PROGRESS IN SEALS FOR SOLID OXIDE FUEL CELLS

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Acknowledgments
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S. Quist – FEA modeling
M. Timper – cell testing

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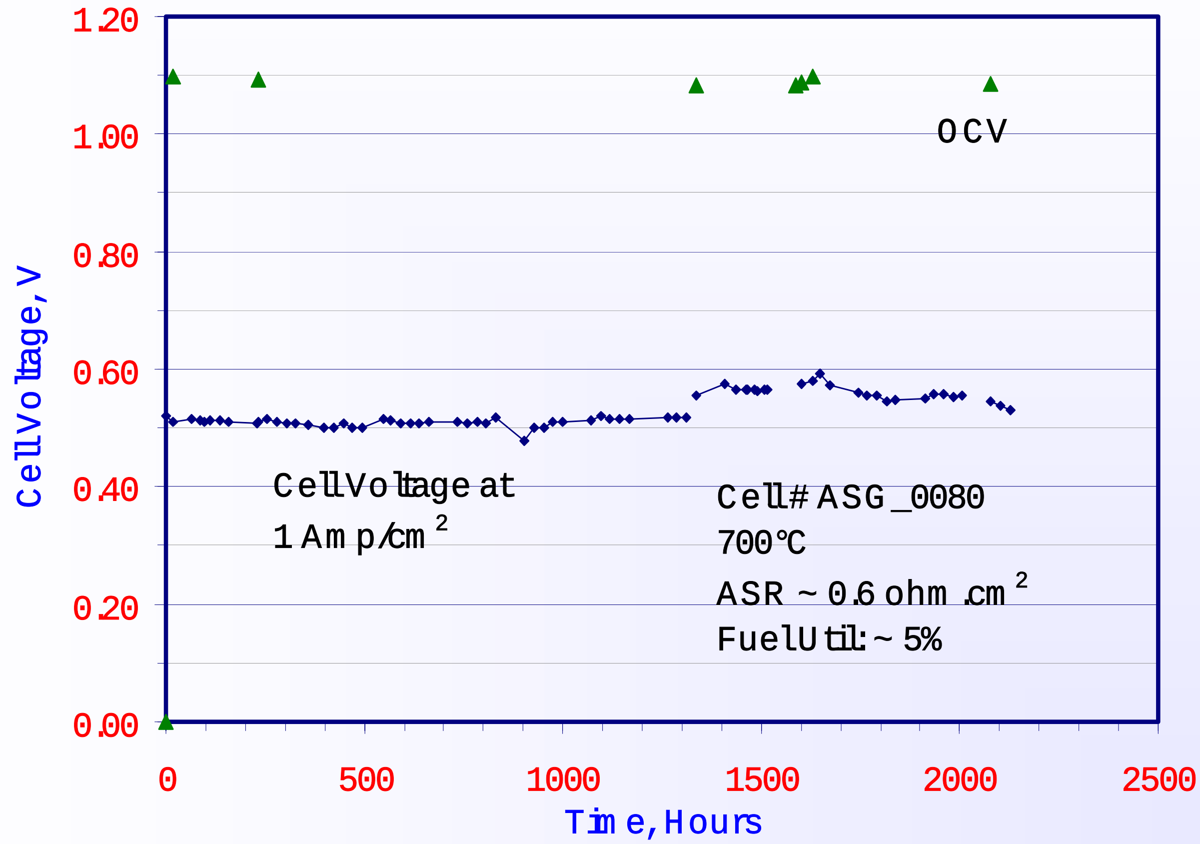
Seal Requirements

- **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.**

Seal Strategies

- **Compressive**
  - **Mica + compression**
  - **Ceramic felt + compression**
  - **Metallic seals + compression**
- **Adhesive**
  - **Cement**
  - **Glass**
  - **Glass-ceramic**
  - **Composite**
  - **Non-reactive metals (gold, hastelloy, etc.)**
  - **Reactive metals (silver, titanium, brazes, etc.)**

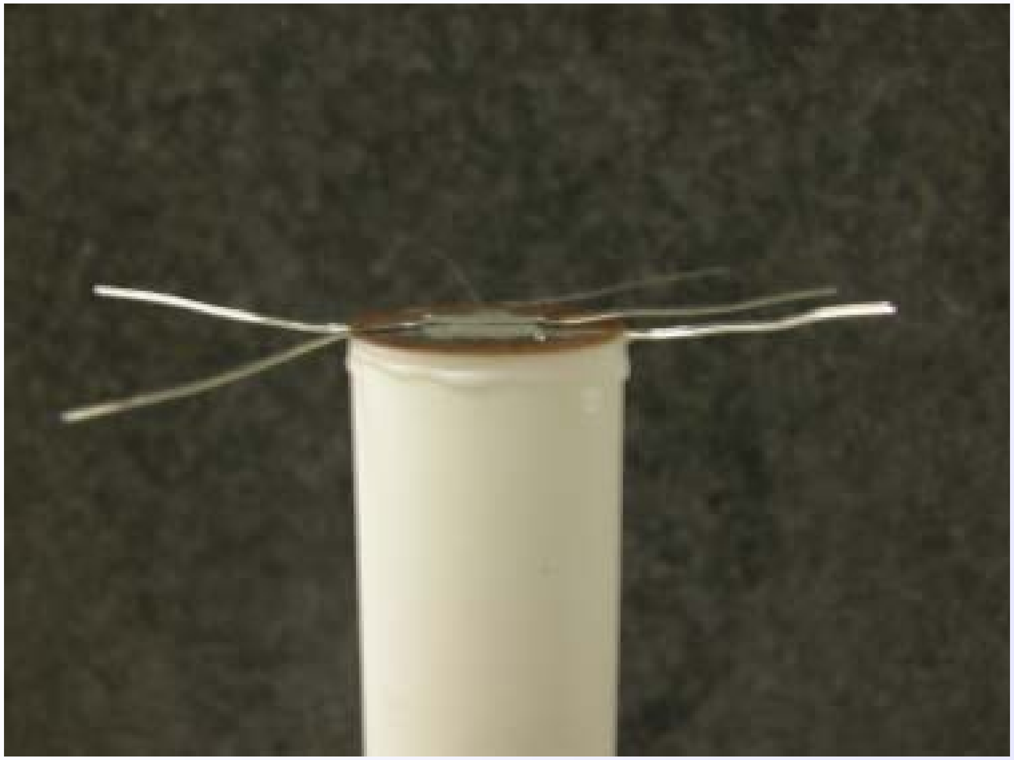
Ceramatec experience: Cement Seal



- **Adequate for new materials (Lanthanum Gallate)**
- **Porous - Stable OCV, but low fuel utilization**
- **Thermal cycle not possible**

