Compressive Seal Development for Solid Oxide Fuel Cells

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Outline

- Status of mica-seal development
- Current work objective
- Results of long-term ageing and thermal cycling
  - Problem of degradation/reaction of mica/G18
  - Solutions to reactive interlayer glasses
  - Ageing and thermal cycling with metallic interlayer
  - Issue of long-term Ag volatilization
  - Reproducibility with Ag interlayers
  - Isothermal ageing in 30v% H_2O fuels
  - fractography
  - Issue of long-term mica volatilization in 30v% H_2O
- Summary and conclusion
- Future work

Status of compressive mica seal

Final goals:
- >40,000 hrs stability
- >10^2 or 10^3 cycle
- No degradation to mating mat'l
- Low stresses
- Low cost in SOFC stack
- Vibrational stability?

Hybrid micas survived, ~4000 hr, 47+30+10 cycles @12 psi, 0.02-0.04 sccm/cm @0.2psi

3 solutions to minimize materials degradation

Hybrid micas showed reproducibility

Hybrid Ag micas aged 1000hrs and 39 cycles in 70%H_2/30%H_2O, 0.02-0.03 sccm/cm

Hybrid micas showed low leakage @ 6 psi and Nernst OCV

Hybrid micas survived 88 cycles@12.5 psi

Hybrid micas survived 1026 thermal cycles and 2052 hrs @800C, ~2.7%H_2/Ar+3% H_2O and 100 psi

Glass-mica composites

Infiltrated micas

Hybrid micas

Plain mica paper

Plain Muscovite mica (monolithic)

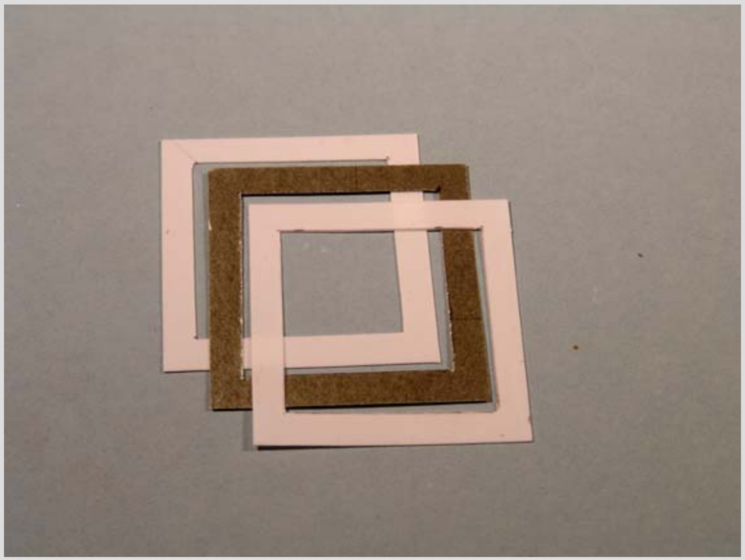
Current work objective

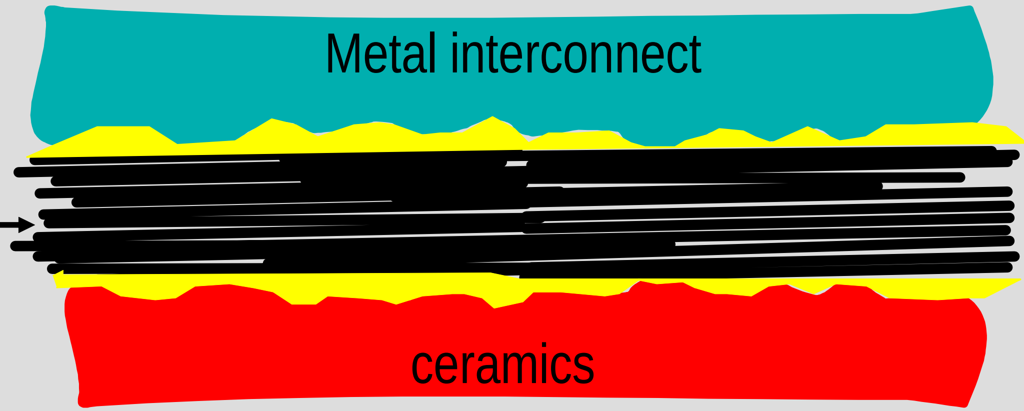
1st and 2nd (FY05) quarters:

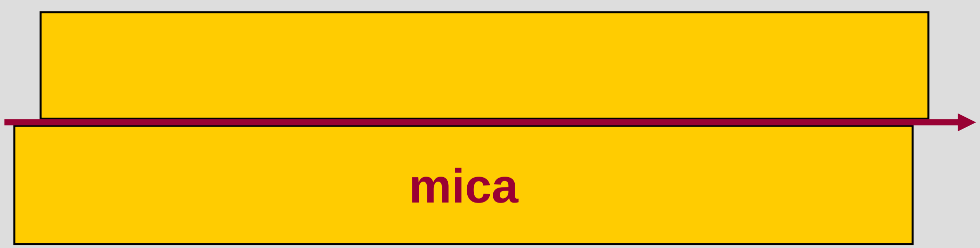
The objective was to evaluate the combined isothermal ageing and thermal cycling effect on hybrid mica seals of metallic interlayers with respect to materials and interfacial degradations in a simulated and high water content (30 v%) SOFC environment.

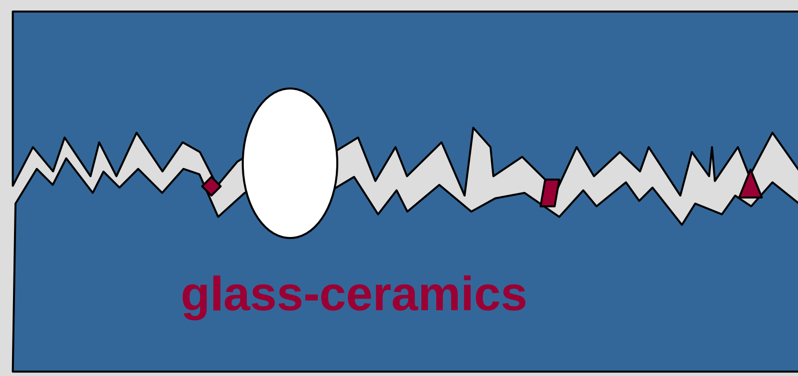
Hybrid Phlogopite mica

Phlogopite is more thermally stable (~960°C) than Muscovite (~600°C)

