Development of Reliable Methods for Sealing Solid Oxide Fuel Cell Stacks

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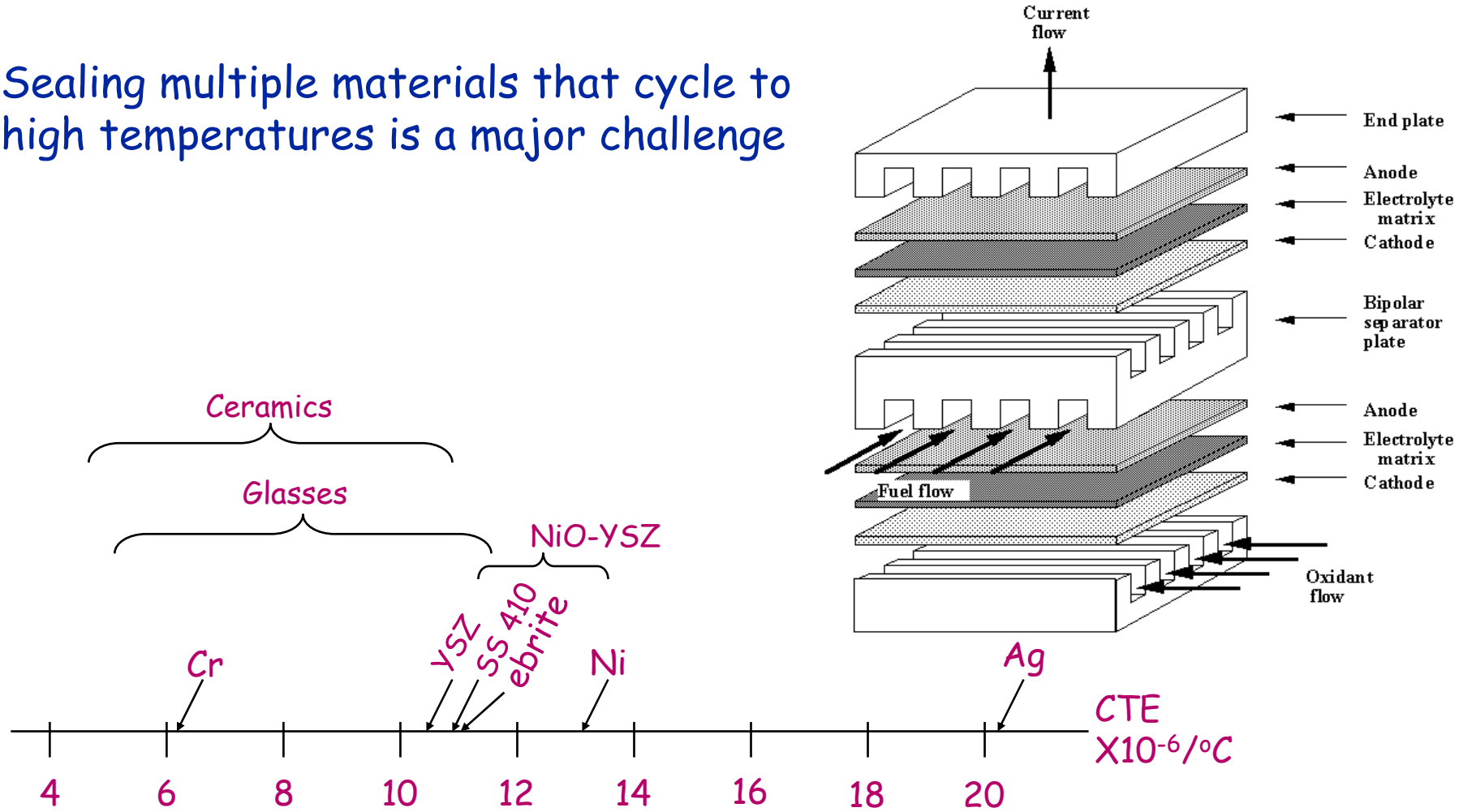
Outline

- Composite approach to SOFC sealing
- Glass and composite properties
- Composites applied to electrolyte and anode-supported SOFCs
- Some composite seal properties
- Summary and conclusions

Development of reliable seals is the major technical barrier to commercializing SOFCs

Sealing multiple materials that cycle to high temperatures is a major challenge



Seals for SOFCs must satisfy some of the most challenging performance criteria in materials engineering

- long-term HT stability in oxidation and reduction (decomposition, vaporization, phase transitions)
- low reactivity with environment and other components
- strength and toughness at the use temperature
- thermal shock resistance
- ability to accommodate CTE mismatch
- hermeticity

All for lifetimes of up to 40,000 hours

Composite Sealing Concept

Assume:	SOFC components bonded in intimate contact
	CTE mismatch
	Stress on thermal cycling
Approach:	A deformable seal based on glass flow above its T_g
	Wetting and reaction controlled by glass chemistry
	Control viscosity and CTE with powder additive
	Slight flow to relieve stress, heal cracks
	Composite is rigid enough to remain in joint

Composite seals can be engineered to provide a wide range of chemical and mechanical properties

Composite CTE depends on individual CTE and modulus values

$$\alpha = \frac{\alpha_1 K_1 V_1 + \alpha_2 K_2 V_2}{K_1 V_1 + K_2 V_2}$$

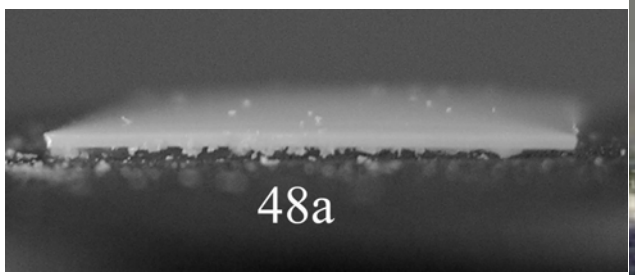
K_i = modulus, V_i = volume fraction

Viscosity increases with decreasing filler particle size and with increasing filler concentration

