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ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Novel Materials for Obtaining Compliant, High-Temperature Seals for SOFCs

SECA Core Technology Program

Ceramatec, Inc.

Supported in part by

US DOE Phase I SBIR DE-FG03-02ER83385

C. Lewinsohn, S. Quist, and S. Elangovan

Presented at

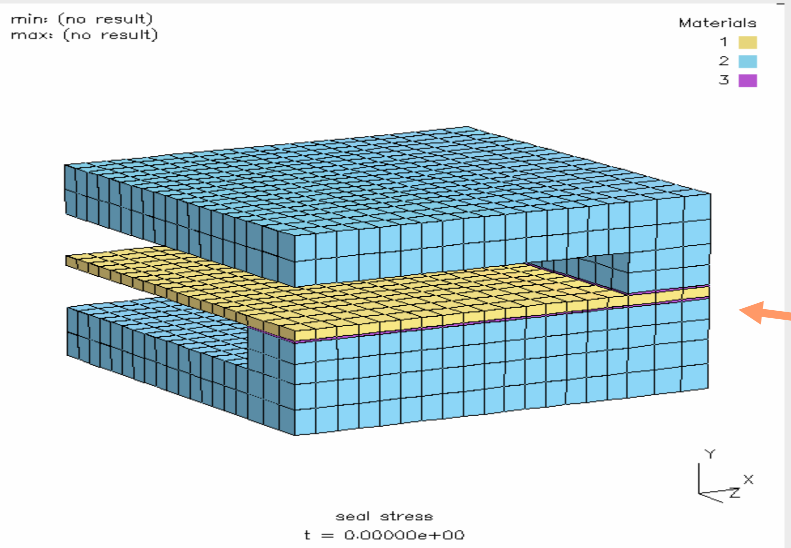
Albany, NY

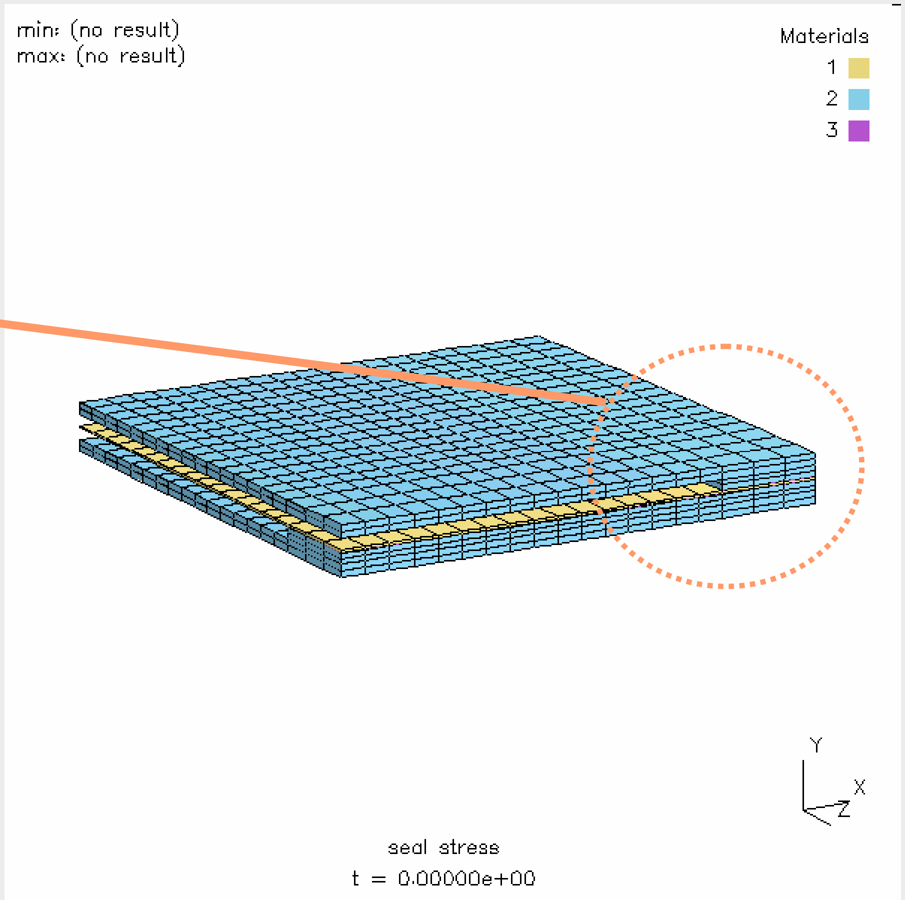
01 October 2003

Seal Requirements

- **Low leak rate: good adhesion, high density.**
- **Ability to withstand thermal cycling/CTE match with cell components.**
- **Compatible with cell materials.**
- **Environmental stability in oxidizing and reducing conditions.**
- **No negative effect on cell performance.**
- **Acceptable cost.**