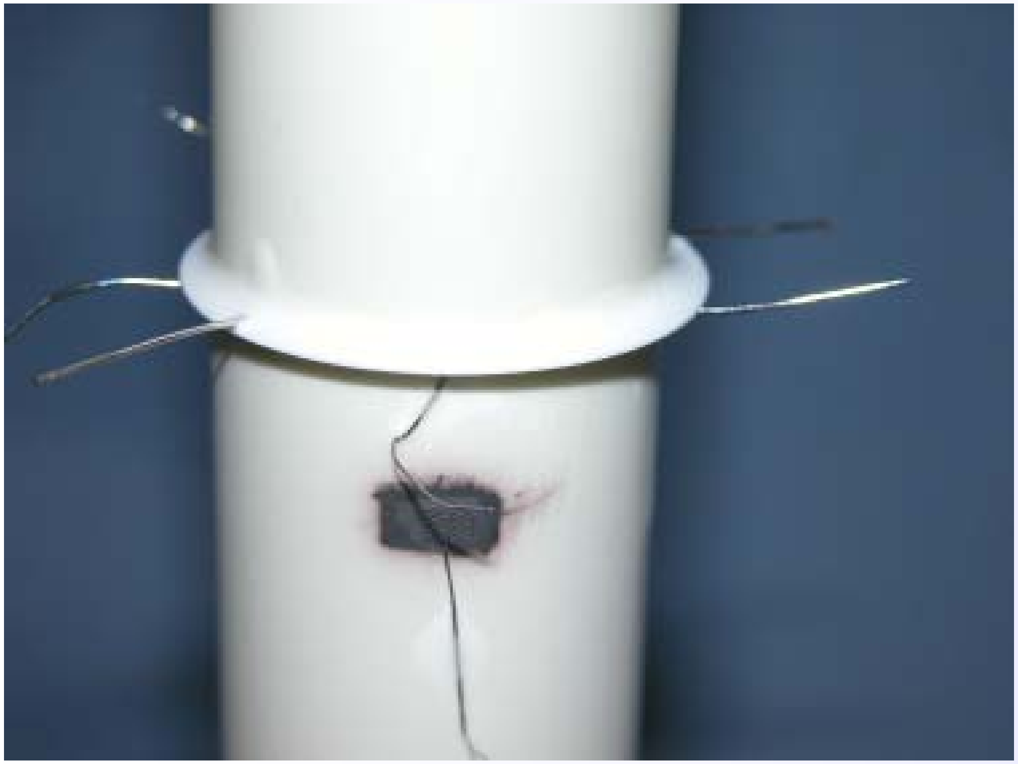
Ceramatec experience: Glass-Ceramic

- Sealed LSGM button cell



Ceramatec experience: Glass Seal

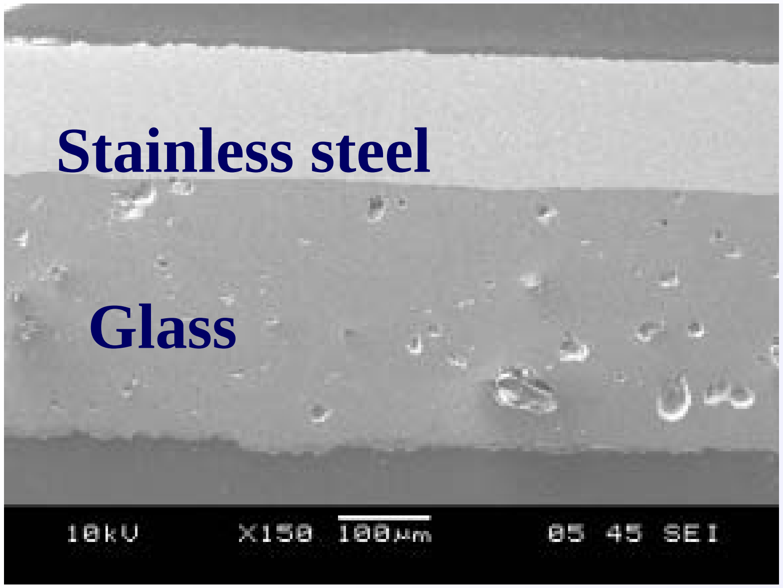
Joining Similar Materials

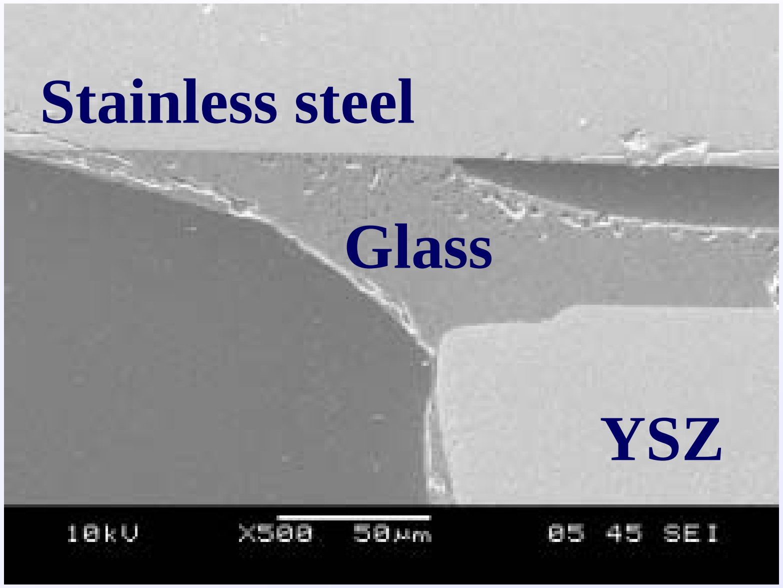


- **Zirconia Electrolyte - Zirconia Tube**

Ceramatec experience: Glass Seal

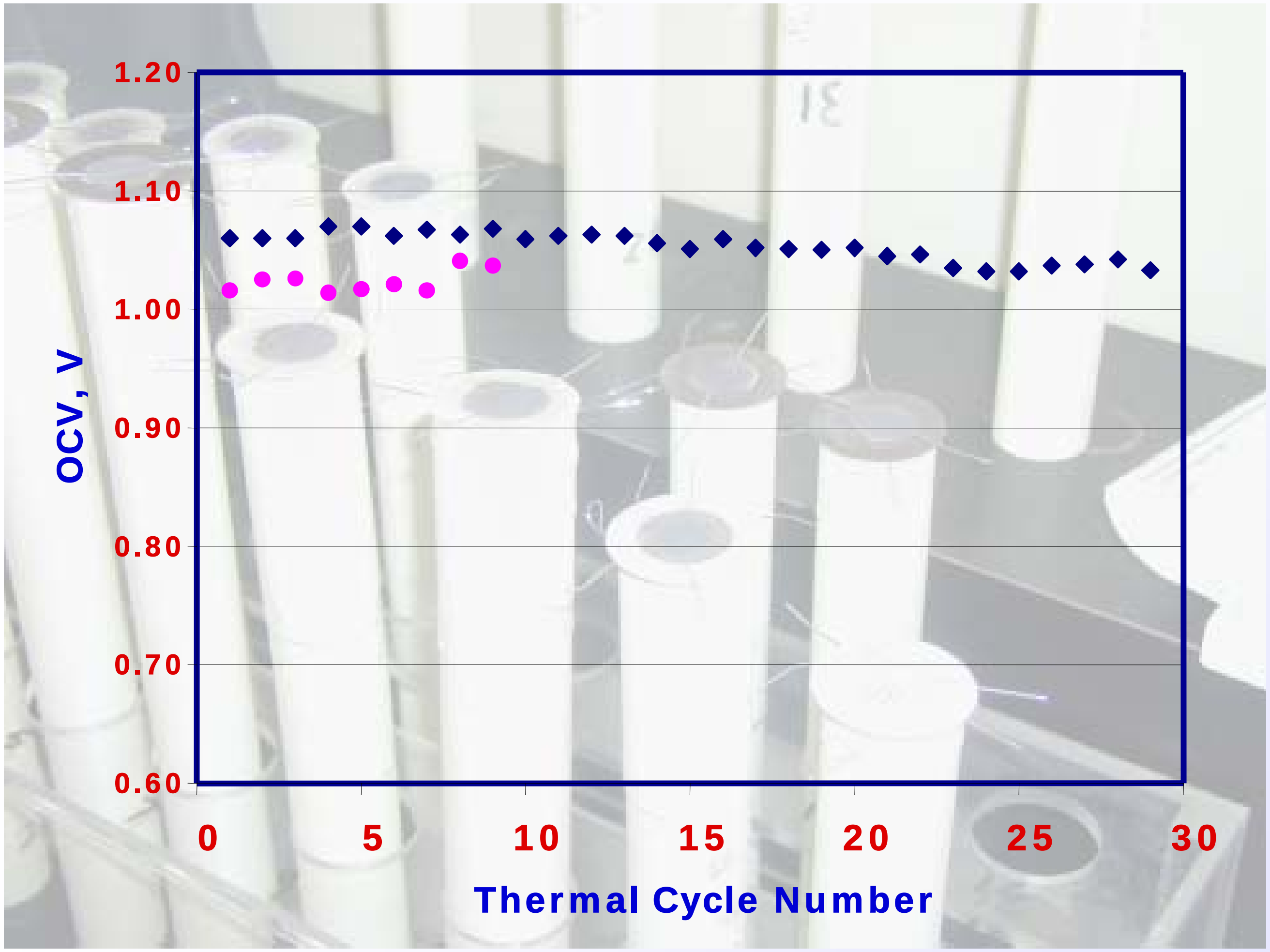
Joining Dissimilar Materials



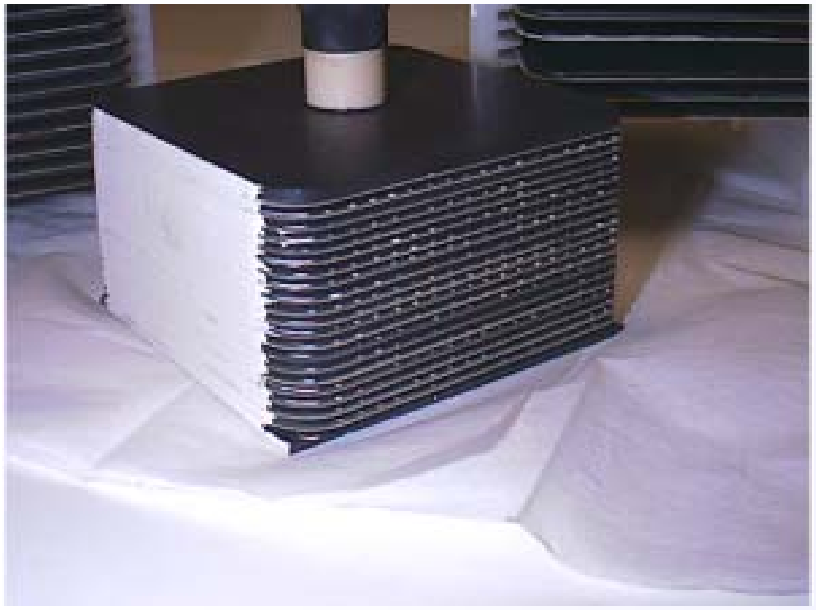


- **Tailored CTE allows joining metal-YSZ**
- **Thermal cycle effect - to be determined**