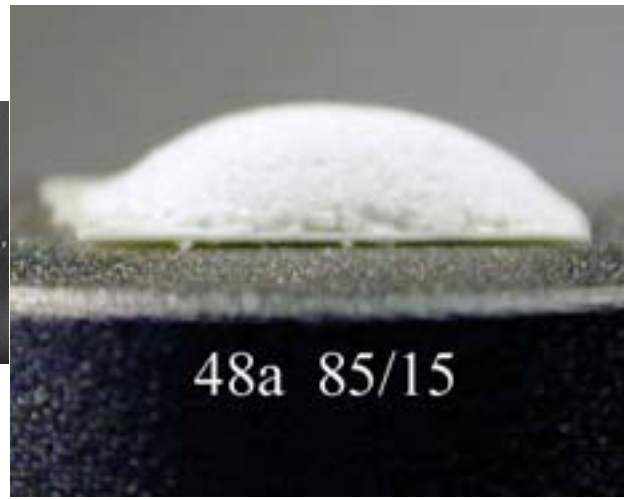
$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\phi / \phi_{max} \right)} \right)^2$$

κ = 1/particle size, ϕ = particle packing density

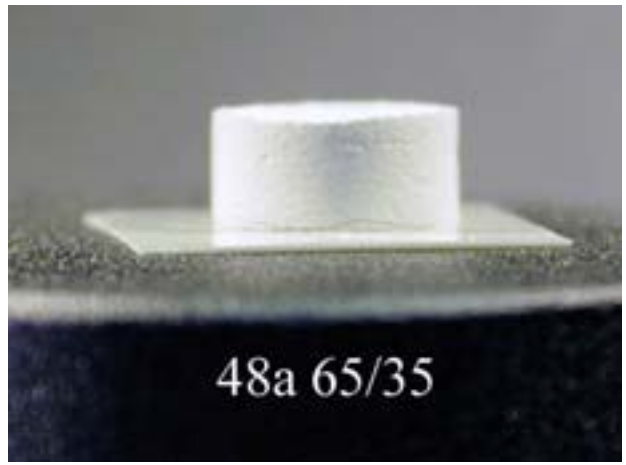
Heating Experiments Show Effect of Glass/Ceramic Powder Ratio on Composite Flow and Viscosity



Glass on YSZ



85 vol% Glass/15%YSZ Powder

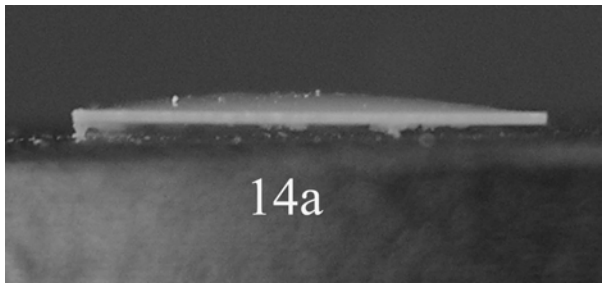


65 vol% Glass/35% YSZ Powder

Thermal Cycle: 10°/min to 1100°C, hold 12 min., cool to 850°C, hold 60 min.

Glass Properties: CTE = 6.1 x 10^{-6}/°C, Tg = 623°C

Heating Experiments Show Interplay of Glass Tg and Ceramic Powder Content on Composite Viscosity



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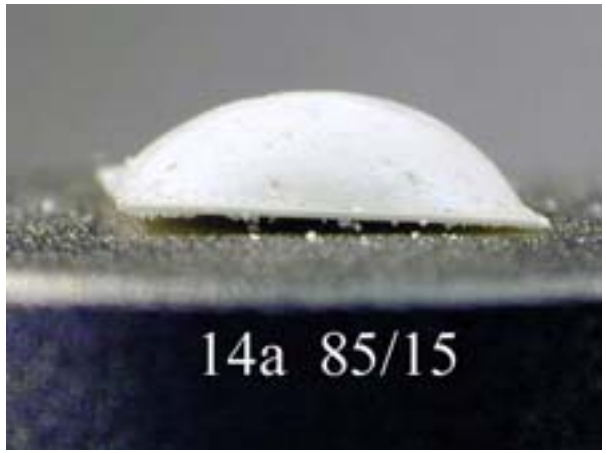

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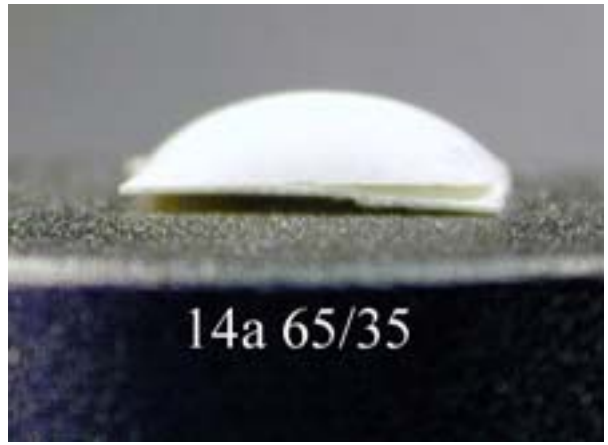


65 vol% Glass/35% YSZ Powder

Thermal Cycle: 10°/min to 1100°C, hold 12 min., cool to 850°C, hold 60 min.

Glass Properties: CTE = 9.1 x 10^{-6}/°C, Tg = 576°C

We are developing glass composites for sealing electrolyte-supported SOFC stacks

Objectives

- Apply glass-composite seal concept to electrolyte-supported SOFCs

- Develop and adjust the properties of a SiO_2- free, composite glass seal using micron to nano-scale additives

- Determine the seal properties during long term exposure at service temperature

Glass composites for sealing electrolyte-supported SOFCs

Seal requirements:

CTE near $10.5 \times 10^{-6}/^{o}C$ to match that of YSZ
minimal interaction with electrolyte
long term stability

Some aspects of glass seal chemistry:

SiO_2 (main glass former) is known to poison YSZ by reducing its ionic conductivity
B_2O_3 is a good glass former, but may be volatile
ZrO_2 is an effective nucleating agent for glass crystallization
MgO, CaO, and BaO are modifiers, stable under reduction
Al_2O_3 can act as glass former or modifier

Experimental Procedures

Raw materials:

- BaO -CaO-MgO-Al_2O_3- B_2O_3 glass
- Ceramic powder additives, emphasize nano-YSZ; 27nm diam; 2.5-30 vol%

Glass-composite fabrication:

- Mechanical mixing of raw materials in Spex mill
- Powder mixture was pressed and consolidated at 50°C above T_g

Analysis:

