SOFC Seals: Materials Status

SECA Core Technology Program – SOFC Seal Meeting

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SOFC SEALS

Functions

- SOFC seals prevent mixing of fuel and oxidant within stack
- SOFC seals prevent leaking of fuel and oxidant from stack
- SOFC seals electrically isolate cells in stack
- SOFC seals may provide mechanical bonding of components

Requirements

While fulfilling the above functions, seal materials must remain:

- **structurally stable**
- **chemically compatible with other stack components**
- **inexpensive**

SOFC SEALS

Notes

- Much of SOFC seal work to date is proprietary (design-specific)
  - Limited SOFC seal information in open literature
- Planar designs typically require multiple seals per stack “repeat unit”
  - Several different types of seal might be used per repeat unit

SOFC SEALS

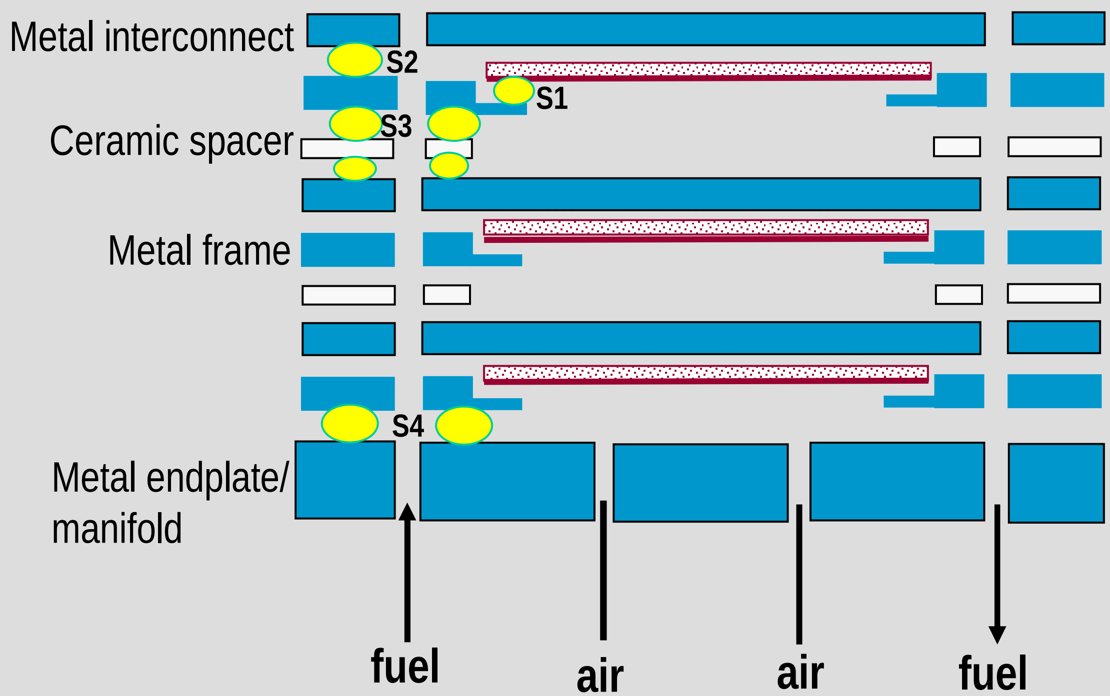
Possible Seals include:

S1: Cell to Metal Frame

S2: Metal Frame to Metal Interconnect

S3: Frame/Interconnect to Spacer (for electrical insulation)

S4: Stack to Base Manifold Plate



Seal designs and materials will largely depend on the cell and stack configurations and contacting surfaces / materials

SOFC SEALS

Basic Sealing Approaches

- **1) Rigid, bonded seals**
  - **Room-temperature analog: Epoxy glue**
  - **Materials: Glass, glass-ceramic, braze**
- **2) Compressive seals**
  - **Room-temperature analog: Rubber O-ring, gasket**
  - **Materials: Mica-based**
- **3) Compliant, bonded seals**
  - **Room-temperature analog: Rubber glue**
  - **Materials: ??**

Level of effort, maturity of technology (↑)

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Rigid, Bonded Seals

- Additional Requirements for Rigid, Bonded Seals (typically glass, glass-ceramic)
  - Thermal expansion match
    - Ni/YSZ 12 ppm/K
    - 8-YSZ 10 ppm/K
    - Doped Ceria 12-13 ppm/K
    - Doped Lathanum Gallate 11.5 ppm/K
  - Sealing temperature
    - Must be ≤ all previous cell/stack fabrication steps
    - Higher than the operational temperature
  - Good wetting during sealing

Glass and Glass-ceramic seals: Status

- **"Standard approach" to sealing planar stacks**
- Successfully used to initially seal stacks; limited success reported in terms of thermal cycling and long-term operation
- Pros:
  - Viscous/wetting behavior of glass facilitates hermetic sealing
  - Inexpensive, easy to fabricate (tape casting, slurry dispensing)
  - Properties can be tailored (CTE, T_g, T_s)
  - Glass-ceramics (vs. glasses) avoid viscous flow during operation and uncontrolled, progressive crystallization during operation
- Cons:
  - Brittle behavior (glass-ceramics; glasses below T_g)
  - Few systems with appropriate CTE (AE-Al-Si-O)
  - Chemical interactions w/ adjacent components (e.g. metal interconnects)
  - Volatilization of seal constituents (SiO_2, B_2O_3, alkali metals)

Potential Glass Systems

- P_2O_5 based glasses
  - Low CTE, low strength
- B_2O_3 based glasses
  - Volatile, low softening temperatures
- SiO_2 based glasses
  - Best available glass candidate (?)
  - Alkaline earth aluminosilicate glasses
    - High electrical resistivity
    - High thermal expansion (matching other SOFC stack components)
    - Rapid crystallization kinetics