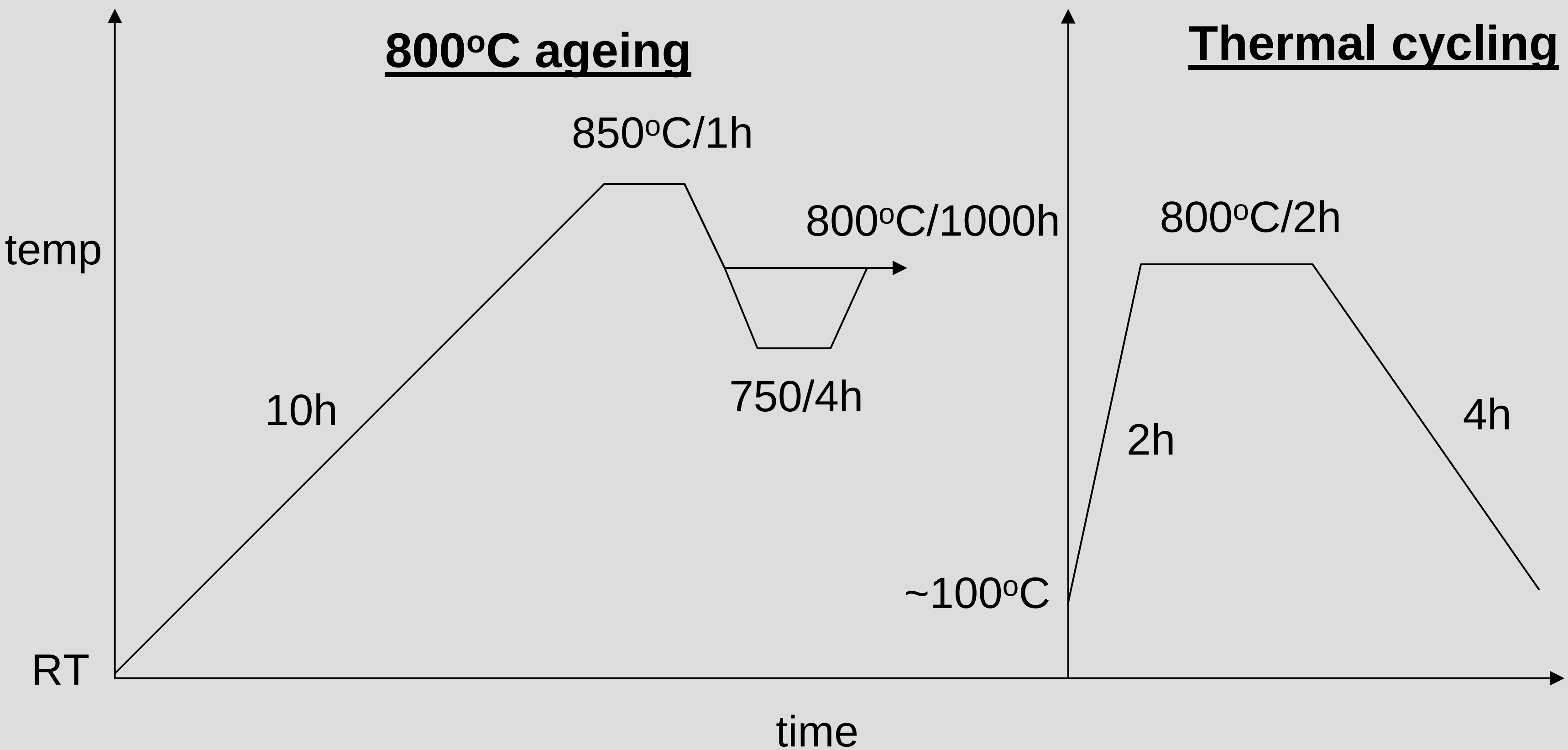






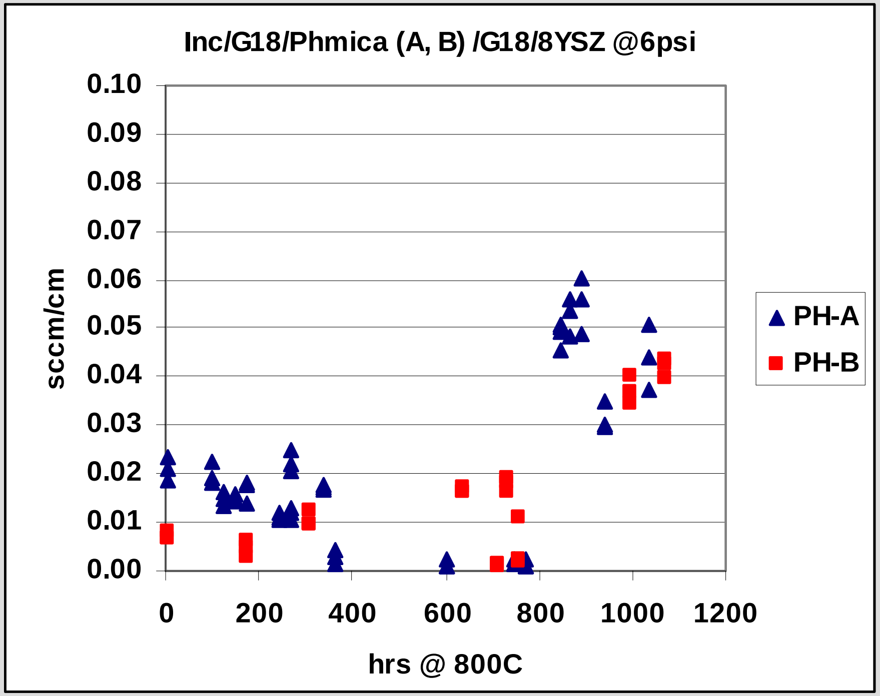


Isothermal ageing and short-term thermal cycling

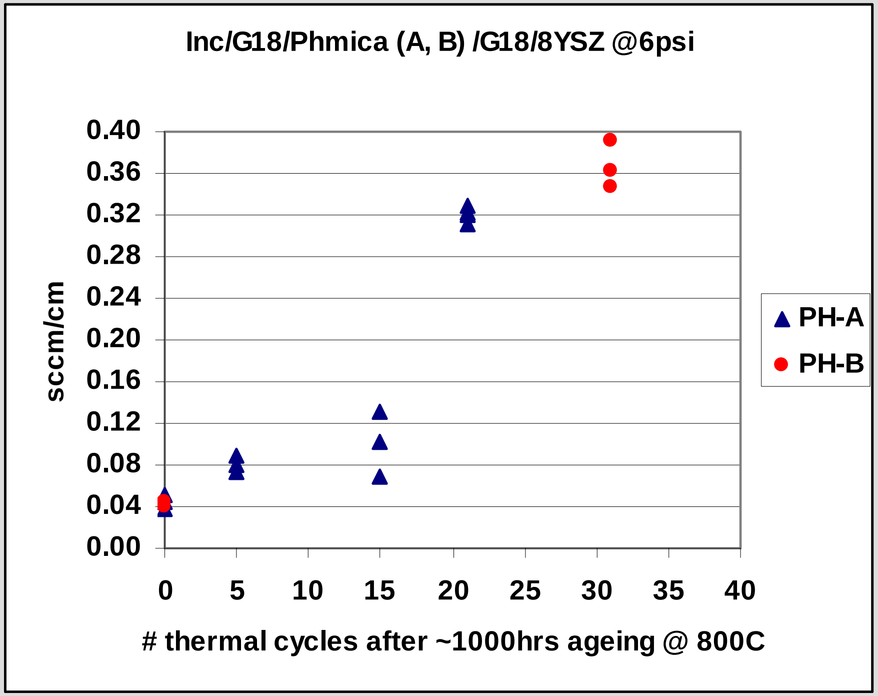


Combined ageing and thermal cycling of hybrid mica with G18 glass interlayers

Inc/G18/PH-A or PH-B/G18/8YSZ @ 6psi with flowing ~2.7%H_2/Ar+~3% H_2O



800°C ageing

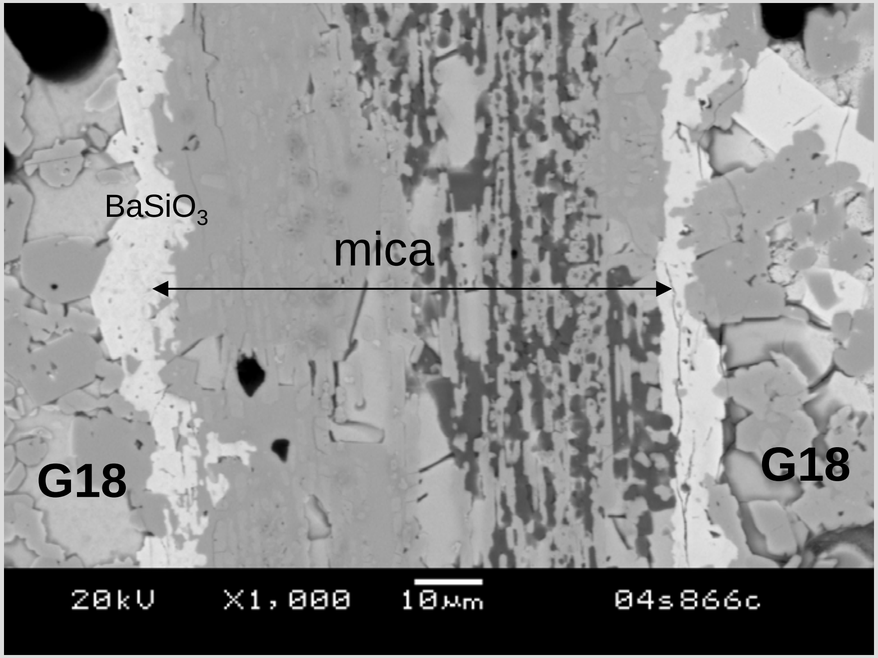


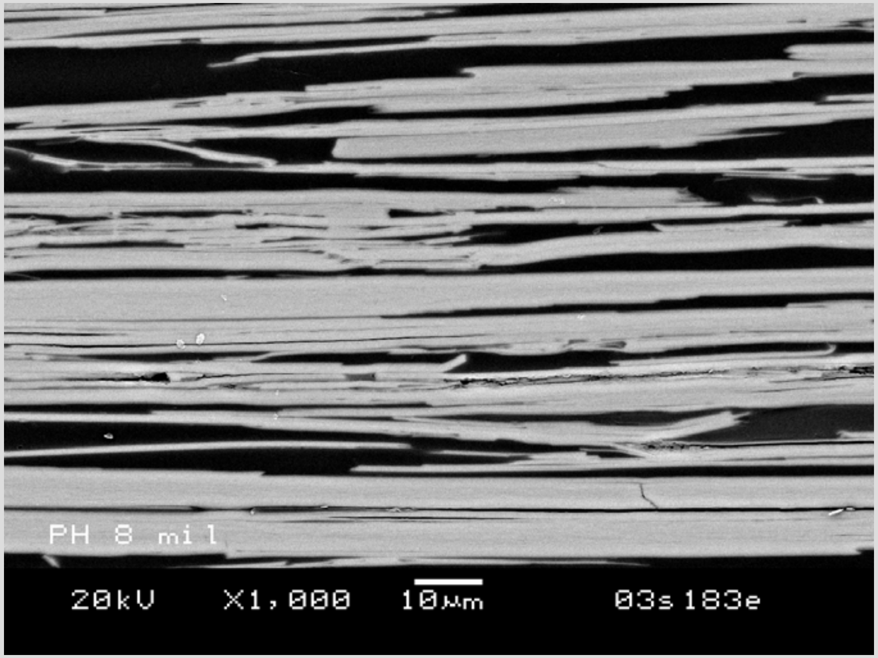
thermal cycling

PH-A: Cogebi, cogemica, PH-B: McMaster Carr

Cross-section of aged and cycled hybrid mica with G18 glass

Pressed @6psi after 1036 hrs ageing and 21 cycles



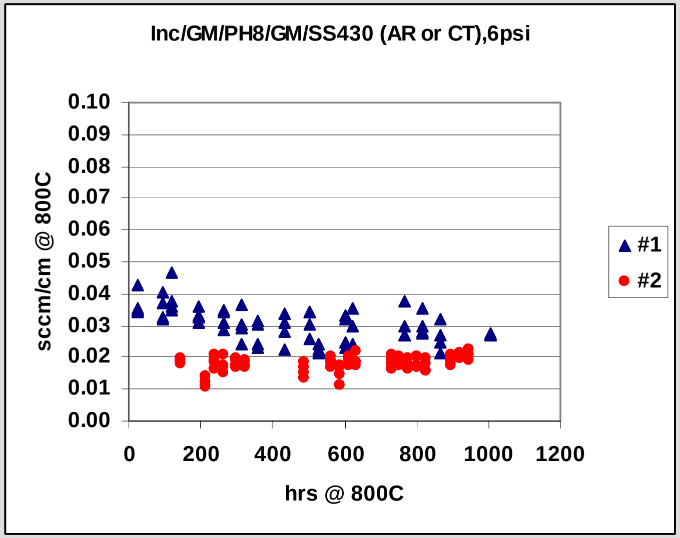


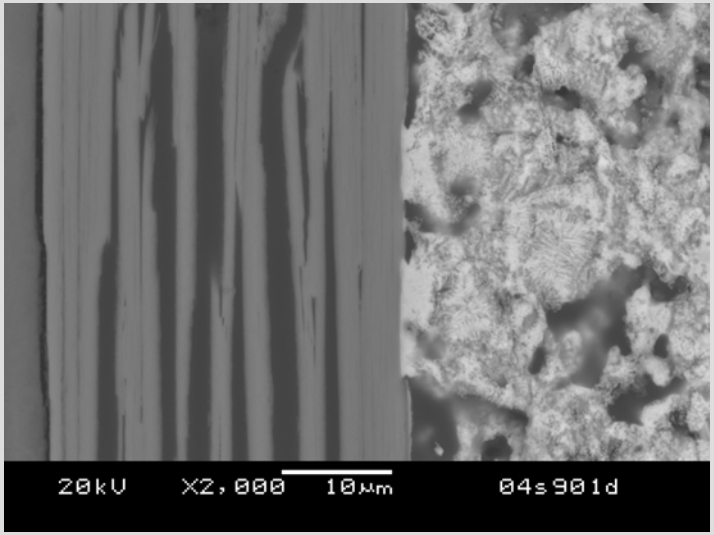
- Fracture occurred along with the G18 glass near the Inconel600 side