- DTA: TA Instruments STD-2960; Pt crucibles; 10°C/min to 1000°C
- XRD: Siemens D500 diffractometer (Cu Kα); 20-70°
- Wettability: Thermolyne 21100 tubular air furnace; 20°C/min to 800-950°C for 10 min.
- Microstructure: JEOL-5800LV coupled with an Oxford EDS system.
- Thermal expansion: Netzch 402 ED dual rod dilatometer ; 50-550°C in air; sapphire standard.
- Long term exposure: Thermolyne 48000; 500 hrs@800°C

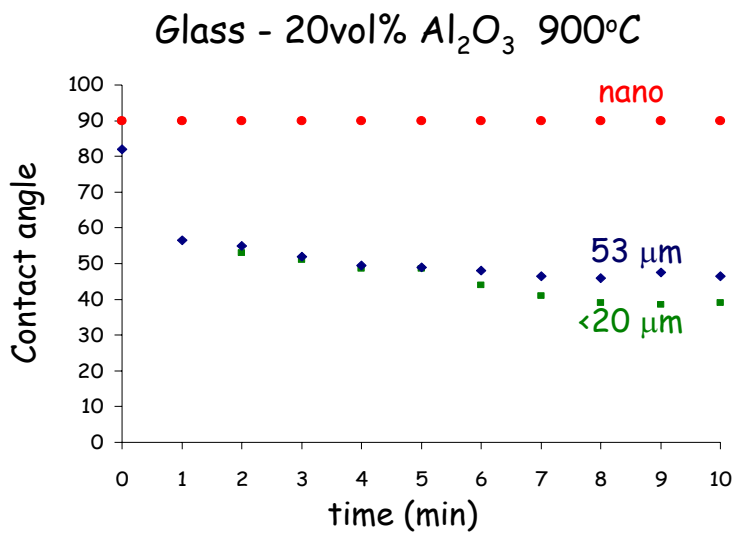
Nano-scale additives have a stronger effect on glass flow than micron-size powder

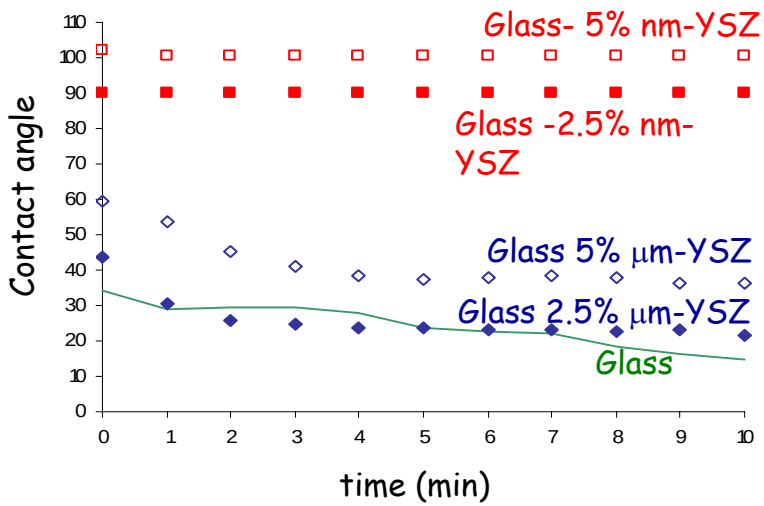
Composite viscosity increases with decreasing filler particle size and with increasing filler concentration

$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\phi / \phi_{max}\right)}\right)^2$$

κ = 1/particle size

ϕ/ϕ_{max}= particle packing density (volume fraction)

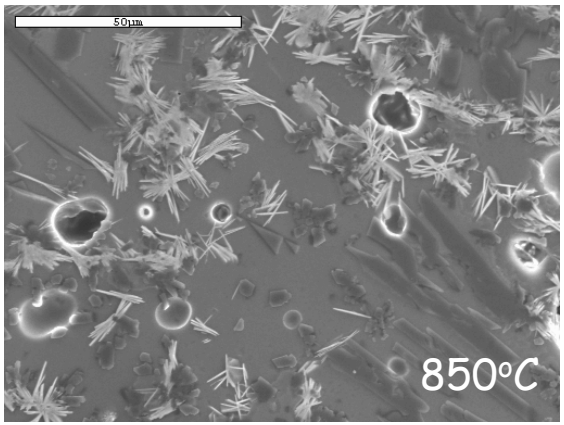


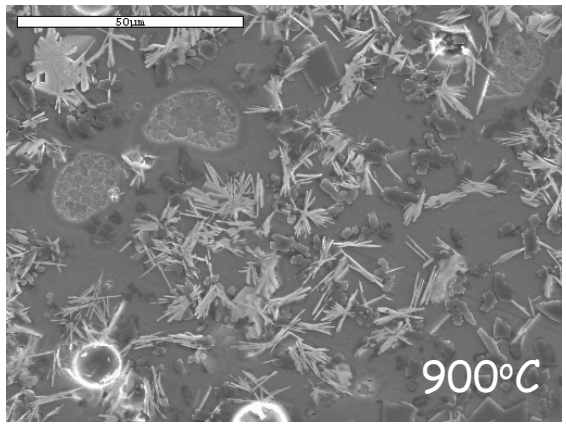


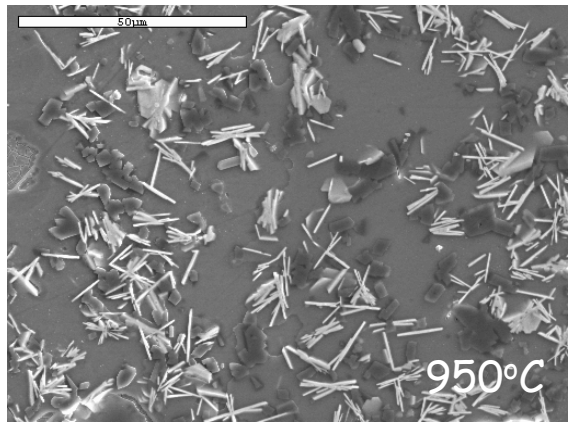
(Spreading rate is a surrogate for viscosity)

