SOFC Seals: SECA CTP Seal Meeting Overview

(Meeting held at Sandia National Laboratory, July 8-9, 2003)

NETL

Wayne Surdoval

Don Collins

Lane Wilson

PNNL

Prabhakar Singh

Jeff Stevenson

Moe Khaleel

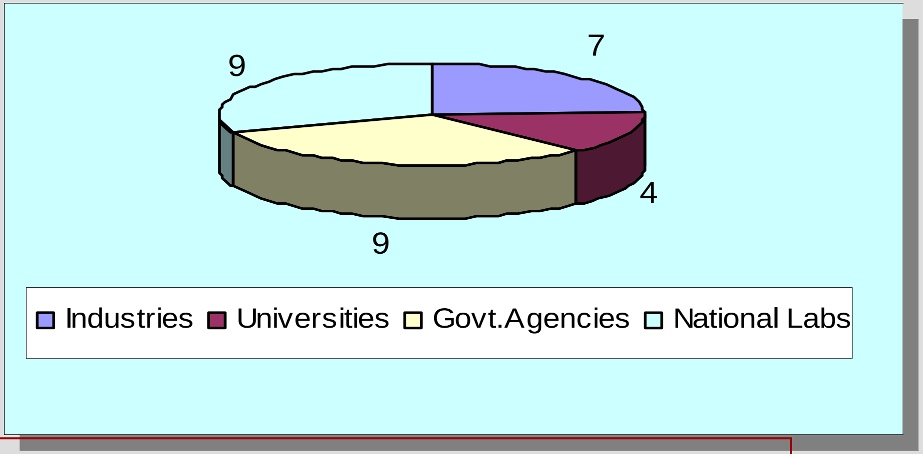
Presented at SECA Core Technology Meeting, Albany, NY

Sept 30-Oct.1, 2003

Acknowledgements

- ***We thank Sandia National Laboratory, specially Drs. Ron Loehman and Bill Hammeter for hosting the SECA-CTP seal meeting. We also thank other staff at Sandia for sharing information about their capabilities with meeting participants.***
- ***We thank Kevin Moore for facilitation at the meeting.***

Participants



NAME	AFFILIATION	PHONE	EMAIL ADDRESS
Bill Hammetter	Sandia Nat'l Labs	505) 272-7603	wfhamme@sandia.gov
Wayne Surdoval	DOE/NETL	(412) 386-6002	wayne.surdoval@netl.doe.gov
Prabhakar Singh	PNNL	(509) 375-5945	Prabhakar.Singh@pnl.gov
Kevin Moore	DOE/NETL	(304) 594-1450	kevin.moore@en.netl.doe.gov
Jianmin Qu	Georgia Tech	(404) 894-5687	jianmin.qu@me.gatech.edu
Matthew Seabaugh	NexTech Materials	(614) 842-6606	seabaugh@nextechmaterials.com
Marvin Singer	DOE/Science	(202) 586-4336	marvin.singer@science.doe.gov
Stephen Veyo	Siemens Westinghouse	(412) 256-1901	stephen.veyo@siemen.com
Raj Singh	Univ. of Cincinnati	(513) 556-5172	raj.singh@uc.edu
Nguyen Minh	GE Power Systems	(310) 538-7250	nguyen.minh@ps.ge.com
Bruce Steinetz	NASA Glenn	(216) 433-3302	bruce.steinetz@grc.nasa.gov
Michael Krumpelt	Argonne Nat'l Lab	(630) 252-8520	krumpelt@cmt.anl.gov
Ron Loehman	Sandia Nat'l Labs	(505) 272-7601	loehman@sandia.gov
S. Elangovan	Ceramatec, Inc.	(801) 978-2162	elango@ceramatec.com
Charles Lewinsohn	Ceramatec. Inc.	(801) 956-1001	clewinsohn@ceramatec.com
Jeff Stevenson	PNNL	(509) 372-4697	jeff.stevenson@pnl.gov
Richard Brow	Univ. Missouri-Rolla	(573) 341-6812	brow@umr.edu
Moe A. Khaleel	PNNL	(509) 375-2438	moe.khaleel@pnl.gov
Anil V. Virkar	MSRS/Univ. of Utah	(801) 581-5396	anil.virkar@m.cc.utah.edu
Narottam P. Bansal	NASA Glenn Res. Ctr.	(216) 433-3855	narottam.p.bansal@grc.nasa.gov
Mark C. Williams	NETL – DOE	(304) 285-4747	mark.williams@netl.doe.gov
Don Collins	NETL - DOE	(304) 285-4156	donald.collins@netl.doe.gov
Mike Santella	Oak Ridge Nat'l Lab	(865) 574-4805	santellaml@ornl.gov
Pinakin Patel	Fuel Cell Energy	(203) 825-6072	ppatel@fce.com
Lane Wilson	NETL - DOE	(304) 285-1336	lane.wilson@netl.doe.gov
Bob Lashway	Ceramatec	(801) 978-2154	rlashway@ceramatec.com
John Dunning	DOE/Albany Res. Ctr.	(541) 967-5876	dunning@alrc.doe.gov
Jill Glass	Sandia Nat'l Labs	(505) 845-8050	sjglass@sandia.gov
Steve Burchett	Sandia Nat'l Labs	(505) 844-6446	snburch@sandia.gov

