Compressive Seal Development for Solid Oxide Fuel Cells

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Outline

- Technical issues
- R&D Objectives and Approach
- Results to Date

  Long-term thermal cycling of hybrid micas: OCV results

  Effect of compressive stress on leak rate versus thermal cycling

  Effect of stack size on the fuel loss

  Effect of temperature gradient on leak rate versus thermal cycling

  Thermal cycling of large sample in pure hydrogen environment

  Allowable leak rate: electrochemical consideration
- Applicability to SOFC commercialization
- Activities for the next 18 months

Current technical issues for compressive mica seals

- Will hybrid mica seals survive long-term thermal cycling (10^2-10^3 cycles) in SOFC environments?
- Will hybrid mica seals have sufficiently low leak rates after repeated thermal cycling?
- How low can the applied compressive load be?
- Will they survive thermal cycling with temperature gradients?
- How low a leak rate is allowable, both electrochemically and mechanically?
- Does the hybrid mica seal have long-term ($40x10^3$ hrs) mechanical, thermal, and chemical stability in SOFC environments?
- Will the compressive stresses cause undesirable creep or plastic deformation of the metallic stack components?
- Will they cause degradation or corrosion to mating materials?

R&D Objective

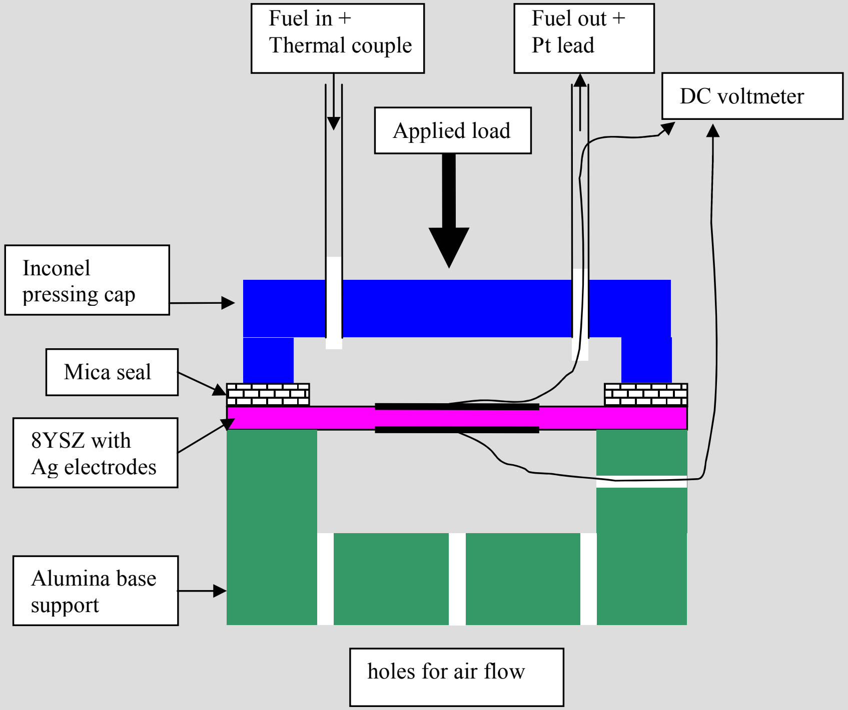
The R&D objective of this project is to develop a ***durable*** and ***low-cost*** compressive seal technology with properties to meet all SOFC stack requirements at very ***low compressive stresses***.

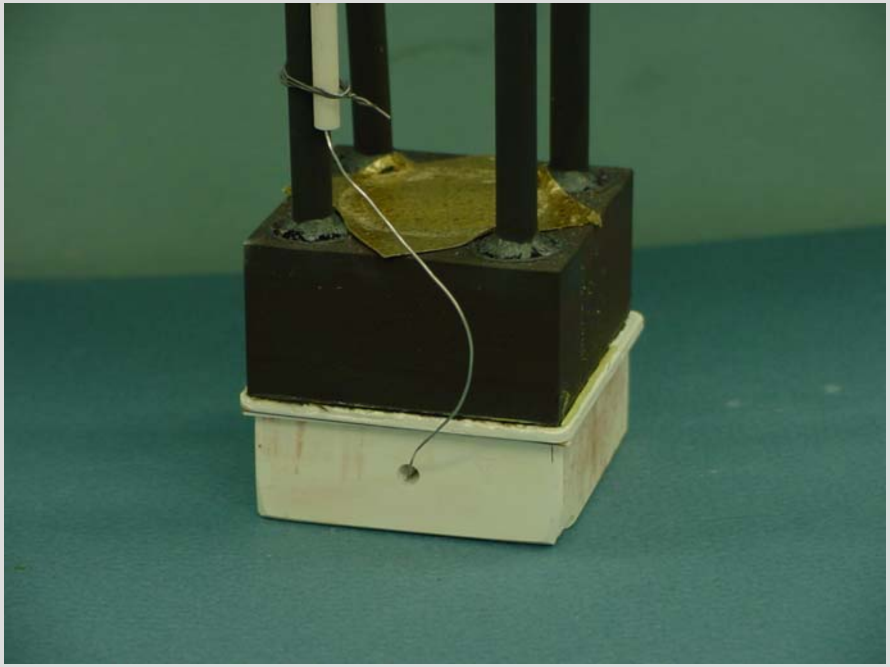
R&D Approaches

- Hybrid mica seals were developed after identification of major leak path at interfaces of compressive mica gasket seals. The concept was tested successfully with a glass or metallic inter-layers.
- Infiltrated Phlogopite micas can further lower the leak rates while maintaining thermal cycle stability. Good chemicals for infiltration yet to be identified.
- Concept of “infiltrated” mica was also successfully demonstrated on glass-mica composites at lower stresses. Processing technique yet to be identified.
- Evaluation of the hybrid micas and glass-mica composites under long-term thermal cycling in a simulated SOFC environments is in progress.
- Testing hybrid micas in a temperature gradient profile.
- Leak rate data is being obtained for hybrid micas and glass-mica composites over a wide range of compressive stresses (6 to 100 psi).

