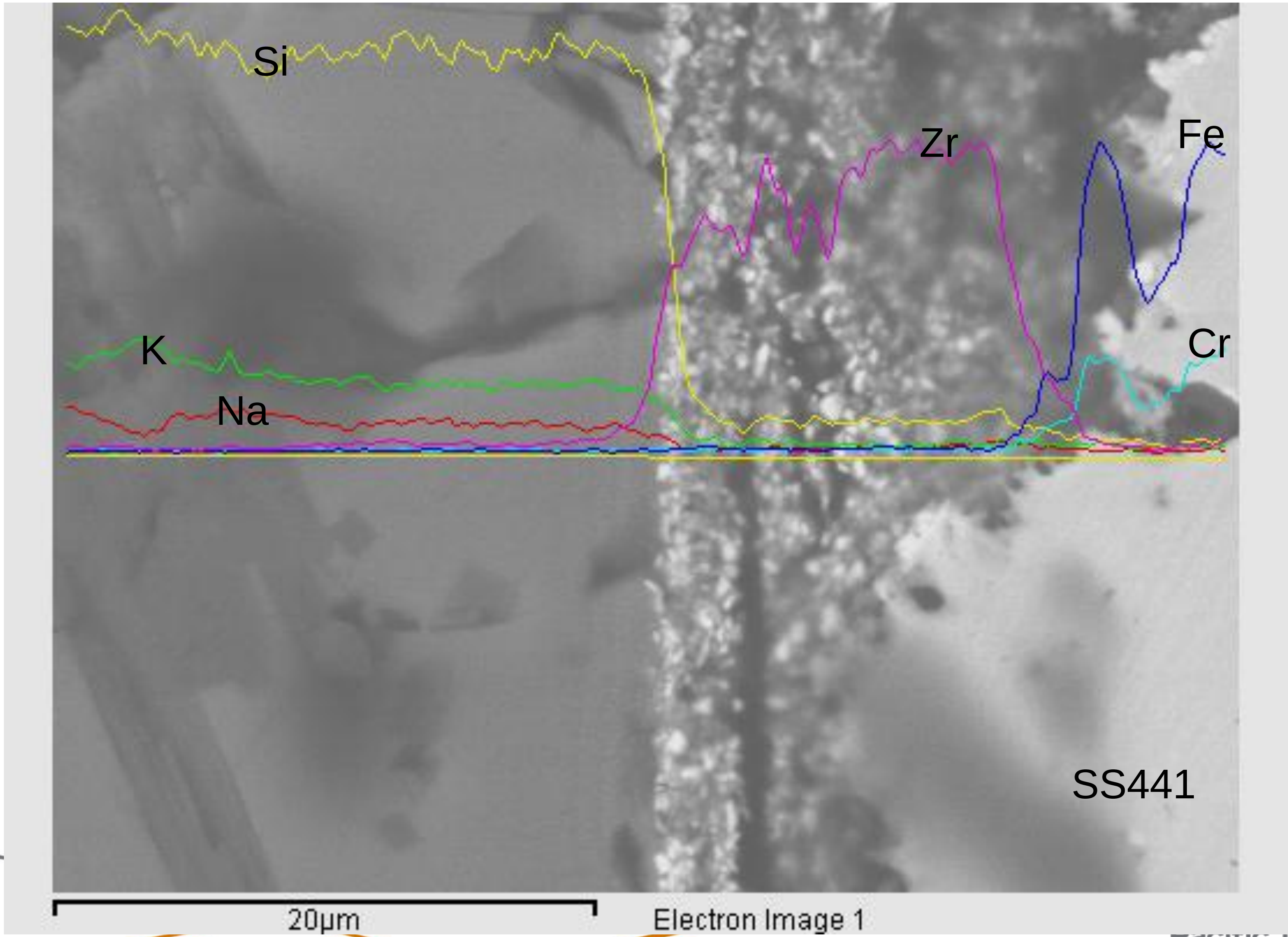
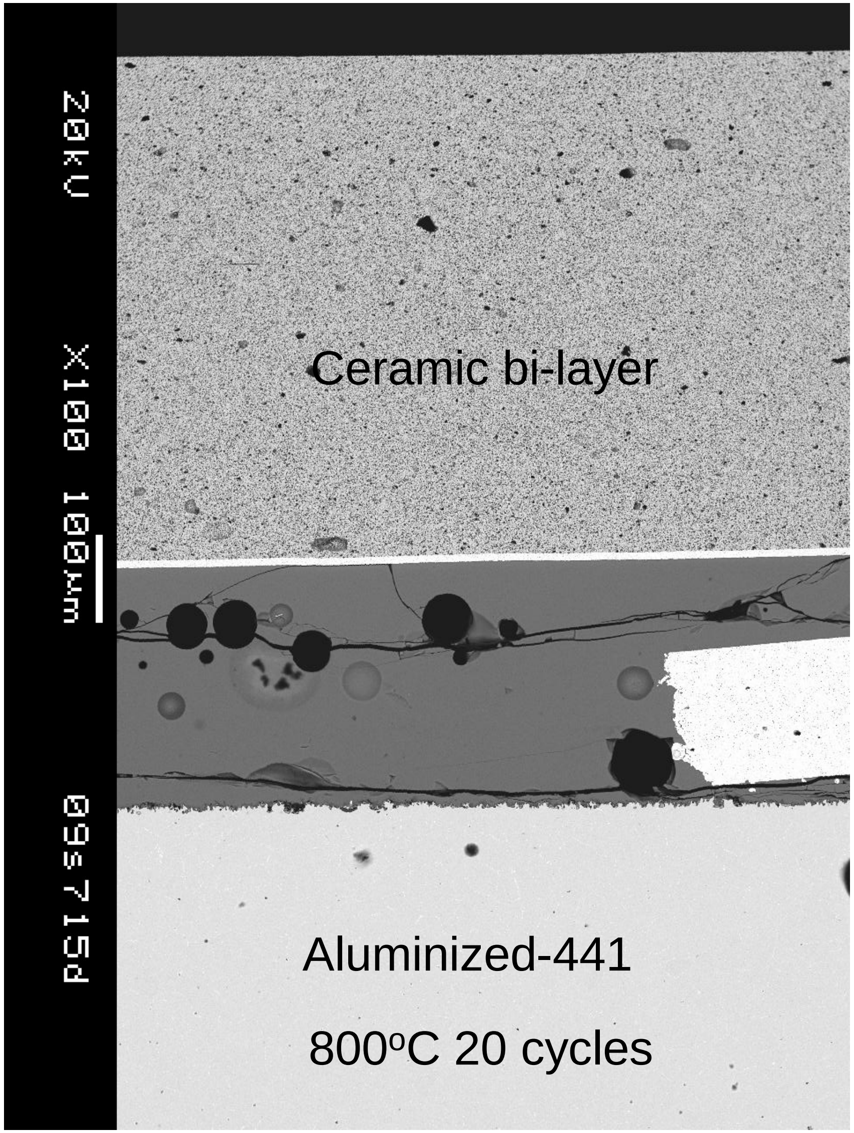
Post-mortem analysis: glass/YSZ electrolyte interface near air side