Ceramatec experience: YSZ Button Cell Thermal Cycle Effect

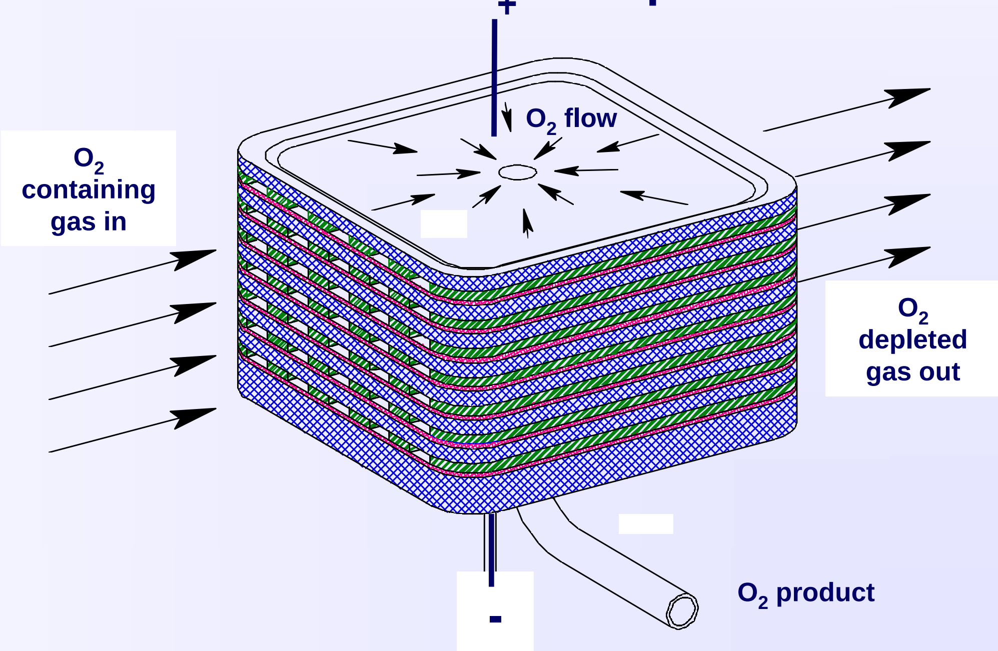


Ceramatec experience:
Electrochemical oxygen generation devices

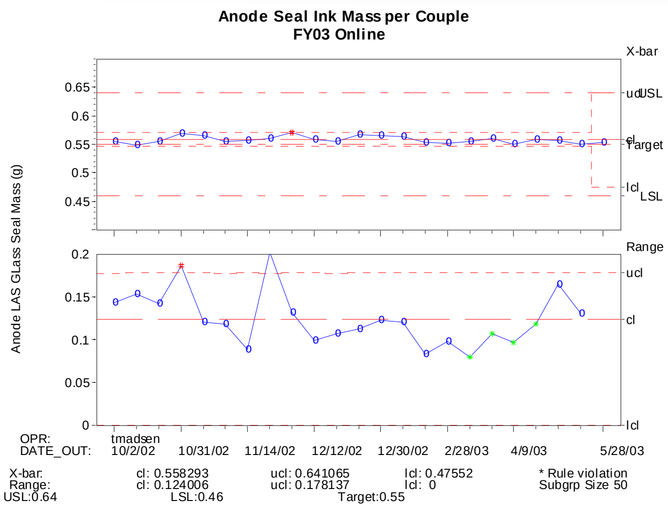


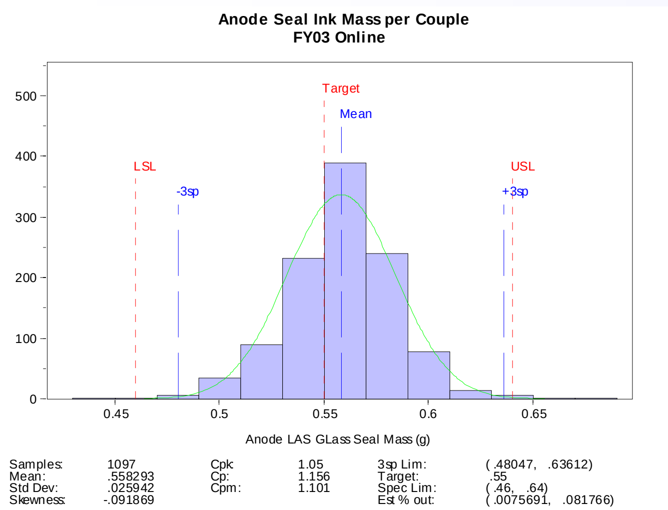
- **Ceramic stack**
  - **front - inlet air**
  - **left - insulated air baffle**
  - **top - O_2 gas port**
- **Cells electrically in series**

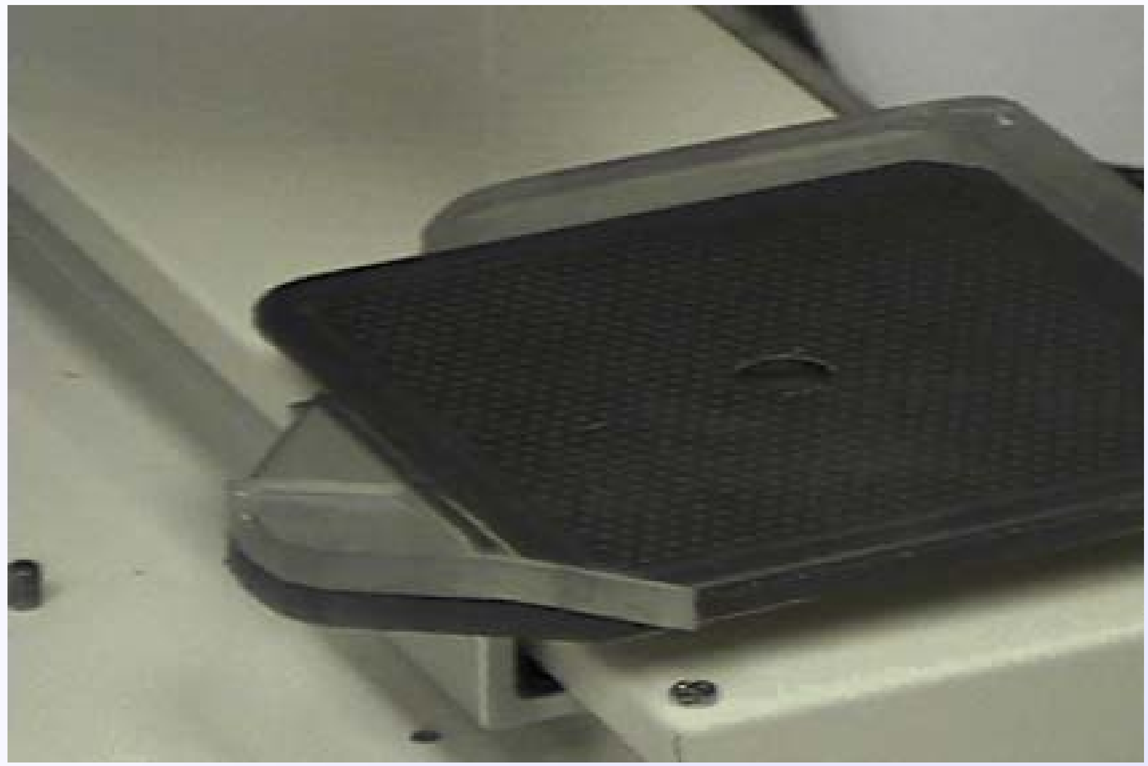
- **Layered components**
  - **interconnect**
  - **cell**
  - **insulator**
- **Gas flow**
  - **air - cross flow**
  - **O_2 - radial flow**
    - **central port out**



Ceramatec experience: Electrochemical oxygen generation devices

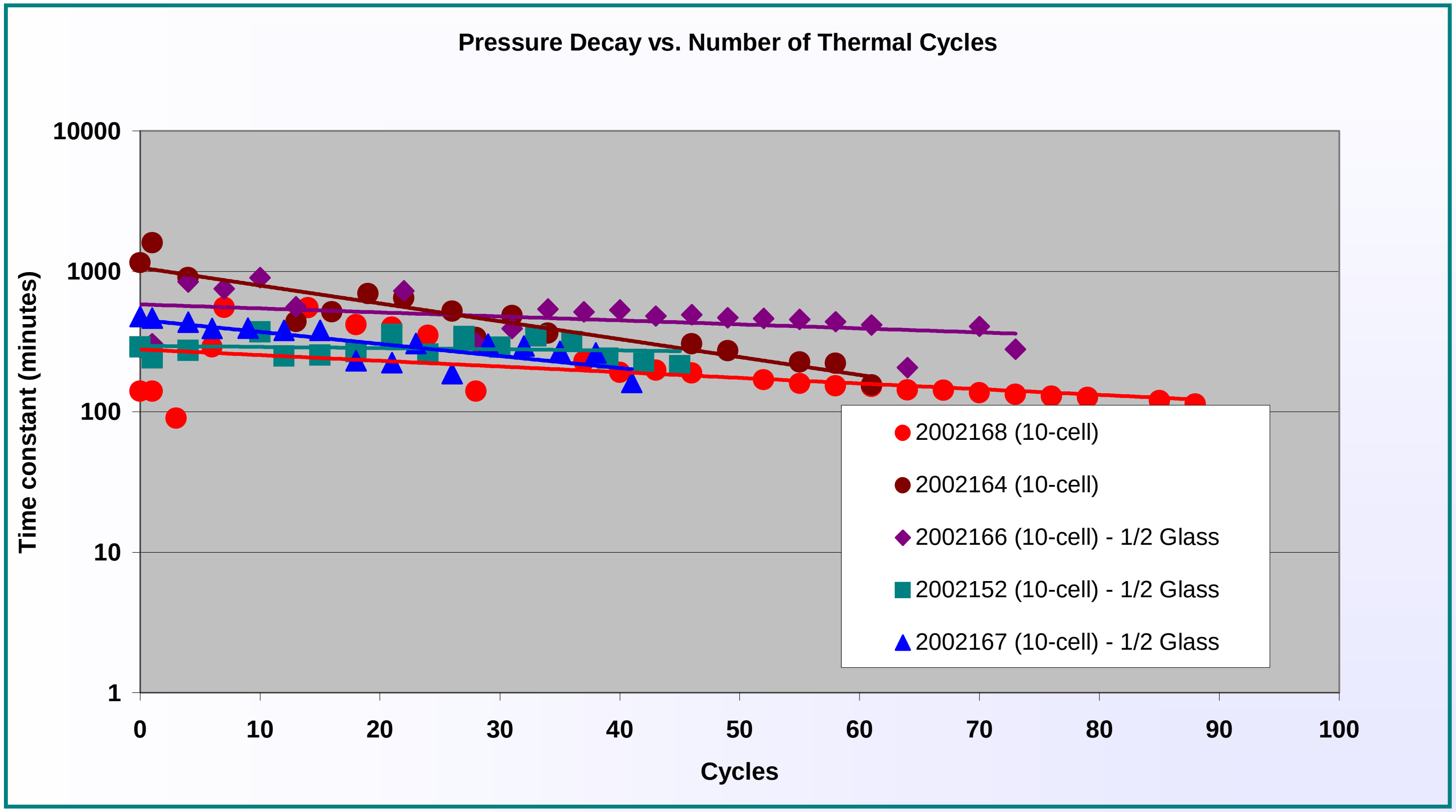






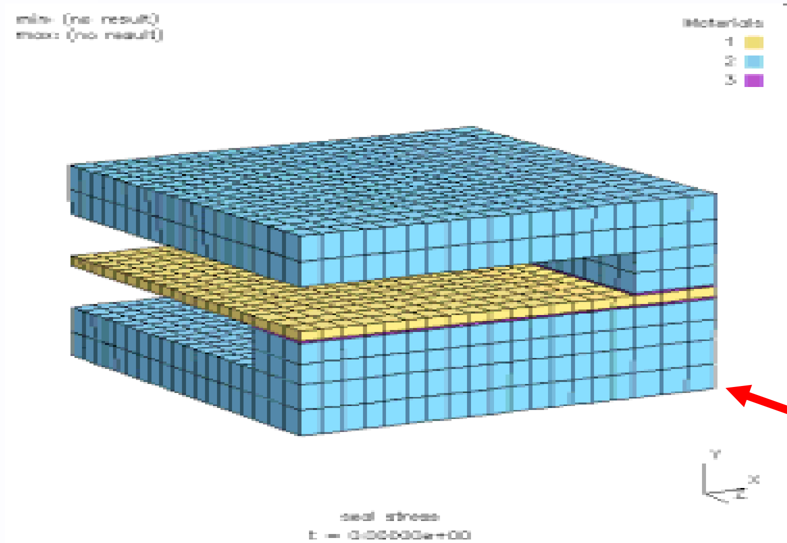
➤**Process control and monitoring affects performance and reliability**