- Thick G18 glass showed undesirable porous microstructure

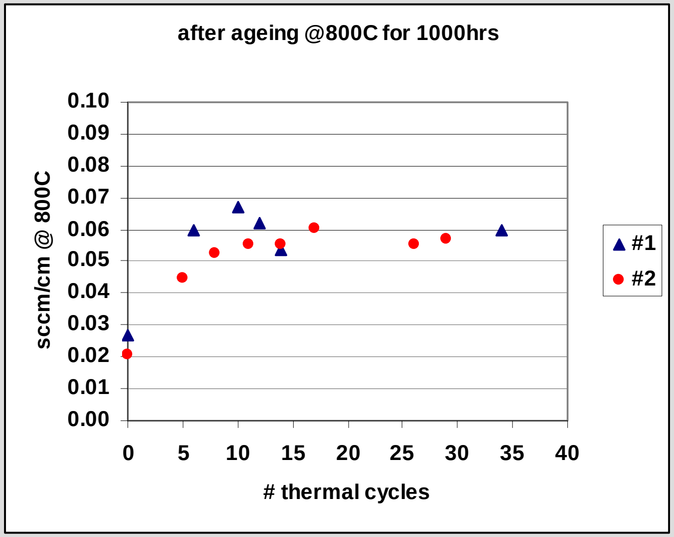
Solutions to minimize mica degradation

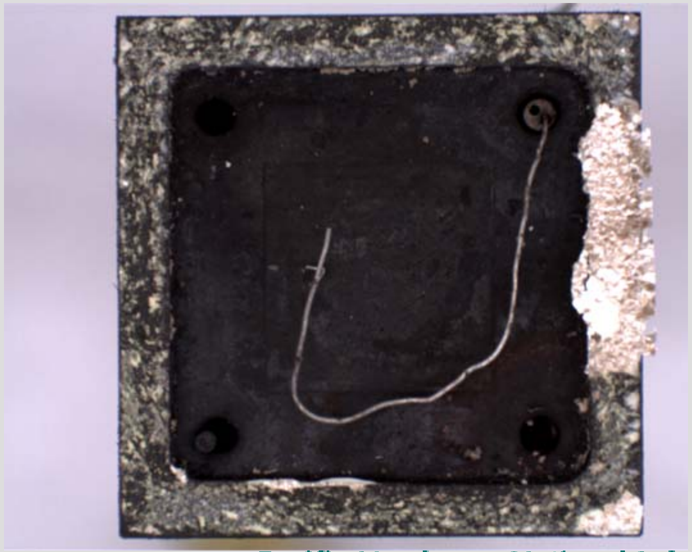
- Promote rapid crystallization of G18 by adding nucleation agent (e.g., TiO_2)
- Use less reactive (more "refractory") glass G-M (less B_2O_3)
- Use of non-reactive metallic materials (Ag, Cu, etc)

No degradation of mica with glass G-M









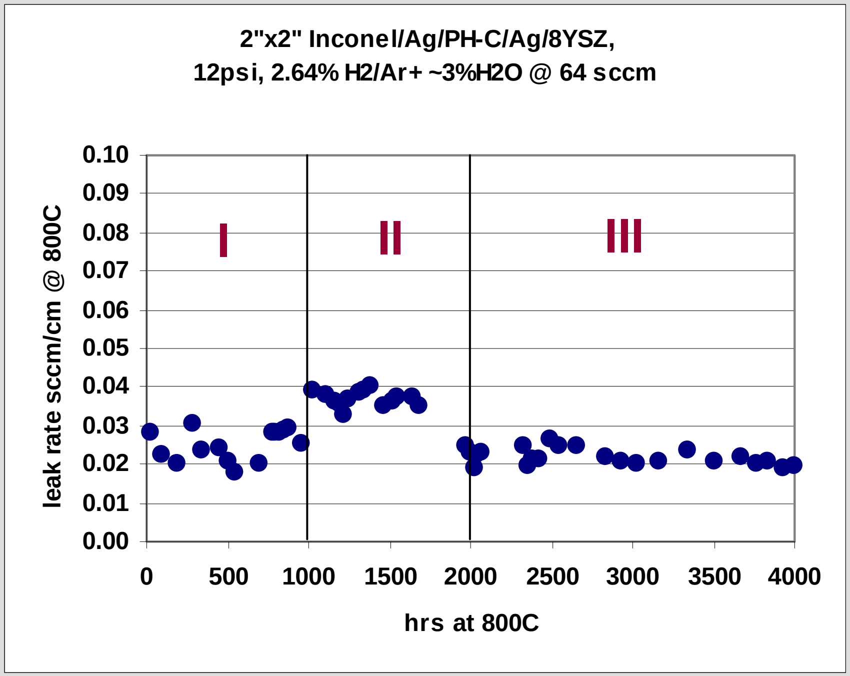
Inconel/GM/PH8/GM/CT SS430 @ 6psi
after 1000 hrs 800ºC and 34 cycles

Hybrid mica with metallic interlayers

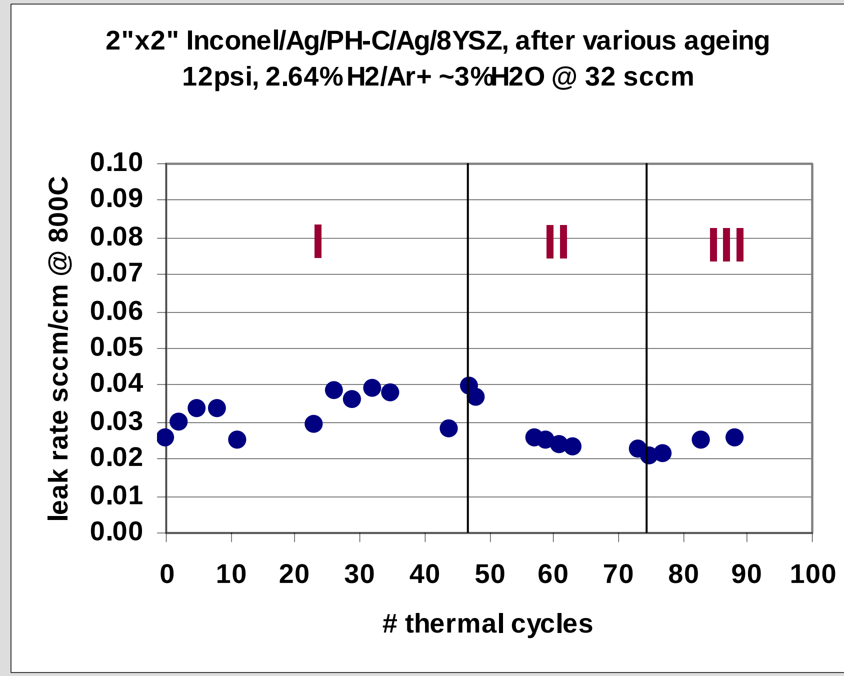
- Non-reactive with Mica
- Volatilization issue
- Oxidation issue
- Poison issue
- High water content fuels
- Easily deformed
- Adhere or bonding to metal of high CTE
- Ag, Cu, and brazes