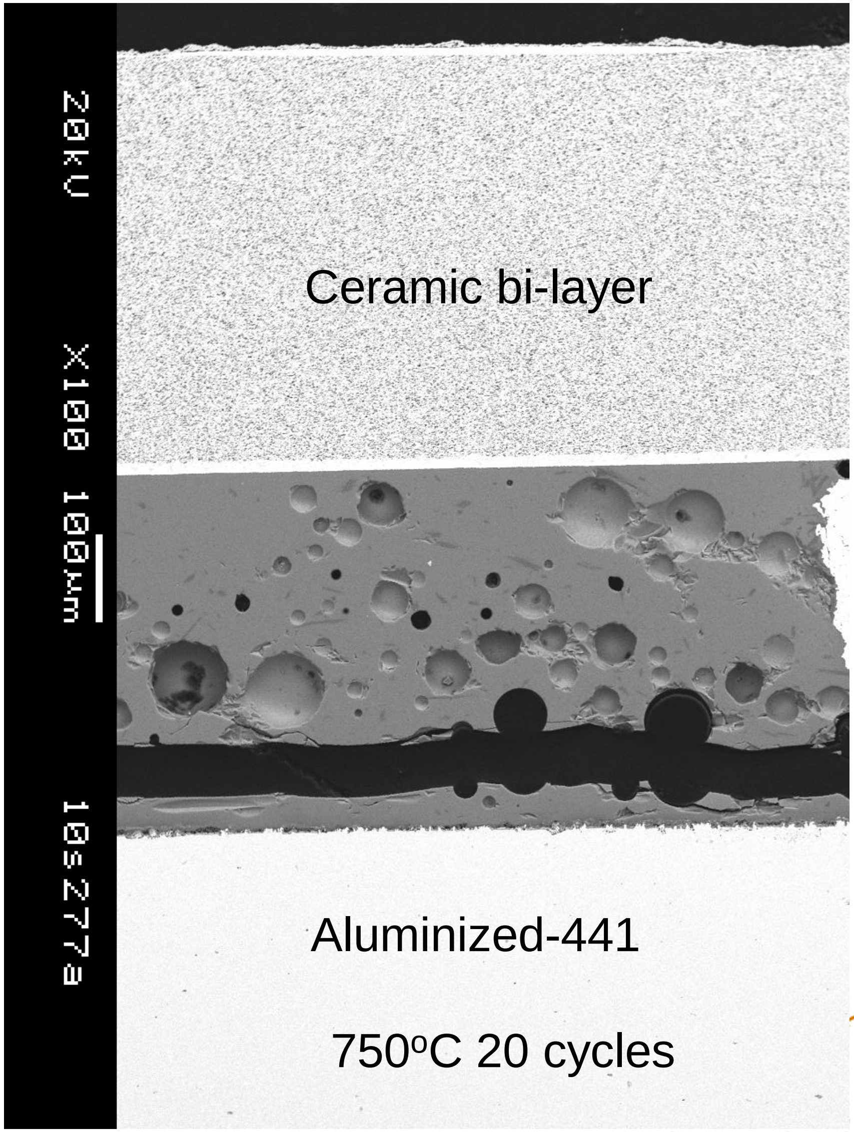


Post-mortem analysis: glass/YSZ coating interface near air side

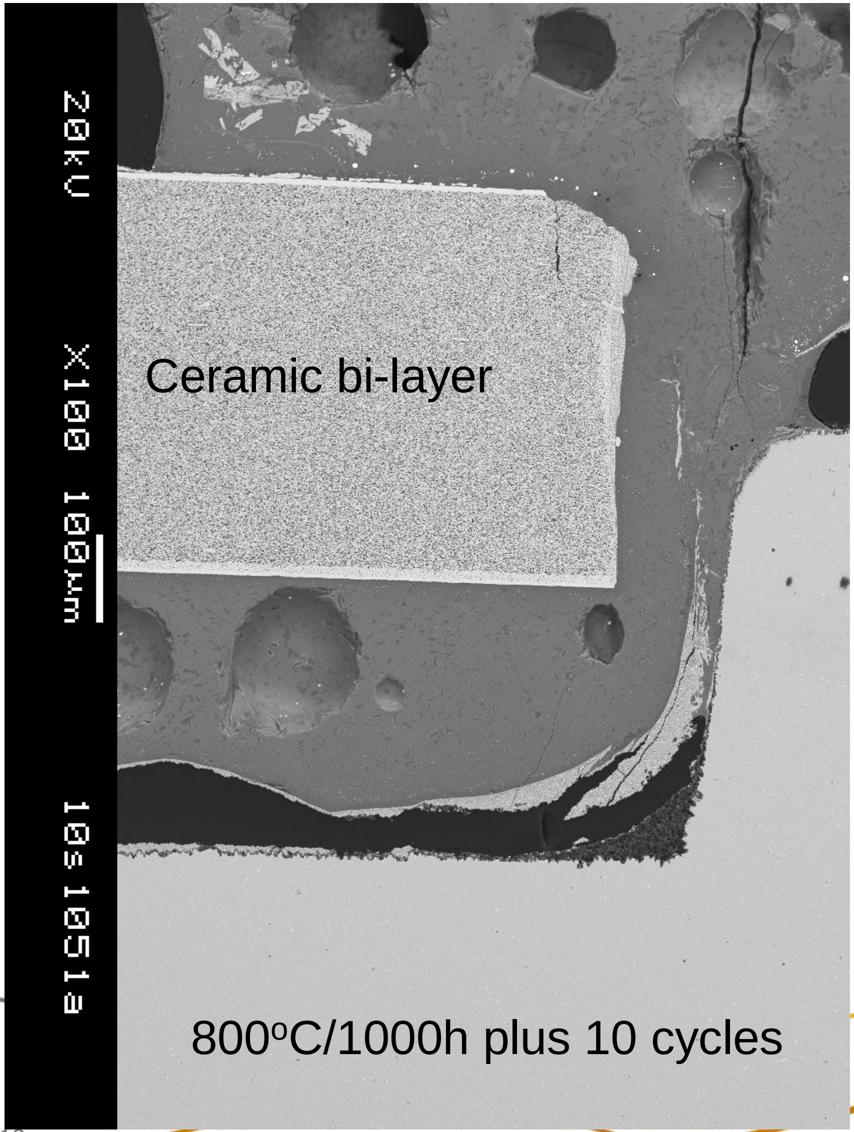


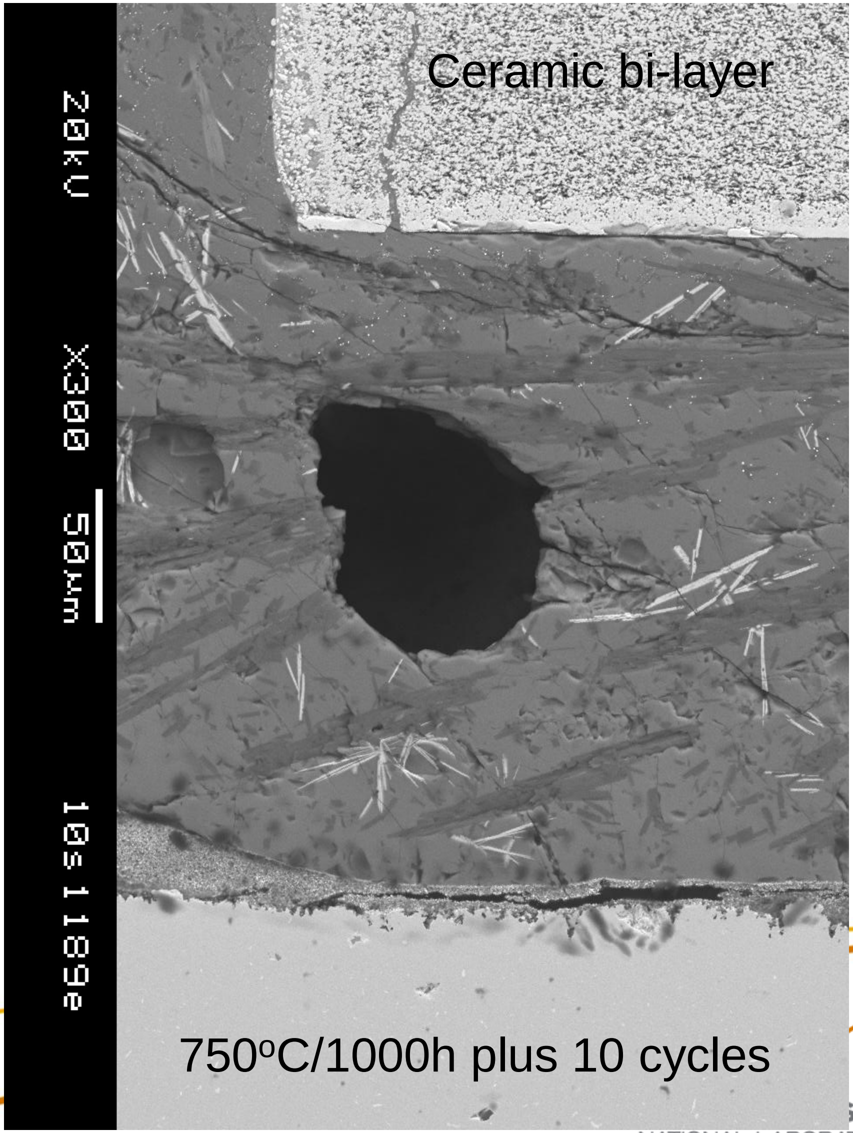
Minimal crystallization during pure thermal cycling