Outline

- SECA CTP Priorities
- Seal Meeting Objectives
- Accomplishments
- Workshop Presentations
- Group Discussions and Story Board
- Path Forward

Current Priorities: *Core Technology Program*

	What	*How*
1	Gas seals	• Glass and compressive seals
1	Interconnect	• Modifying components in alloys • Coatings
2	Modeling	• Models with electrochemistry • Structural characterization
2	Cathode performance	• Micro structure optimization • Mixed conduction • Interface modification
2	Anode/ fuel processing	• Metal oxides with interface modification • Catalyst surface modification • Characterize thermodynamics/kinetics
3	Power electronics	• Direct DC to AC conversion • DC to DC design for fuel cells
4	Material cost	• Lower cost precursor processing • Cost model methodology

❖ Rita Bajura, SECA Annual Meeting, Seattle 2003

Objective

- **Review SOFC sealing issues and requirements**
- **Present current status of SOFC sealing technology**
  - ***Seal materials***
  - ***Materials interactions***
  - ***Failure processes***
- **Identify**
  - ***Advance concepts***
  - ***Designs and development approaches***

Develop group consensus on promising R&D concepts / directions

Utilize information for scoping and coordination of SECA-SOFC sealing activities

Meeting results

- Obtained input from participants on new seal concepts including materials design and fabrication processes
- Established consensus (via facilitated break-out sessions) on promising concepts and future R&D directions
- Published results from the meeting regarding new sealing technologies
- SECA CTP meeting results are available on:

  http://www.seca.doe.gov

SOFC Seal functions

SOFC seals:

- **Prevent mixing of fuel and oxidant within a cell stack**
- **Prevent leaking of fuel and oxidant from stack**
- **Electrically isolate cells in stack**
- **May provide mechanical bonding of cell components**