SOFC Glass Seal Studies

- $SrO-La_2O_3-Al_2O_3-B_2O_3-SiO_2$
  - High B_2O_3, very low softening points
    - K. Ley et al., J. Mater. Res., 11, 1489 (1996)
- $BaO-Al_2O_3-B_2O_3-SiO_2-As_2O_3$
  - Volatilization of B_2O_3 and As_2O_3 (pore formation)
    - C. Gunther et al., in Solid Oxide Fuel Cells – V, 746 (1997)
  - Crystallization rate adjustable with MgO additions; interactions with interconnect alloy ($MgCr_2O_4$)
    - K. et al., J. Eur. Cer. Soc., 19, 1101 (1999); Proc. 4th European SOFC Forum, 899 (2000)

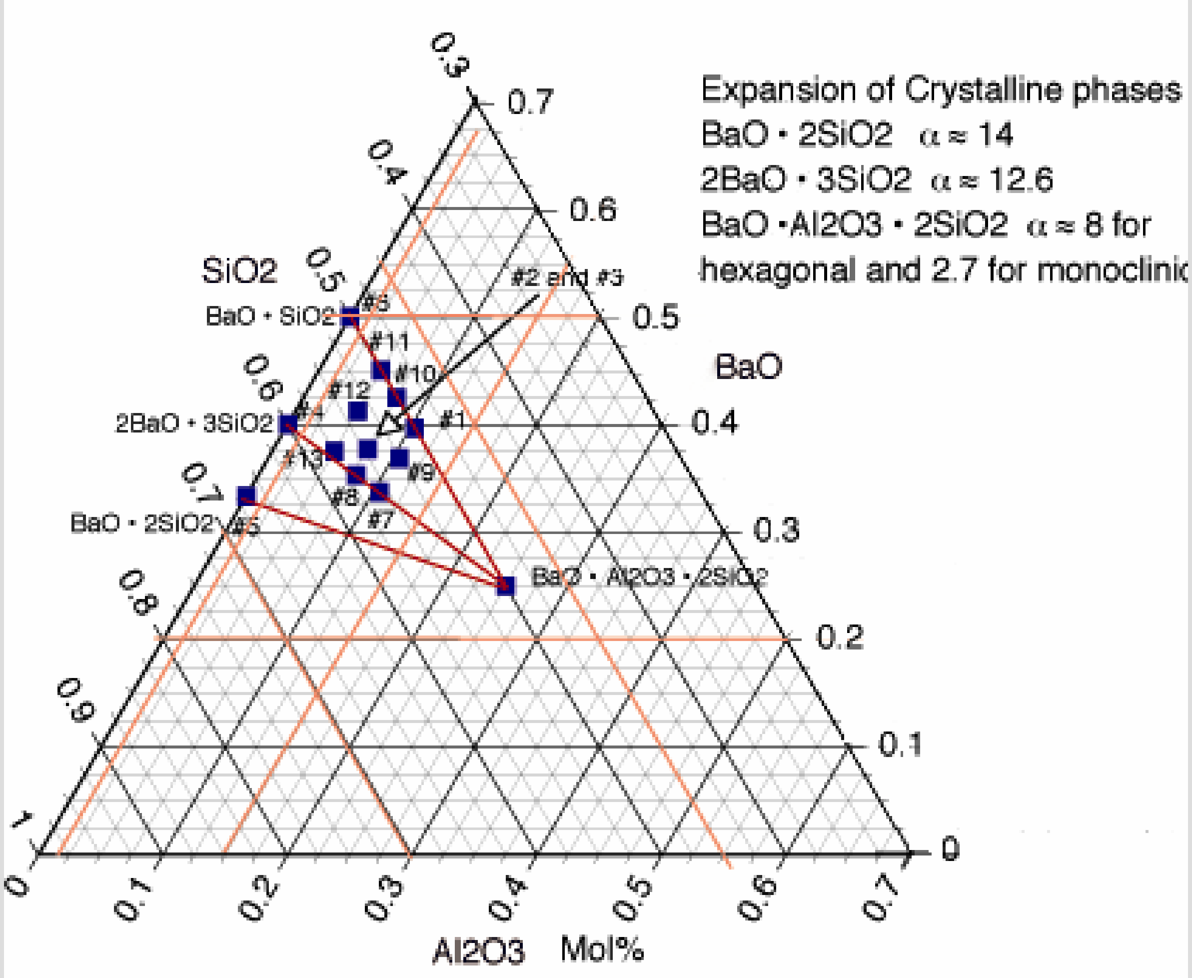
SOFC Glass Seal Studies

- $AO-Al_2O_3-B_2O_3-SiO_2$ (A = Ba, Ca, Mg)
  - Ba: Higher CTE, lower T_g than Ca, Mg
    - N. Lahl et al., in Solid Oxide Fuel Cells – VI, 1057 (1999)
- $CaO-Al_2O_3-SiO_2$
  - Primary crystallization product: Wollastonite ($CaSiO_3$)
    - Y. Sakaki et al., in Solid Oxide Fuel Cells – V, 652 (1997)