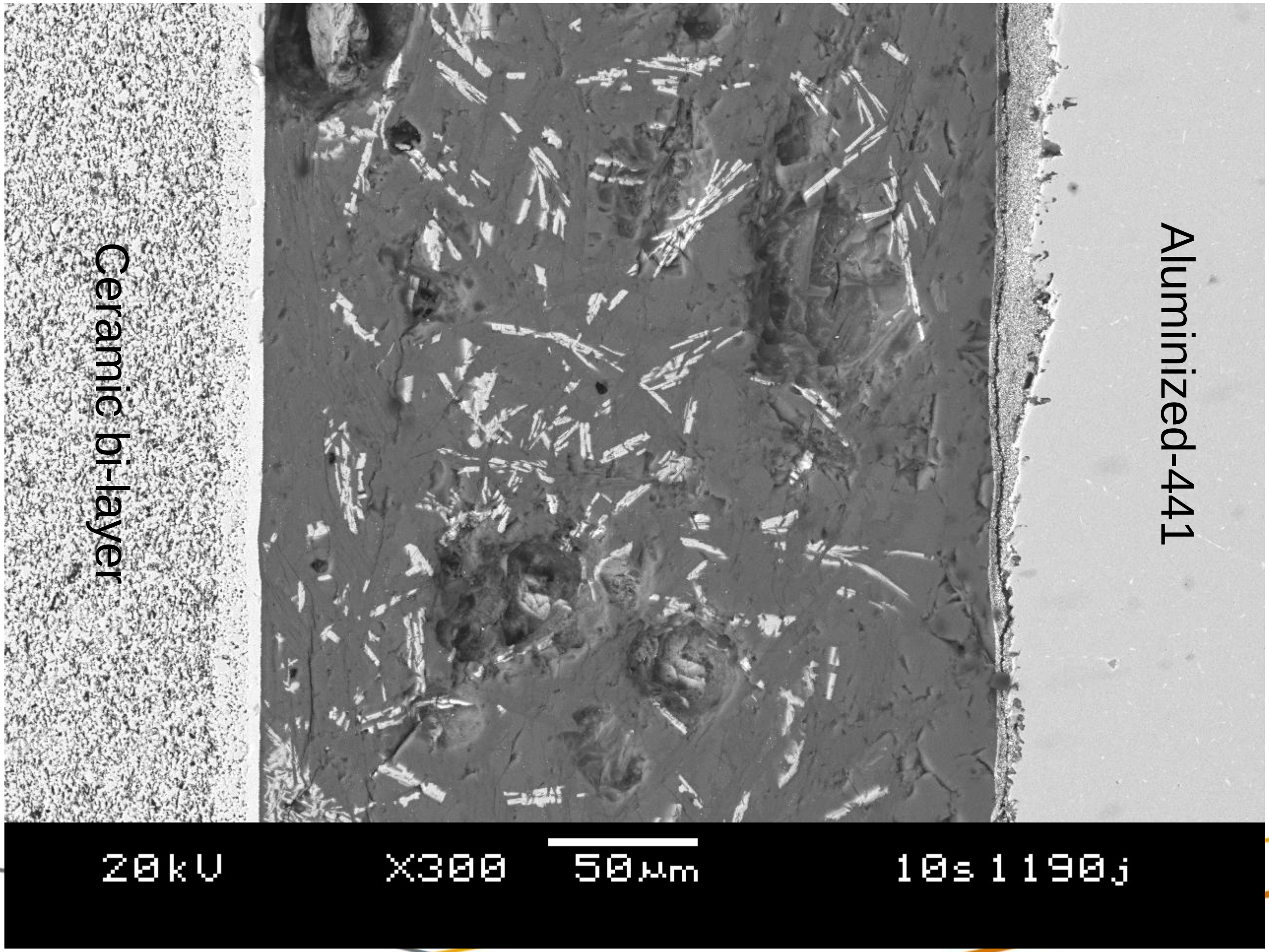
More crystallization during isothermal ageing





More crystallization during isothermal ageing

700^{o}C/1000h plus 10 cycles: Ba-silicate and K-Al silicate



oxide	mole%
Al2O3	1.84
BaO	3.57
CaO	3.96
Fe2O3	0.09
K2O	7.07
MgO	1.03
Na2O	7.83
TiO2	0.45
ZnO	0.01
ZrO2	0.01
Li2O	0.05
B2O3	0.03
SiO2	74.06

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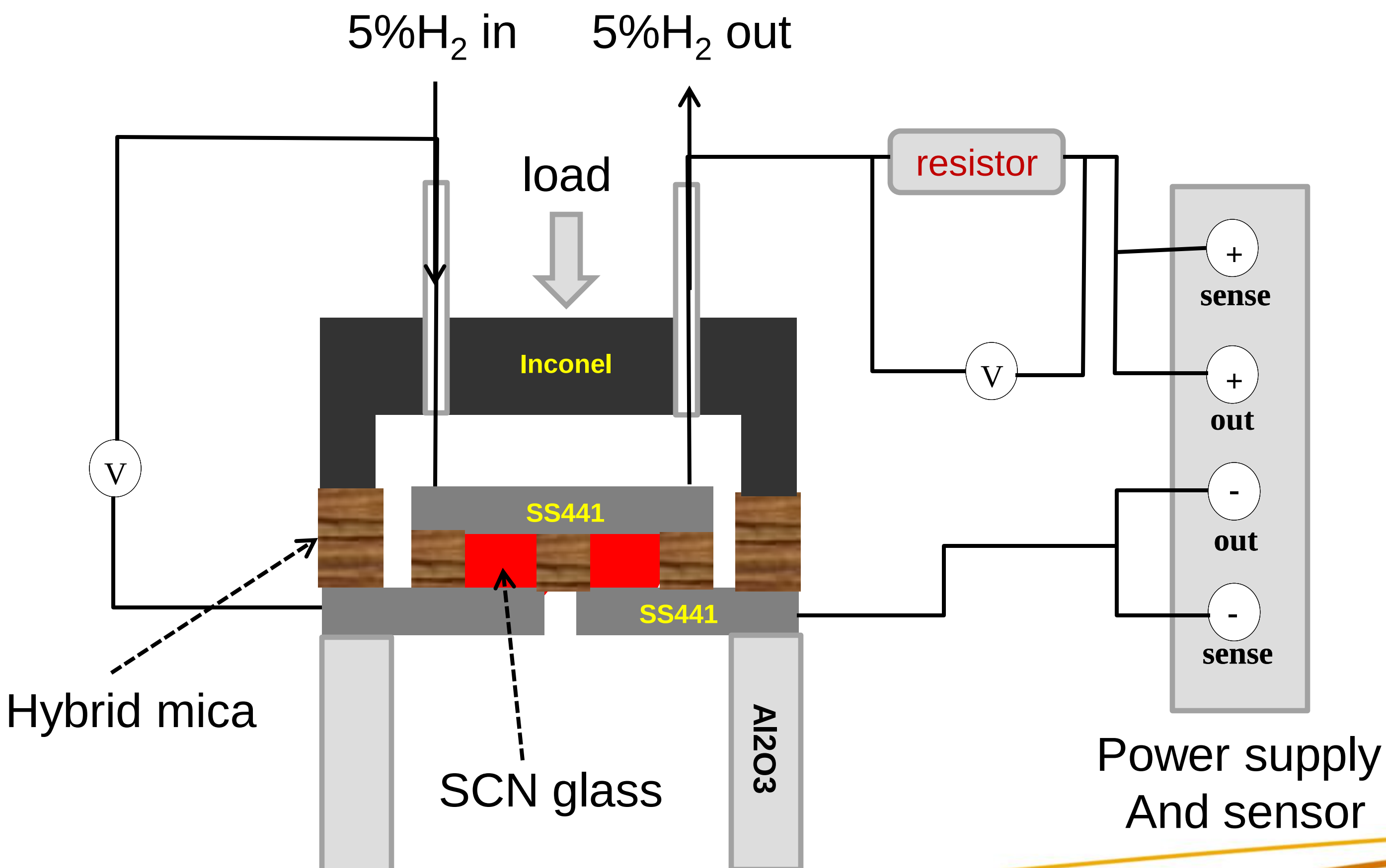
Q2: Electrical stability test