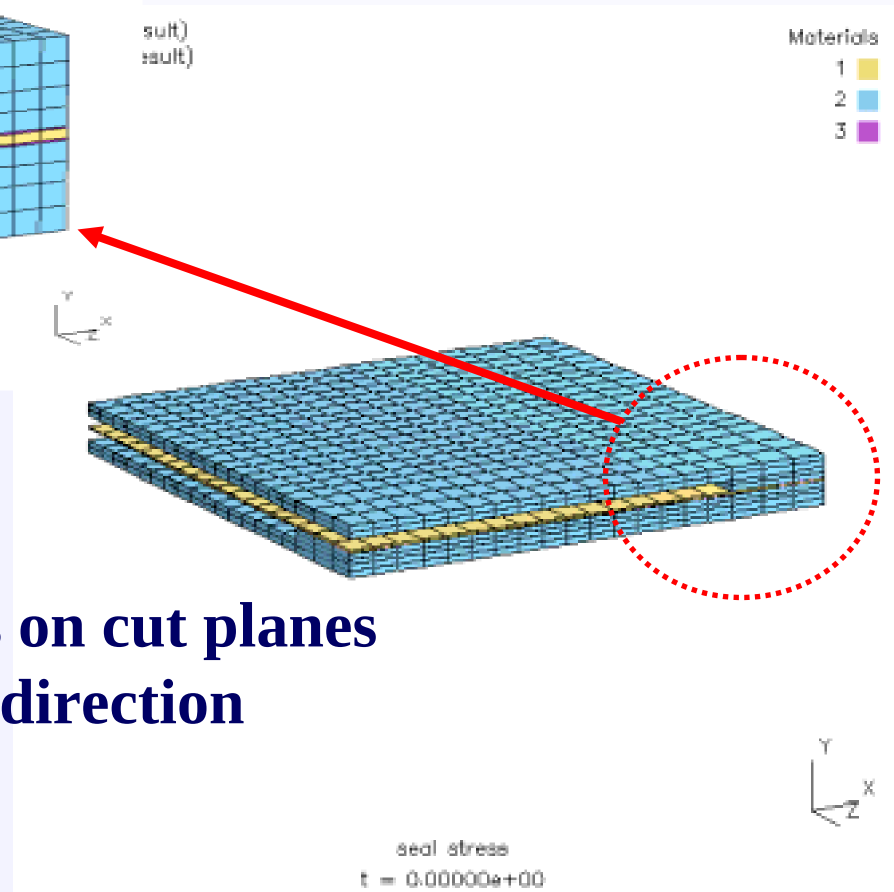
Ceramatec experience: Electrochemical oxygen generation devices



- **Cells cycled between RT and 700C, 100 times**
- **Stacks cycles > 90 times**

Mechanical behavior of seals – FEA analysis





- **10 x 10 cm stack**
- **¼ stack model**
- **Symmetric boundary conditions on cut planes**
- **Bottom surface fixed in vertical direction**
- **Upper surface unconstrained**