Results update
OCV v.s. long thermal cycle test

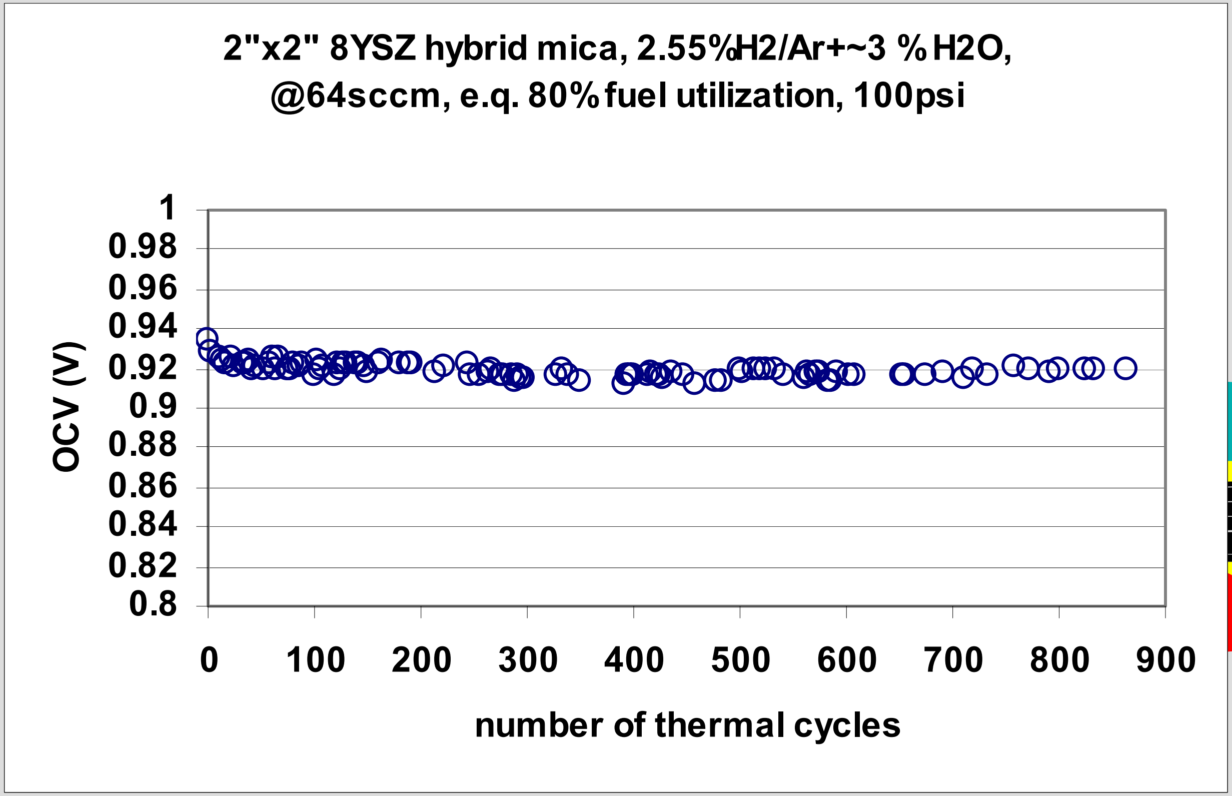
2”x2” 8YSZ dense plate with hybrid mica seals at 100 psi
Ag electrodes, Pt lead wire, and Inconel600 or SS430 block on alumina block



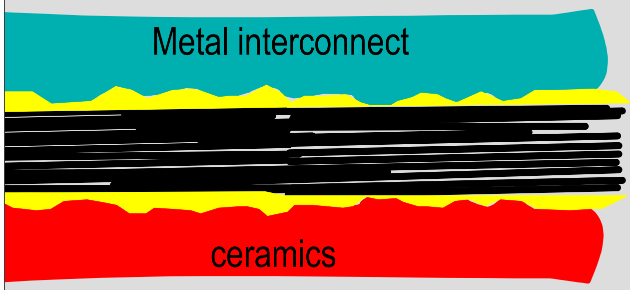


Long-term thermal cycling and OCV tests

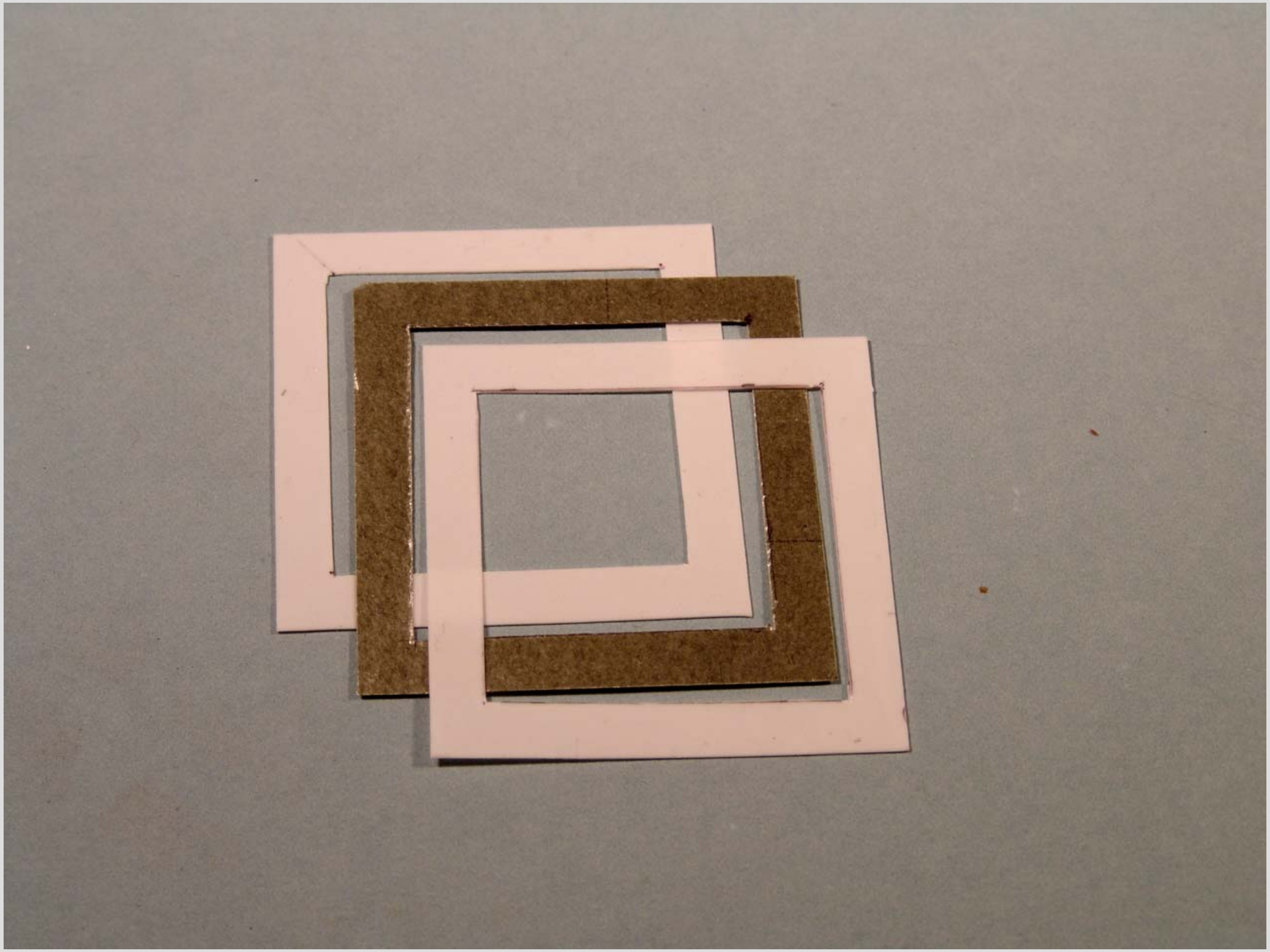
Loss of ~1.4% (OCV=0.919 V) after 864 thermal cycles (@ 100 psi)
At 63 sccm of 2.55% H_2/Ar + ~3% H_2O versus air