Chemical compositions

Alkali ions (Na^+ and K^+) are major charge carriers for conductivity in silicate glasses
Two concerns: **liquid glassy phases**, and **alkali** effect

SCN-1 glass

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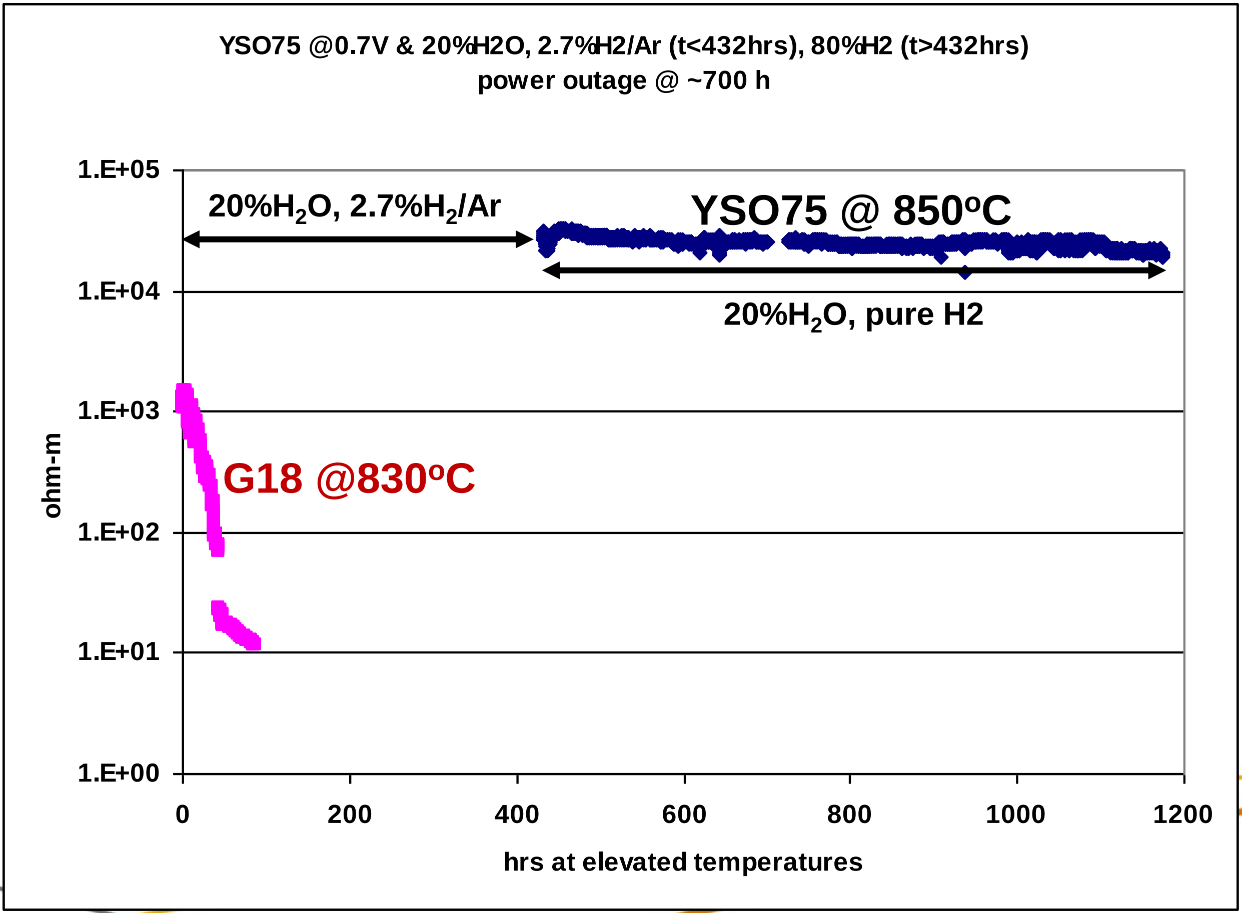
Refractory glass
YSO77

oxide	mole%
Y2O3	6.00
BaO	6.00
SrO	42.50
B2O3	10.00
SiO2	35.50

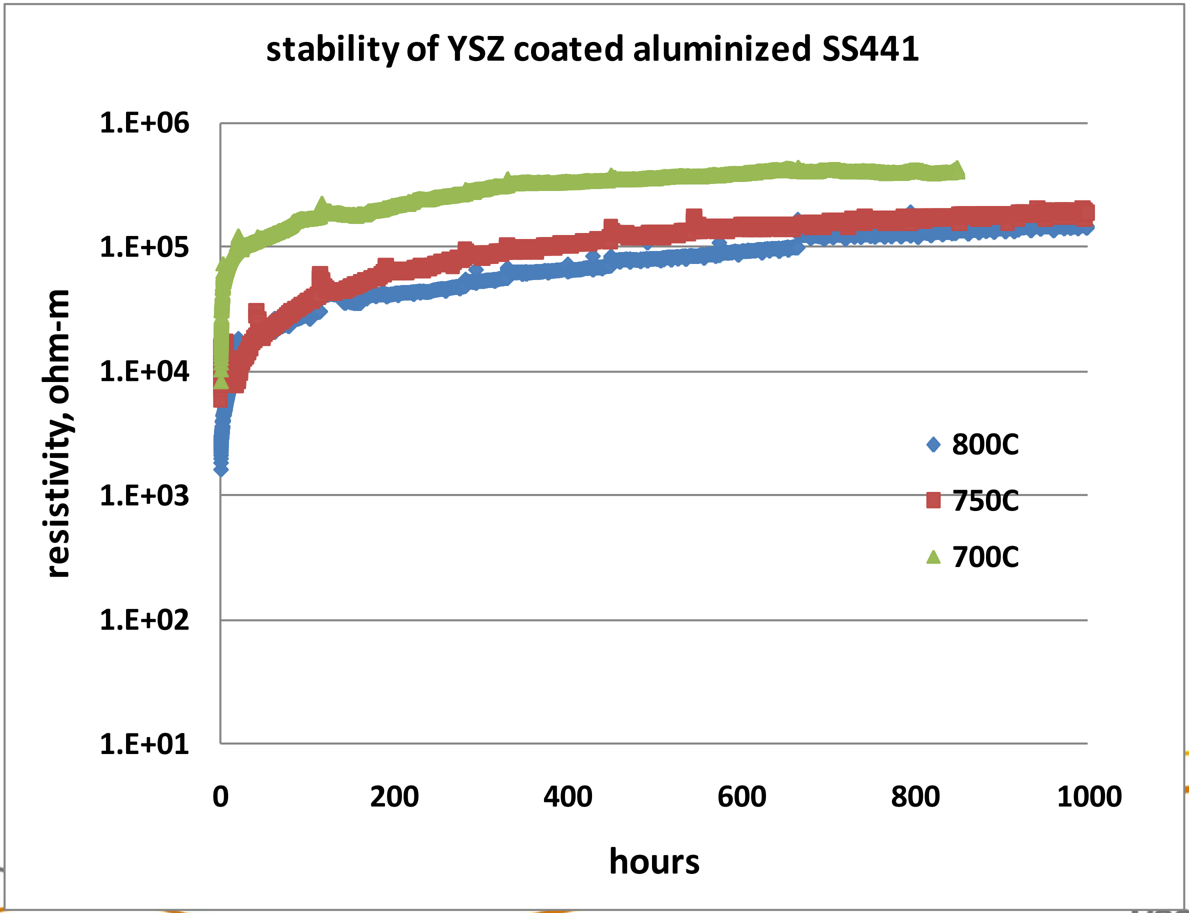
Comparison of crystallized glass (YSO75) and less crystallized glass (G18) with as-received crofer

G18 (less crystallized compared to refractory glass) showed rapid decrease In resistivity, suggesting dissolution/diffusion of metal ions from crofer22APU



Electrical stability with YSZ coated Aluminized SS441

Tested with flowing 5%H_2 (~3%H_2O) and a DC load of 0.8V across glass
Stable apparent resistivity (calculated by ohm x area/thickness neglecting coating contribution) indicates coatings remain intact (compatible) with SCN-1 glass.