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FEA model

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

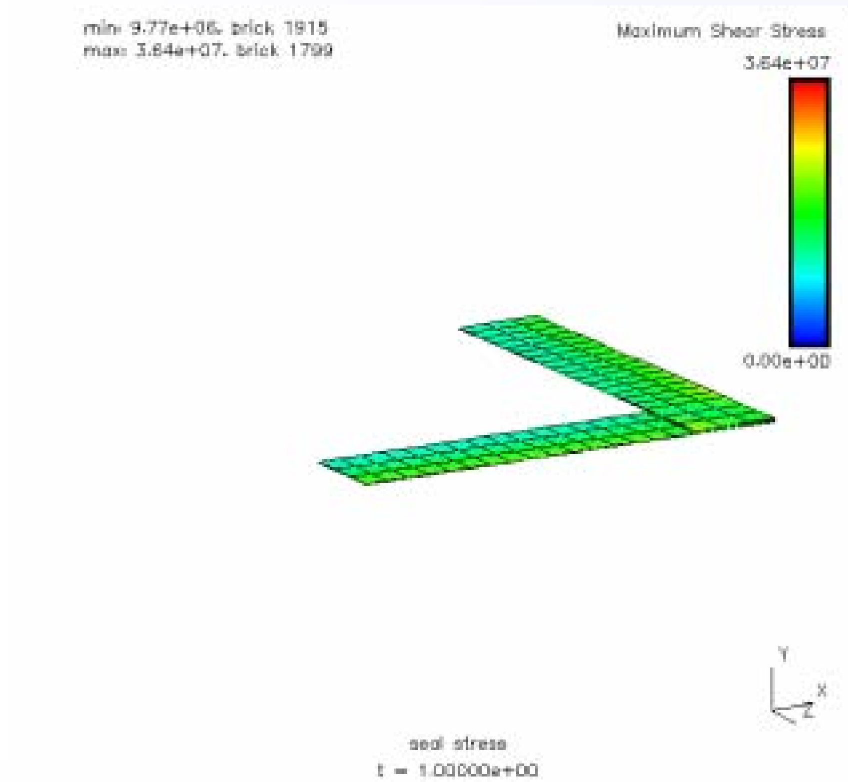
Material Properties

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

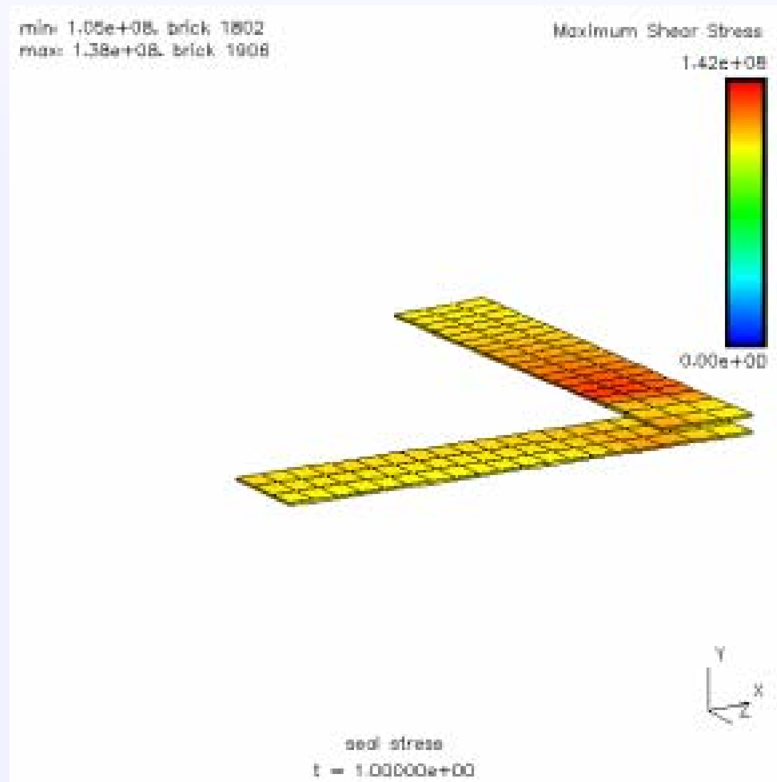
Seal Stresses – FEA analysis

Maximum shear stress occurs near corner

E_{seal} = 20 GPa



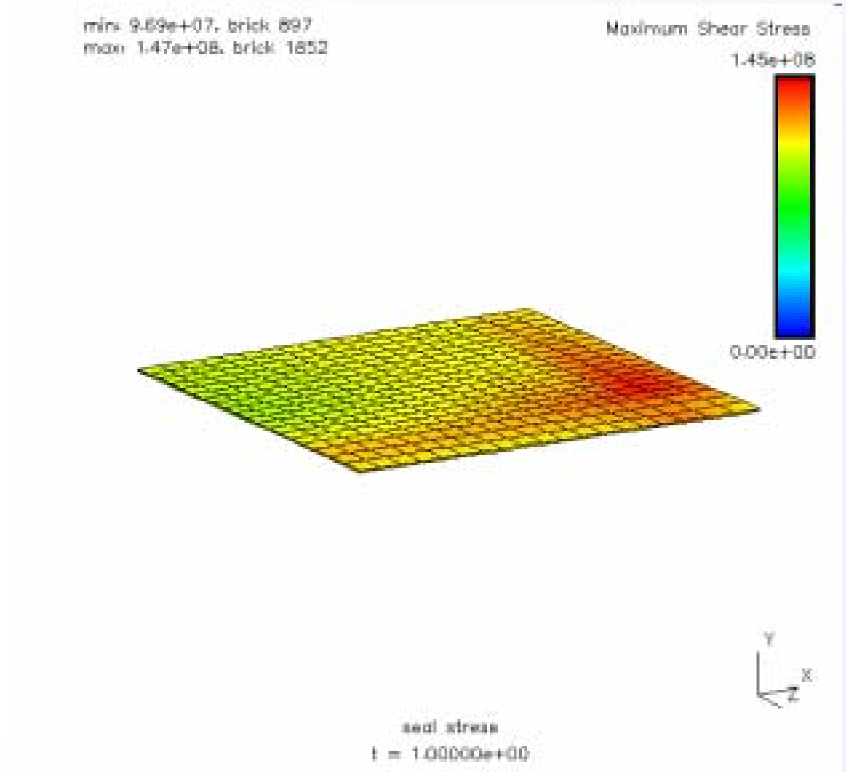
E_{seal} = 200 GPa



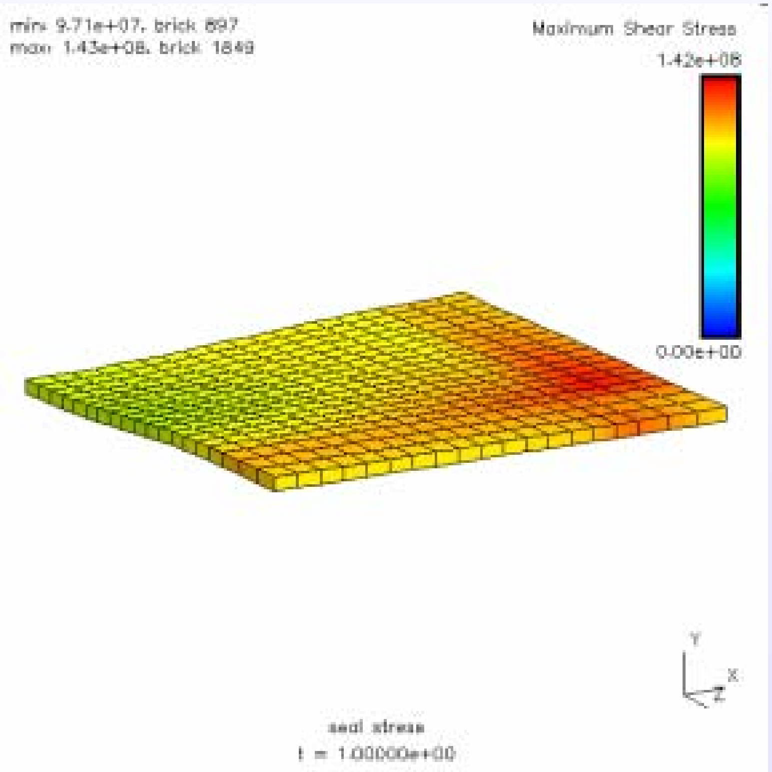
Electrolyte Stresses – FEA analysis

Maximum shear stress occurs near corner

E_{seal} = 20 GPa

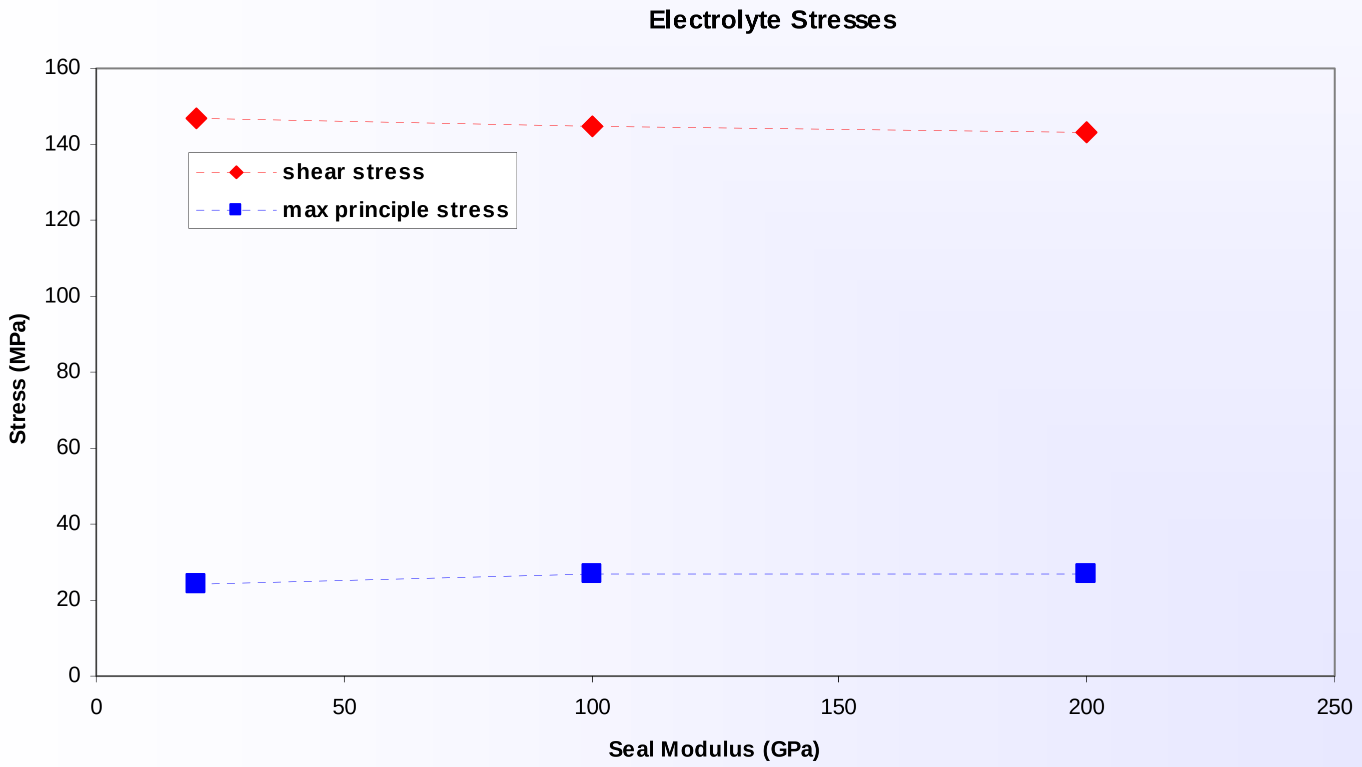


E_{seal} = 200 GPa

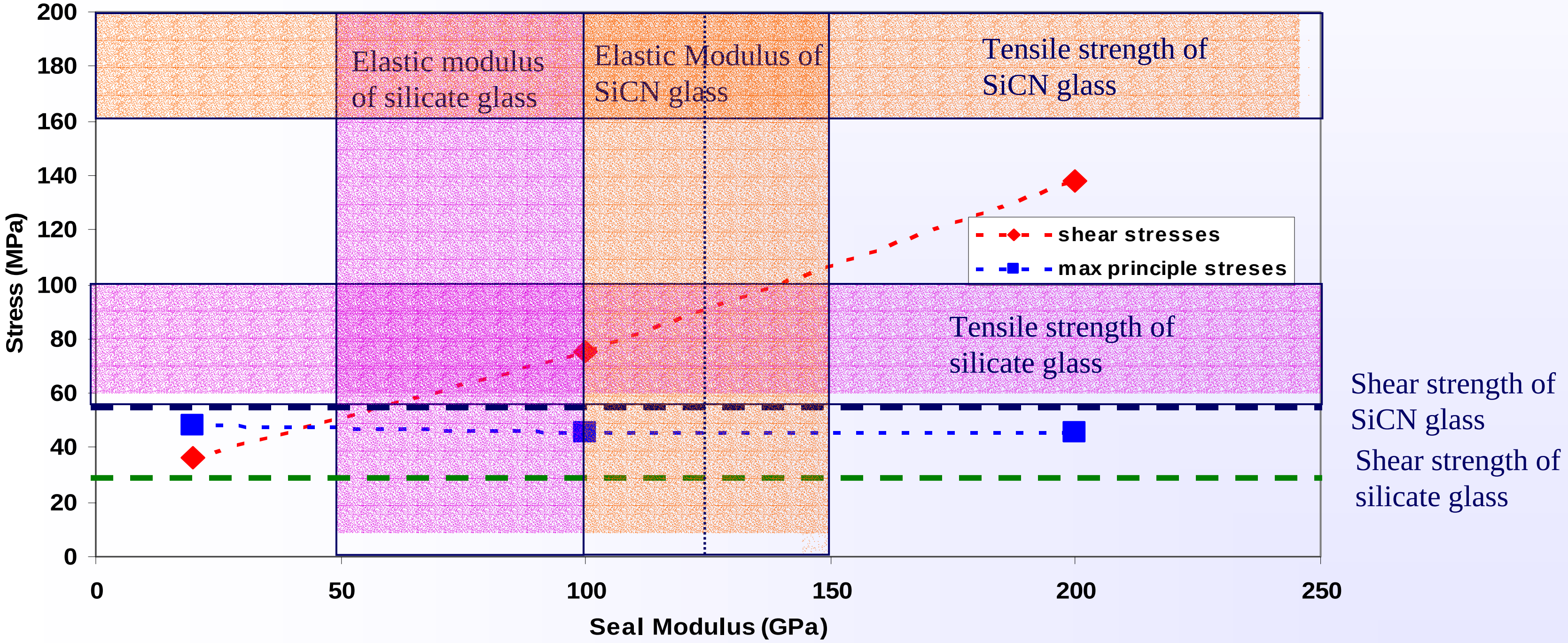


Electrolyte Stresses – FEA analysis

Seal compliance doesn't significantly affect electrolyte stresses



Seal Stresses – FEA analysis



Thermal Shock

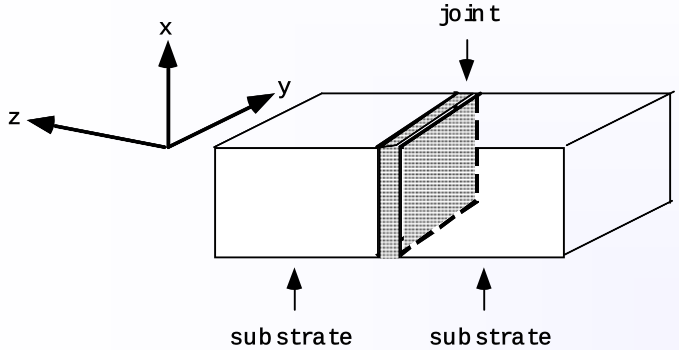
$$R' = k\sigma_{max}(1-\nu)/(E\alpha)$$

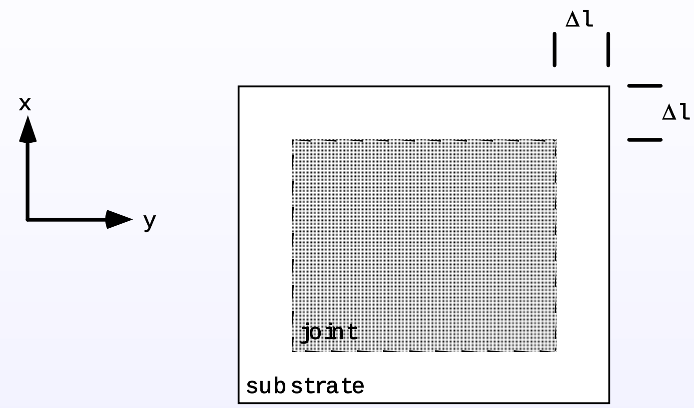
composition	**k (W/m-K)**	**E (GPa)**	**α (ppm-C^{-1})**	**ν**	**σ_{max} (MPa)**	**R'**
silicate	1	75	10	0.2	60-100	85.3
SiCN	10	120	10	0.2	160-200	**1200**