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

Technology Status

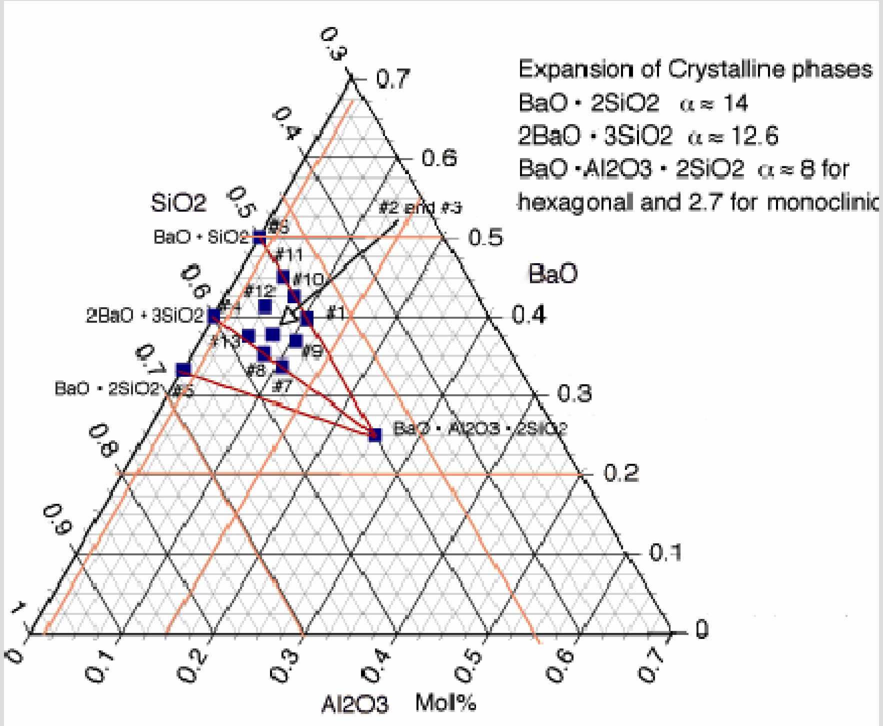
- ❖ Rigid seals – most mature, easy to fabricate but require CTE match, chemical stability
- ❖ Compressive seals – promising with respect to CTE but limited development, requires external load frame
- ❖ Cross cutting tools –
  - ❖ Computational tools – available to study various failure modes during steady state and thermal cyclic conditions
  - ❖ Other experimental tools - characterization, mechanical and chemical behavior