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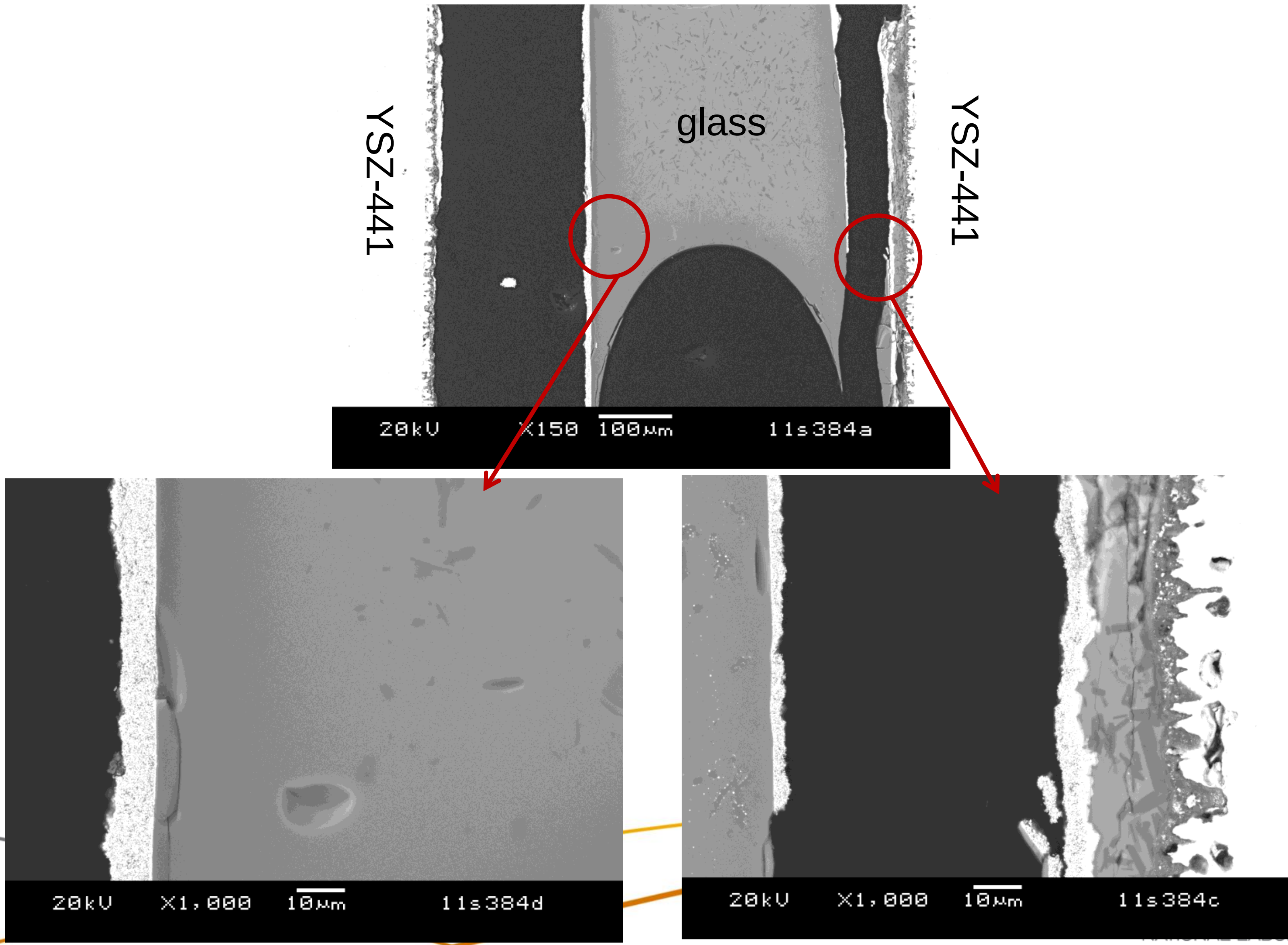
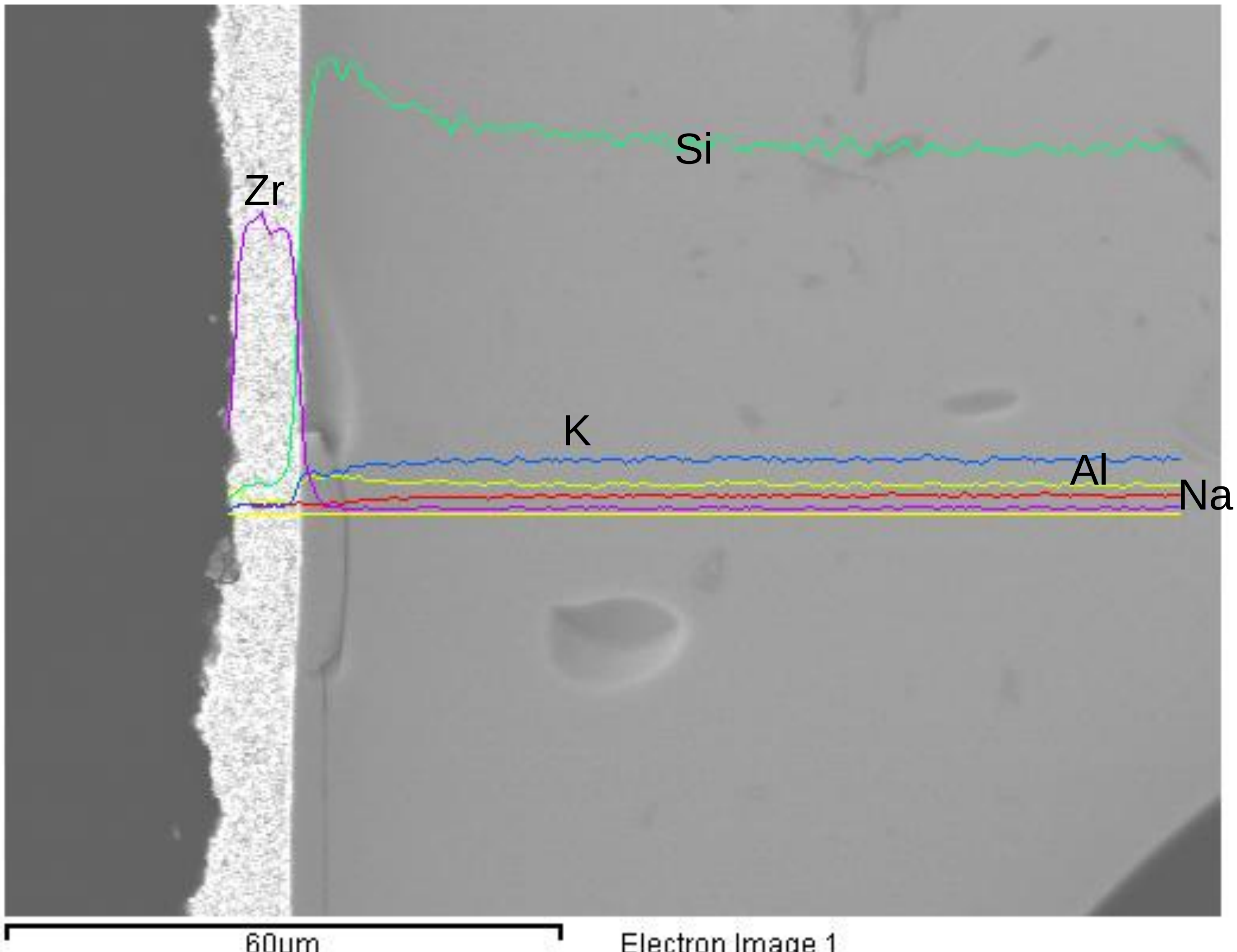
Microstructure of 800ºC/1000h electrically tested sample with YSZ coating