Mechanical behavior of seals – FEA analysis





- ¼ stack model
- 10 x 10 cm stack
- Upper surface unconstrained
- Bottom surface fixed in vertical direction
- Symmetric boundary conditions on cut planes
- Stresses calculated for cooling from fabrication temperature

FEA model

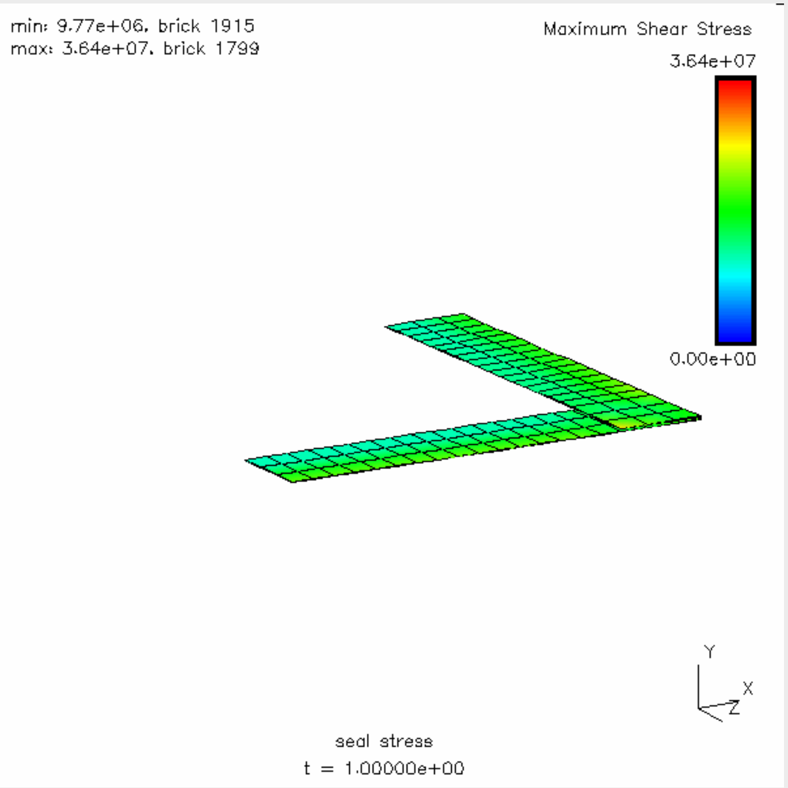
Material Properties

Component	**E (GPa)**	**ν**	**CTE (ppm $^{o}C^{-1}$)**
Interconnect	200	0.29	12
Electrolyte	185	0.31	11
Seal	20, 100, 200	0.20	11

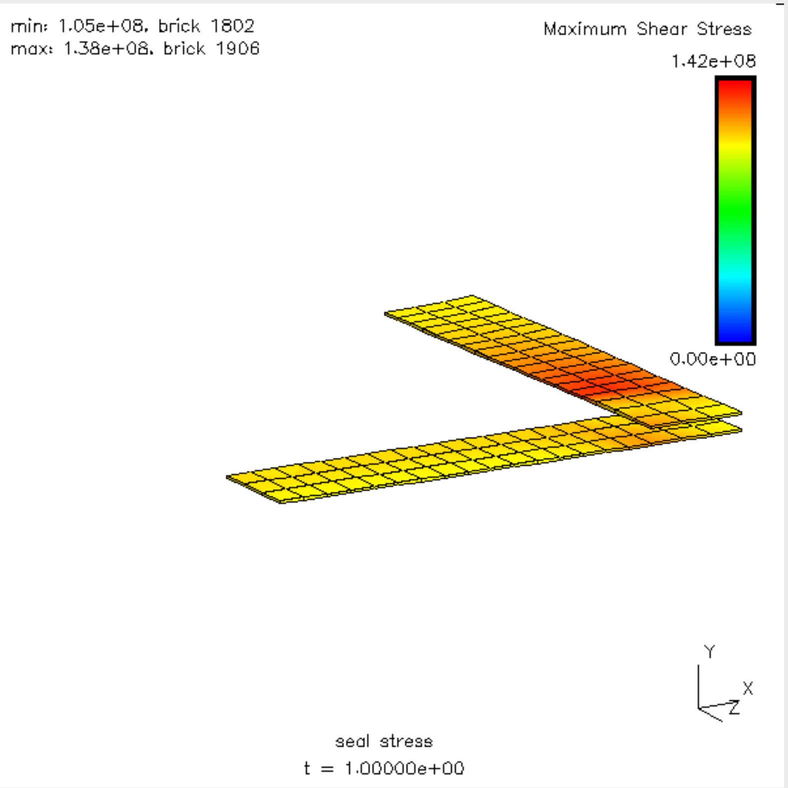
- **Stress free temperature: 1000ºC**
- **Seal dimensions: 50 microns thick, 1 cm wide**