The sealing temperature influences the microstructure

Competition between $BaZrO_3$ growth and $MgCaB_2O_5$ dissolution





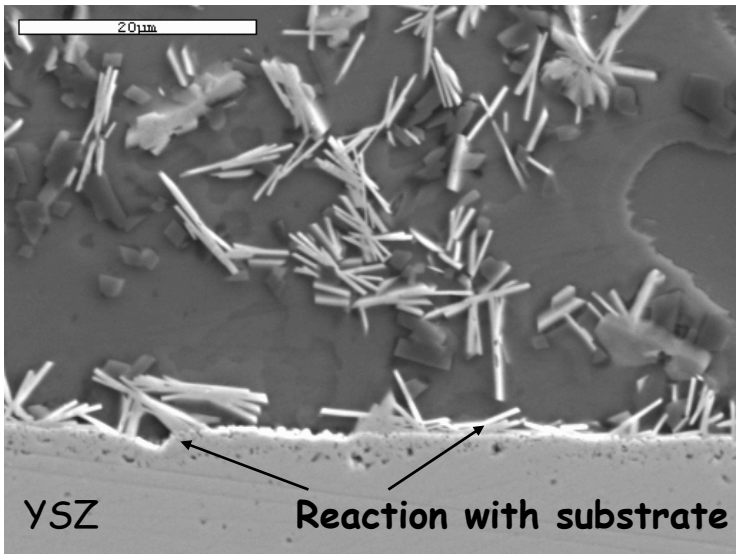


- Reaction between BaO in glass and YSZ forms $BaZrO_3$ (CTE:7.9x10^{-6}/°C)
- $BaZrO_3$ forms as micron-scale needles
- With increasing sealing temperature:
  - Vol% of $BaZrO_3$ increases.
  - Dissolution of $MgCaB_2O_5$ crystals

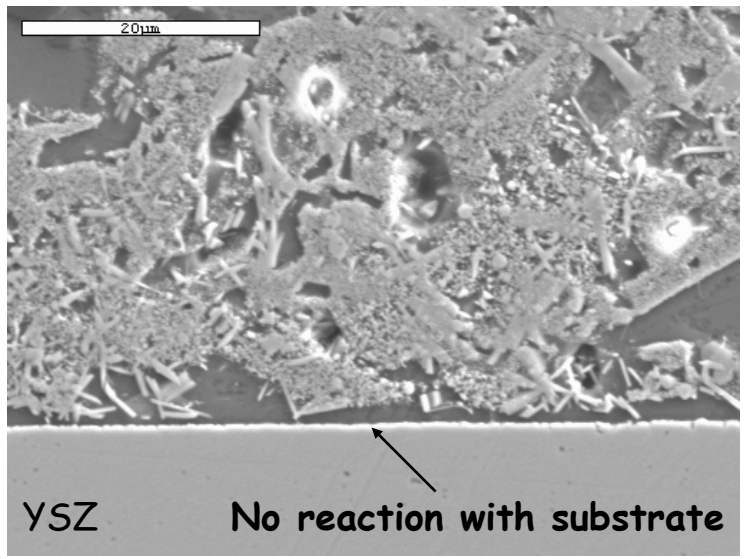
Dark phase = $MgCaB_2O_5$

Light needles = $BaZrO_3$

Preferential reaction of BaO with nano-YSZ additive reduces its reaction with electrolyte



5vol%; 950°C; 10min



30vol%; 950°C; 10min

Reaction of BaO with nano-scale YSZ to form $BaZrO_3$ reduces the amount of BaOavailable for reaction with the YSZ substrate

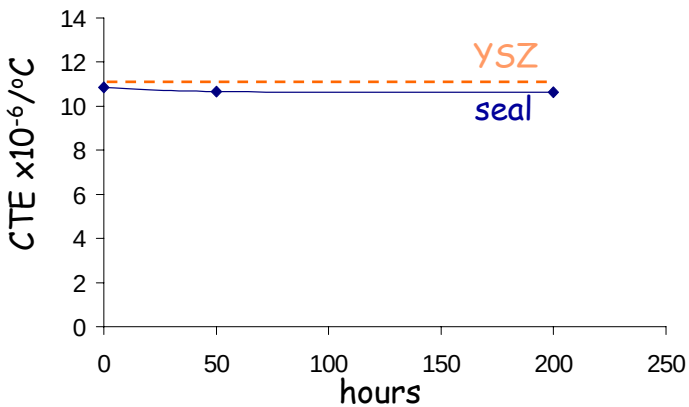
The composite CTE can be adjusted by adding Ag powder and varying the sealing cycle

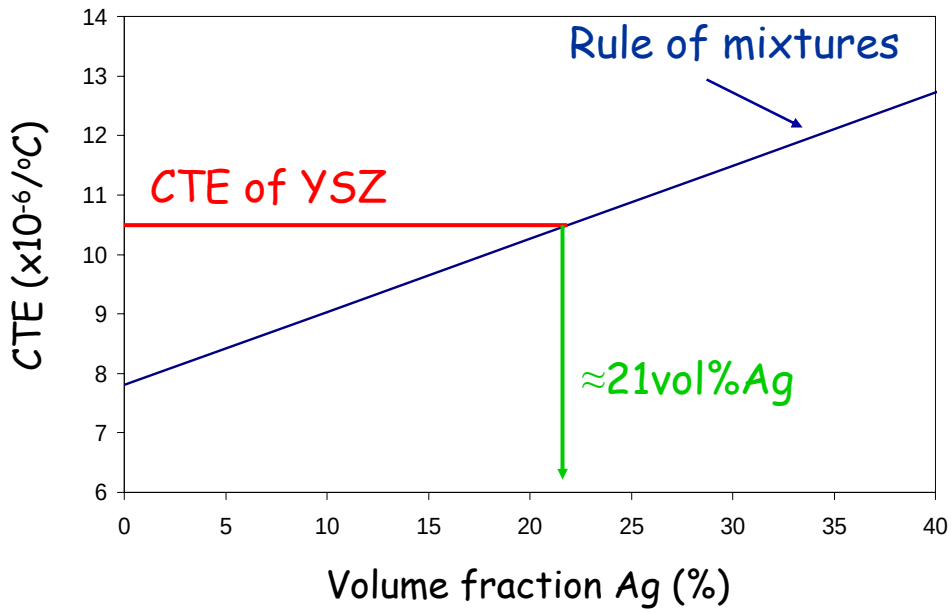
Previous results showed minimal changes of CTE over time @800°C after sealing at 900°C

$$\alpha_{seal} = \alpha_{gc} + (\alpha_{Ag} - \alpha_{gc})V_{Ag}$$

$\alpha_{gc} = 7.8 \times 10^{-6}/°C$

$\alpha_{Ag} = 20.1 \times 10^{-6}/°C$





Summary of results on seals for electrolyte-supported SOFCs

- We are developing reliable SiO_2 - free composite seals for electrolyte supported SOFCs
- Sealing glasses that contain BaO react with YSZ to form $BaZrO_3$, which lowers composite CTE ($BaZrO_3$ CTE = $7.9 \times 10^{-6}/^{o}C$)
- Nano-scale ceramic additives have higher reactivity
  - affects the location of the reaction (additive vs. electrolyte)
  - more rapid stabilization of seal properties (kinetics of $BaZrO_3$ formation)
- Properties of an equilibrium glass-composite can be adjusted to match substrate material properties