Ageing and thermal cycling of hybrid mica with Ag interlayers (0-4000 hrs)

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi



Isothermal ageing



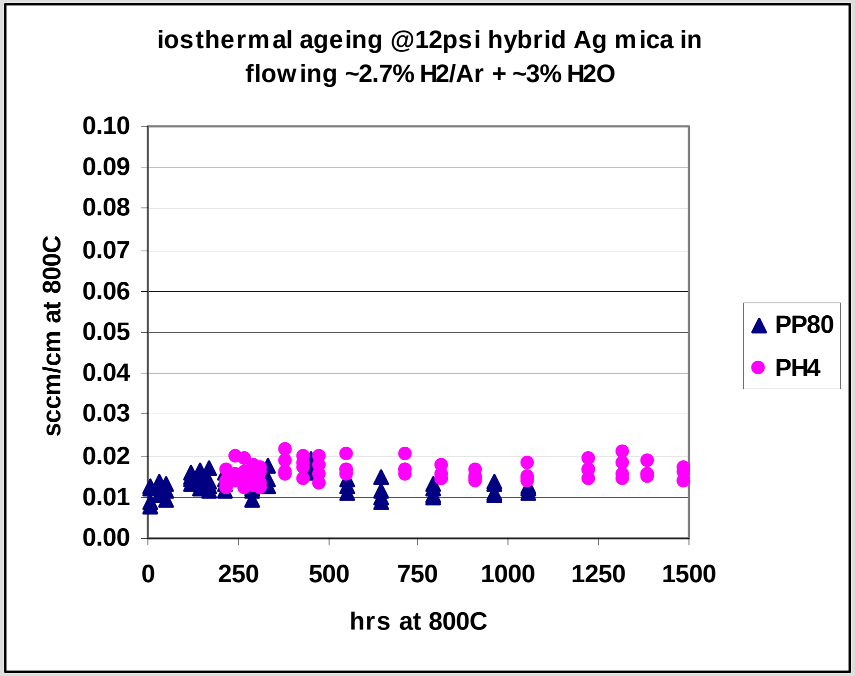
Thermal cycling after ageing

fuel loss = 0.2% @0.03 sccm/cm, 0.2 psid, 0.7V, 0.5 W/cm^2, 800^{o}C, 80% fuel utilization of pure hydrogen of a 6”x6” SOFC cell

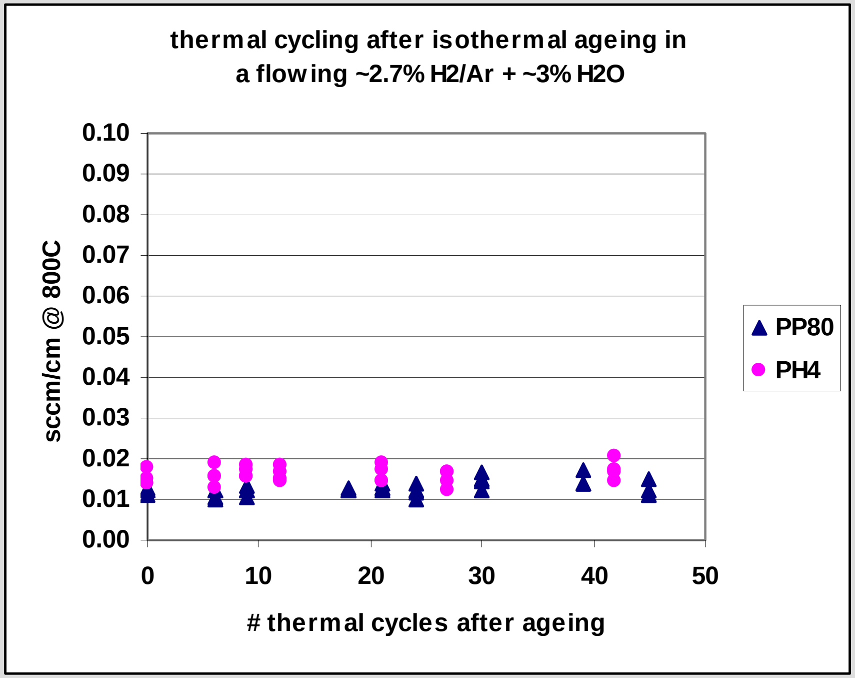
SECA target: fuel loss <1% @ 0.1 psid after 10 thermal cycles for 6”x6”