Seal Stresses – FEA analysis

$E_{seal} = 20$ GPa

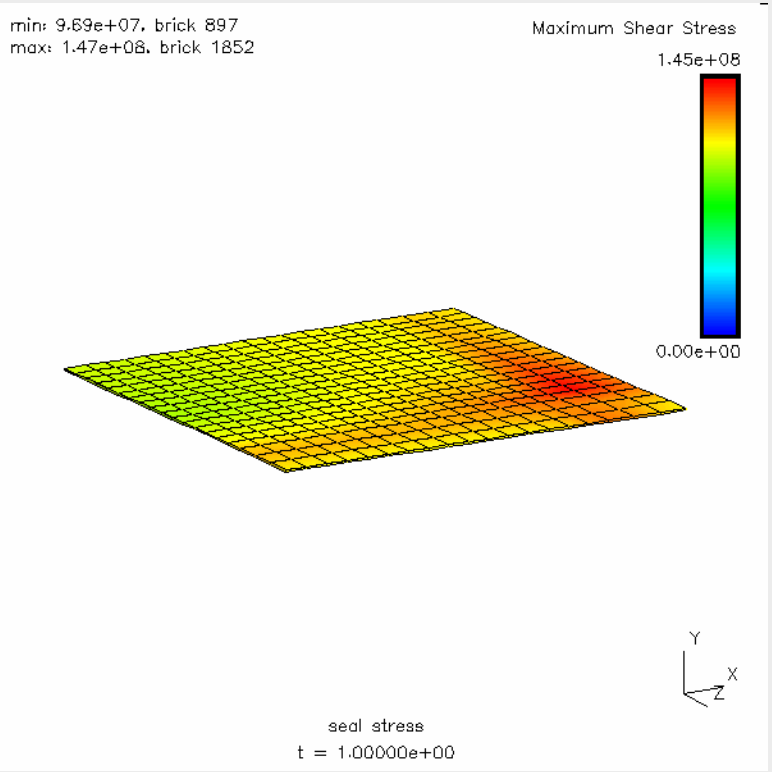


$E_{seal} = 200$ GPa

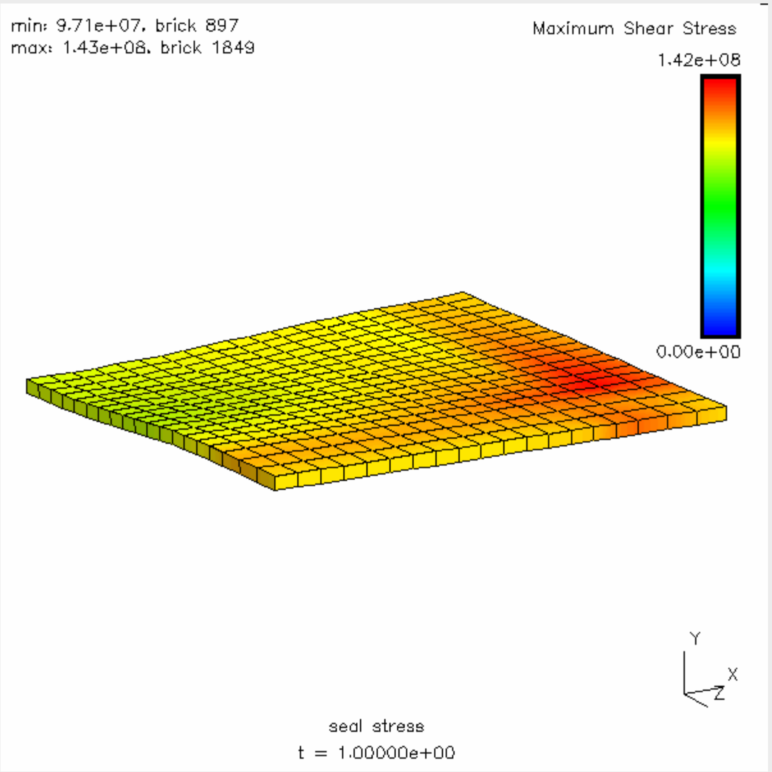


Electrolyte Stresses – FEA analysis

$E_{seal} = 20$ GPa

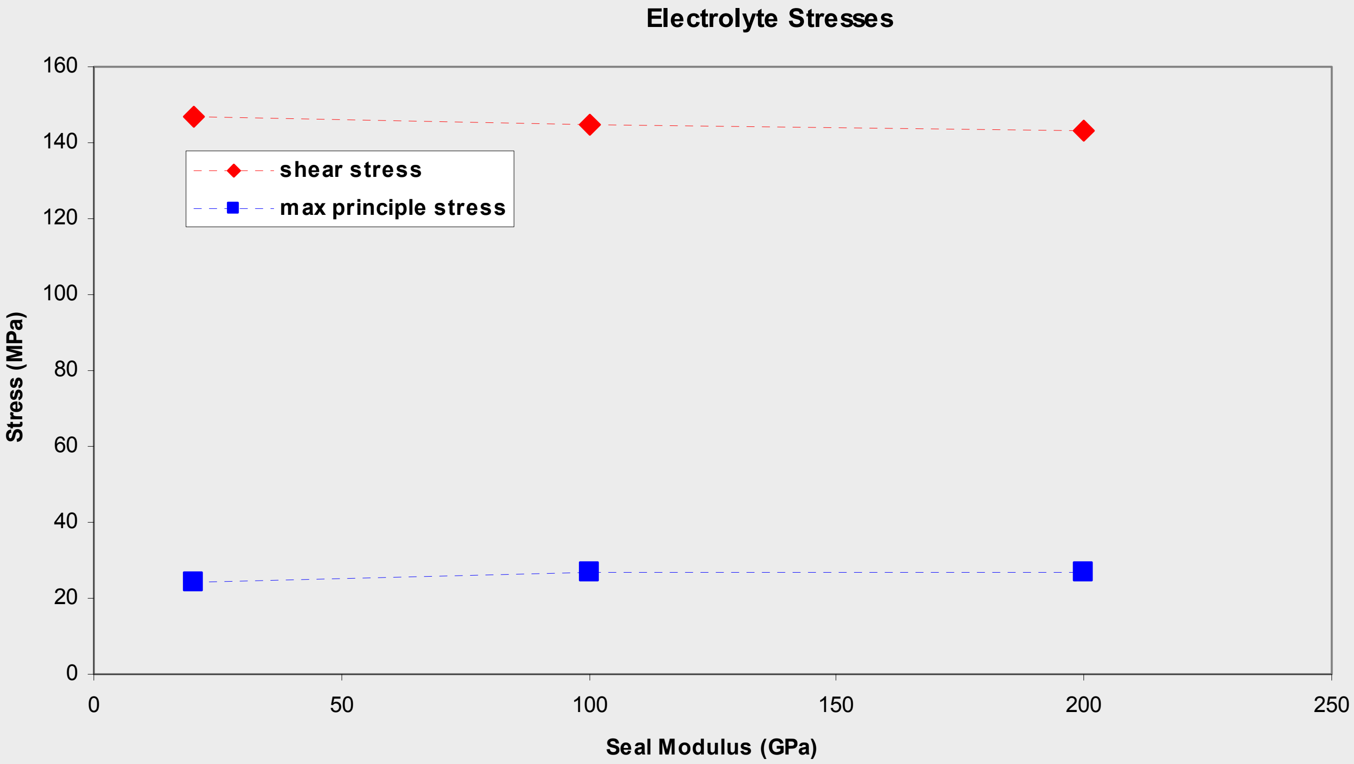


$E_{seal} = 200$ GPa

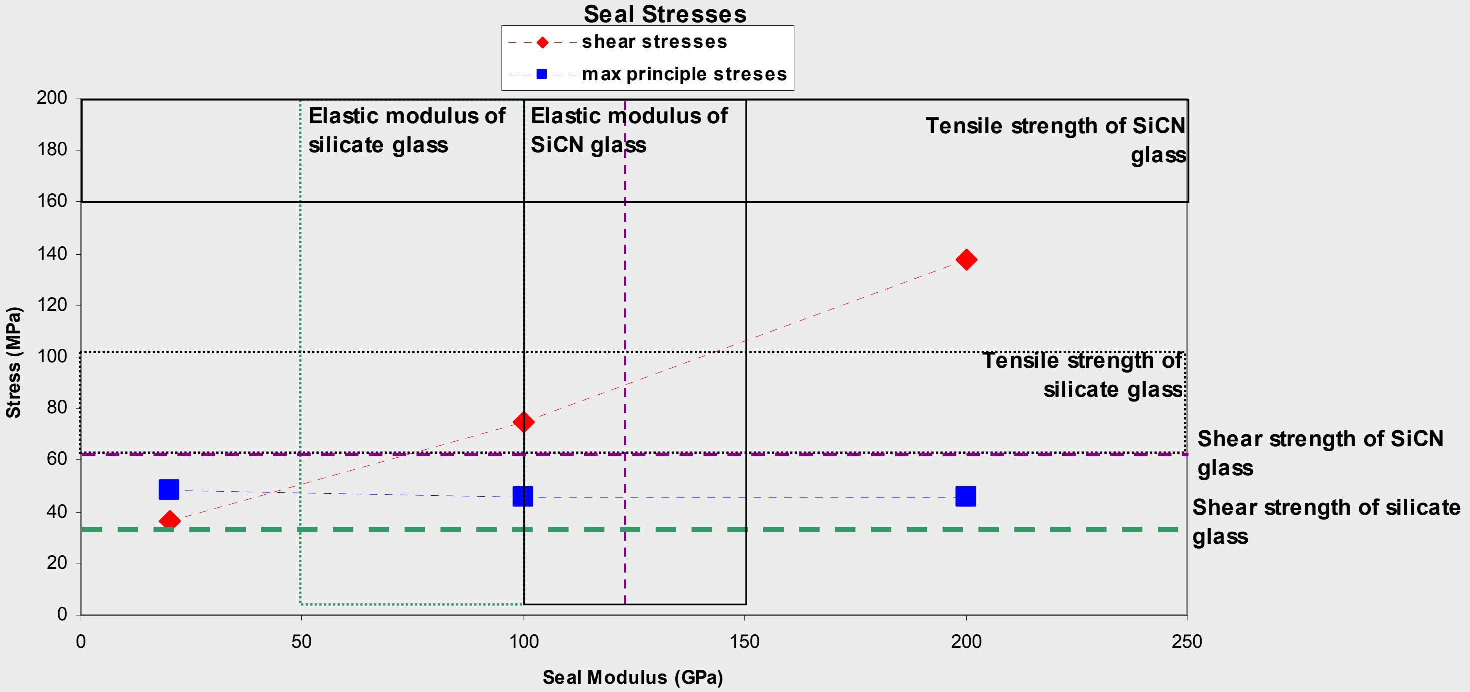


Electrolyte Stresses – FEA analysis