Objectives of this phase of the work

- Develop a glass-composite seal suitable for anode supported SOFCs
- Adjust the properties of a SiO_2-based glass to be compatible with anode and interconnect simultaneously (Glass # 27 provided by Prof. R. Brow)
- Determine the seal properties after long-term exposure at service temperature

Experimental procedures

Raw materials:

- SiO_2-SrO-ZnO-Al_2O_3-CaO-B_2O_3 glass
- Ni additive; 2-3 μm diam; 5-30 vol%

Glass-composite fabrication:

- Mechanical mixing of raw materials in Spex mill
- Powder mixture was pressed and consolidated at 50°C above T_g

Analysis:

- DTA: TA Instruments STD-2960; Pt crucibles; 10°C/min to 1000°C
- XRD: Siemens D500 diffractometer (Cu Kα); 20-70°
- Heat treatment: Controlled atmosphere – W elements; 20°C/min to 950°C for 10 min (Ar and Ar-H_2 atmosphere).
- Microstructure: JEOL-5800LV coupled with an Oxford EDS system.
- Thermal expansion: Netzch 402 ED dual rod dilatometer ; 50-550°C in air; sapphire standard.
- Long term exposure: Thermolyne 48000; 500 hrs@800°C

The properties of the glass are suitable for SOFCs seals

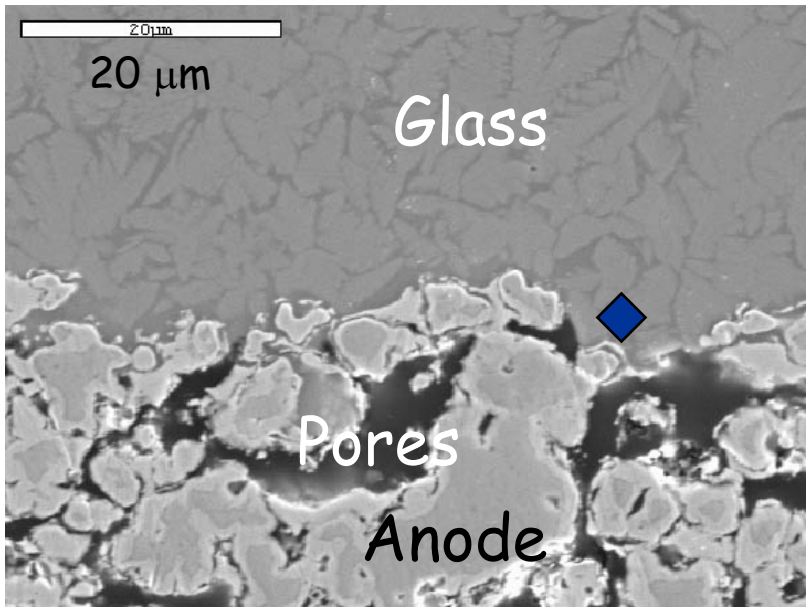
Thermal events during heating

Glass transition temp	700°C
Softening temperature	730°C
Crystallization temp	904°C

Thermal expansion behavior (RT-600°C)

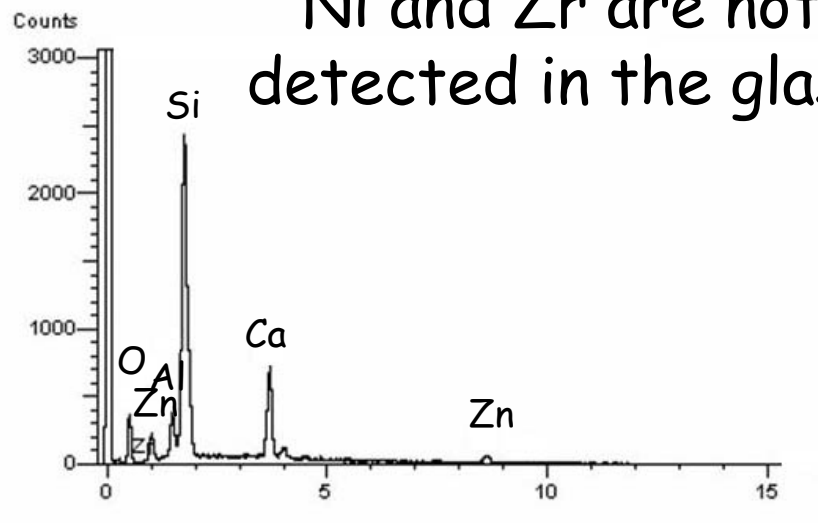
Glassy state	$9.7 \times 10^{-6}/°C$
After heat treatment	$9.8 \times 10^{-6}/°C$
After 3 days @ 750°C	$9.8 \times 10^{-6}/°C$
After 7 days @ 750°C	$9.9 \times 10^{-6}/°C$
After 14 days @ 750°C	$10 \times 10^{-6}/°C$