Hybrid mica seal:
As-received mica paper sandwiched between 2 glass interlayers

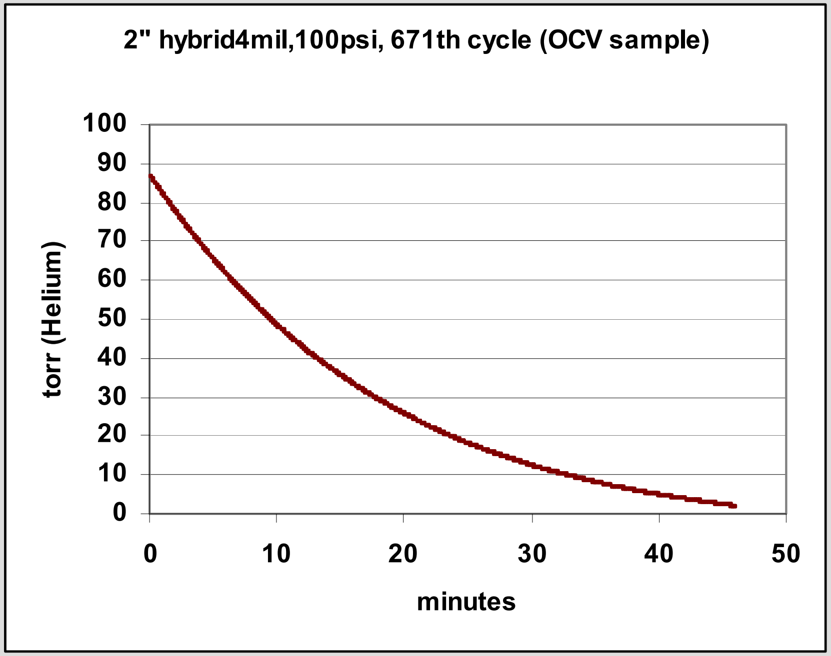


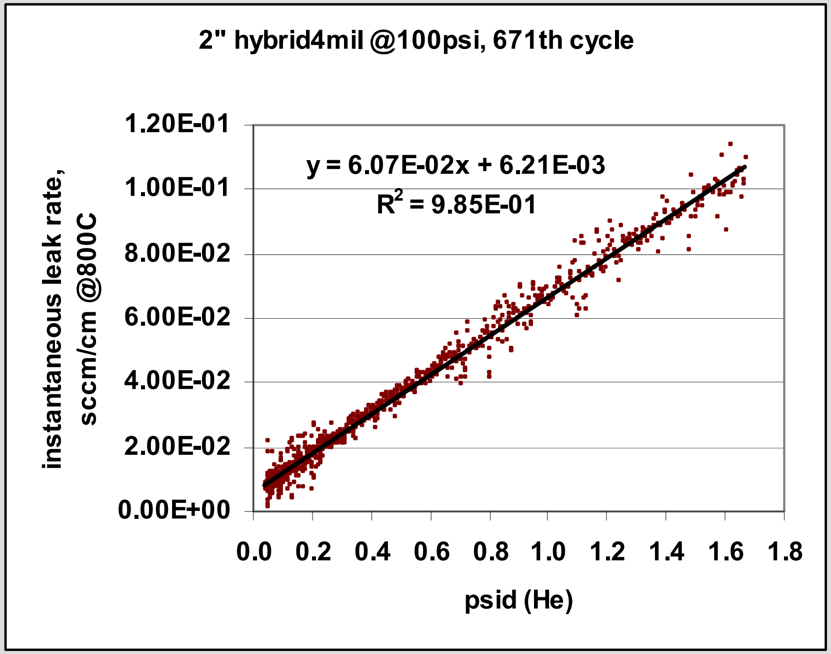
Hybrid micas



Leak rate determination of 2"x2" hybrid mica (100psi) after 671 thermal cycles

Leak rate = 0.018 sccm/cm @ 0.2 psig





Comparison measured and calculated leak rate and at 864th cycle

Theoretical (Nernst) voltage @ 800°C of 2"x2" hybrid mica 100psi = 0.932 V (2.55% H_2/Ar + ~3% H_2O versus air)

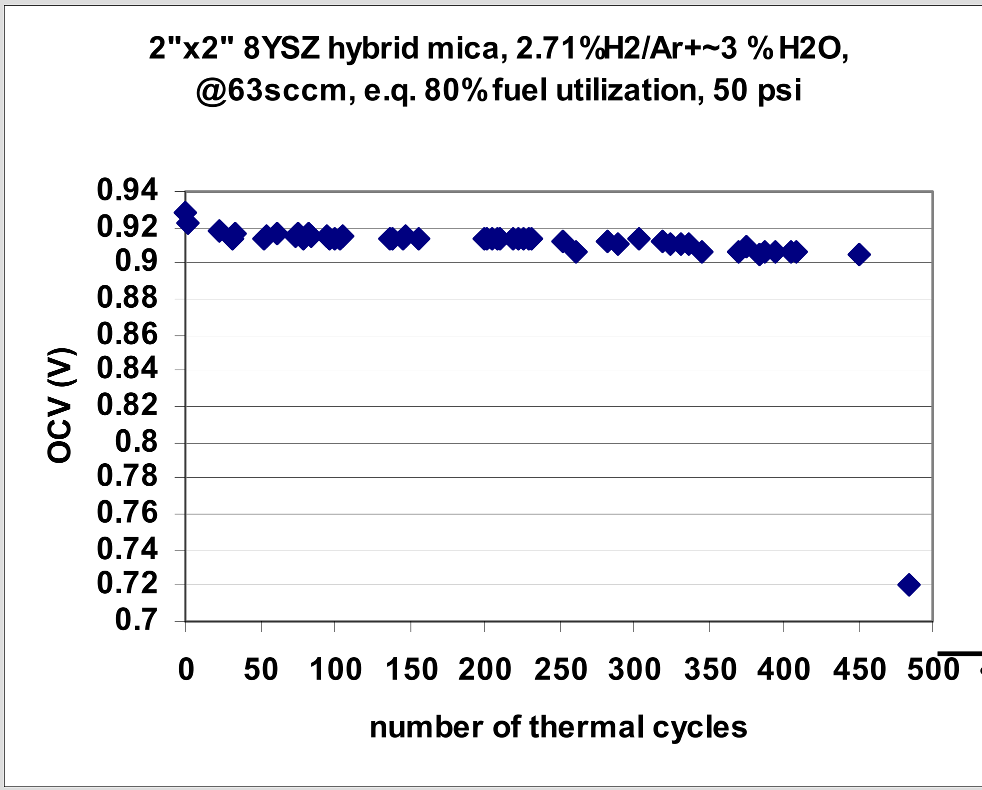
Measured OCV = 0.919 V (@ flow rate = 63 sccm)
Measured leak rates @0.2 psi = 0.018 sccm/cm

At 0.919 V, 800C and 63 sccm fuel (2.55% H_2/Ar)
Calculated air leak rate = 0.027 sccm/cm

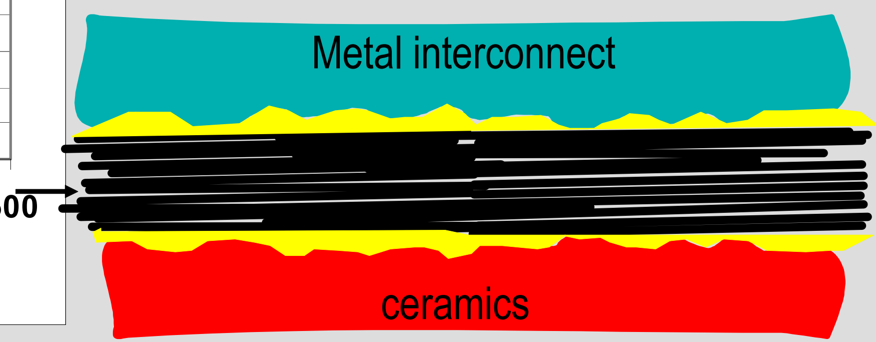
May suggest some background leaks.