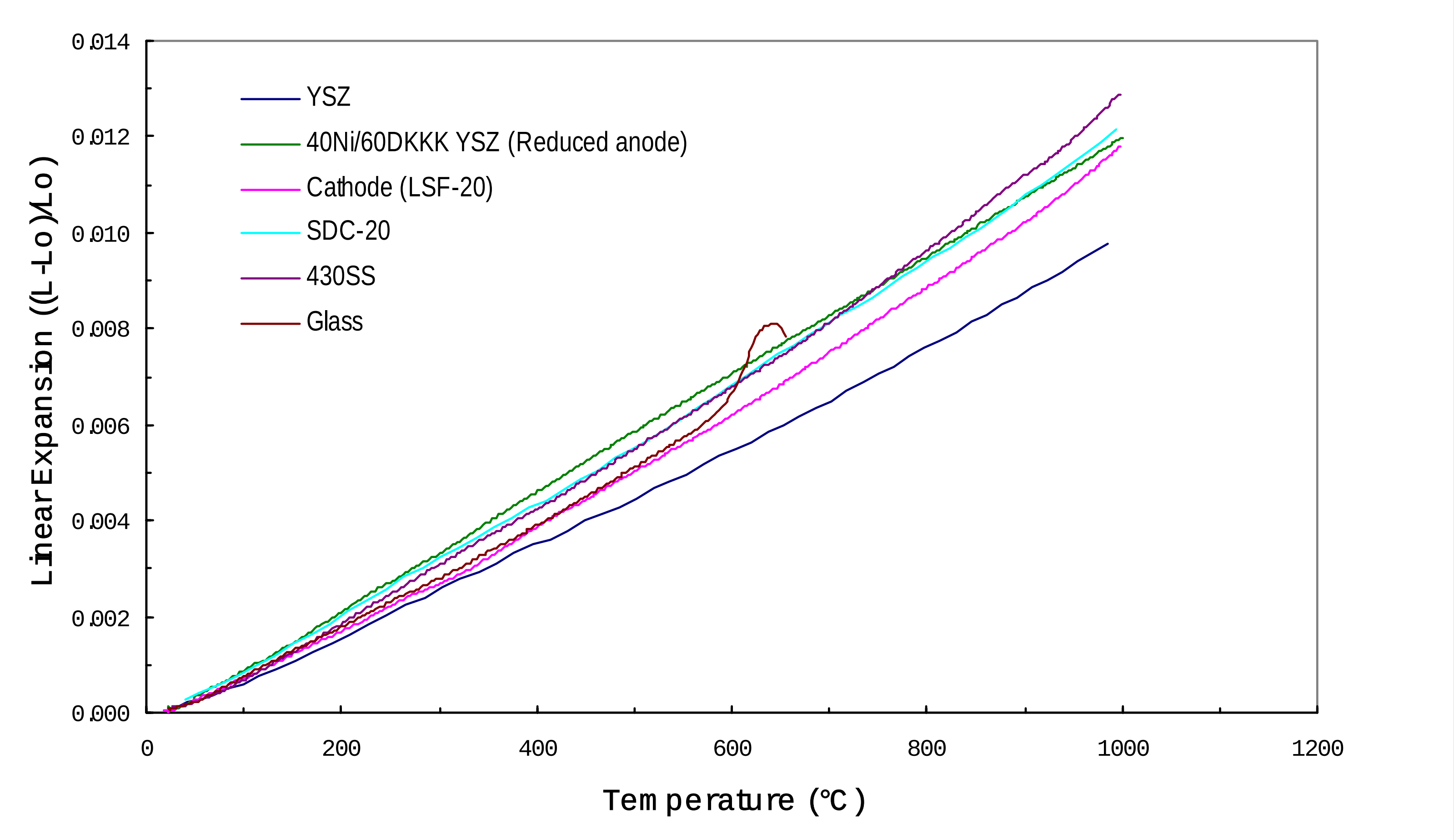
Note Emphasis on Alkaline Earth Aluminosilicate Glasses

BaO-Al$_2$O$_3$-SiO$_2$ Seals

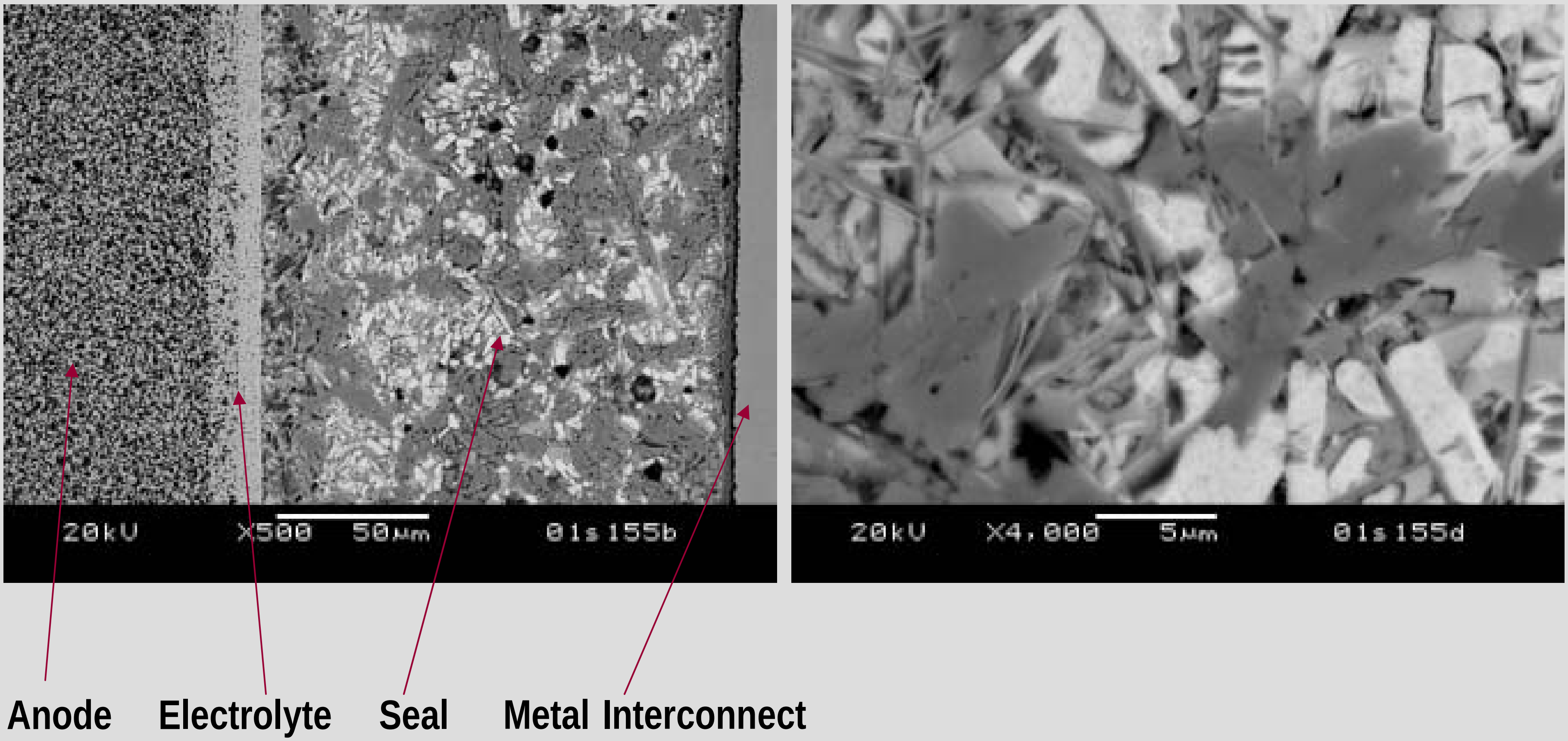
PNNL Patents:
US 6,430,966;
US 6,532,769