No sign of reaction between the Brow 27 glass and the anode material



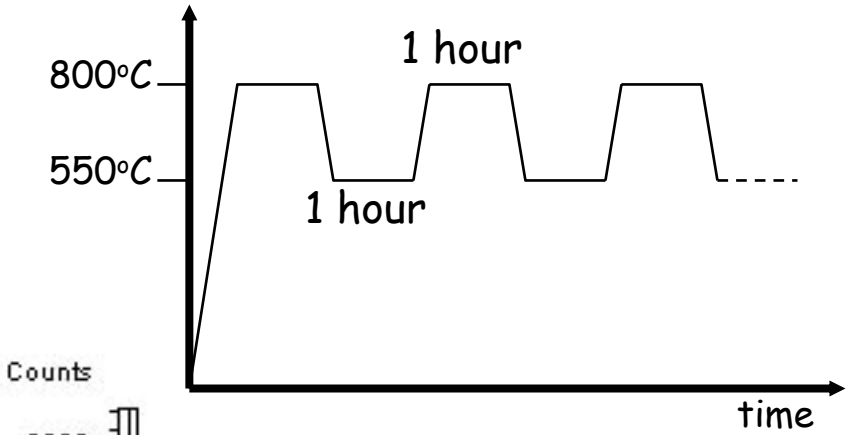
EDS ◆

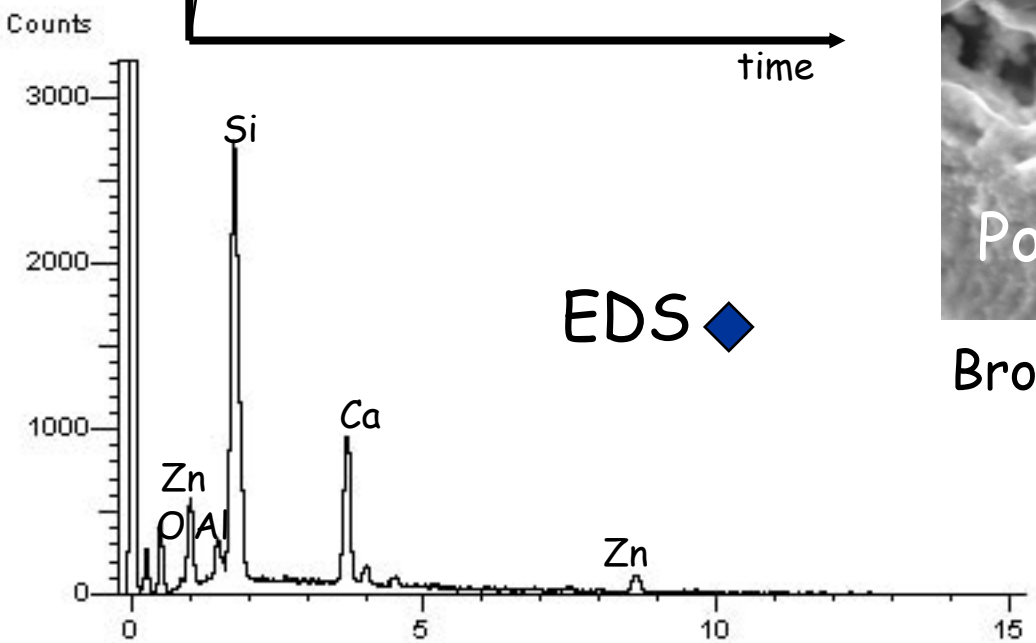
Ni and Zr are not detected in the glass

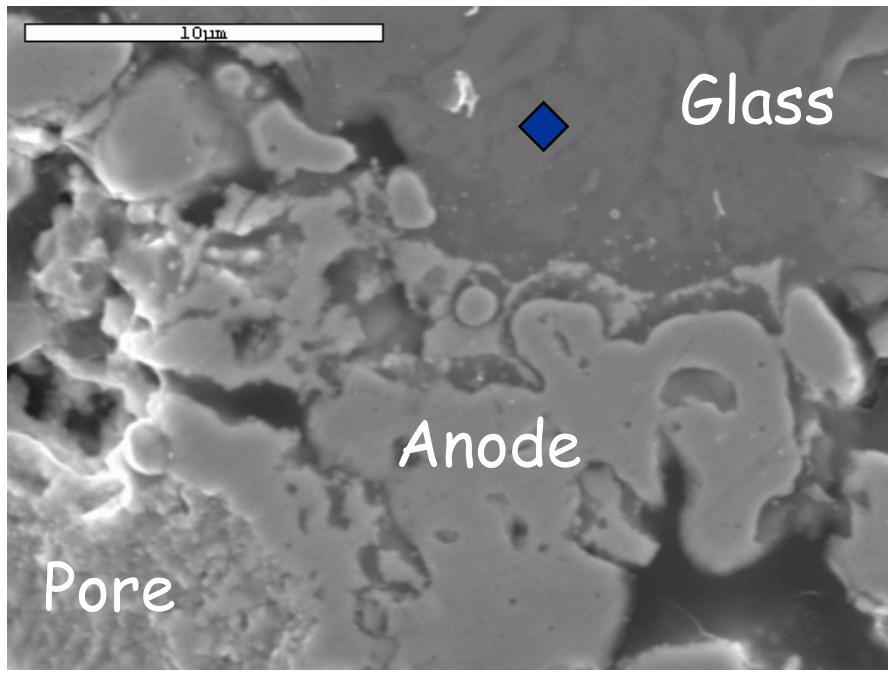


- Adhesion between the glass and the anode
- No dissolution of anode in glass at this scale
- No penetration of the glass into the anode is observed