Good reproducibility for hybrid mica with Ag interlayers

Inconel/Ag/Ph-mica/Ag/SS430 @12psi, 2.7%H_2/Ar+~3% H_2O

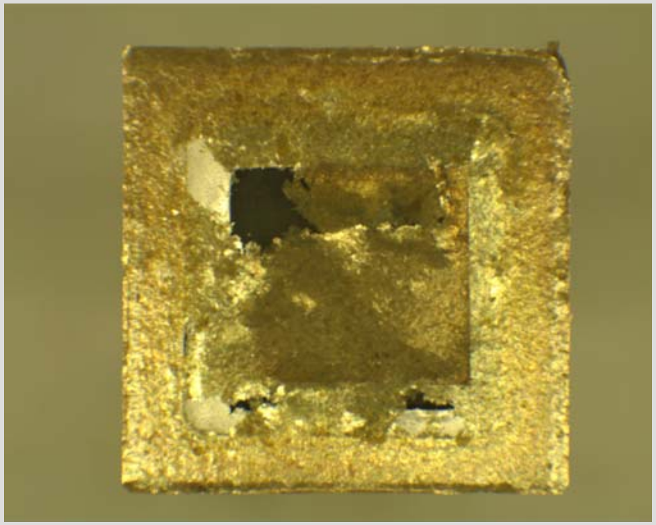


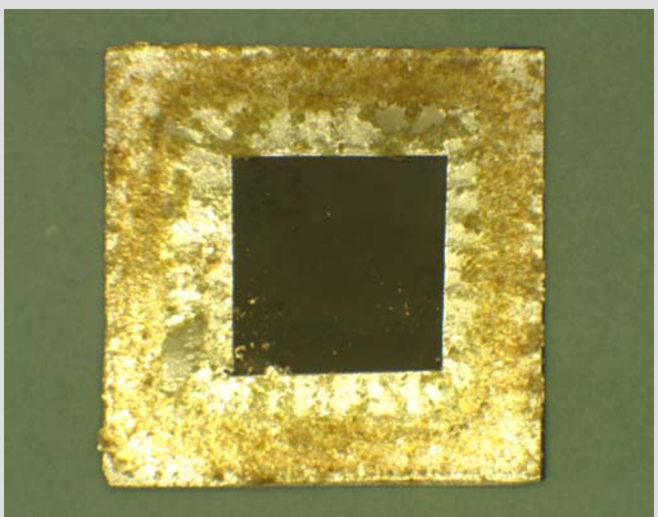
Isothermal ageing

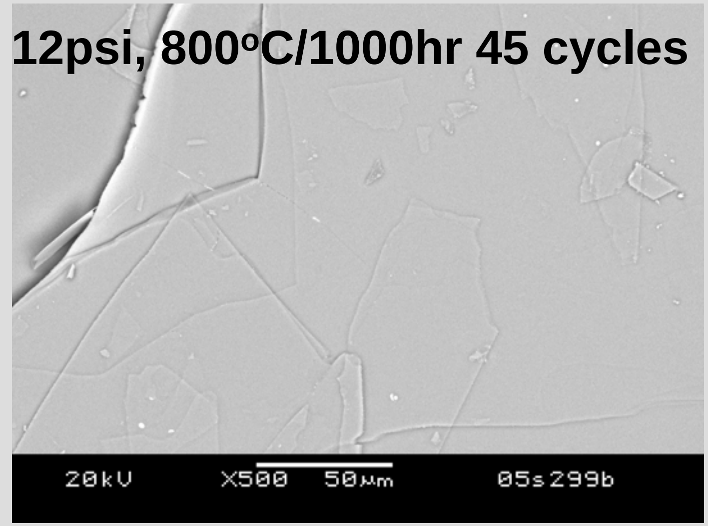


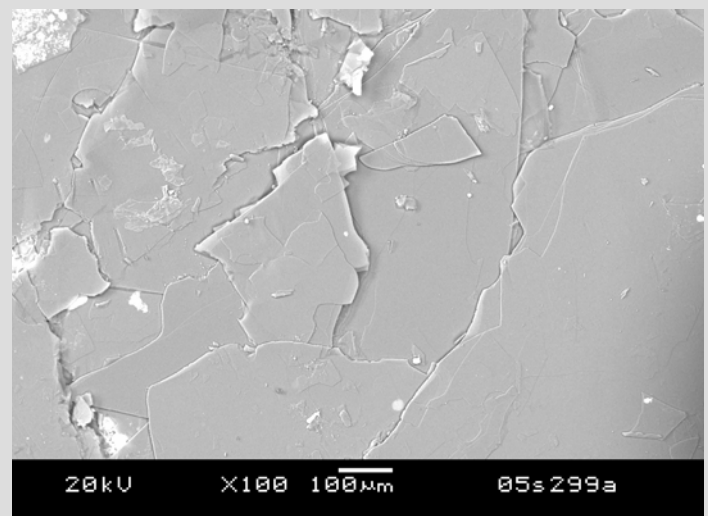
Thermal cycling after ageing

Fracture surface of aged and cycled hybrid mica with Ag interlayers



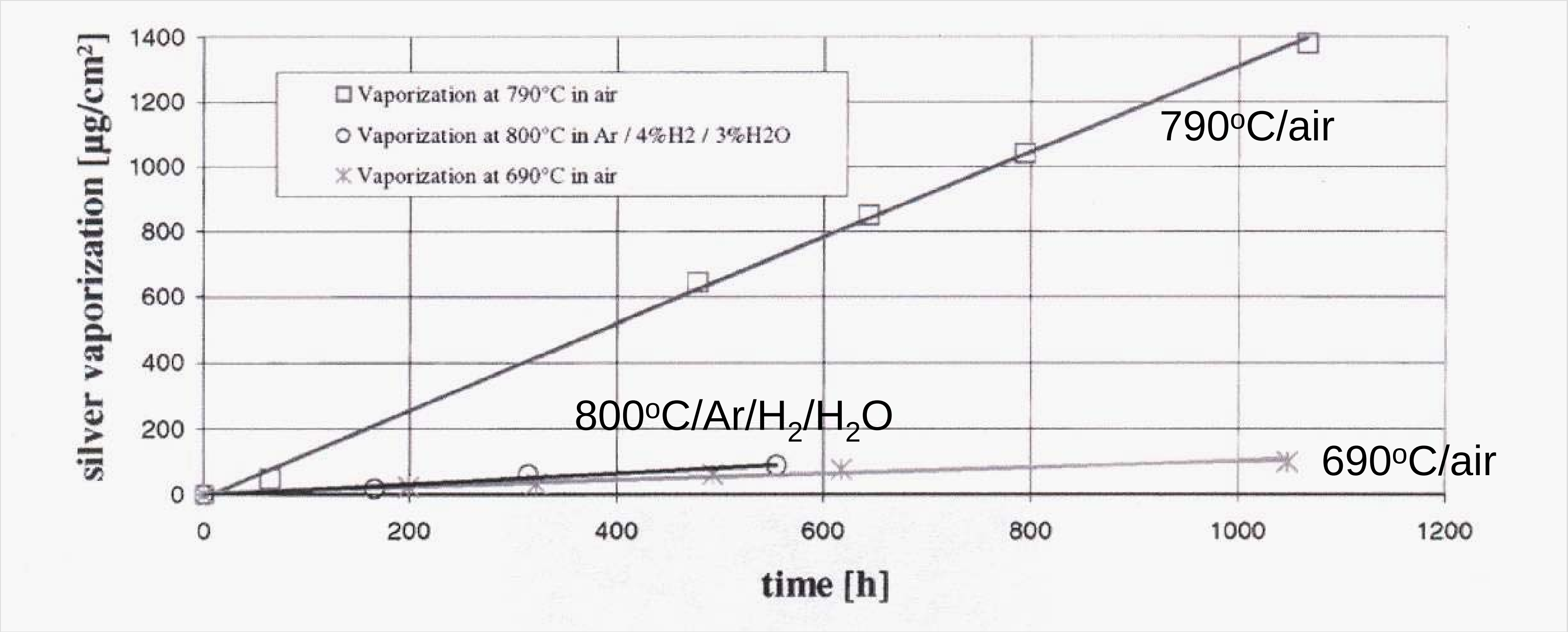






Issue of vaporization loss of Ag

From Meulenberg etal J. mater. Sci., 36 [6] 3189-3195 (2001)

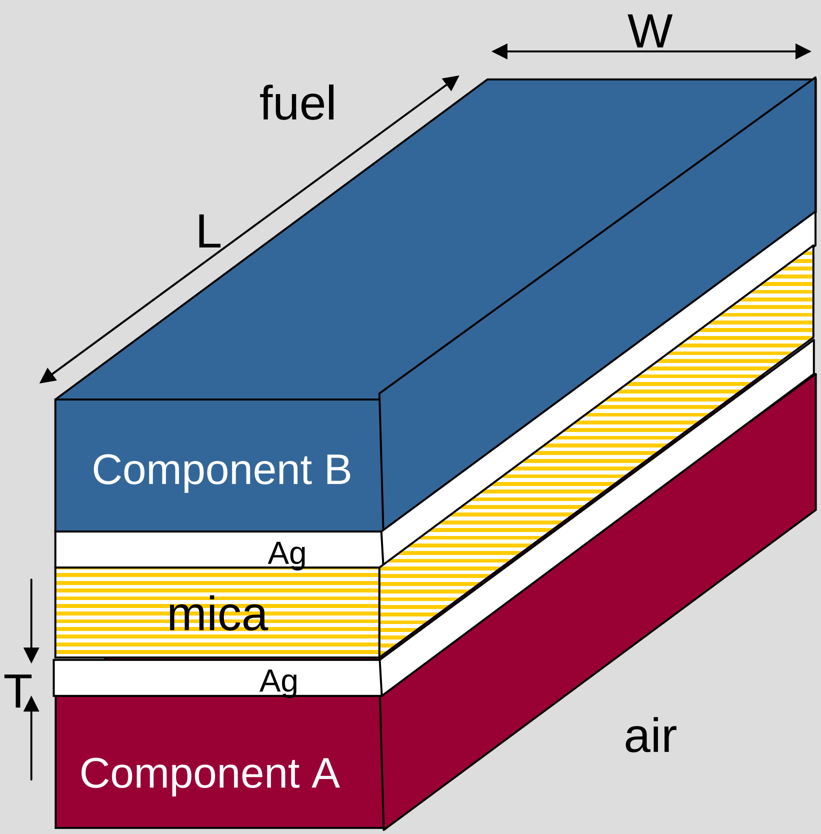


690^oC/air: 0.094 $\mu g/cm^2/h$ — 2.16% @40,000hrs

790^oC/air: 1.29 $\mu g/cm^2/h$ — 28.7% @40,000 hrs

$800^oC/Ar/H_2/H_2O$: 0.161 $\mu g/cm^2/h$ — 2.33% @40,000 hrs

~1 wt% loss of Ag in hybrid mica over 40,000 hrs @ 790-800ºC



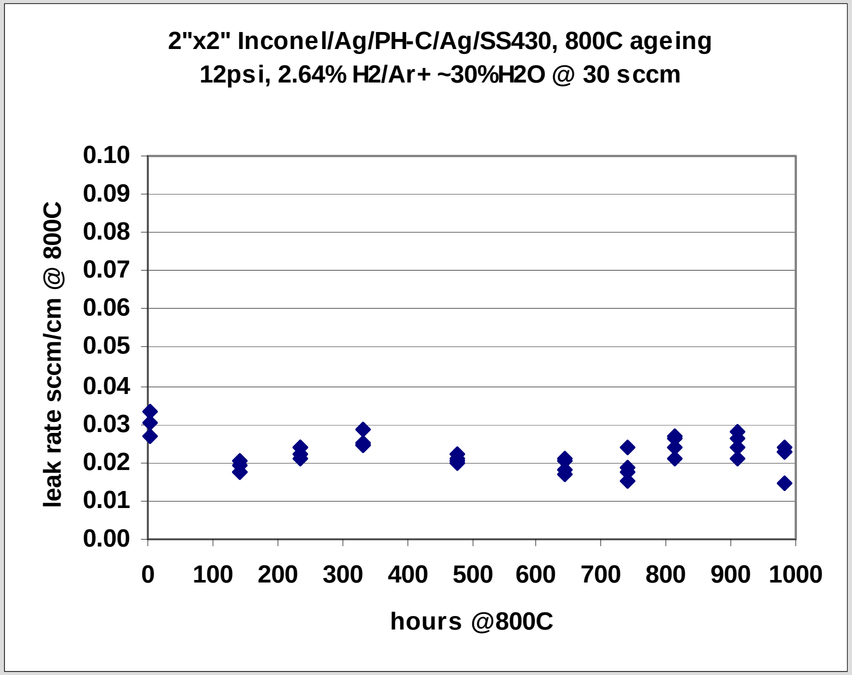
For a width (W) = 0.5 cm
ρ(Ag) = 10.5 g/cc

Ag loss on fuel side
=40,000(aTL)/(ρTWL) = 0.12%
Ag loss on air side
=40,000(bTL)/(ρTWL) = 0.98%