THERMAL CYCLING AT LOWER STRESSES (50 psi)

Loss of ~3% (OCV=0.906V) after 451 thermal cycles, 8YSZ fractured 484 cycle

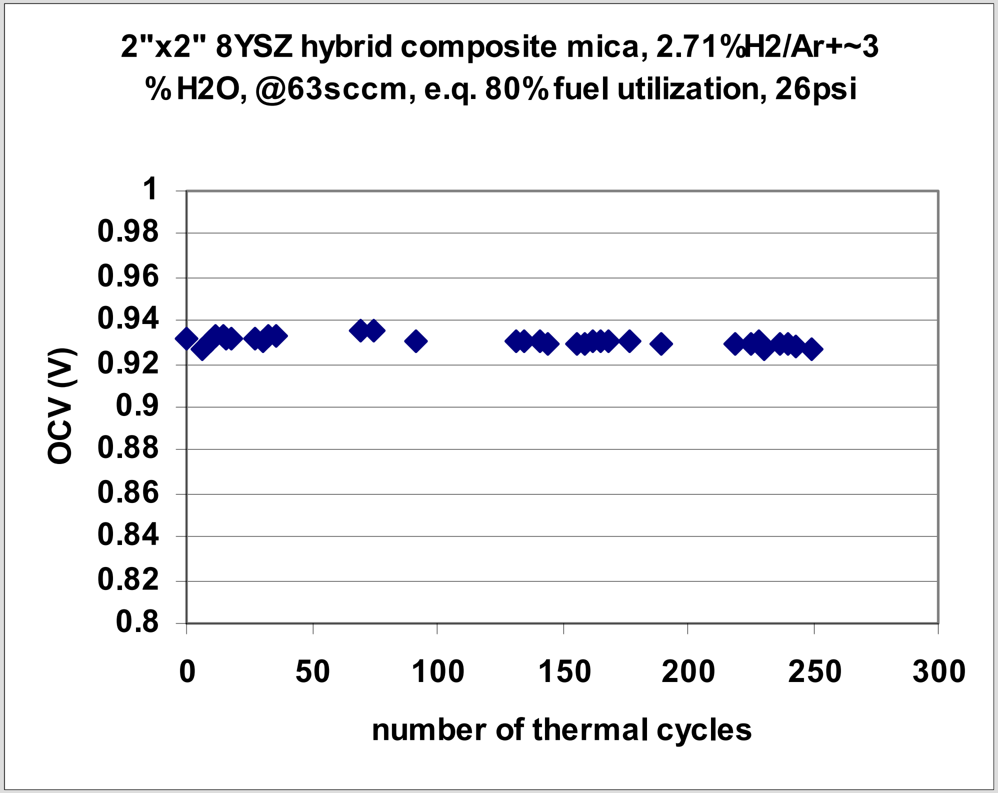


Estimated leak rate @ cycle #484 3.64 sccm or ~1.4 sccm/cm from OCV=0.72 V

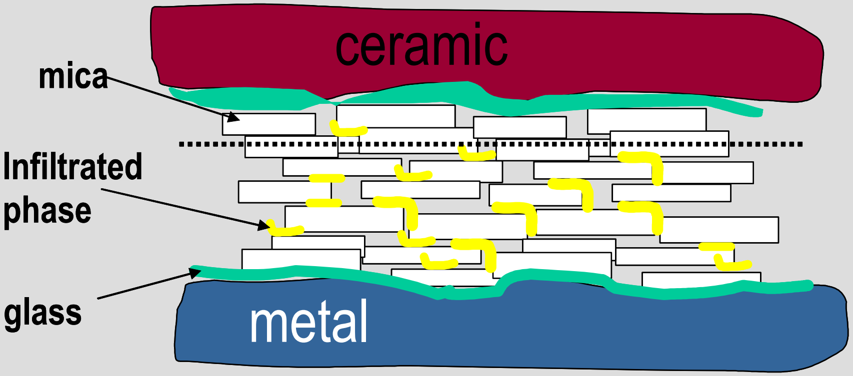


Thermal Cycle Test w/ Reduced Compressive Stress (26 psi)

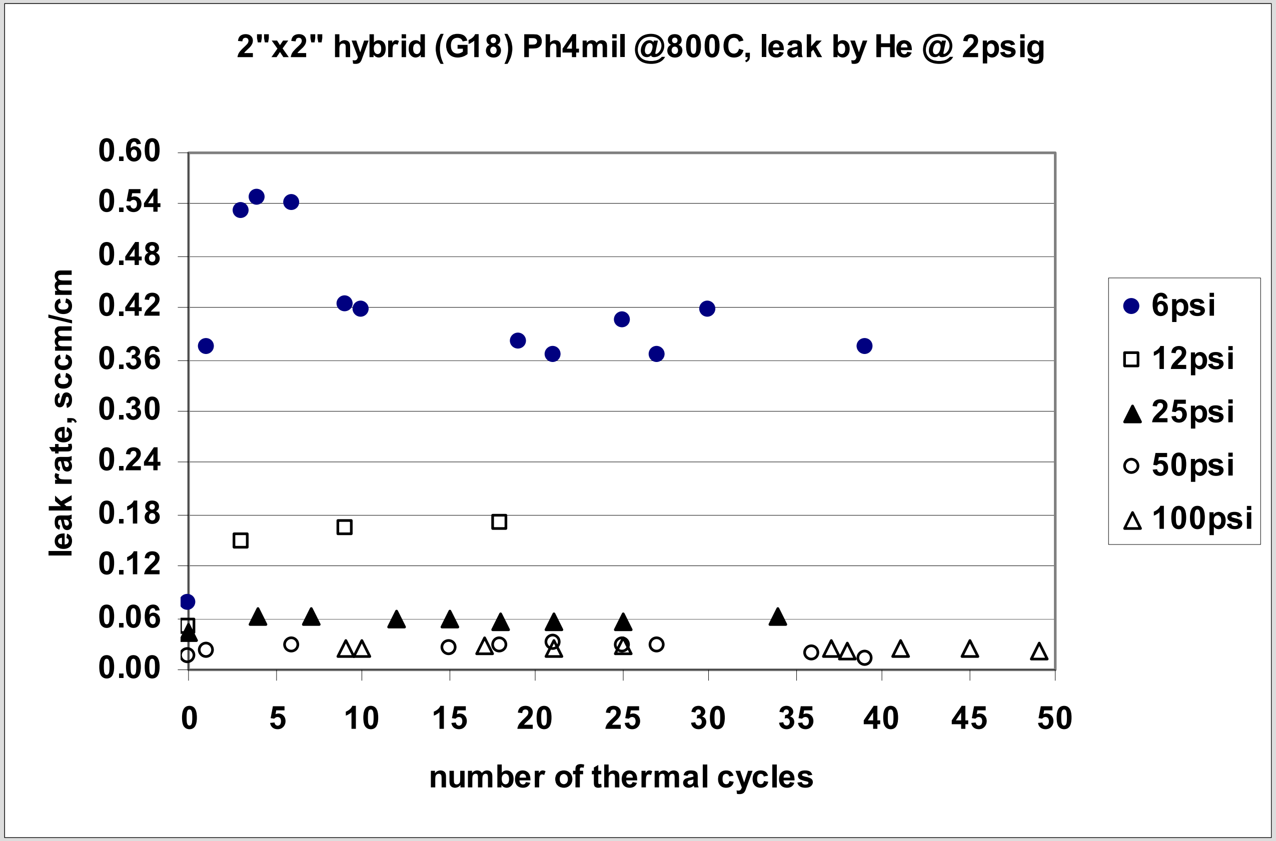
OCV=0.927 V after 250 thermal cycles (0.5% loss). Hybrid seal based on glass-mica composite