Interface unchanged after multiple thermal cycles



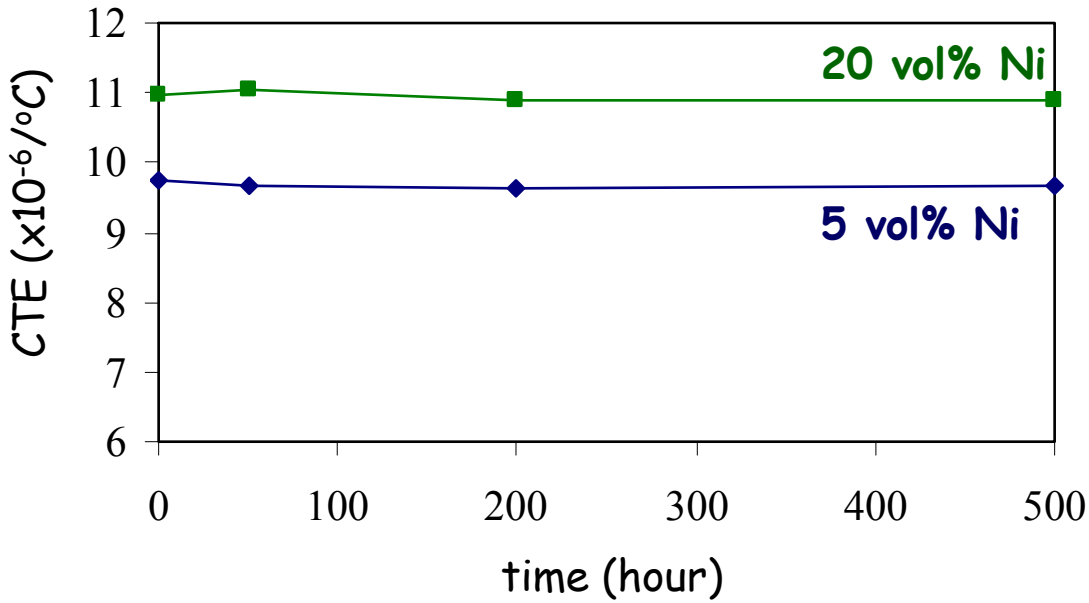


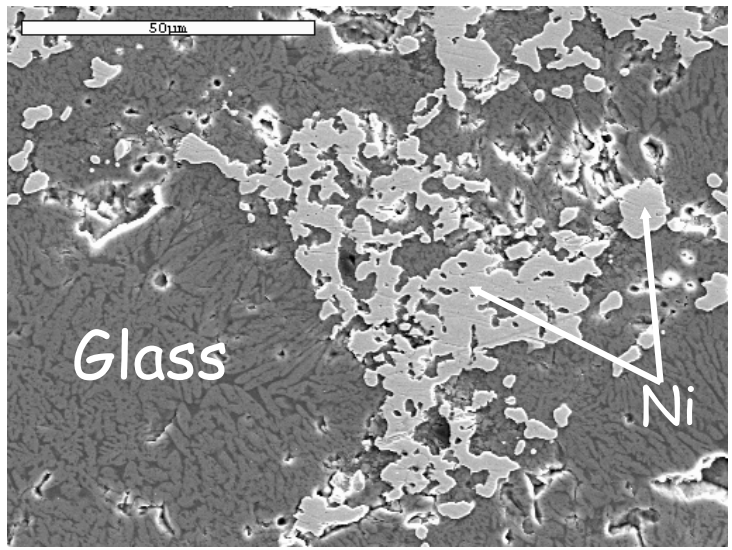


Brow 27 glass-anode interface after 11 thermal cycles in Ar-H_2 atmosphere

The CTE of composite is stable over time @ 800°C

Lack of Ni reactivity with the glass makes Ni powder suitable for adjusting the composite CTE

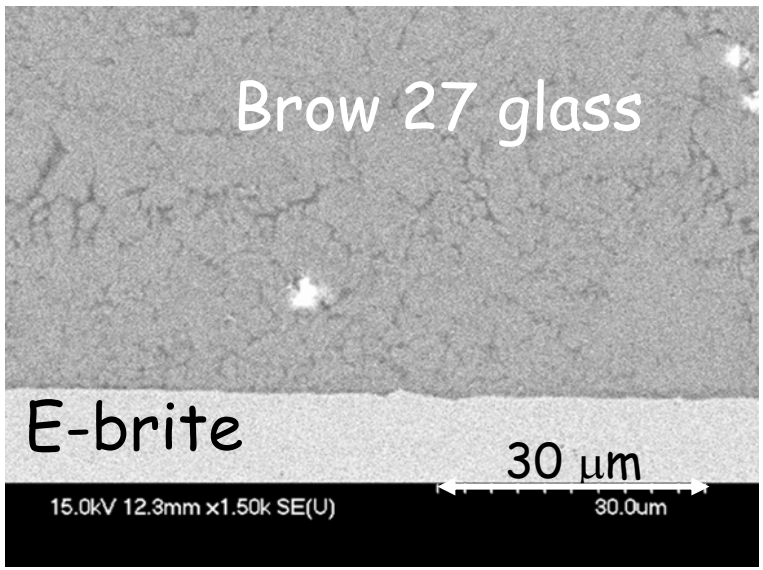




Brow 27 glass-20vol%Ni after sealing cycle of 10 min@950°C

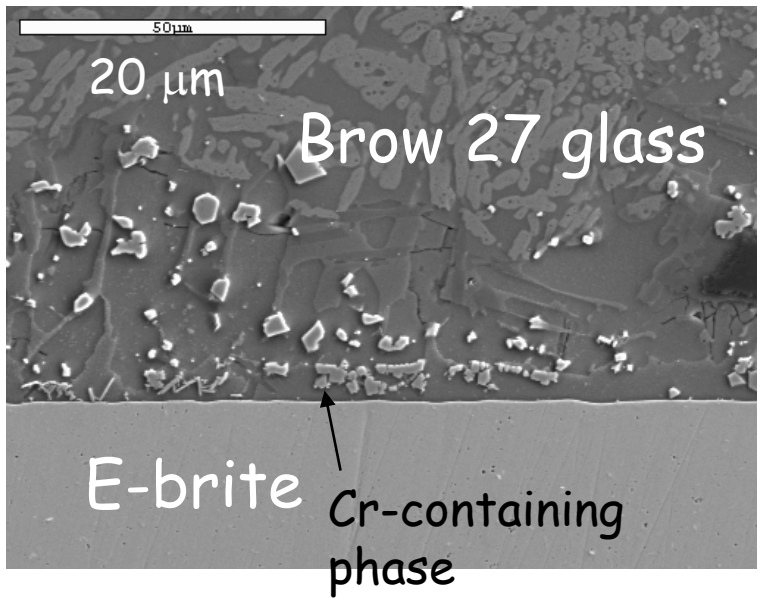
The sealing cycle greatly influences the interaction between the glass and interconnect

Heat treated 2 hours at 800°C and held @ 750°C for 4 days



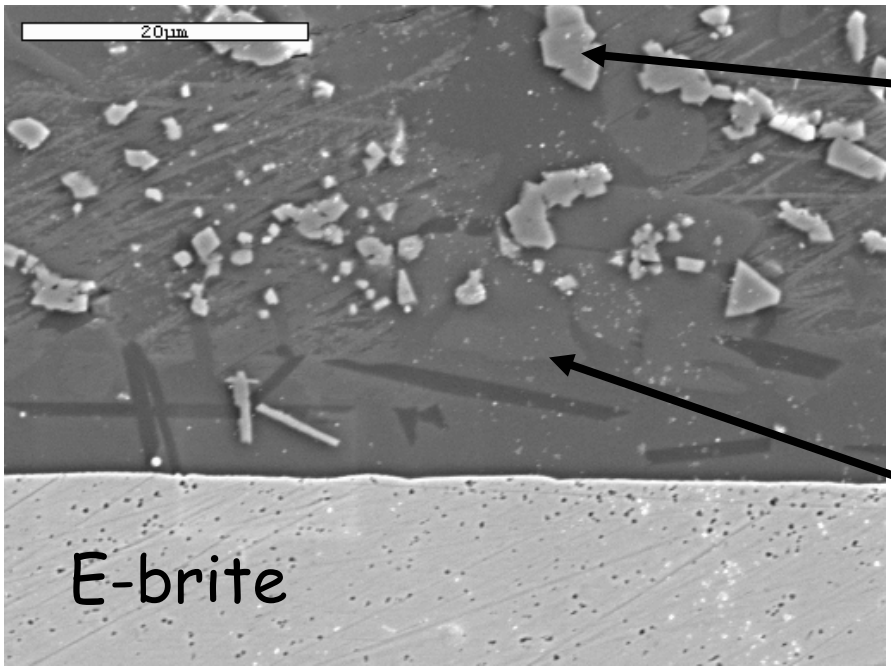
- No major sign of reaction
- Cr was not detected in the glass by EDS