- Seal compliance doesn't significantly affect electrolyte stresses, since weight of stack constrains displacements.



Seal material selection



- ➢Compliant materials, with required properties, have low strength.
- ➢High strength materials, with required properties, have low compliance.
- ➢Composite seals combine benefits of high-temperature materials and compliant materials.
- ➢Seal designs can also be used to modify stress states.

Thermal Shock

$$R' = k\sigma_{max}(1-\nu)/(E\alpha)$$

composition	**k (W/m-K)**	**E (GPa)**	**α (ppm-C^{-1})**	**ν**	**σ_{max} (MPa)**	**R'**
silicate	1	75	10	0.2	60-100	85.3
SiCN	10	120	10	0.2	160-200	**1200**

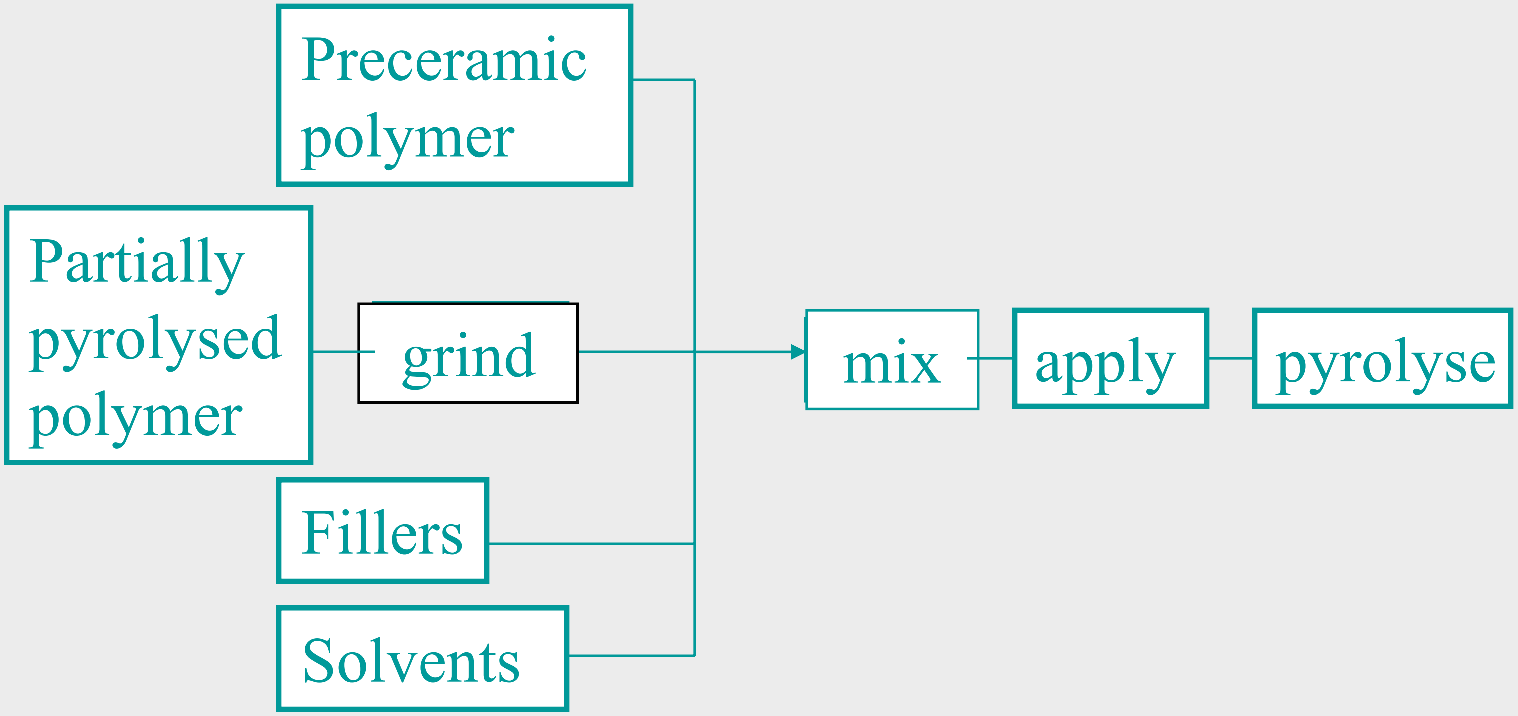
- Amorphous, non-oxide-based seal materials should have significantly higher resistance to thermal shock and, hence, thermal cycling.