Thermal Expansion of Cell and Stack Materials



Glass G18 After Crystallization



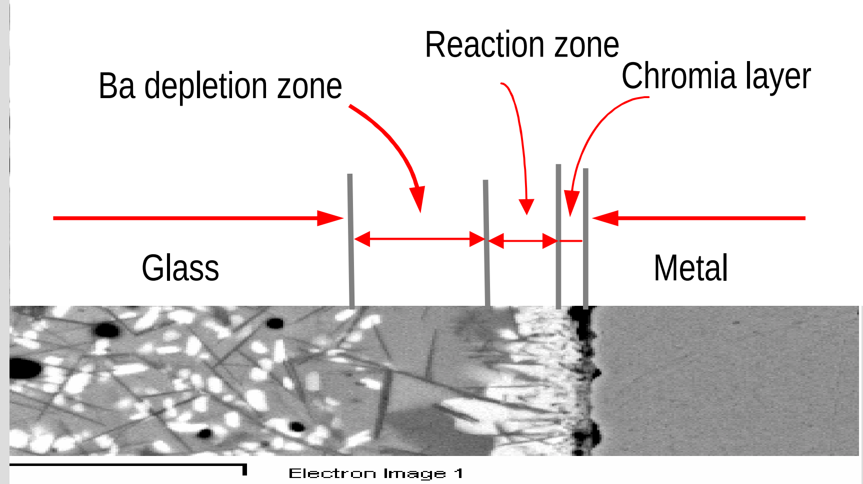
Glass/Metal Chemical Interactions

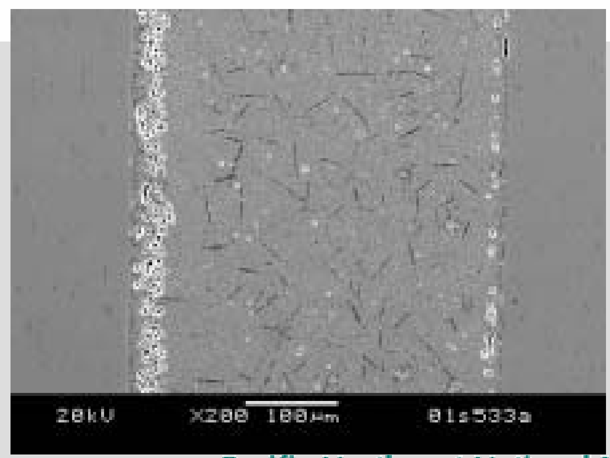
Challenges of glass-sealing metal interconnects in SOFC stacks include:

•Formation of interfacial compounds (e.g., barium chromate for barium aluminosilicate sealing glass bonded to chromia forming alloys)

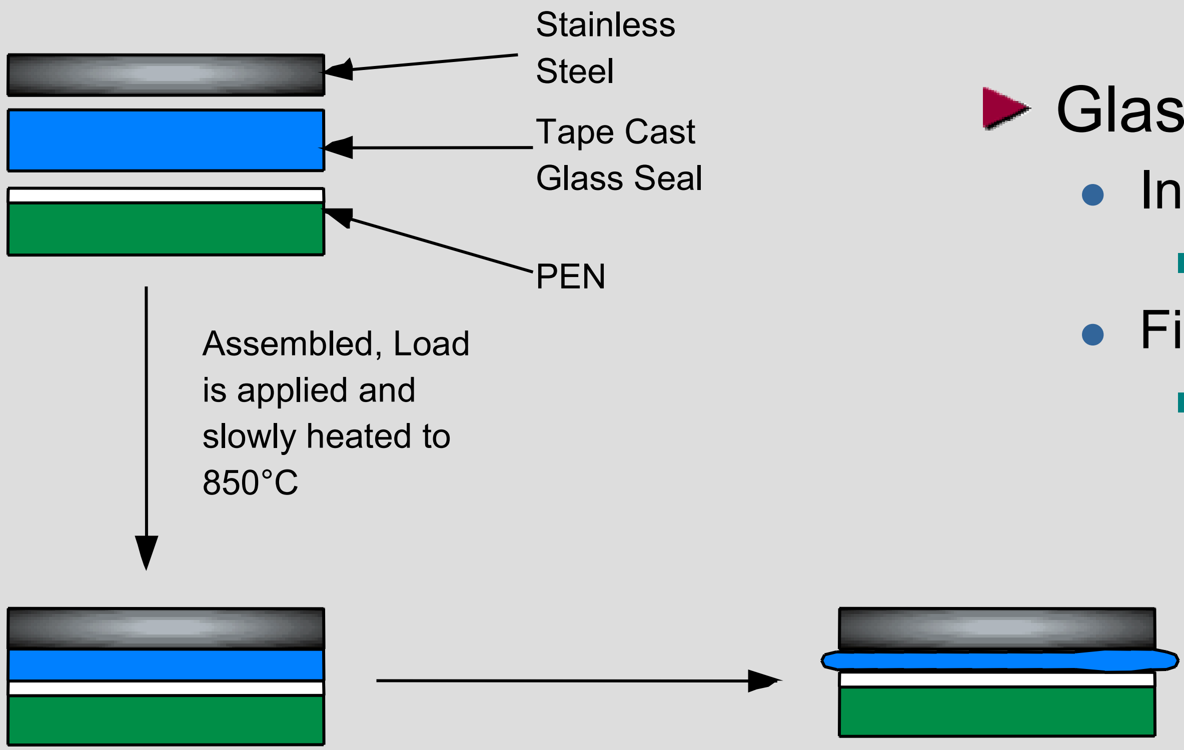
•Development of extensive porosity in glass near glass/alloy interface