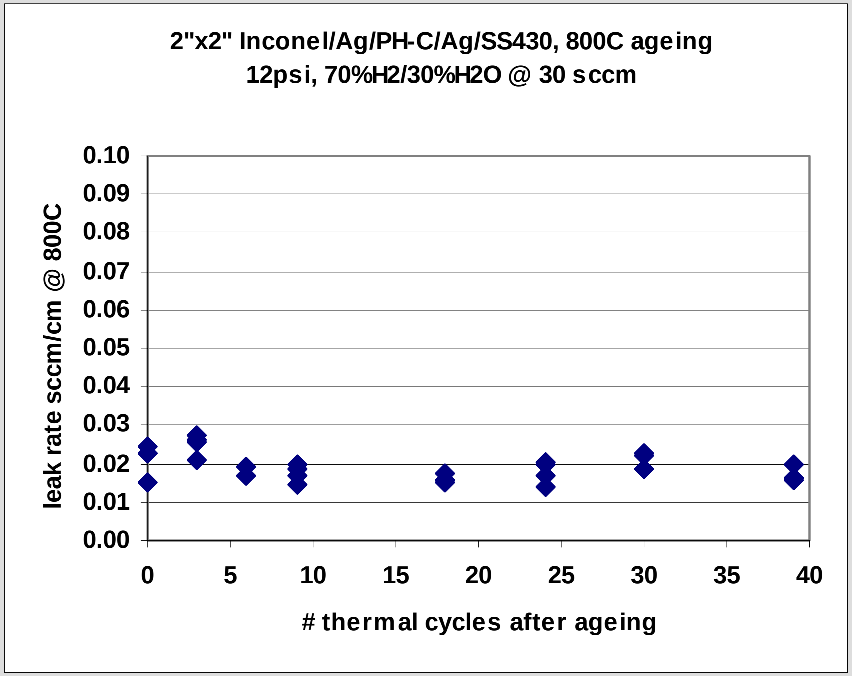
- **Loss from exposed edges only**
- **No diffusion loss to metals**
- **Electrical shorting?**
- **Degradation of electrochemical performance unknown; however, possible solutions are available.**

Ageing and thermal cycling of hybrid mica in high humidity (30v%) fuel gas

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi



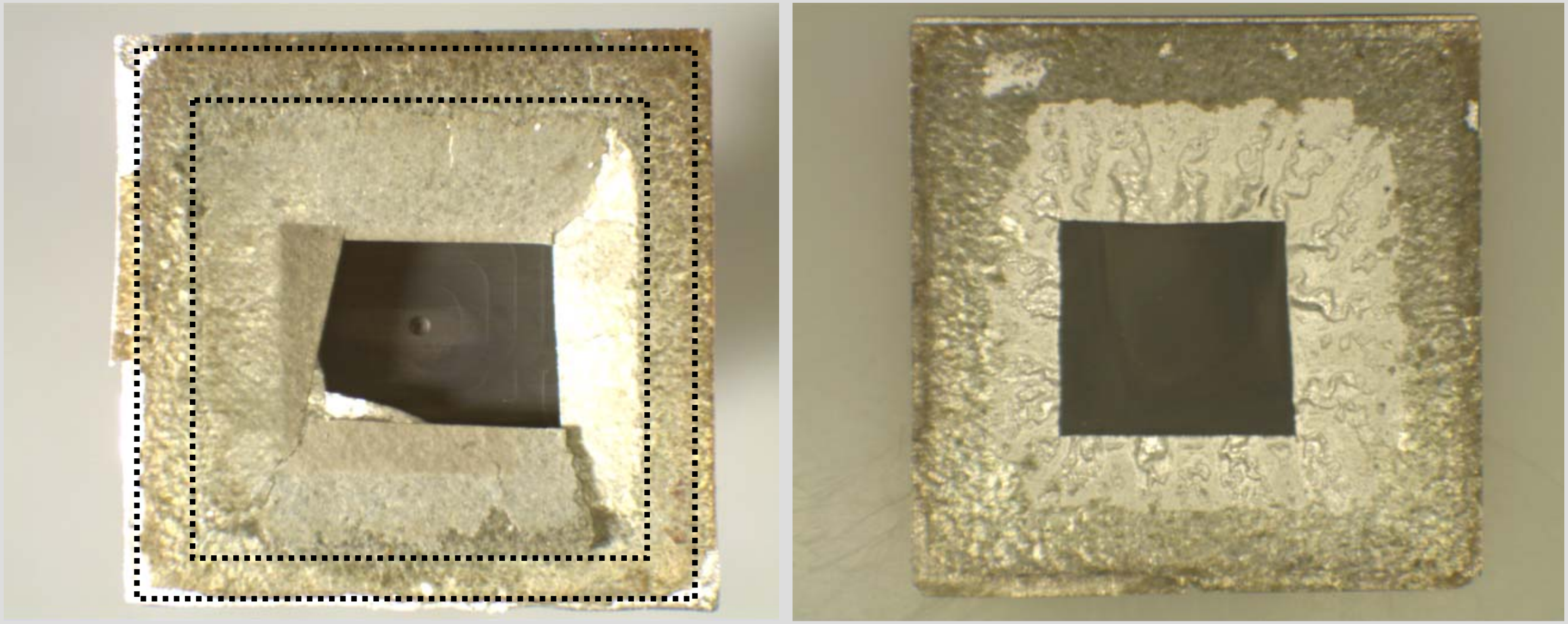
Isothermal ageing



Thermal cycling after ageing

Fracture surface of aged hybrid mica in 70% H_2/30% H_2O @800^oC

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi, 1000hrs and 39 cycles



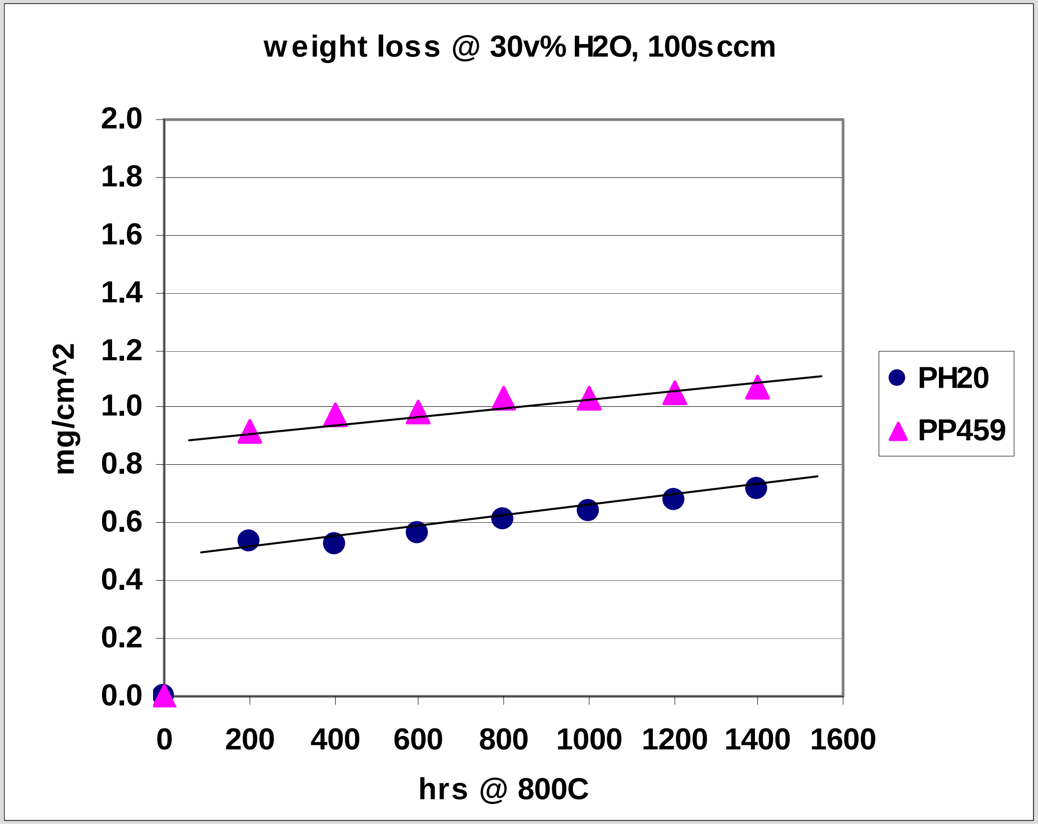
Majority fracture between mica flakes, one spot of mica/Ag interface

Issue of vaporization loss of Phlogopite mica, $KMg_3(AlSi_3O_{10})(F,OH)_2$

- Silicate glass material loss by $Si(OH)_4$ g
- 1”x1” mica exposed in 2.7% H_2/bal. Ar + ~30v% H_2O @ 100 sccm, 800°C