Heat treated 10 min @ 950°C



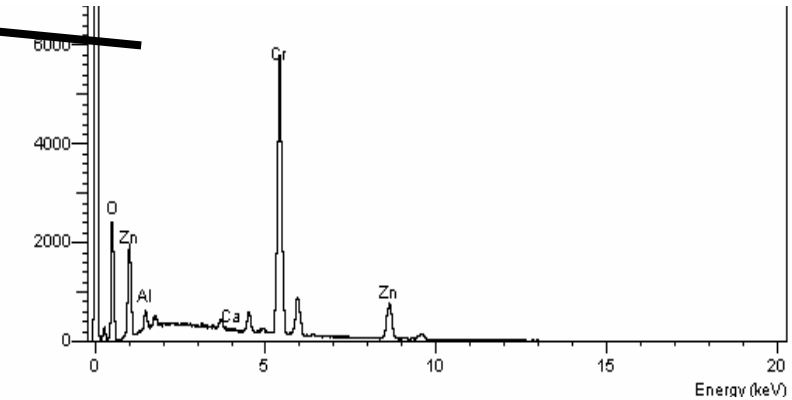
- Some dissolution of Cr from E-brite

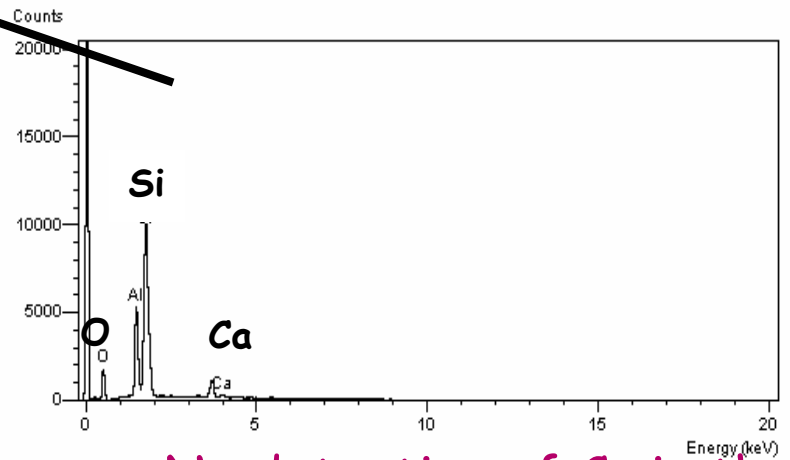
Brow 27 glass seems to be compatible with E-brite alloy at lower temperatures, but reacts at 950°C



After sealing cycle of 10 min @ 950°C

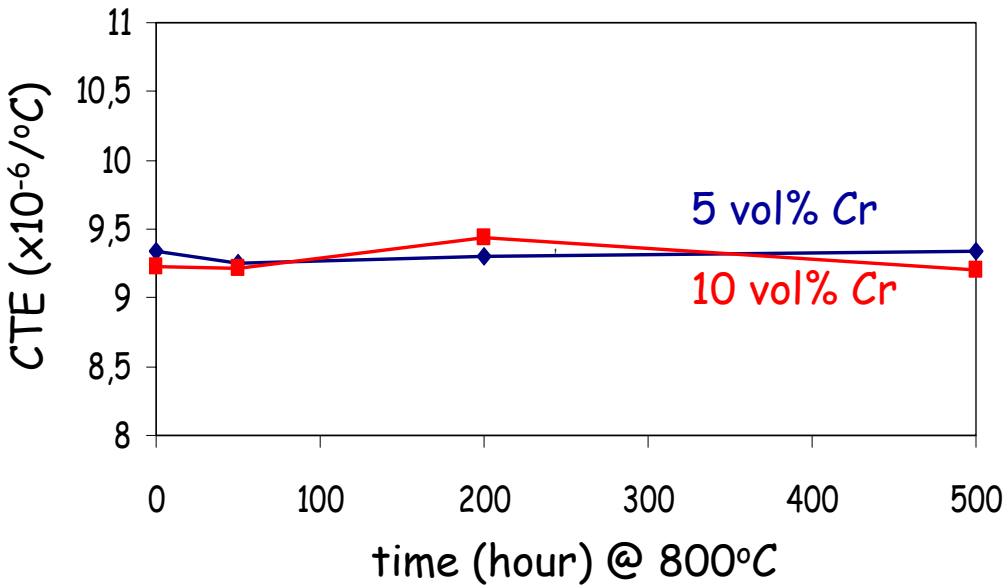
Precipitates contain Zn, Cr, Al, and O





No detection of Cr in the glass matrix

Cr was added to the Brow 27 glass to simulate the effect of Cr dissolution on change of CTE over time



- Compared to pure glass, the addition of Cr reduces slightly the CTE after sealing cycle (10 min@ 950°C)

- The CTE of the composite remains stable after the initial decrease

- This result suggests that once the glass matrix is saturated with Cr, no further dissolution will occur (compatible with SS)

- Possibility of reducing Cr dissolution by pre-reaction with glass

Conclusions

- This glass system (Brow 27) shows no reaction with the anode materials below 1000°C
- The interface maintains adhesion and structure after thermal cycling
- The glass CTE is around 9.5 x 10^{-6}/°C but it can be raised by addition of Ni powder
- The glass seems to have a low solubility for Cr_2O_3, but some formation of precipitates is observed
- Once the glass is saturated in Cr, the CTE of the glass is stable at about 9.3x10^{-6}/°C