$$2Cr_2O_3+4BaO+3O_2 = 4BaCrO_4$$





Glass Sealing Procedure



After Binder removal (500°C) thickness is reduced by about half. Glass starts to sinter and flow

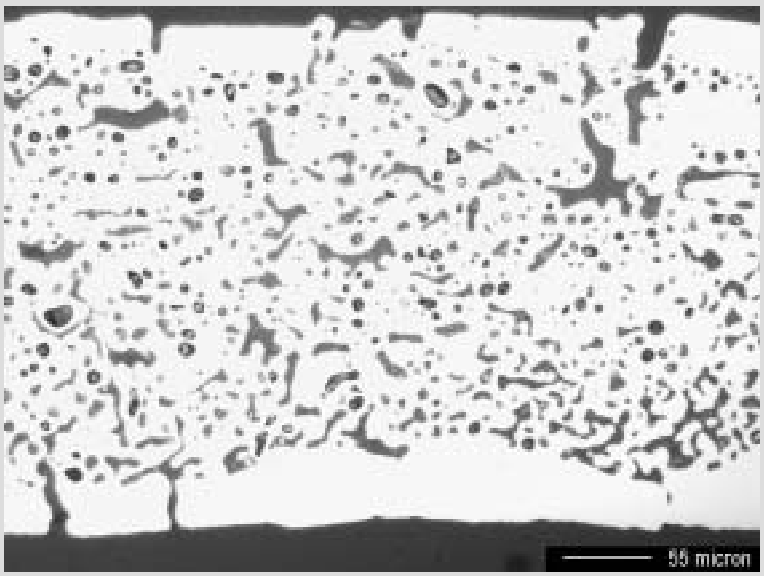
Between 600 -850 °C the glass becomes viscous and flows to conform to the stack parts. 750° -850° Crystallization begins

- Glass Seal
  - Initial Thickness
    - ~750 µm
  - Final Thickness
    - ~200 µm

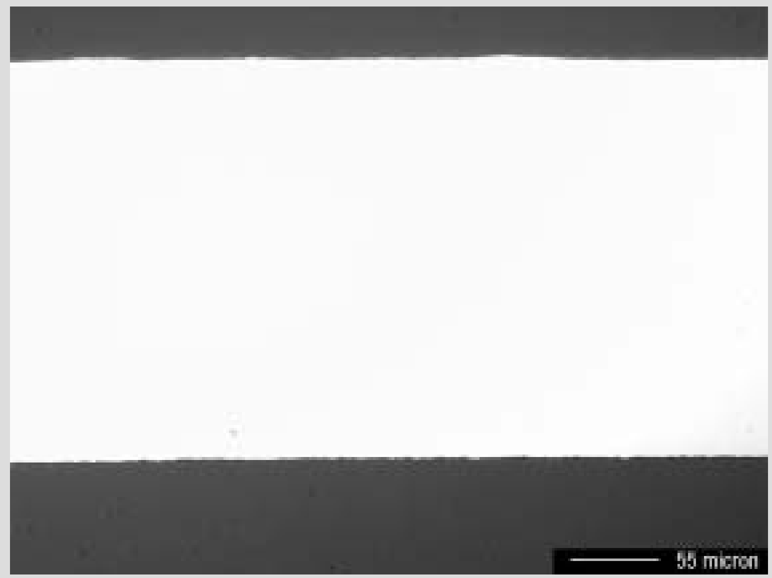
Brazed seals

- Potential alternative to glass-based seals
- Involves use of molten filler metal which flows and fills gap between components
- Pros:
  - Wetting behavior of molten metal facilitates hermetic sealing
  - Easy to fabricate
  - Properties can be tailored (CTE, T_m)
- Cons:
  - **Electrically conductive!**
  - Few systems compatible with sealing under oxidizing conditions
    - Noble metal brazes expensive
    - Ag relatively inexpensive, but is unstable in dual environment

Silver: Unstable in dual atmospheres



Exposed to fuel/air environment, 100hrs, 700C



Exposed to air/air environment, 100hrs, 700C

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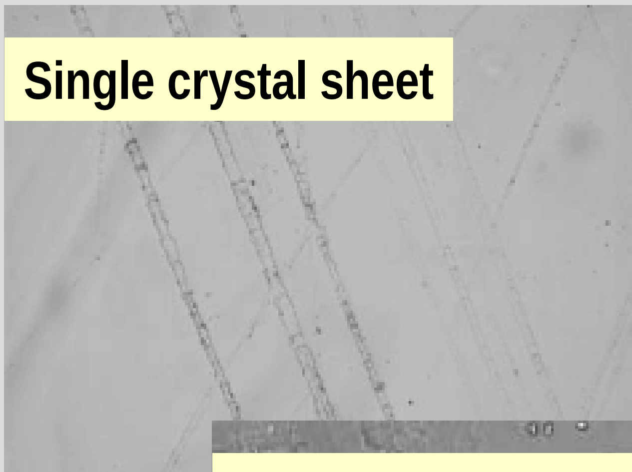
↑ Level of effort, maturity of technology