Chemical compatible with YSZ coating

No reaction and segregation of alkalis at interfaces under DC loading



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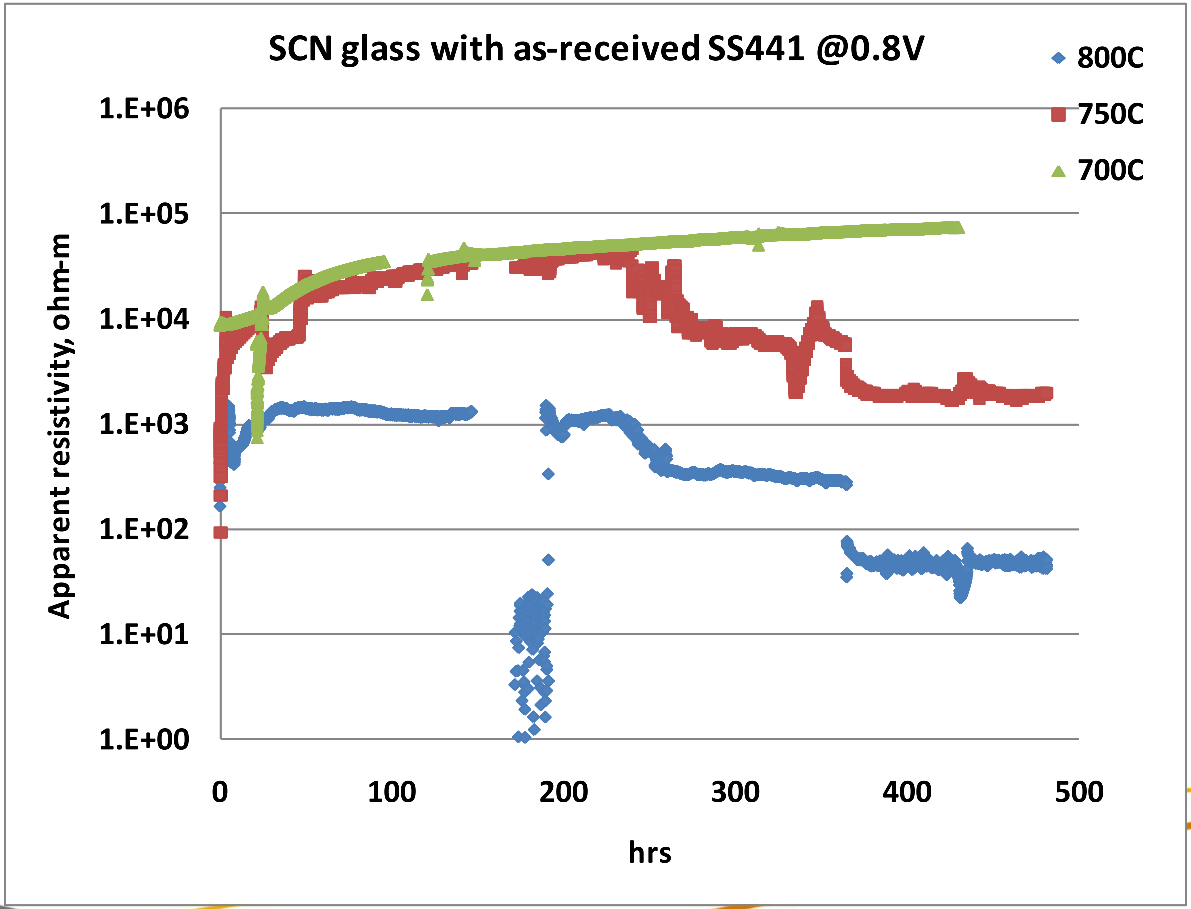
electrical stability with plain SS441



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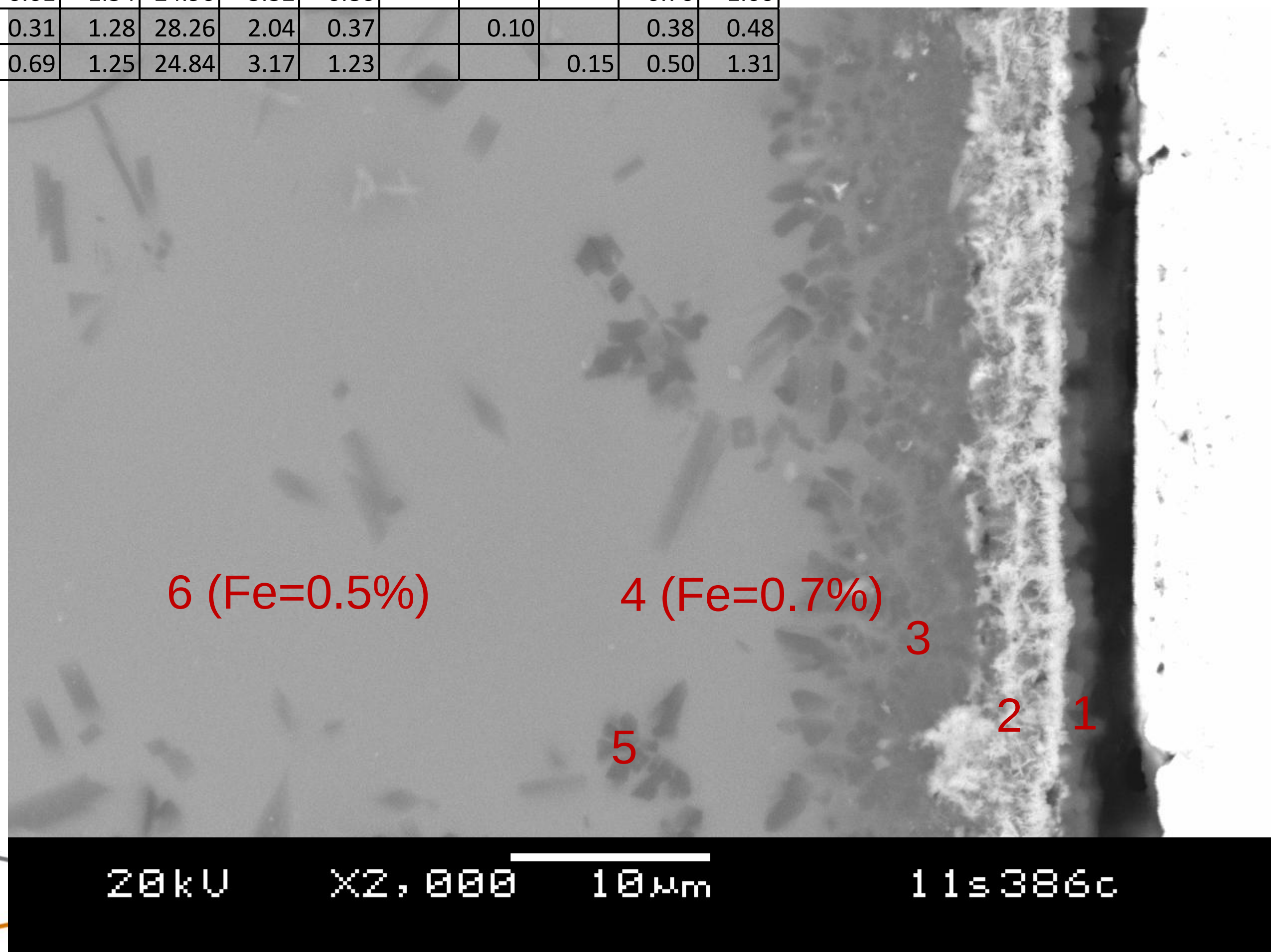
Presence of Fe in SCN-1 glass

spot #	O	Na	Mg	Al	Si	K	Ca	Ti	Cr	Mn	Fe	Ba
1	67.09				26.46			0.35	4.90		1.20	
2	65.41				13.52			0.84	19.43	0.51	0.29	
3	66.89	0.63	0.25	1.55	27.67	1.92	0.14	0.14	0.53		0.29	
4	64.84	2.24	0.61	1.54	24.90	3.32	0.86				0.70	1.00
5	65.83	0.95	0.31	1.28	28.26	2.04	0.37		0.10		0.38	0.48
6	64.44	2.43	0.69	1.25	24.84	3.17	1.23			0.15	0.50	1.31