Preceramic polymer precursor derived seals - rationale

- **Leads to formation of amorphous, non-oxide materials with enhanced mechanical properties compared to alternative materials.**
- **Allows liquid and polymeric processing methods – dip coating, spray coating, molding, injection, etc.**
- **Allows for introduction of a variety of fillers and additives.**
- **Precursors wet and adhere to a variety of substrates.**
- **Relatively lower processing temperature (900 - 1000ºC).**

Stress due to constrained densification



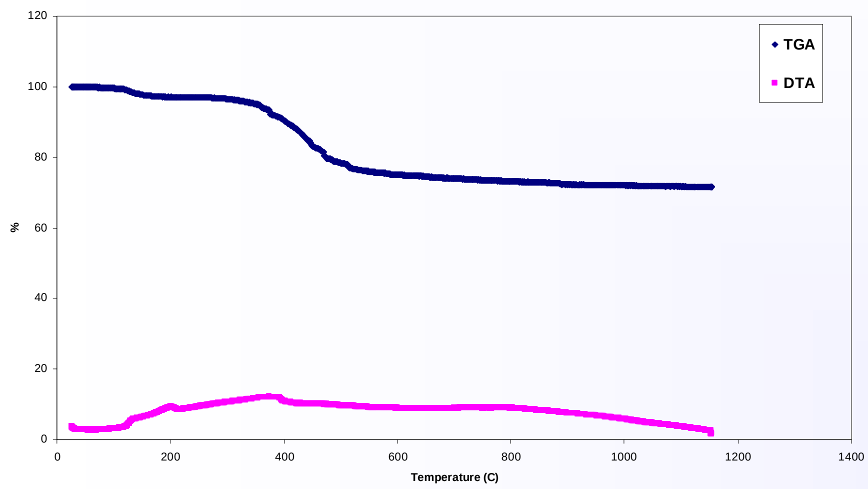


$$\sigma_P = 3\eta_f \left[\rho \big/ (3-2\rho) \right] \dot{\varepsilon} \Big/ \left[1 - \tfrac{1}{2} \left[\rho \big/ (3-2\rho) \right]^{1/2} \right]$$

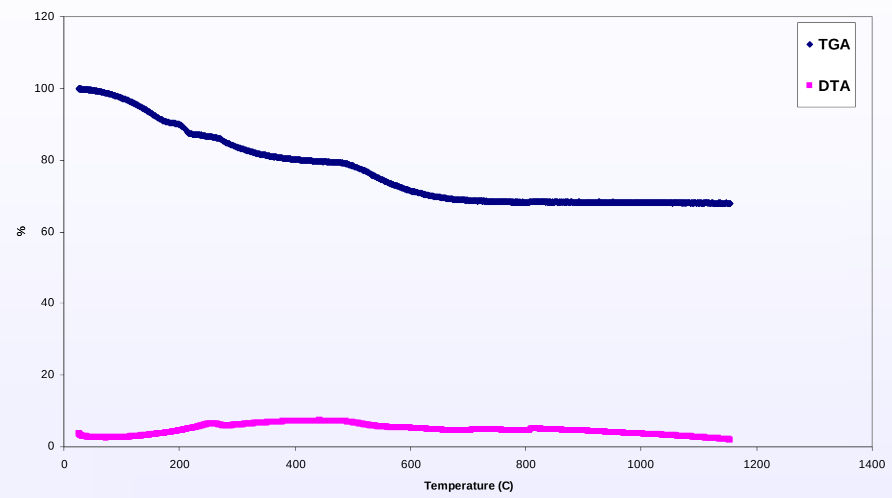
Critical parameters:

- **material viscosity**
- **shrinkage rate**

TGA/DTA – heating schedule



polycarbosilane



polycarbosilazane

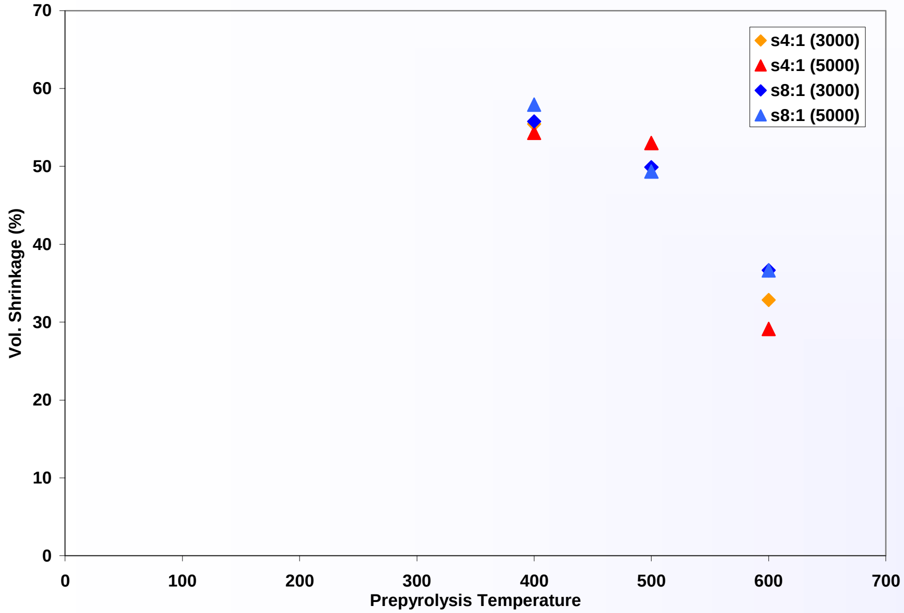
- **Rate of change greatest between 200 - 600ºC**
- **Slow heating rate must be used prior to 600ºC.**

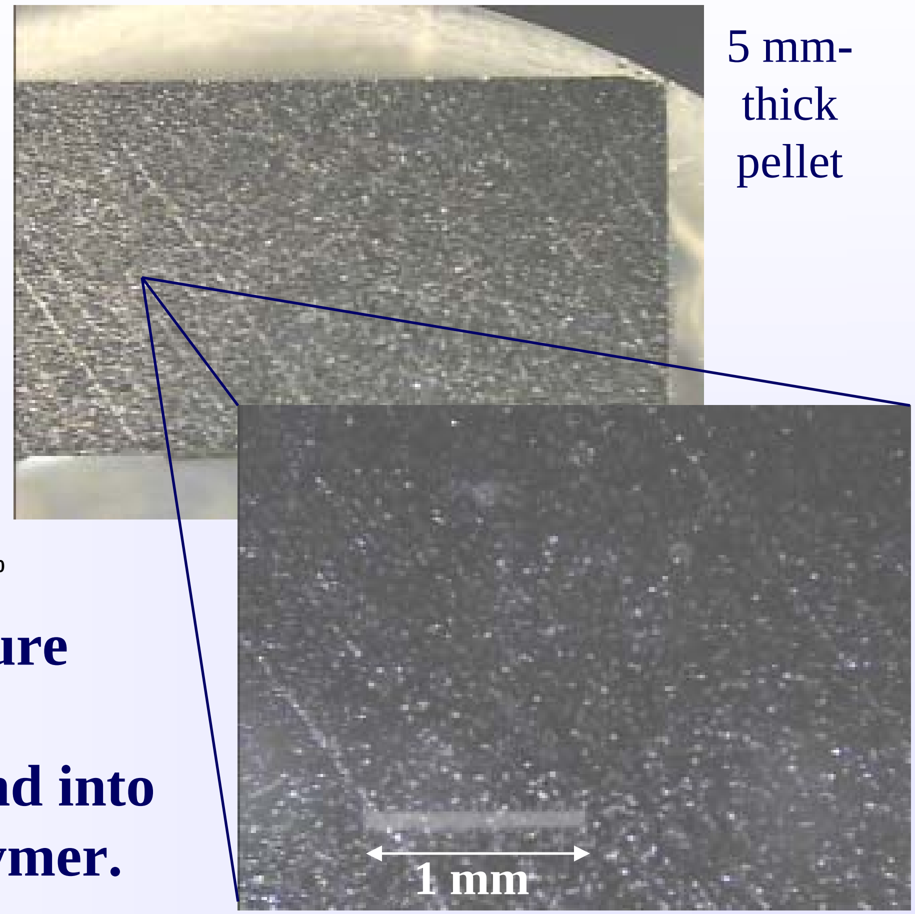
Mitigating shrinkage stresses

- **Inert and active fillers:**
  - **Inert fillers can be used to reduce overall shrinkage**
  - **Inert fillers reduce initial polymer volume**
  - **Inert fillers can also be used to modify properties: CTE, compliance**
  - **Certain active fillers can also be used to reduce overall shrinkage**

- **Pre-cure, or Partially-pyrolyse precursor to reduce the amount of shrinkage (“quasi-inert filler”):**
  - **Example - A 24% reduction in stress can be obtained by partial pyrolysis of polycarbosilane to reduce the shrinkage during joint processing by 40%.**