Compressive seals

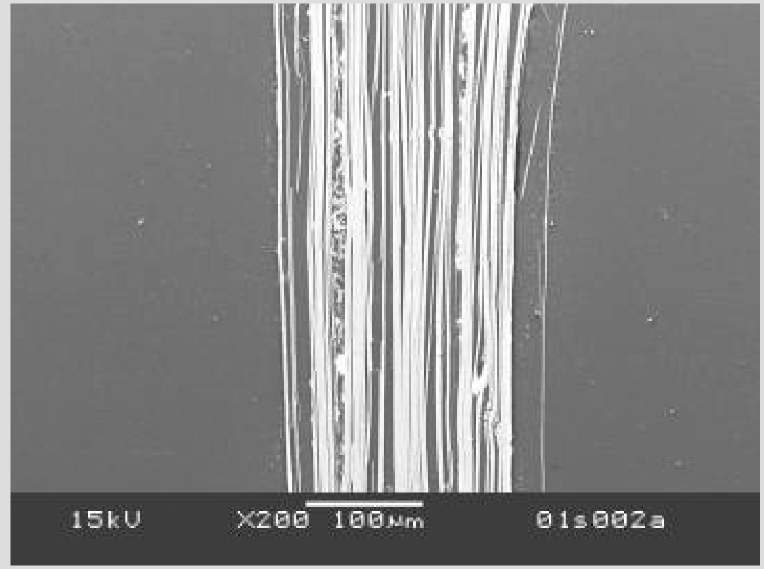
- **Very little reported development work compared to rigid seals**
- **Pros:**
  - May provide mechanical "de-coupling" of adjacent stack components (avoid thermal stress development during fabrication, operation, thermal cycling)
  - Potentially easy to fabricate
  - In simplest form, no viscous/liquid sealing step required
- **Cons:**
  - Potential for high leak rates through seal/component interfaces for simple gasket approaches
  - Few stable, compliant, hermetic candidate materials
  - Load frame required to maintain compressive stress
    - Adds expense, complexity
    - Effect of long-term compressive load on dimensional stability of other stack components?

Basis of compressive seal: Mica

- Muscovite: $KAl_2\ (AlSi_3O_{10})\ (F,OH)_2$
- Phlogopite: $KMg_3(AlSi_3O_{10})(OH)_2$


Single crystal sheet

Paper: Discrete flakes with binders

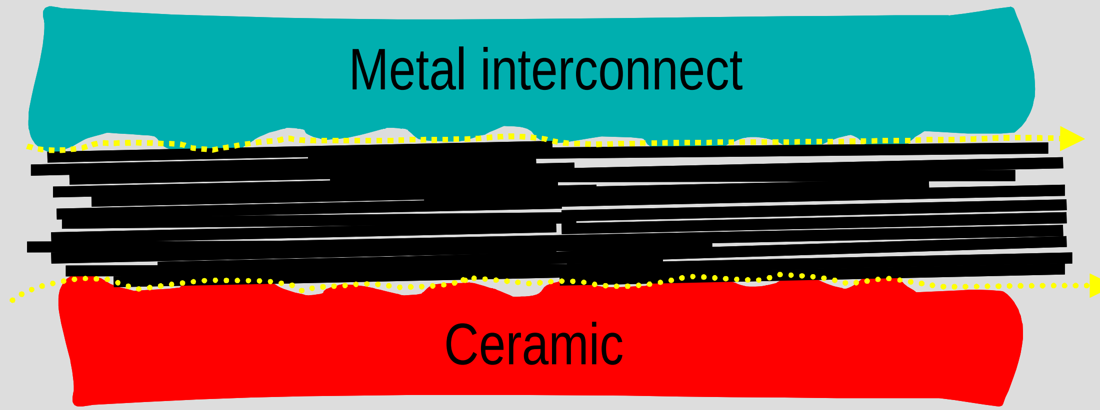


Layered silicate structure

Goal is to develop seals which can tolerate CTE mismatch between adjacent components