Fe at%=0.06% SCN-1



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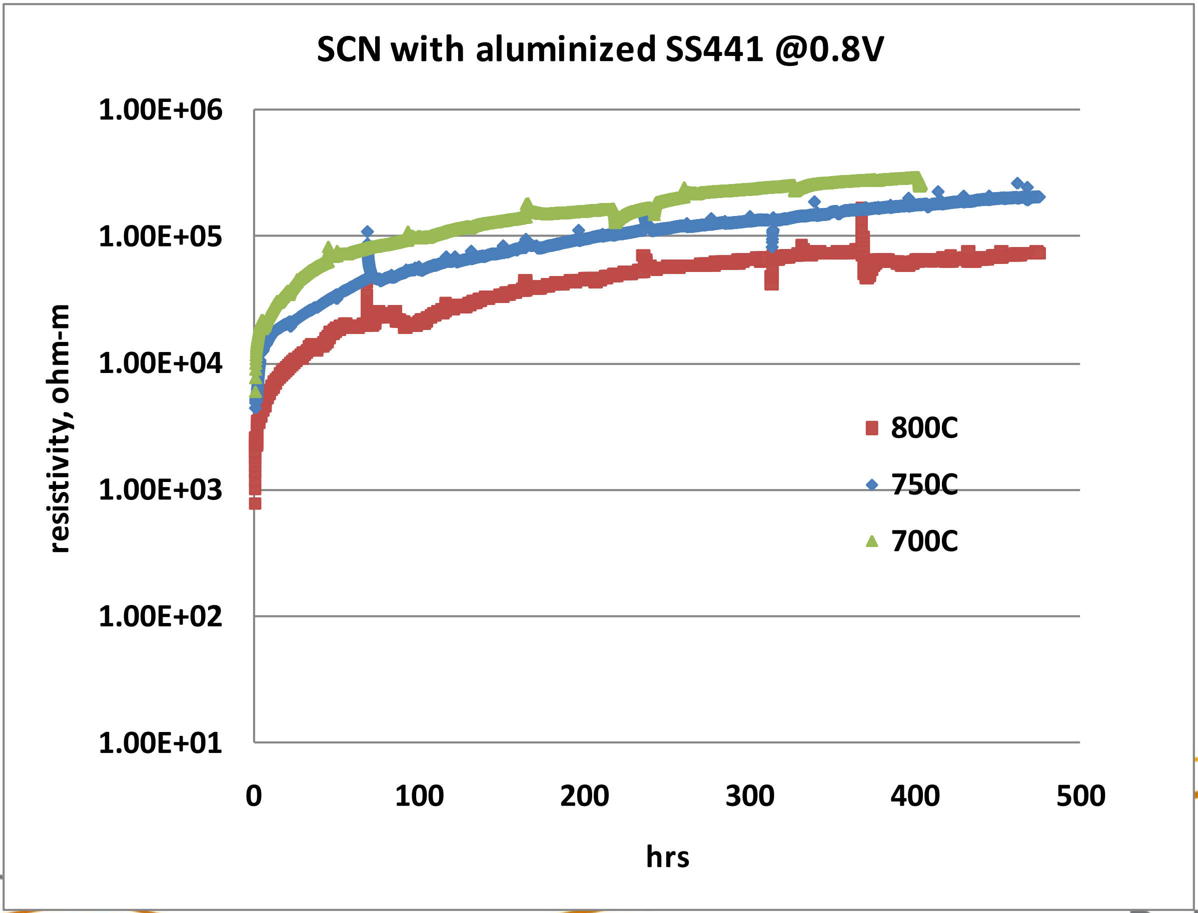

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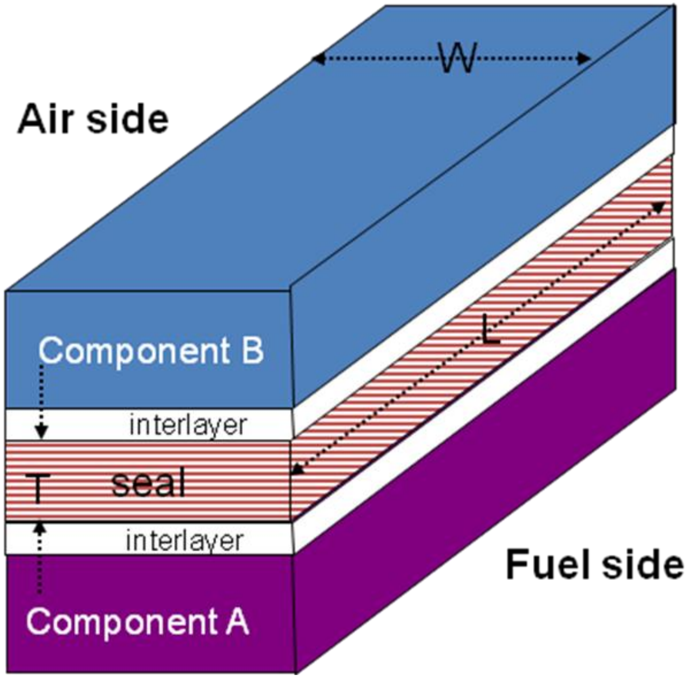
Q3: volatility issue

Weight loss vs. time data provided by ORNL of SCN-1 pellets at 800ºC in stagnant air or flowing steam

Linear volatility rate (R) was averaged for 5000h (steam) or 10000h (air)