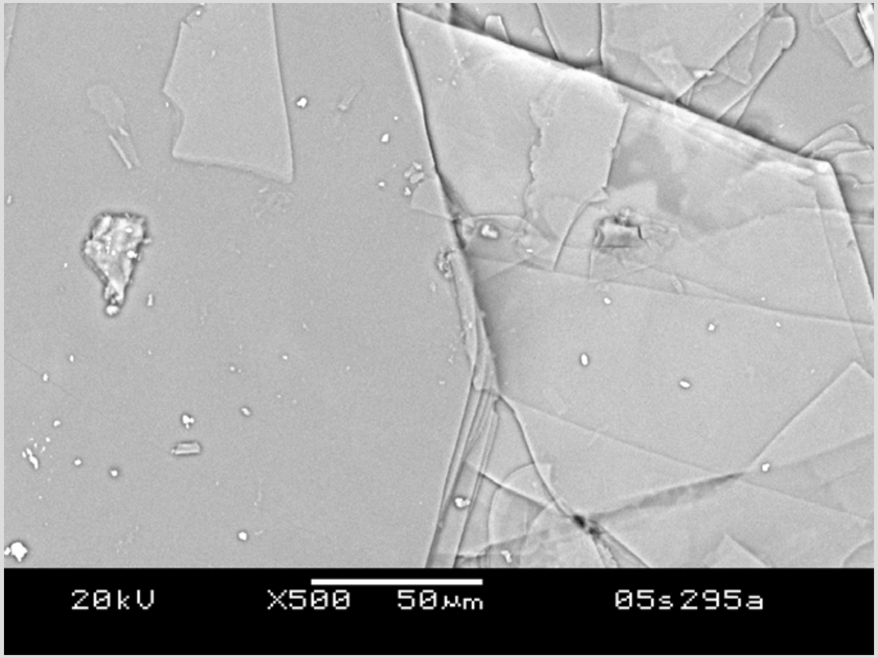
slope =
~1.2×10^{-4} mg/cm²/h
~1.6×10^{-4} mg/cm²/h

Incomplete binder
Burnout <200 hrs

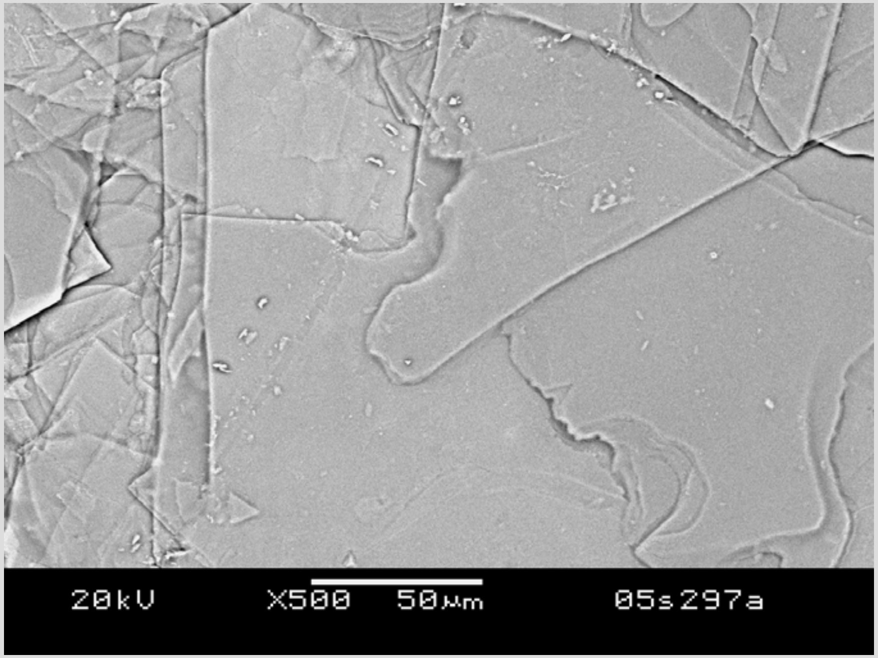


No degradation to mica exposed to 30 v% H_2O @ 800°C/1400hrs

1"x1" mica in 2.7% H_2/bal. Ar + ~30v% H_2O @ 100 sccm, 800°C/1400 hrs

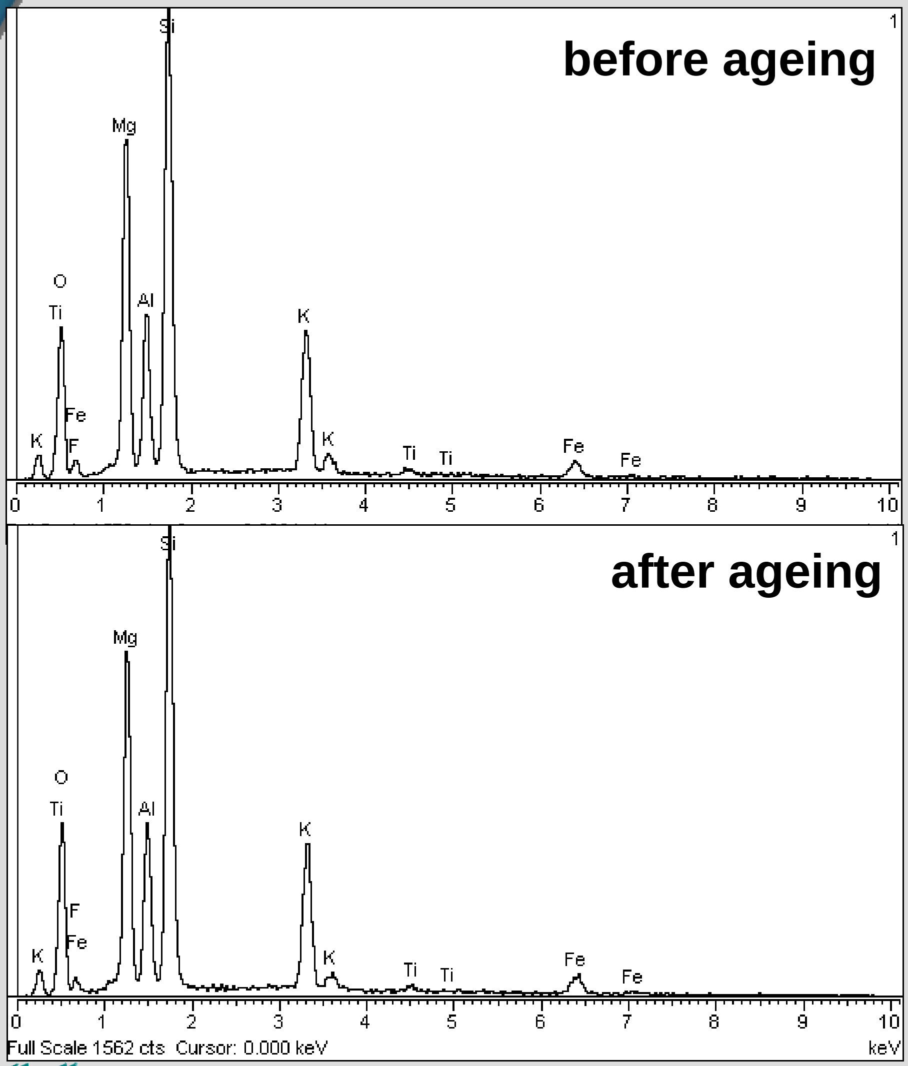


before ageing



after ageing

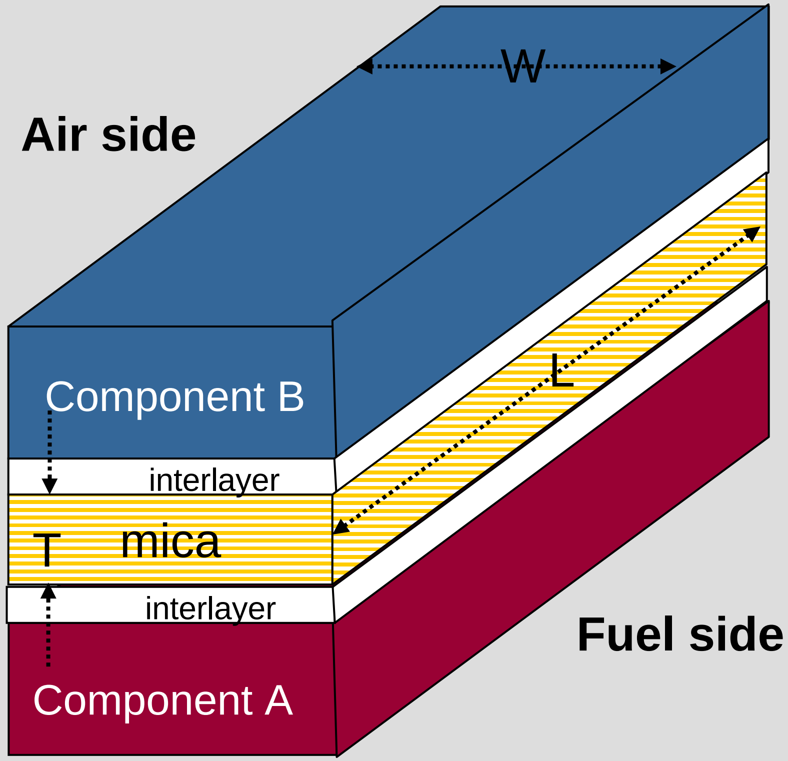
No degradation to mica exposed to 30 v% H_2O @ 800^{o}C/1400 hrs



1”x1” mica in 2.7% H_2/bal. Ar + ~30v% H_2O @ 100 sccm, 800^{o}C/1400 hrs

Element	before	after
O K	46.3	48.1
F K	4.34	4.1
Mg K	14.97	14.44
Al K	6.69	6.56
Si K	20.15	19.51
K K	6.09	5.75
Ti K	0.25	0.23
Fe K	1.22	1.32