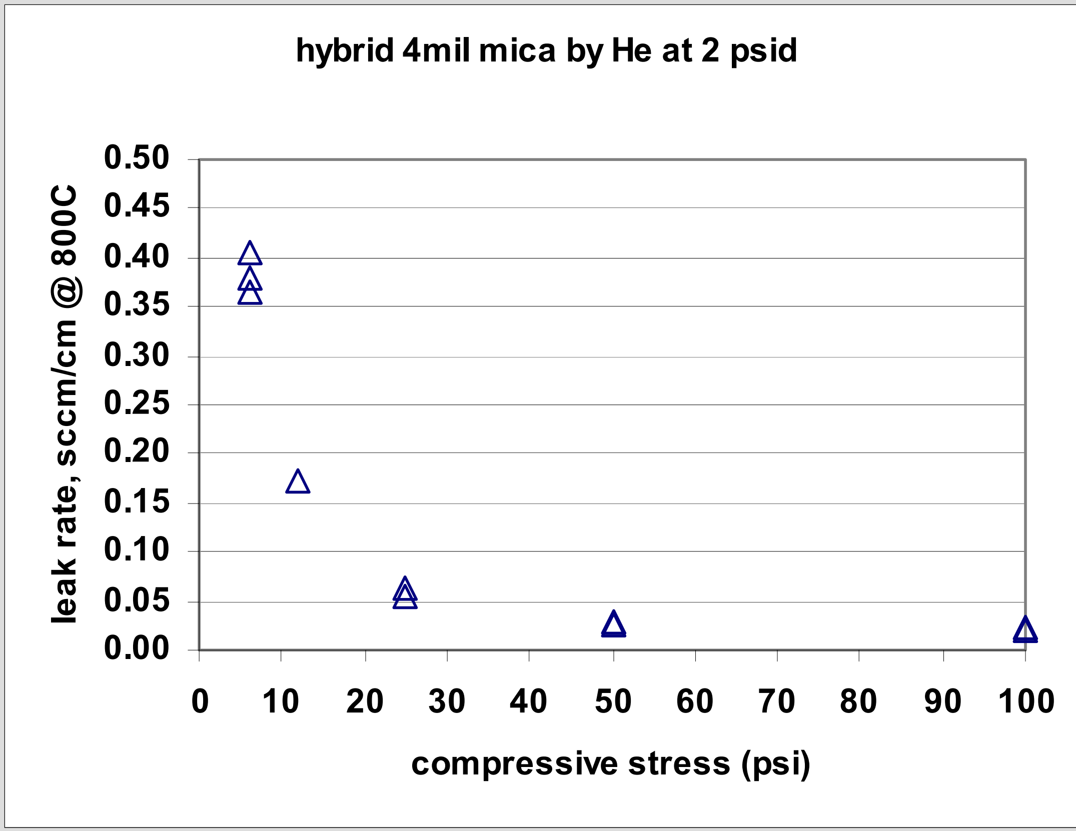
Pt wire broke after 250 cycles.
Estimated leak rate=0.011 sccm/cm from OCV=0.927 V

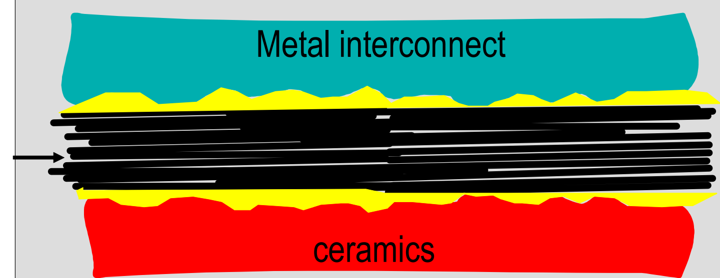


Effect of compressive stress on the leak rates of hybrid mica (4mil) at high (2 psi) helium pressure