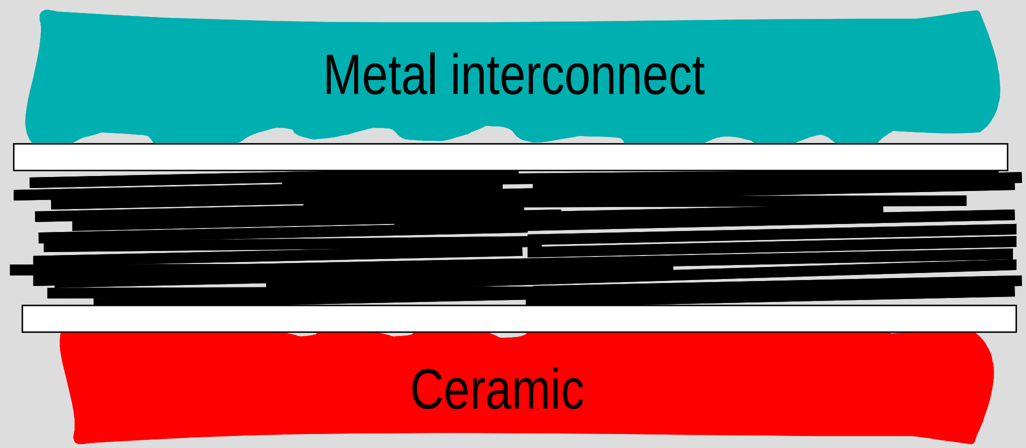
Concept of hybrid compressive seal

Simple mica layer yields excessively high leak rates through interfaces



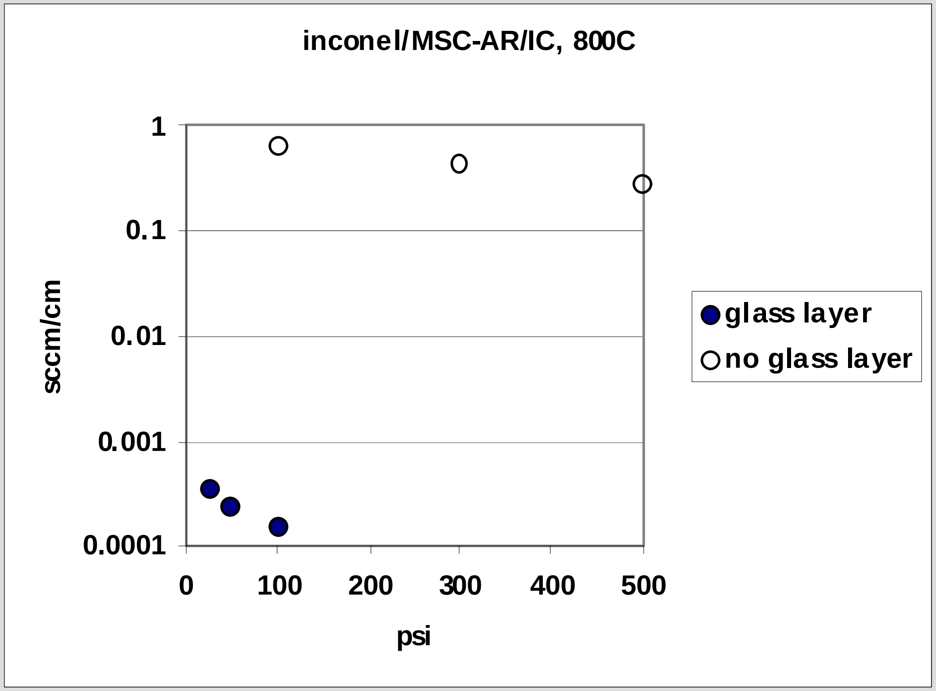
Mica: compliant in 2-D (x-y plane)