Preceramic polymer precursor derived seals - rationale

- Allows for introduction of a variety of fillers and additives that provide for thermophysical compatibility and mechanical compliance.
- Leads to formation of chemically inert, microstructurally stable, non-reactive (w/SOFC components) amorphous, non-oxide materials with enhanced mechanical properties compared to alternative, high temperature materials.
- Allows liquid and polymeric processing methods – dip coating, spray coating, molding, injection, etc.
- Relatively low processing temperature (900 - 1000ºC).
- Suitable for intermediate and high temperature operation.

Seal Fabrication

Process Flowchart



Preceramic polymer

Partially pyrolysed polymer

grind

Fillers

Solvents

mix

apply

pyrolyse

Test seals - fabrication

Application

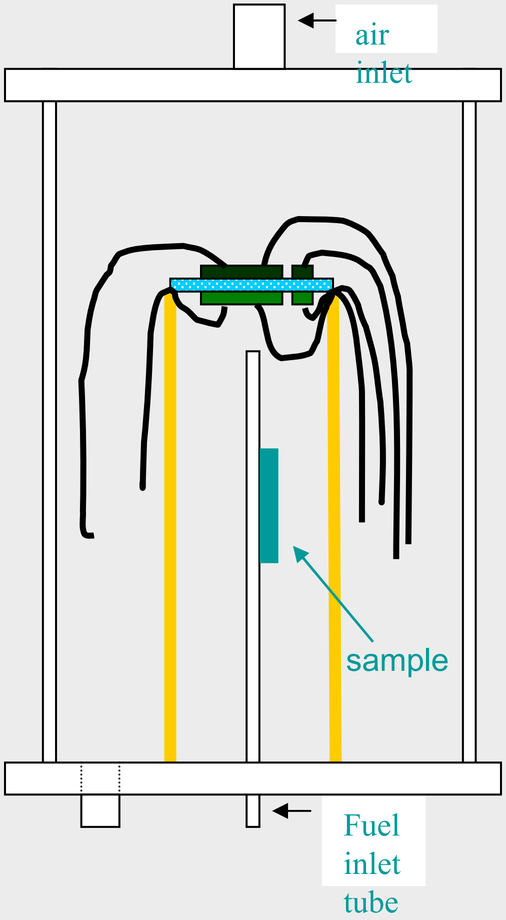
Pyrolysed seals

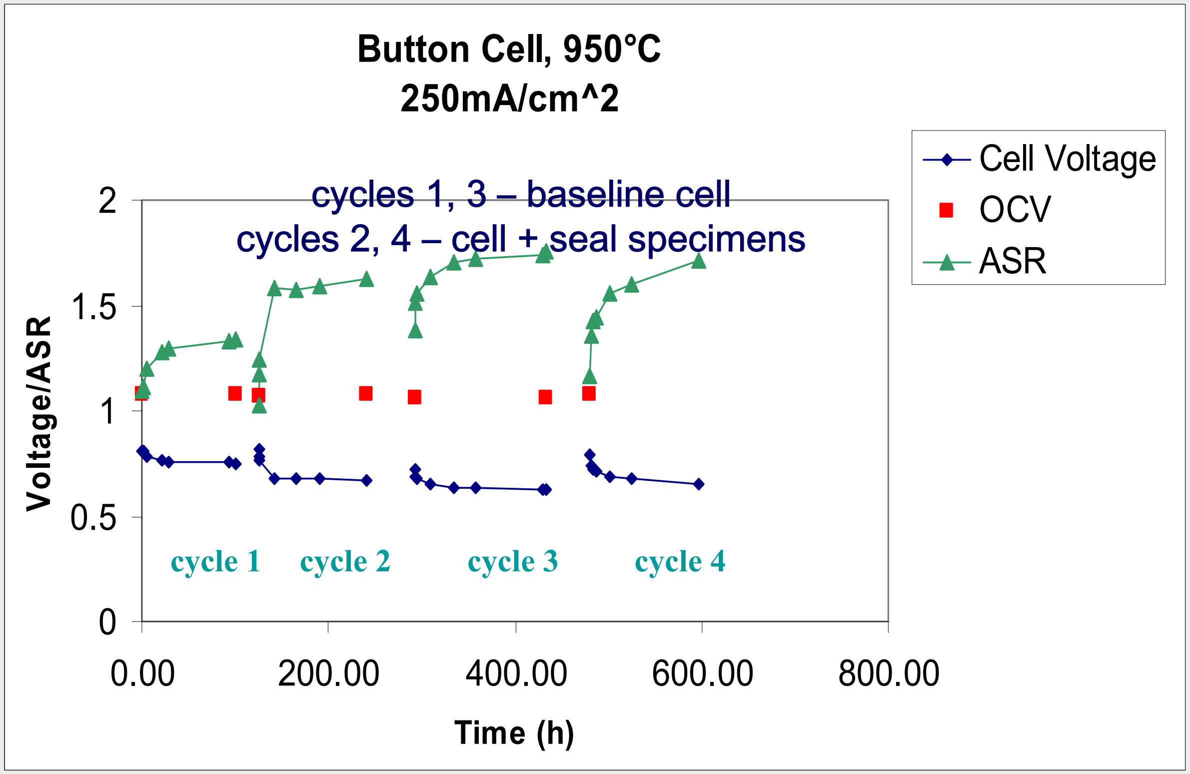
High thermal expansion, inert fillers used to control CTE

Composition	Temperature Range (ºC)	CTE (ppm ºC^{-1})
8 mol% yttria-doped zirconia	*25-1000*	*10.6-11.1*
polycarbosilane/Metal 1	200-700	10.0
polycarbosilane/Metal 2	200-700	7.0
polycarbosilane/Metal 3	200-700	9.0
polycarbosilane/Ceramic 1	200-700	7.0
polycarbosilane/Glass 1*	200-600	7.0
polycarbosilazane/Metal 1	200-600	10.0
polycarbosilazane/Metal 2	200-700	5.0
polycarbosilazane/Metal 3	200-700	10
polycarbosilazane/Ceramic 1	200-700	8.0

* Glass provided by Dr. R. Loehman, Sandia National Laboratory, Albuquerque, NM..

Compatibility with SOFCs





- Preliminary results indicate cell performance is not affected by the presence of seal material in the fuel stream