Minute loss (<0.5 wt%) of Phlogopite @ 800°C and 30 v% H_2O fuel gas



For a width (W) = 0.5 cm
ρ(mica) = ~2.82 g/cc
a=1.2-1.6 mg/cm^2/hr

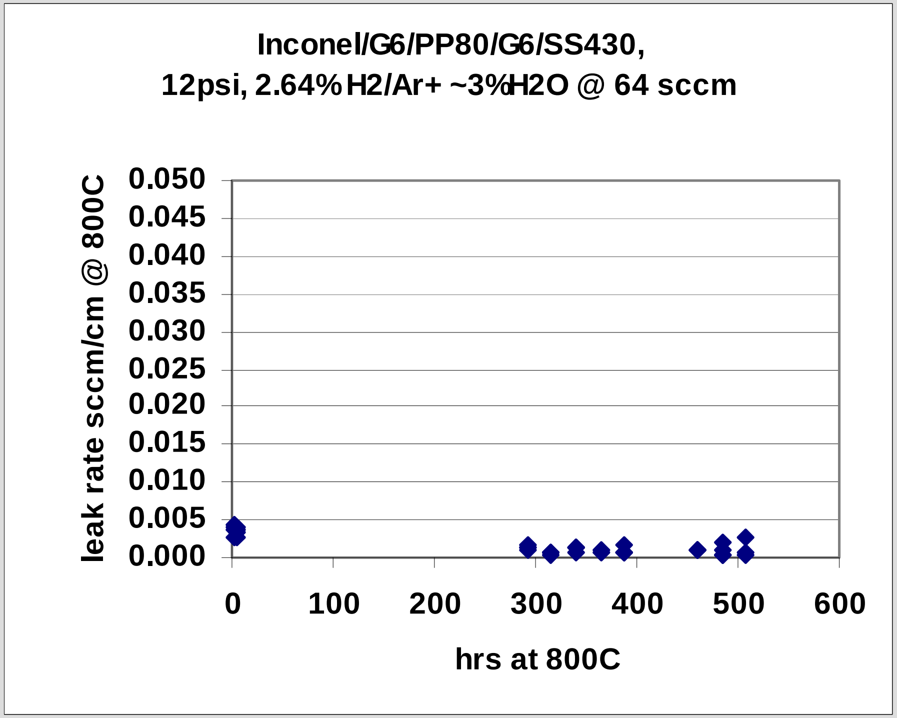
mica loss on fuel side
= 40,000(aTL)/(ρTWL)
= ~0.34-0.45 wt%

- mica loss from free exposed edges at fuel side only

Engineering control the leak rate

$$\text{total leak} = K_{eff} A \frac{dP}{dx} + D_{eff} A \frac{dC}{dx}$$

Reduce leak by increasing seal width and/or reducing mica thickness



Conclusion

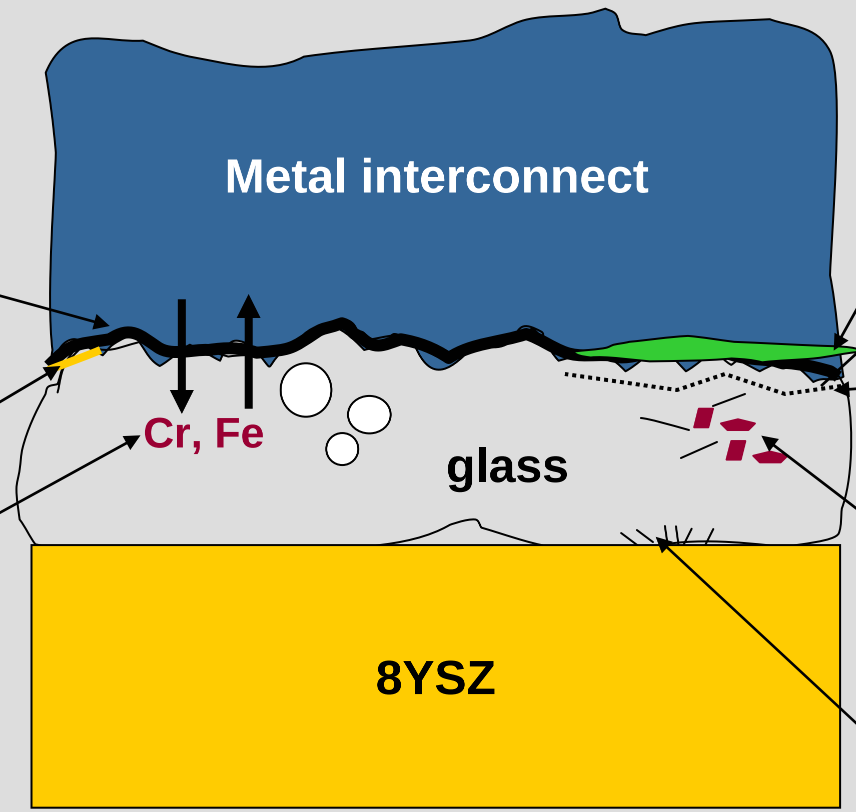
Hybrid Phlogopite mica demonstrated desirable properties as a strong candidate for SOFC sealing:

- Long-term thermal cycle stability over 1026 cycles.
- Long-term ageing stability with constant leak rates (~0.02 sccm/cm) over 4,000 hrs.
- Constant leakage during combined ageing and thermal cycling.
- Low leakage (~0.01-0.02 sccm/cm) at minimal stress of 6 psi.
- Good thermal stability in high water content fuels (30 v%), lean and rich in hydrogen.
- Calculated minute materials loss due to volatilization over 40,000 hrs.
- Identified the effect of mica thickness and compressive stresses.
- Identified cause for mica degradations and 3 solutions demonstrated.
- Good reproducibility and scale-up from 2”x2” to 3.5”x3.5”.
- No effect of temperature gradients on leakage during thermal cycling.
- Low leakage (~0.02 sccm/cm) satisfied SECA’s target of <1% fuel loss.
- Low cost, easy processing, and engineering.

Future work

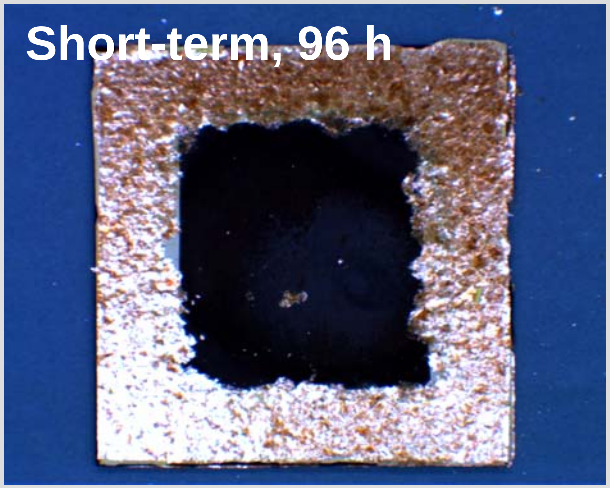
- Development of durable low-cost glass (glass-ceramics) seals with minimal materials/interfacial interaction/degradation and engineered interface for optimal shear strength at various sealing temperatures.
- Study interfacial reaction/degradation of G/M and G/C at various stages of operation, temperatures, and environments
- Understand and model engineered interface for optimal interfacial strength: to prevent Mode II and III fracture
- Evaluate "refractory" glass compositional effect on basic thermal properties (T_g, T_s, T_c, CTE, sealing temperatures, 850-1100^{o}C)
- Identify the microstructural effect due to crystallization on basic thermal and mechanical properties
- Candidate metals: Crofer22 and FeCrAl and surface treatment
- Candidate ceramics: 8YSZ/NiO-YSZ anode bilayers
- Candidate glasses: alkaline earth-Al-Ca-Silicates

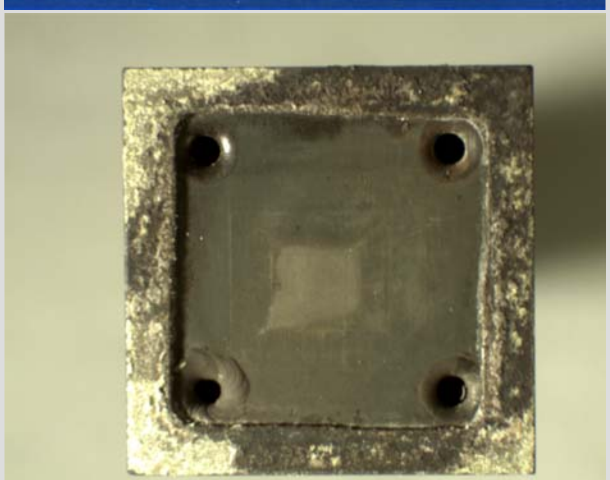
Weakest link is at the metal/glass interface



Oxidation scale or reaction/corrosion products at the metal/glass interfaces often have mismatched CTE.

proposed fracture of a rigid glass (glass-ceramic) seal at various stages





Intermediate stage, 1000 h