Metal/glass interlayer: compliant in 3-D; seals off interfaces

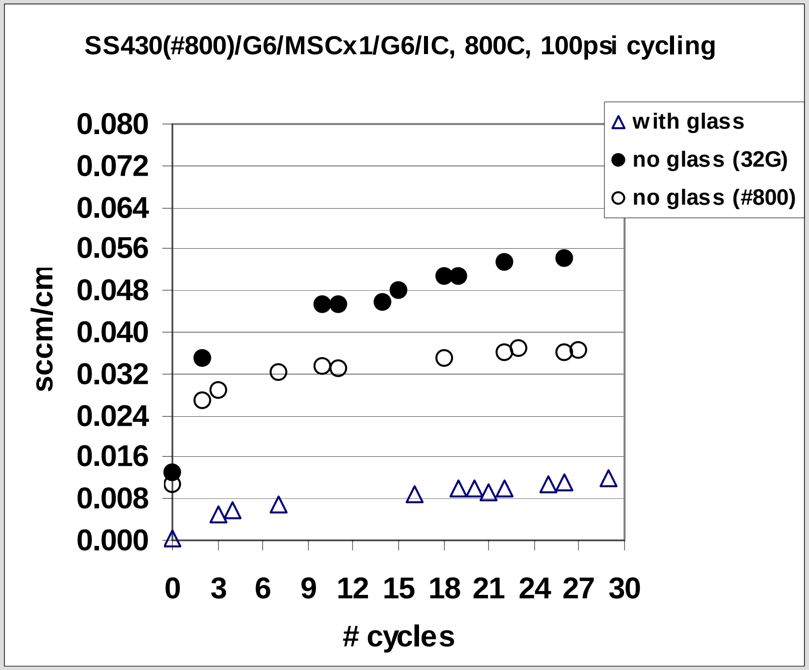


Reduction of leak rate by insertion of glass interlayers

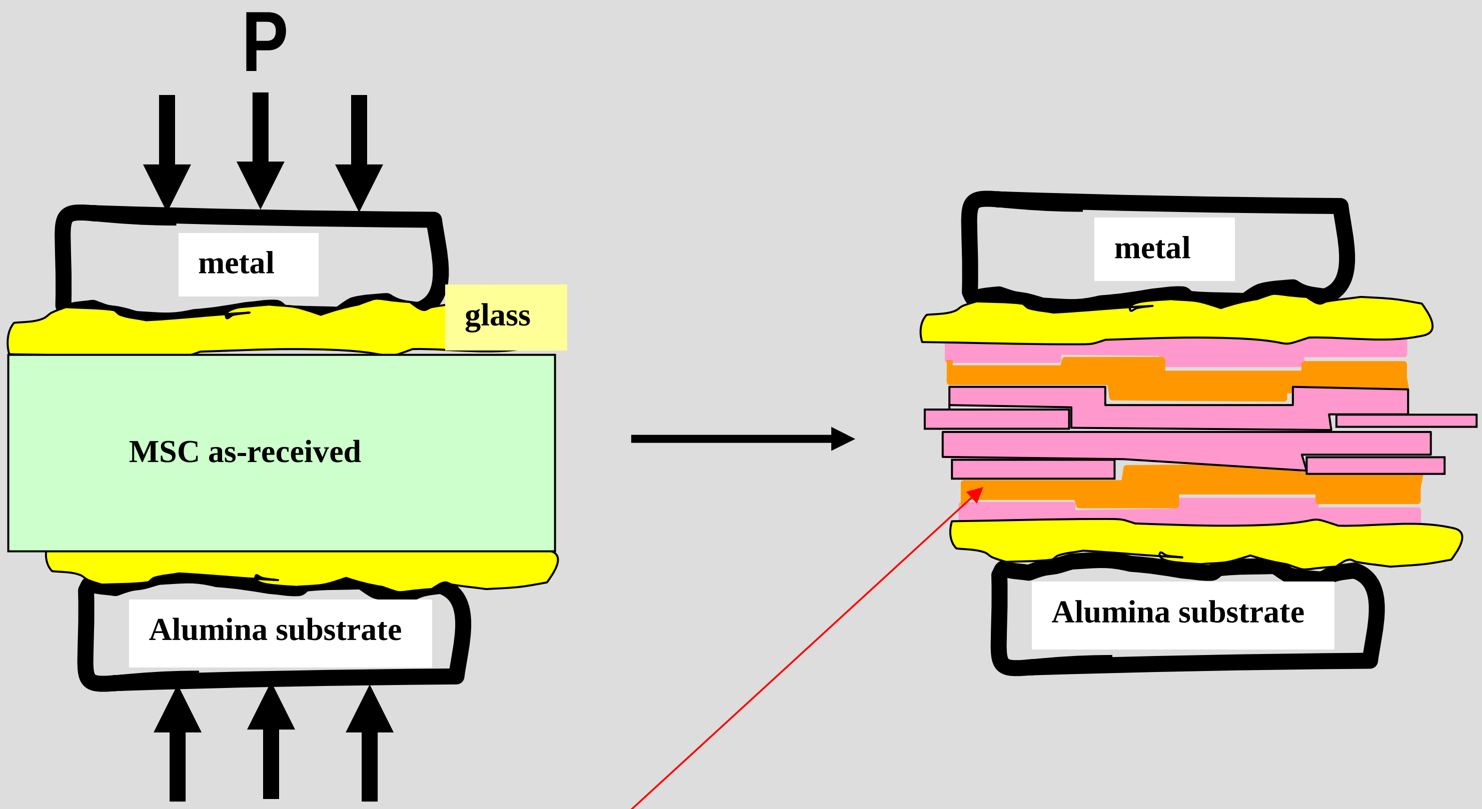
Orders of magnitude reduction in leak rate (vs. plain mica) for single crystal type mica in hybrid design with glass interlayers



Abrupt increase in leak rate during initial cycles –
Modest increase in leak rate subsequently



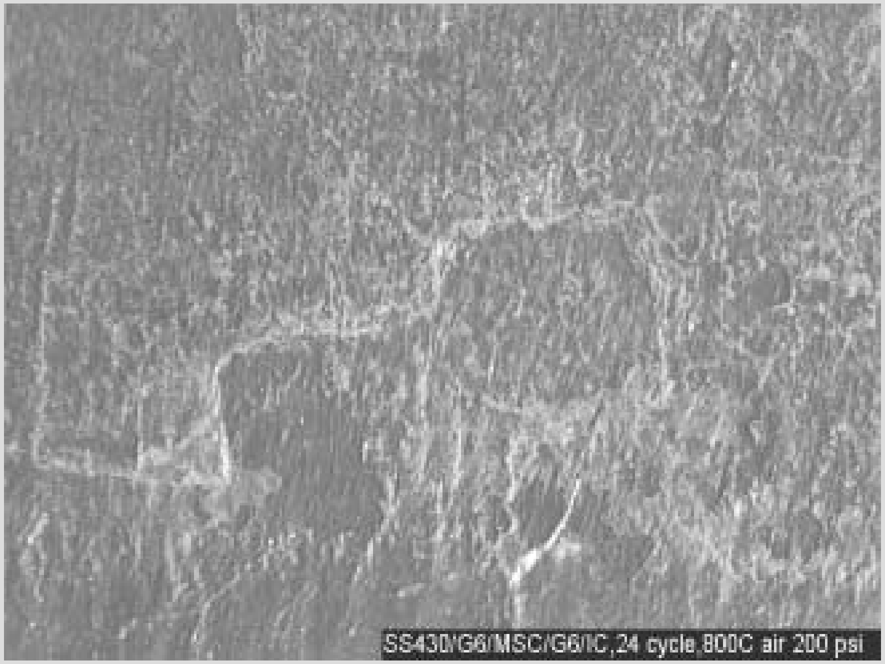
Thermal cycling degradation of hybrid seals



Frictional damage is limited to the first several sub-layers below glass/mica interface; CTE of mica (~6.9 ppm/K) substantially less than CTE of SS or glass (10-13 ppm/K)

Damage to mica during thermal cycling

MSC after 24 thermal cycling to 800ºC in air (applied stress:100 psi (SS430/G6/MSC-ar/G6/IC))



Y-S Chou, J.W. Stevenson, and L.A. Chick, "Ultra-low leak rate of hybrid compressive mica seals for solid oxide fuel cells", Journal of Power Sources, 112, 130 (2002).

Y-S Chou and J.W. Stevenson, "Thermal cycling and degradation mechanisms of compressive mica-based seals for solid oxide fuel cells," J. Power Sources, 112, 376 (2002).

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Recap: SOFC Seal Requirements

Functional requirements and materials selection parameters	
Mechanical	•Hermetic (or near hermetic) •Minimal CTE mismatch (or ability to yield or deform to mitigate CTE mismatch stresses) •Acceptable bonding strength (or deformation under compressive loading) •Thermal cycle stability •Vibration and shock resistance (for mobile applications)
Chemical	•Long-term chemical stability under simultaneous oxidizing/wet fuel environments •Long-term chemical compatibility with respect to the adjacent sealing surface materials •Resistance to hydrogen embrittlement/corrosion
Electrical	•Non-conductive
Fabrication	•Low cost •High reliability with respect to forming a hermetic seal •Sealing conditions compatible with other stack components

Recap: SOFC Seal Materials "Issues"

- Long term structural stability
  - Bulk cracking
  - Re-crystallization
  - Interface de-bonding
  - Reaction products: Layer formation, Porosity formation
- Chemical stability
  - Interface reactions
  - Evaporation
  - Dissolution
  - Hydrogen-assisted corrosion