Crack-free parts fabricated by controlled processing



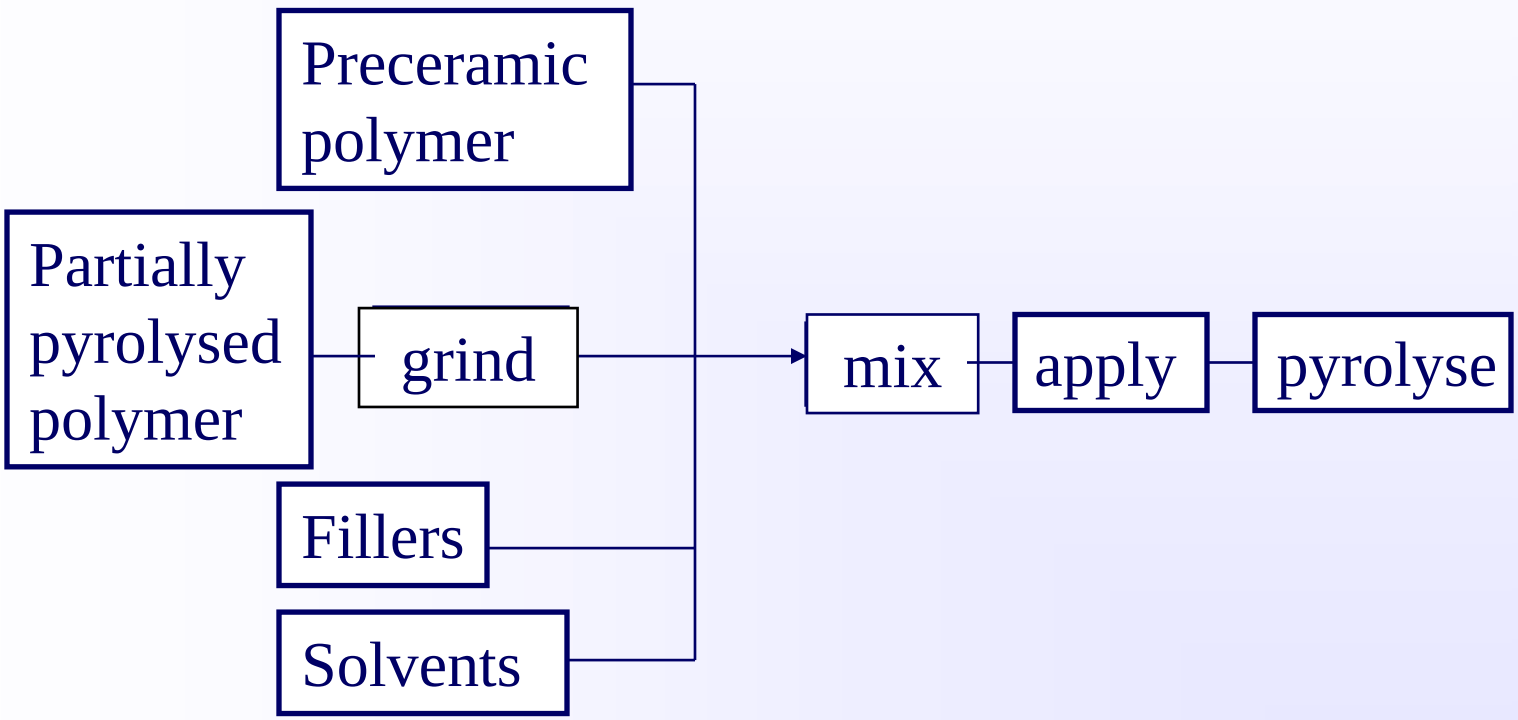


5 mm-thick pellet

- **Higher partial pyrolysis temperature decreases overall shrinkage**
- **Partially pyrolysed material ground into powder and blended with fresh polymer.**
- **Blended mixture pyrolysed to dense material.**

Seal Fabrication

Process Flowchart



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Test seals - fabrication

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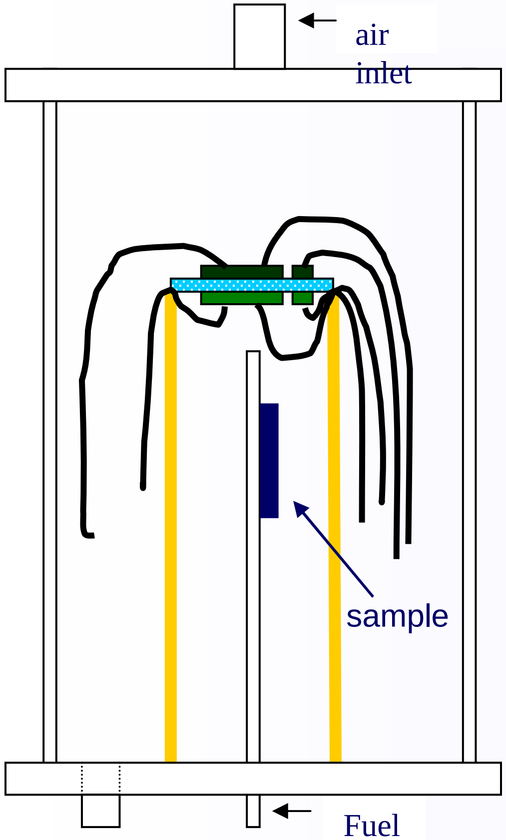
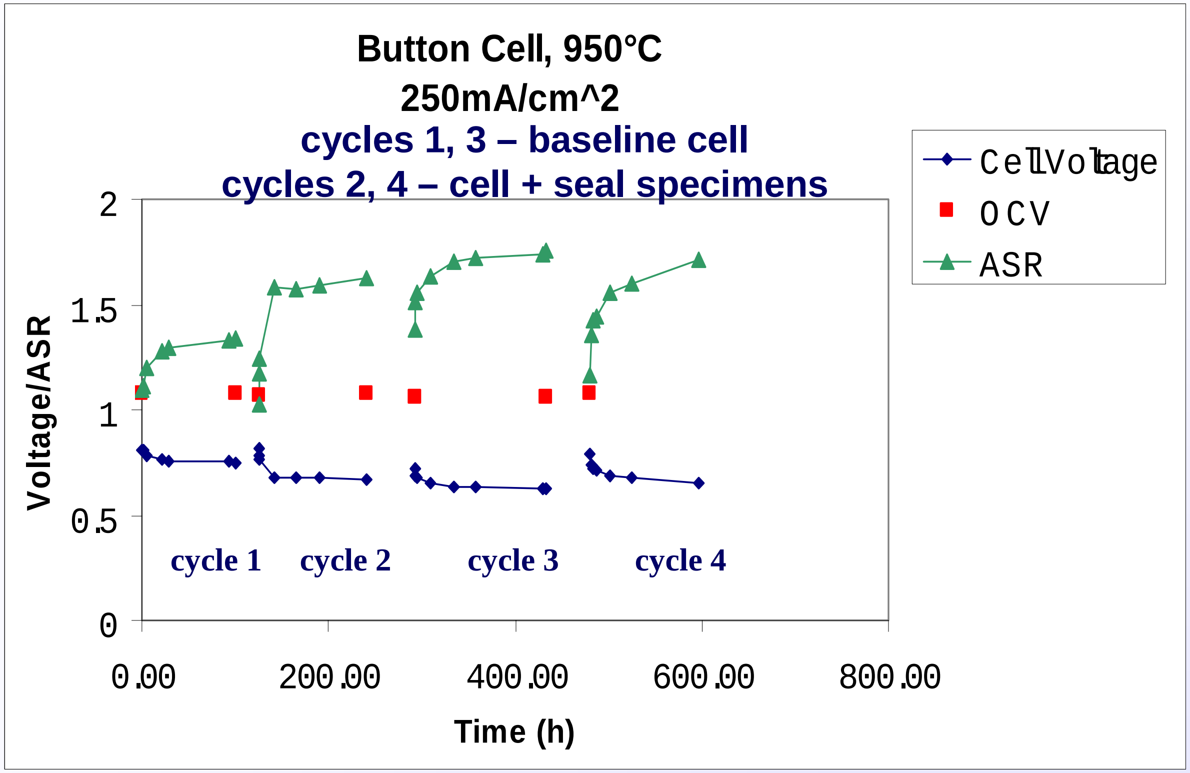
Test seals - pyrolysed

High thermal expansion, inert fillers used to control CTE

Composition	**Temperature Range (ºC)**	**CTE (ppm $^{o}C^{-1}$)**
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