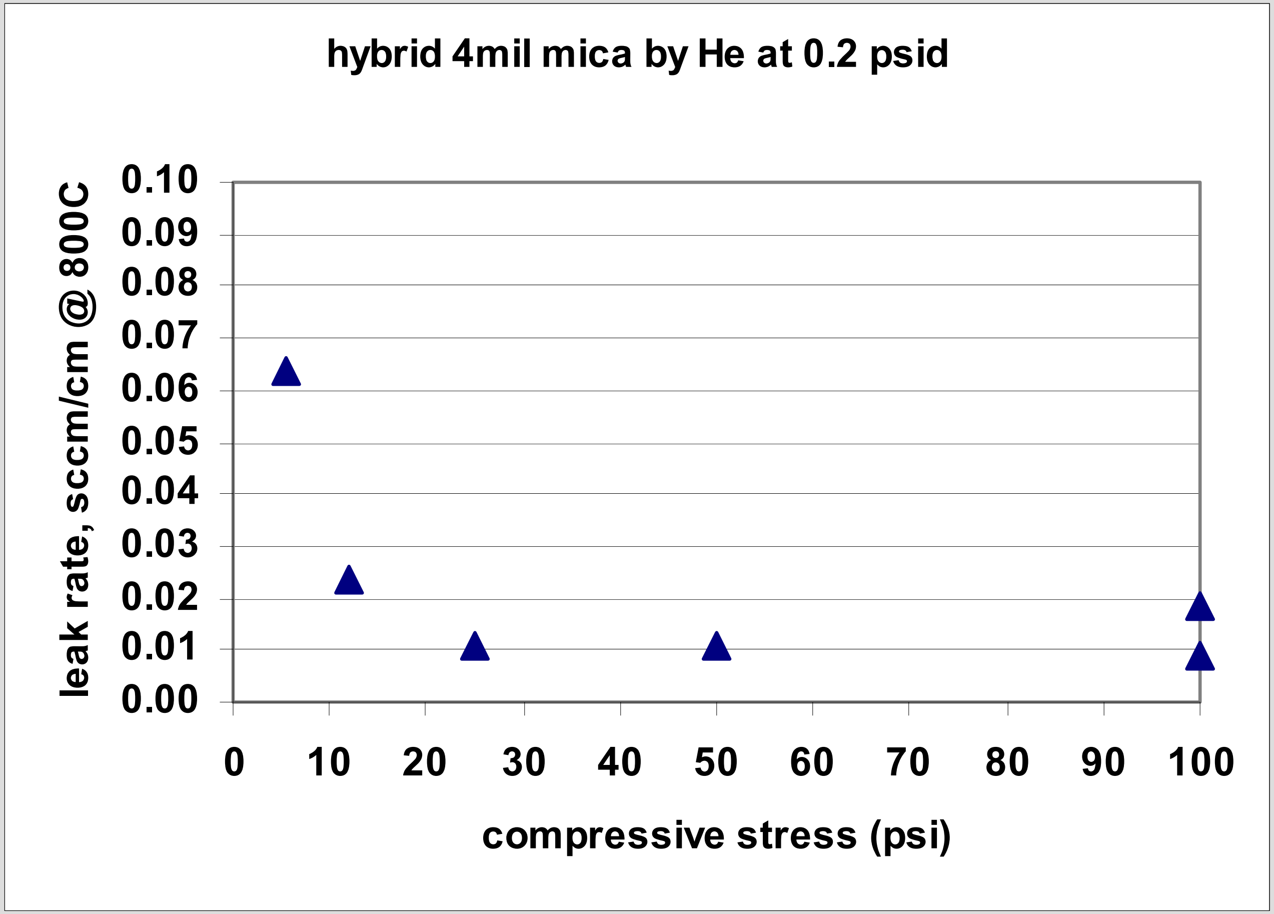


Effect of compressive stress on the leak rates, 4mil thick @ 2psig





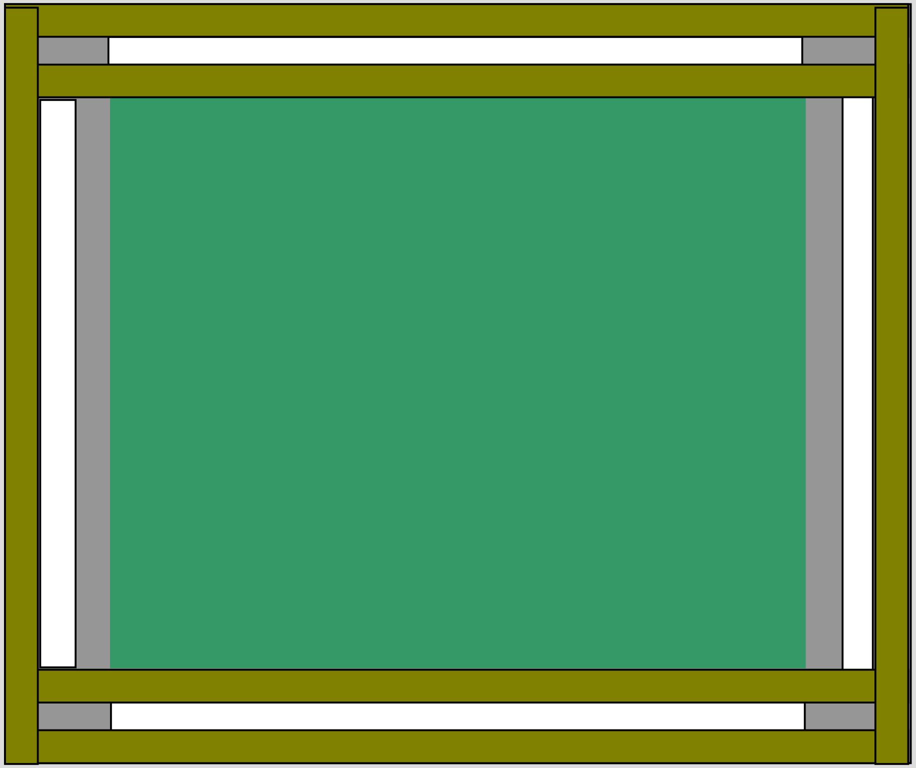
Effect of compressive stress on the leak rate of hybrid mica (4mil) at low (0.2 psi) helium pressure



Fuel loss for hybrid mica at low differential pressure (0.2 psid)

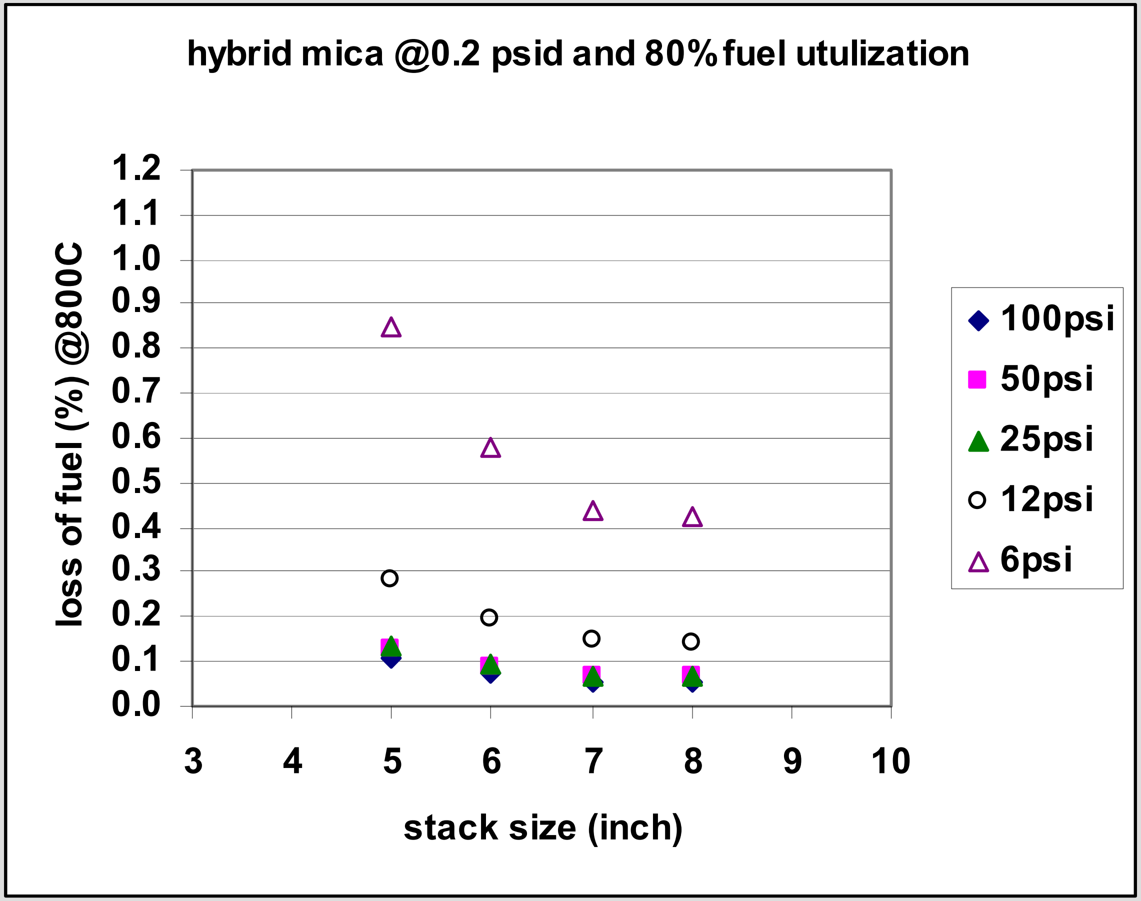
Consider square stack with square active area and 1" space between active side and edge of stack

Leak length (inch) =
18" (5"x5" stack)
22" (6"x6" stack)
26" (7"x7" stack)
30" (8"x8" stack)



Fuel loss for hybrid mica at low pressure gradient (0.2 psid) and 80% fuel utilization

Assume 0.7 V, 0.75 A/cm², and 0.5 W/cm² @ 800°C with pure hydrogen



Allowable leak rate is design-specific

- Stack-size dependent:

fuel needed @ certain power density is α d^2

Leak rate (mica seal) is α d

- Leak location dependent: e.g., inlet and outlet
- Fuel concentration dependent
- Electrochemical and mechanical consideration
- Mica seal may be more robust from mechanical point of view since the leak is rather uniform while rigid seals are prone to localized leaks, which can lead to catastrophic failure.