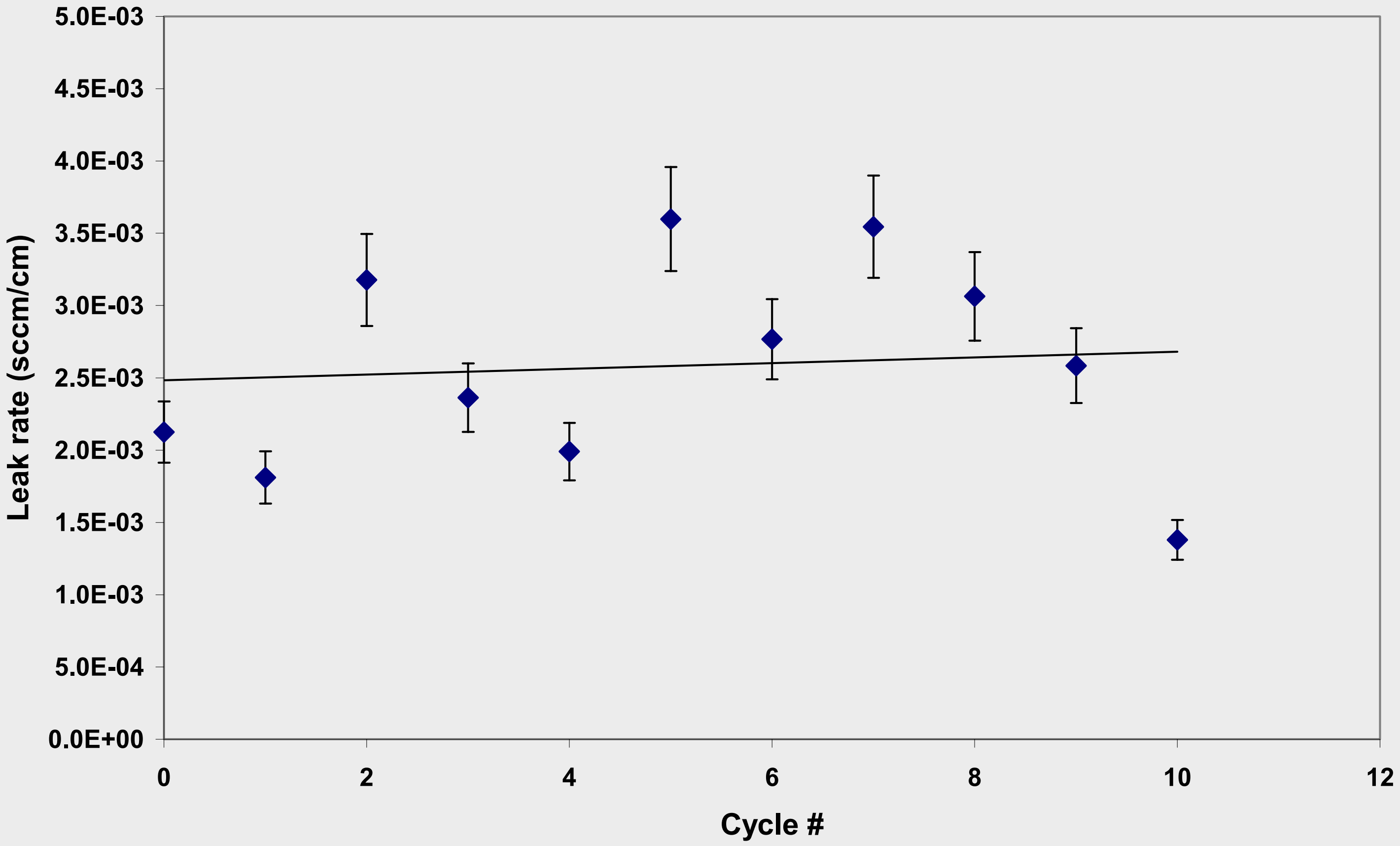
Leak rate

Substrates	Leak rate (sccm/cm)
Zirconia electrolyte/zirconia electrolyte	1.3×10^{-3} *
Zirconia electrolyte/metal interconnect	1.9×10^{-3}
Metal interconnect/metal interconnect	2.7×10^{-2}
Alumina/inconel sealed w/compressive, hybrid mica seal (PNNL data measured at 800ºC)	*1.6×10^{-4}*

- **Seals tested without applied, compressive force**

* Same as for a proprietary glass seal w/matched thermal expansion but higher reactivity with ceramic SOFC components.

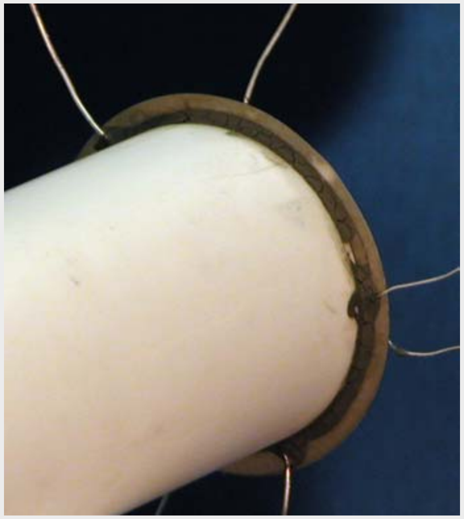
Leak rate – effect of thermal cycling



RT – 800ºC in 8 h
800ºC – RT in 8h
10 cycles

- Very little degradation in leak rate due to thermal cycling

Seal performance



4 cm diameter SOFC tests

Temp. (ºC)	polycarbosilane + metal filler	polycarbosilane + ceramic filler
800	1.038 V	1.065 V
850	1.030 V	1.052 V
900	1.008 V	1.042 V
cooled to 50ºC		
800	1.031	1.073
850	0.992	1.062
900	0.949	1.050

Summary

- Pyrolysis of preceramic polymer precursors offers a promising method for sealing SOFCs.
- Fillers and partial-pyrolysis can be used to mitigate shrinkage stresses and to control thermoelastic properties.
- Additional studies of leak rate reduction, adhesion, CTE, and and environmental stability are underway, but preliminary results are encouraging.