Compatibility with SOFCs





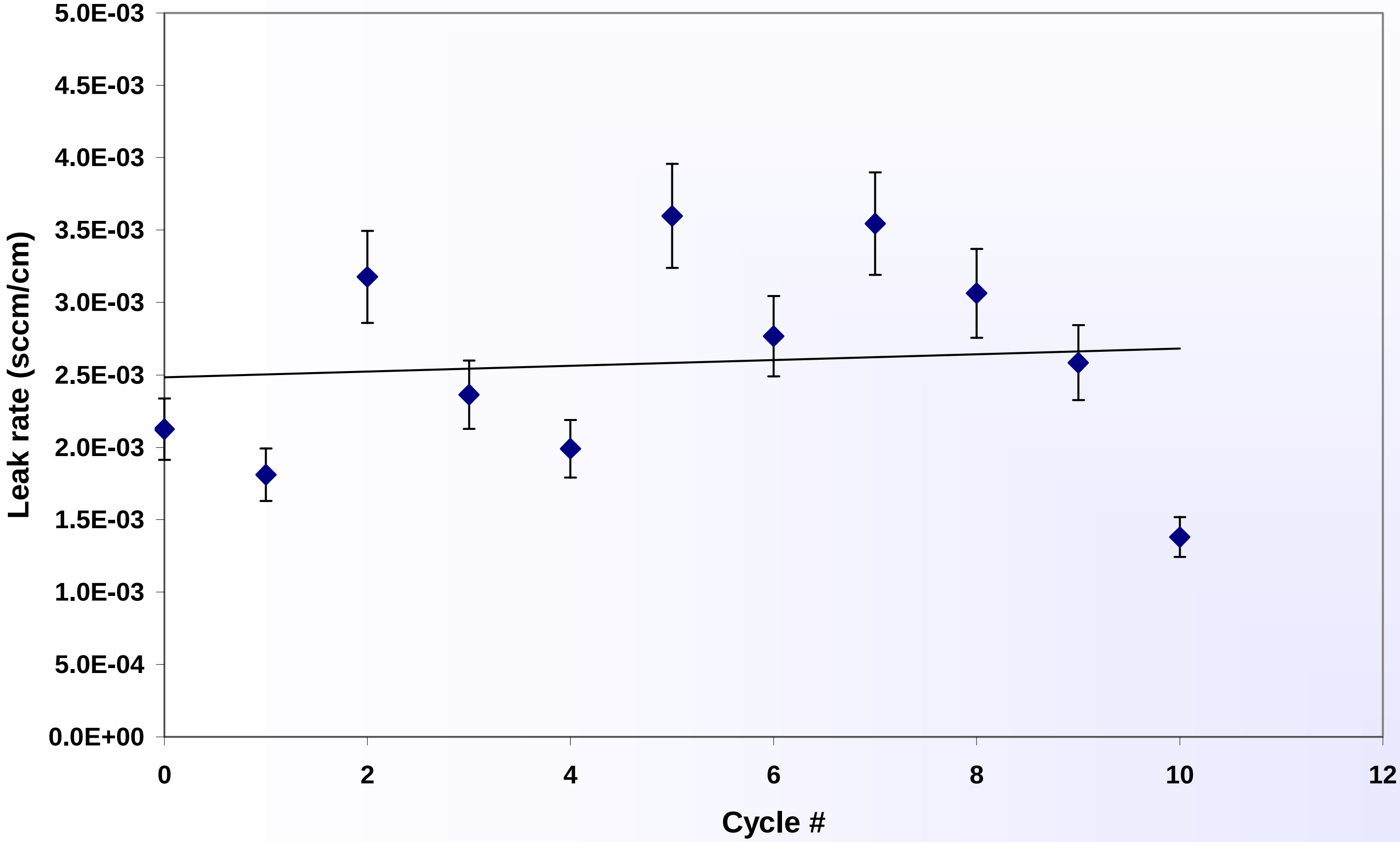
- **Preliminary results indicate cell performance is not affected by the presence of seal material in the fuel stream**

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}*

* 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**

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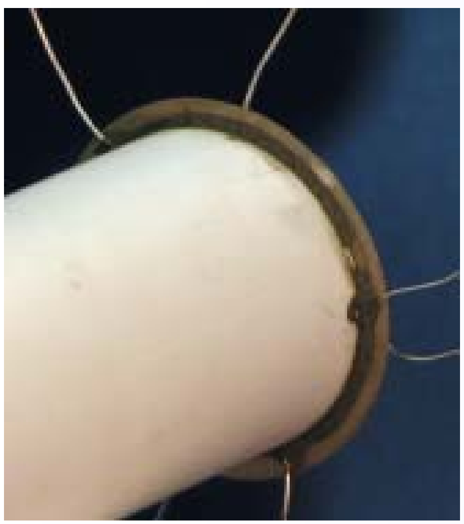
Seal performance



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

Seal and SOFC Standards

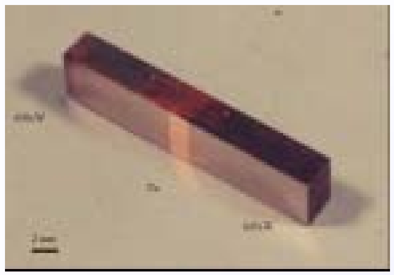
- **Standards allow for comparison among various seal materials**
- **Standards facilitate design evaluation and modeling**

  – ***Seal leak rate***
  – ***Seal material shear strength***

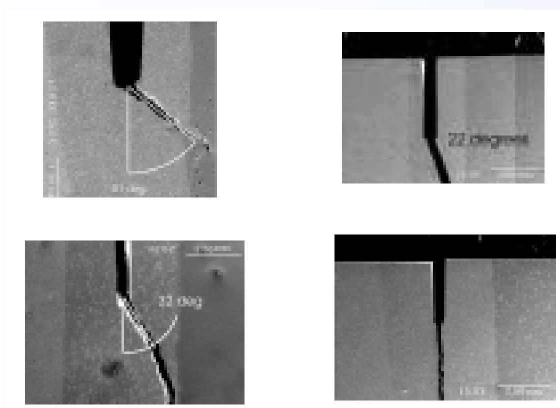
ASTM C28: Advanced Ceramics
Committee chairs: Michael Jenkins, Steve Gonzcy

Applications - SOFCs
Task Leader: C.Lewinsohn, Ceramatec Inc.

Opportunities for Graded Seals



Cu/W Graded Bend Bar



Crack Trajectories

- It is well established that proper design of graded interlayers in joints:
  - Reduces magnitude of peak residual stresses compared with monolithic interlayer
  - Allows positioning of the location of peak stresses away from brittle regions
  - Reduces edge stress singularities
- Recent research has found:
  - Crack trajectories may be manipulated by control of geometry and interlayer properties

J. Chapa-Cabrera and I. E. Reimanis. “Effects of Residual Stress and Geometry on Crack Kink Angles in Graded Composites”, *International Journal of Engineering Fracture Mechanics,*Vol. 69, Issues 14-16, pp 1667-1678, (2002).

J. Chapa-Cabrera and I. Reimanis, “Crack Deflection in Compositionally Graded Cu-W Composites”, *Philosophical Magazine A*, volume 82, number 17/18, 3393-3403 (2002).

Approach for Seal Design

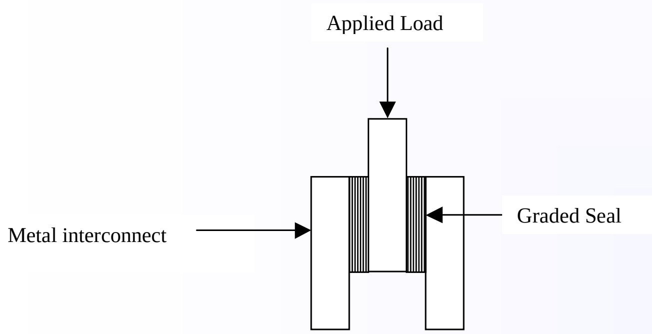


Figure 1. Double lap shear test sample schematic.

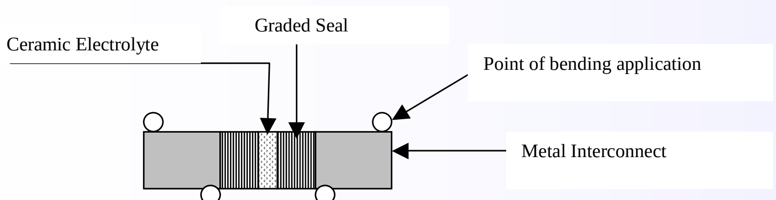


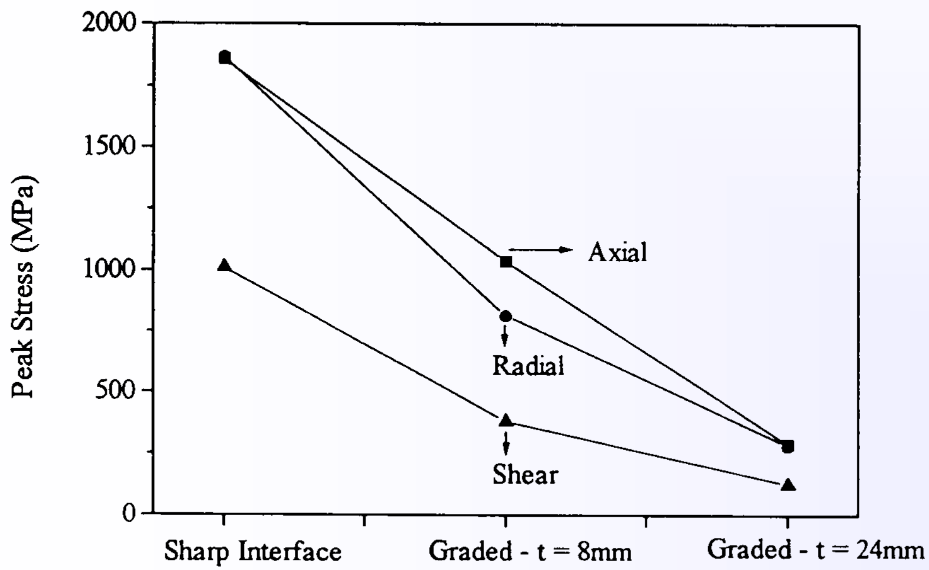
Figure 2. Four point bending sample schematic.

- Discrete layers of different compositions
  - Ceramic and metal fillers used to vary thermal expansion coefficient of seal
  - Individual layers applied by spin coating
  - Effects of joint architecture and microstructure to be examined
- Objectives
  - Establish optimum conditions for strength
  - Find relationship between strength and geometry, microstructure and composition of seal

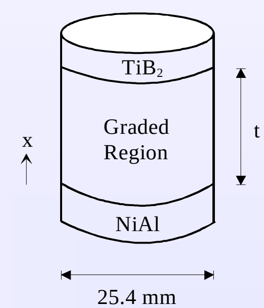
Professor Ivar Reimanis is currently funded for graded materials research by:
DOE/Office of Basic Energy Sciences and U.S. Army Research Office

Reducing Peak Stresses

FEA Results



- Stresses depend on
  - *joint thickness*
  - architecture



R. Torres, G. W. Mustoe, I. E. Reimanis, and J. J. Moore, Processing and Fabrication of Advanced Materials IV (1996).

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Summary

- **Several candidate materials and methods exist for sealing SOFCs.**
- **These materials and methods must be tailored to the devices and applications.**
- **A balance of material properties is required for an effective seal.**
- **Device design can be used to influence seal requirements.**
- **Pyrolysis of preceramic polymer precursors offers a promising method for sealing SOFCs, further study is required.**
- **Further modeling, materials testing, design evaluation, and adoption of standards are strongly recommended.**