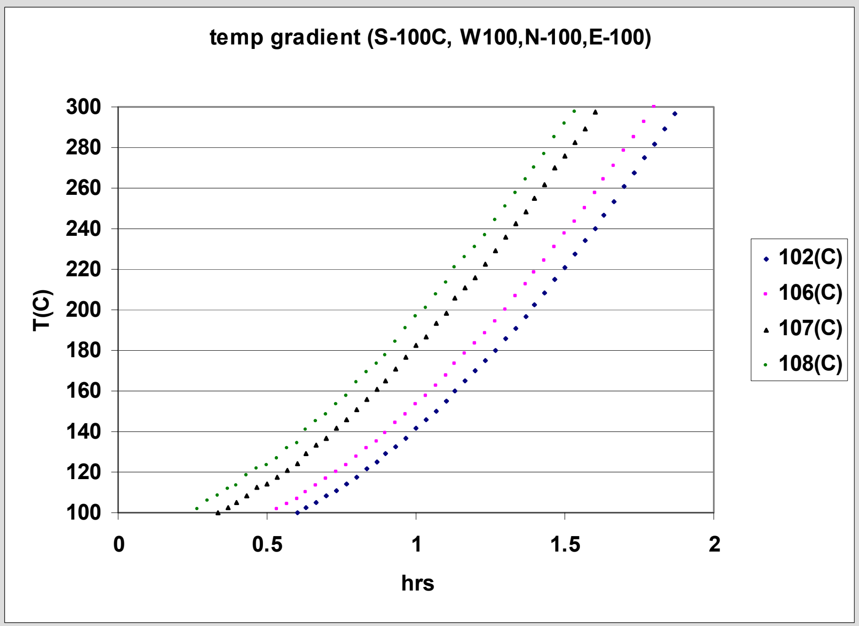
OCV loss for hybrid mica at low pressure gradient (0.2 psid) and 80% fuel utilization

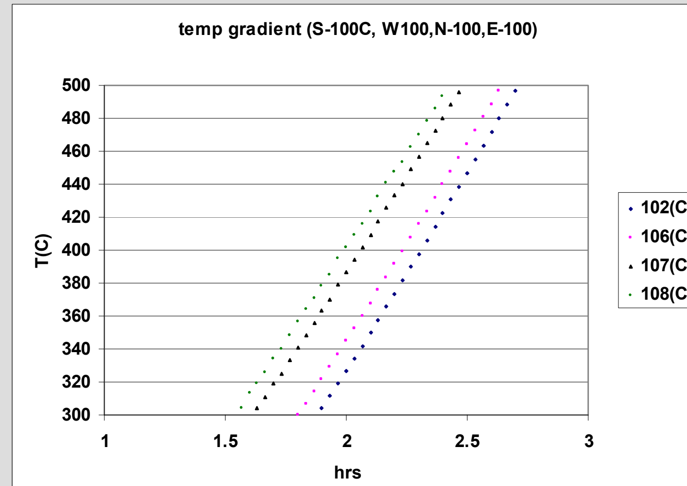
A 6"x6" stack with a 4"x4" active area and total leak length 22" (per cell)
Cell power density of 0.5 W/cm^2, 0.75 A/cm^2 (0.7 V and 800°C)
Need 650 sccm (pure H2) and 1547 sccm air for a 80% fuel utilization

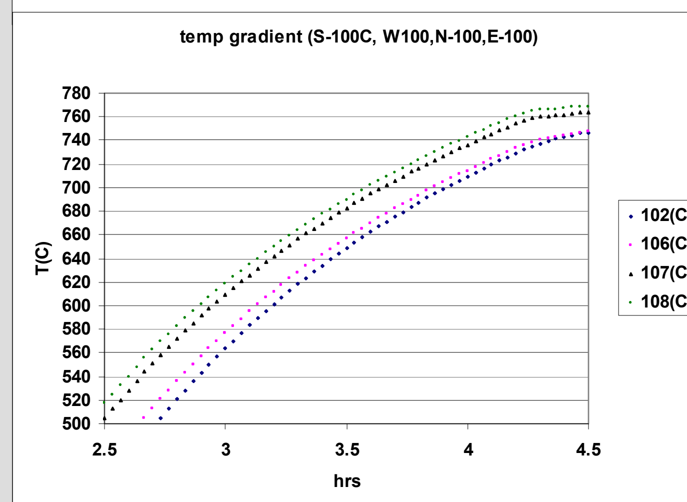
leak rate, sccm/cm @0.2psi	**0.02**	**0.04**	**0.06**	**0.08**	**0.1**
total fuel leak, sccm	1.1	2.2	3.4	4.5	5.6
% of fuel loss	0.17	0.34	0.52	0.69	0.86
initial H2 conc. air side	0.000701	0.001402	0.002102	0.002803	0.003504
initial O2 conc. At fuel side	0.000361	0.000722	0.001083	0.001444	0.001805
OCV (V)	1.1009	1.0998	1.0987	1.0977	1.0966
loss OCV (mV)	0.88	2.03	3.15	4.13	5.21
loss OCV %	**0.08**	**0.18**	**0.29**	**0.38**	**0.47**
Eq. PO2 at fuel side	4.329E-22	4.544E-22	4.764E-22	4.964E-22	5.195E-22
Eq. PO2 at air side	0.2097	0.2094	0.2092	0.2089	0.2086