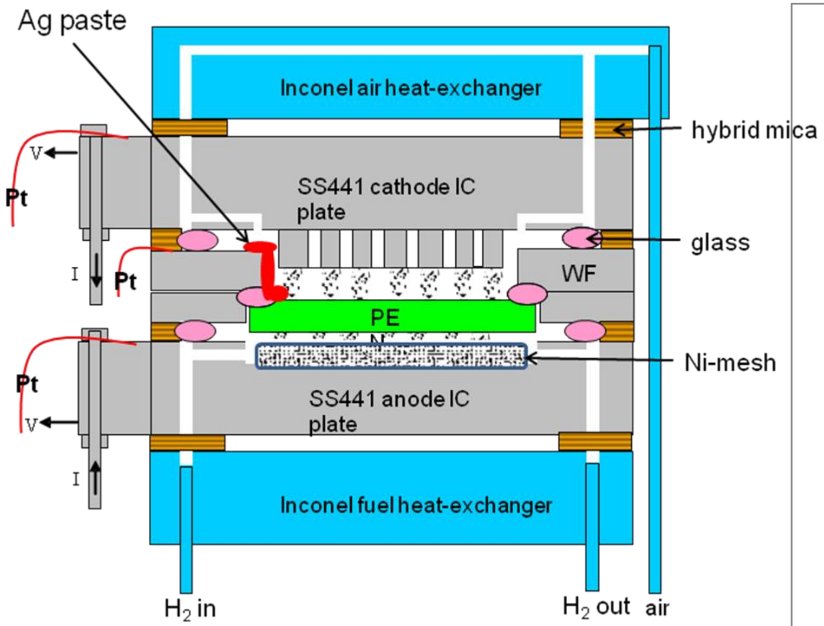
Total weight loss %

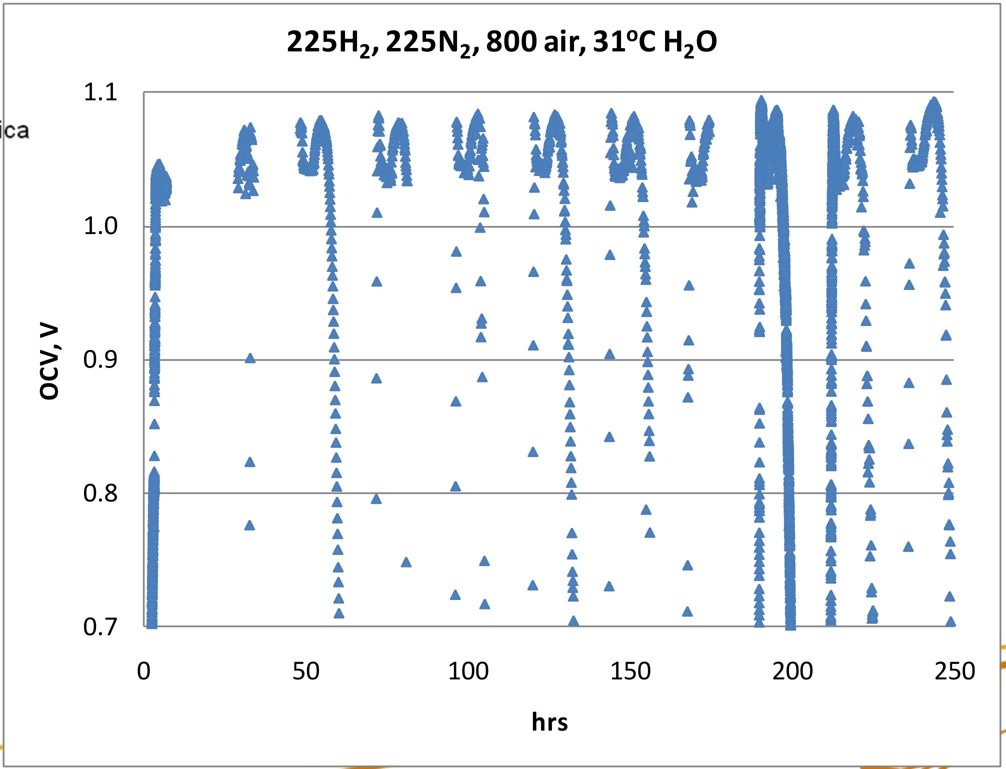
$= (R*L*T*40{,}000*100)/(\rho*L*T*W)$

Test cond. 800ºC	Avg. volatility (g/mm^2-hr)	Total wt. loss (%) in 40,000h
YSZ-air	6.33×10^{-9}	1.7
YSZ-steam	9.90×10^{-10}	0.3
Al_2O_3-air	8.04×10^{-9}	2.1
Al_2O_3-steam	1.08×10^{-9}	0.3

Q4: evaluate glass in stack test fixtures-thermal cycle stability

- Objectives: *thermal cycle stability*, containment/spreading issue, and volatile species interaction in base-line stability for 1000h
- Reasonable consistent OCV at 800ºC (1.040 V) theoretical 1.048V over 10 deep thermal cycles (~50ºC to 800ºC in 3h, 800ºC/3h, 18h to ~50ºC).





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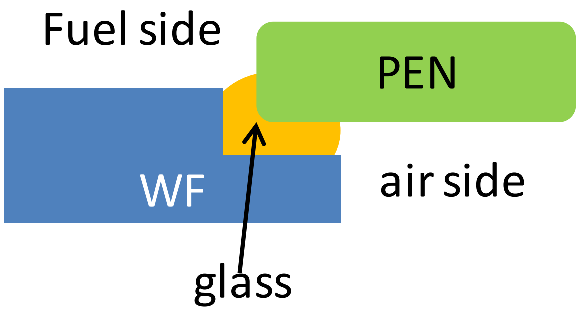
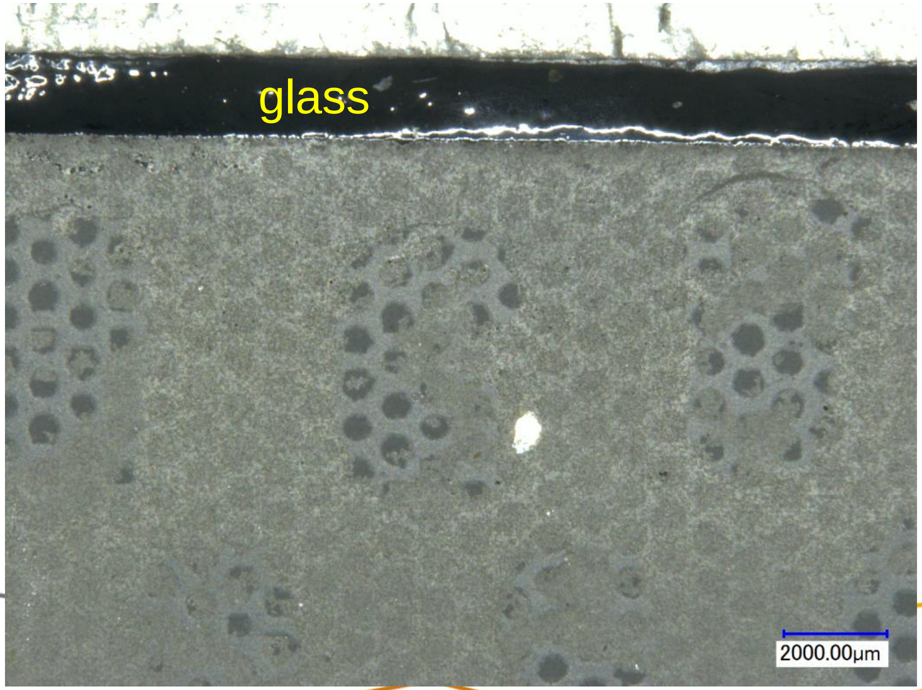
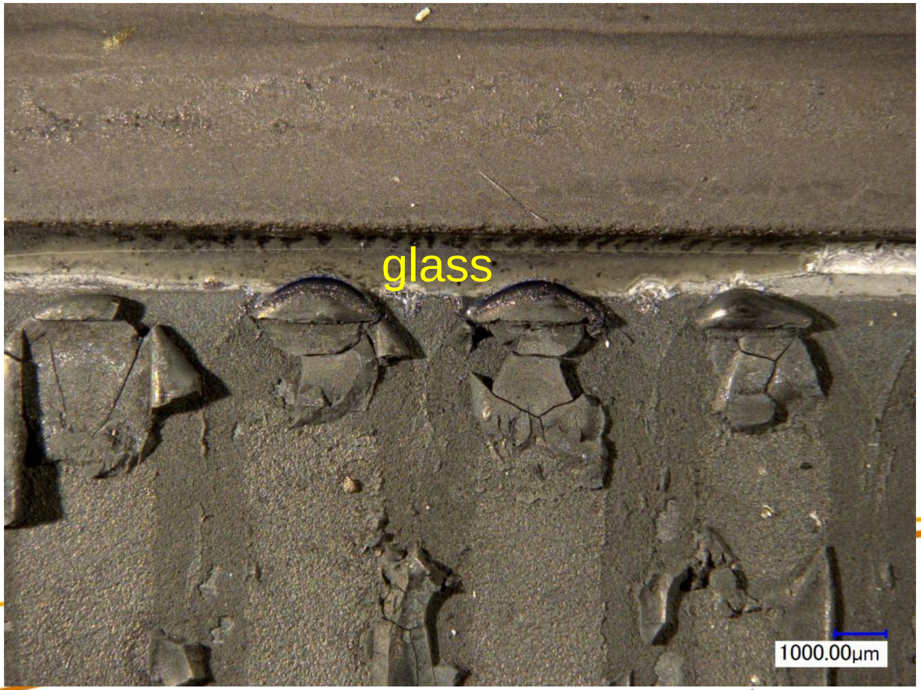
Q4: evaluate glass in stack test fixtures-containment/spreading issue



Fuel side



Air side



Summary and conclusion

- Compliant SCN-1 glass was evaluated comprehensively in thermal cycles stability, thermal stability, and chemical compatibility with candidate SOFC materials.
- The glass demonstrated very good thermal cycle and thermal stability with constant leak rate.
- Interfacial characterization showed minimum reaction at YSZ electrolyte and YSZ coating interfaces.
- Electrical stability test under DC load indicated insulating nature of the glass and no segregation of alkalis. Crystallization was similar as 1000h stability test without DC loading.
- Volatility estimation indicated minimal glass loss in 40,000h operation.
- Preliminary evaluation in stack test fixture showed good thermal cycle stability without containment/spreading issue.

Future work

- Optimize YSZ coating in terms of thickness with collaboration with modeling to stress minimization.
- Evaluate stability (1000h) in stack test fixtures at various temperatures with emphasis on interaction of volatile species with active SOFC components.
- Modify processing and sealing conditions to eliminate large pore formation.
- Collaborate with modeling to predict microstructure evolution effect on compliance, thermal and physical properties.
- Continue evaluating the spreading/containment issue, and predict the life-time flow under differential pressure.
- Design new window frame for robust sealing.