Thermal cycling with temperature gradient

Temperature gradient of 30-100°C across 3.5"x3.5" sample during cycle



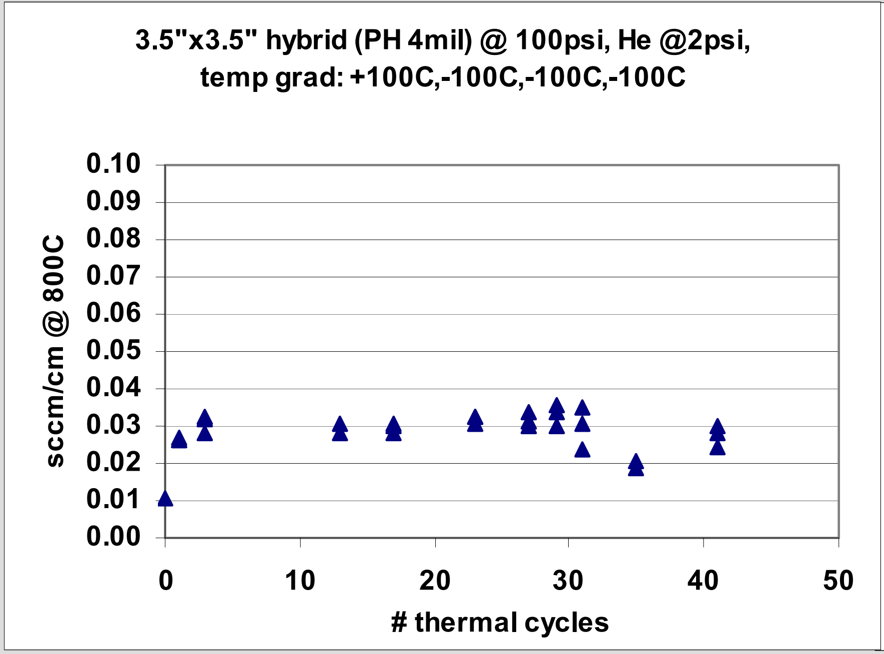




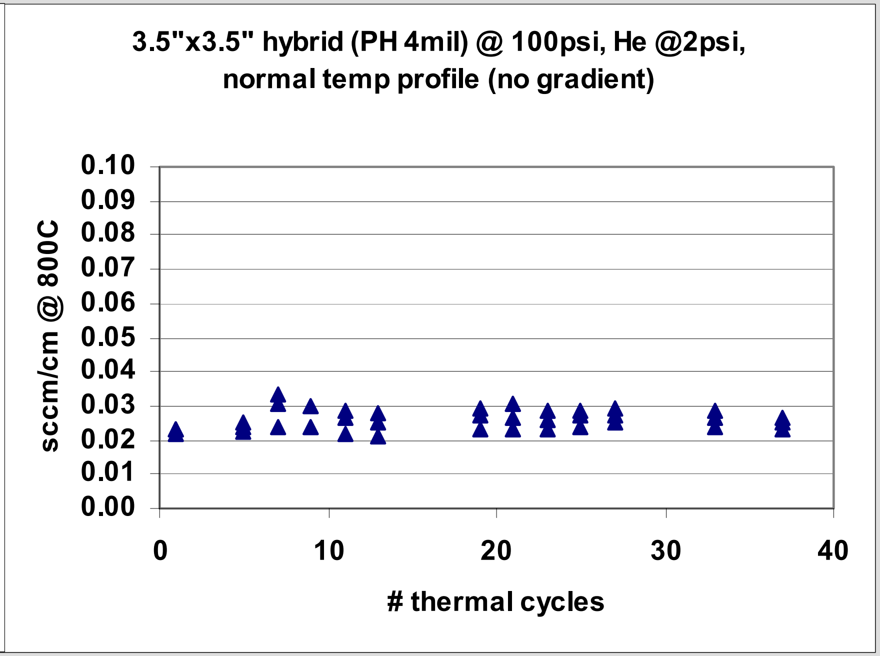
Effect of temperature gradient

3.5”x3.5” hybrid mica @100psi and cycling between 200-800°C

With T gradient

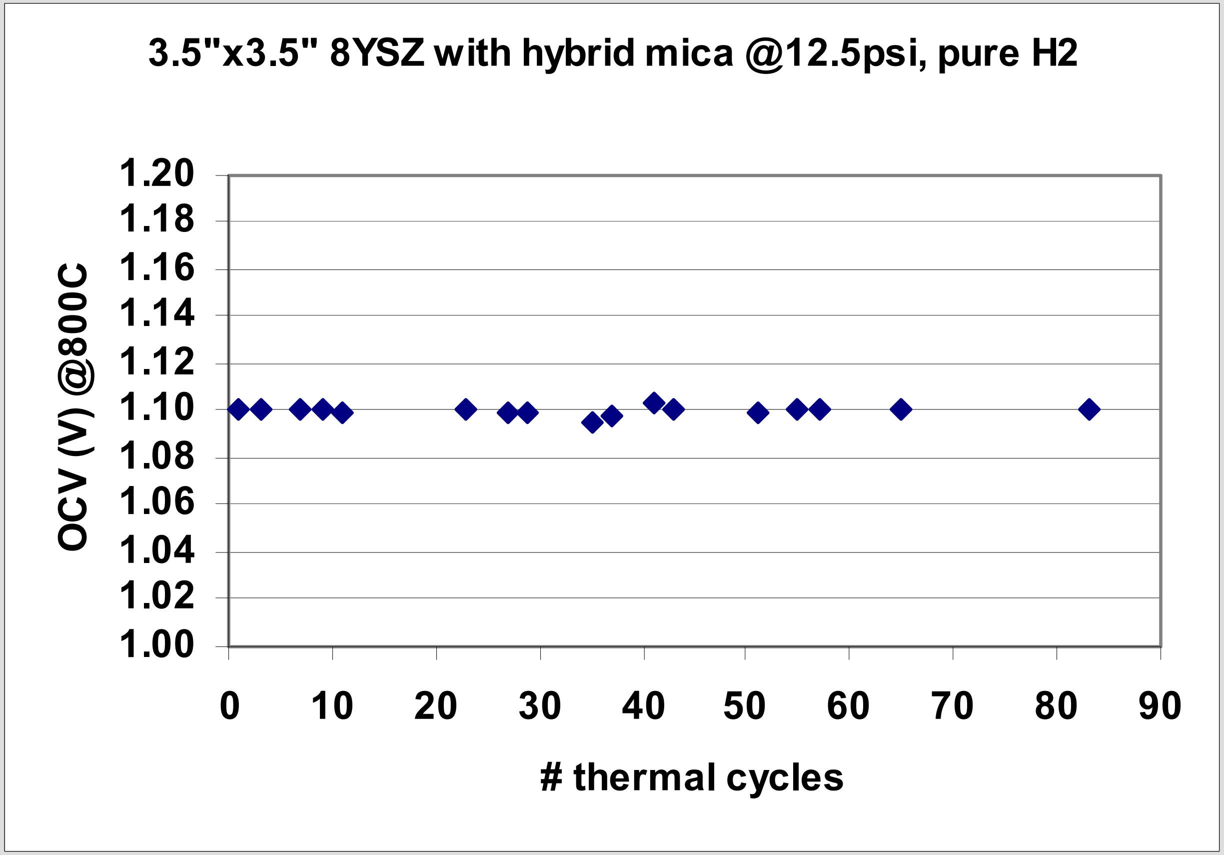


Without T gradient



Thermal cycling in pure hydrogen fuels of large (3.5”x3.5”) hybrid micas @ 12.5psi

Nernst voltage = 1.102 V @800°C for (97% H_2/3% H_2O vs air), flow rate 284 sccm ~ 80% fuel utilization



Summary and Conclusions

- Hybrid micas have demonstrated excellent thermal cycle stability under several different loading conditions: 864 cycles (100psi), 450 cycles (50 psi), and 250 cycles (26 psi) in OCV tests.
- The effect of compressive stress on the leak rate was studied from 6 psi to 100 psi. At all stresses, the hybrid micas showed fairly constant leak rates after ~10-20 thermal cycles.
- The leak rates were linearly proportional to the differential gas pressure.
- Leak test on large (3.5”x3.5”) hybrid mica showed no effect from ~30º-80°C temperature gradients.
- Good thermal cycle stability was demonstrated on large (3.5”x3.5”) hybrid mica in 97% hydrogen / 3% water environment for 85 thermal cycles.
- Fuel loss was estimated for various stacks at different fuel utilizations, and found to be minimal (~0.1%) at low compressive stresses if the stack is to be operated at ambient or small differential pressures.

Applicability to SOFC commercialization

- The developed hybrid mica seals could be quickly adapted for commercialization since the mica layers are commercially available, and the glass interlayers can be easily fabricated by tape casting or other automatic processes.
- The glass-mica composite seal will require further processing optimization to improve distribution of large mica flakes, and the selection of an optimum glass or glass-ceramic to meet SOFC requirements.

Activities for the next 18 months

- Evaluate the low (3 psi) compressive stresses on hybrid micas
- Optimization of glass-mica composite seals by using two different glasses at various volume fractions: a Ba-Al silicate glass (a rigid glass-ceramics) and a glass which tends to remain vitreous instead of crystallizing. Evaluate forming techniques for making thin and uniform thickness mica-glass composites.
- Combined aging (1 month) and thermal cycling (100 cycles) tests of various hybrid micas in a simulated SOFC environment or pure hydrogen versus ambient air conditions.
- Testing leak rate versus limited (30-50) thermal cycles at various low loads (3, 6, and 12psi) for various hybrid micas and glass-mica composites.
- Evaluate allowable leak rates from thermal-mechanical considerations.
- Design an accelerated aging test for evaluating the long-term stability of candidate hybrid mica seals in a simulated SOFC environments.
- Evaluate the degradation by hybrid micas or glass-mica composite seals on various candidate metallic interconnect materials in a simulated SOFC environment: e.g., coated/uncoated ferritic stainless steel, Haynes230, Inconel600 or others.