Rigid glass seals

- *Al-Si-X(Alkaline) system*
- *CTE tailored*

- Porosity formation
- Interaction with scales

$BaO-Al_2O_3-SiO_2$ Seals



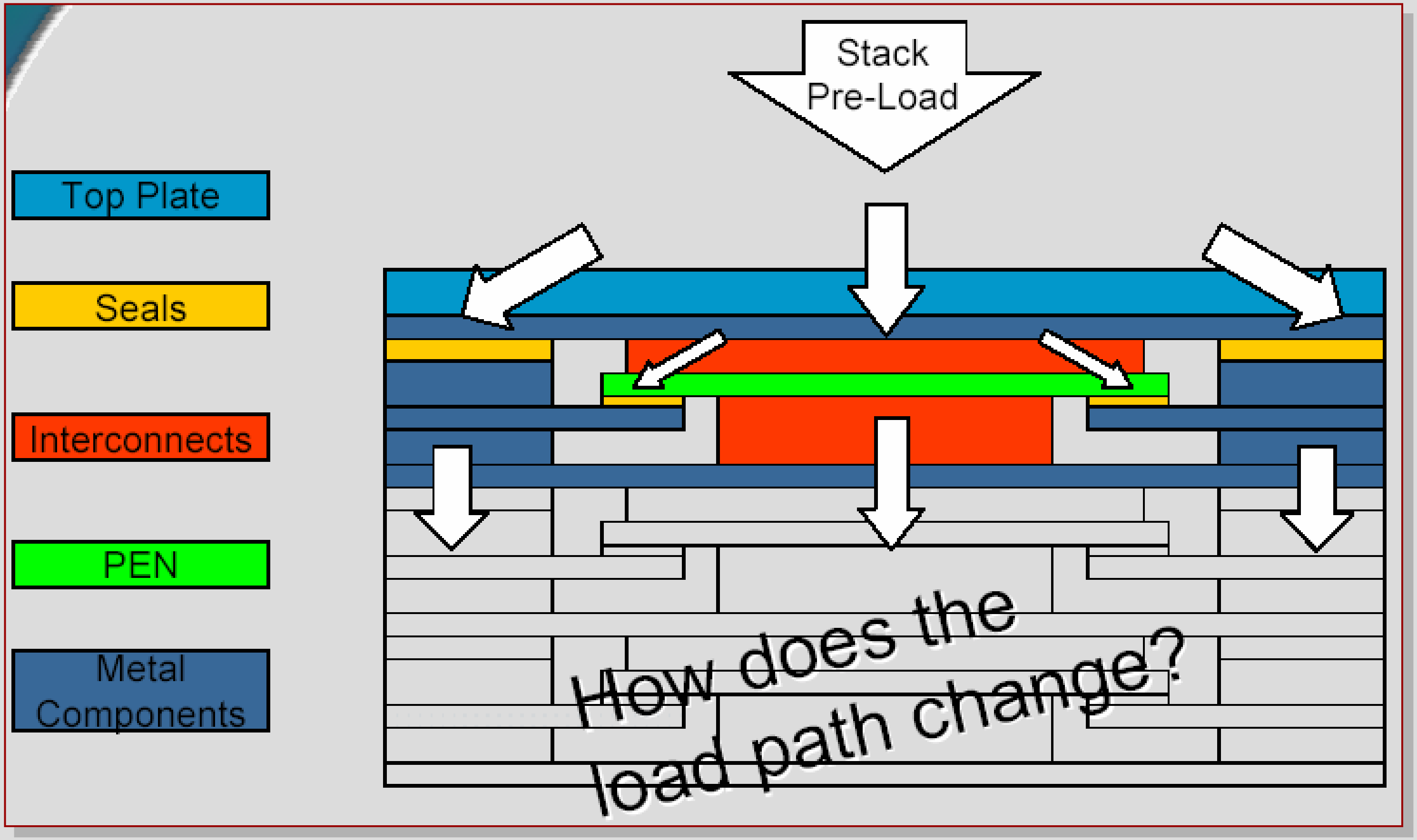
Brazed metal seals

- 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

Compressive 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?

Seal designs



Design Parameters

- What are the PEN stresses as a function of boundary stiffness during steady state or transient conditions?
- What are the cell edge displacements as a function of PEN stresses?
- What are the effects of stack B.C.s on stresses?
- What is the state of stress and displacement in the seal area?
- How does a dead load distributes throughout the stack, especially sealing areas?

SBIR Seal Development Activities

Phase I Conclusions

NEXTECH MATERIALS

- Highly Textured Seal Materials Result from Tape Casting Process
- Green Tapes Amenable to Many Geometries
  - Gasket Approach Can Be Tailored
  - Thickness Controlled Through Lamination
- Seal Performance Controlled by Composition
  - Crystalline Phase: TCE, Mechanical Strength
  - Glass Content, Properties: Wetting, Stability
  - Binder Content

ceramatec

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.

Technical approach

Three approaches considered:

- ***Rigid chemical***
- ***Sliding mechanical***
- ***Compliant wet***

Analyze:

- ***Pros***
- ***Cons***

Identify development needs:

- **Fundamental gaps**
- **Engineering needs**

Technical Challenges

Rigid Chemical	Sliding Mechanical	Compliant Wet
Glass - Pros • Lowest leakage • Inexpensive • Glasses not limited to stoichmetric • Excellent thermal and environmental stability • Processing flexibility (automatable) in-expensive • Successful experience "short-term" Glass - Cons • Constrains cell movement during thermal excursions • Accommodation of CTE mismatch • Increases strength requirement on PEN • Increases tendency for cracking • Metal to ceramic delamination • Different materials thermal capacitance • compositions (tailorable) • Application temperature • Migration of species • Assembly tolerances and compensation • Seal/cell surface debonding, cell component debonding, interface stream • Durometer u/mils • Increases time of heating and cooling (fabrication) • Changing material structure with cycling Cements • Con: CTE – coefficient thermal expansion • Pro: No requires loading Organo precursor cements - Cons • Steam? • CTE mismatch • Porosity or density • Hydrogen Nonconductive braze system All - Con • Interfacial reactivity	Pros • Tolerance for CTE mismatch • Less demanding on strength of cell • Easier to disassemble - repairable Cons • Requires pressure • Surface preparation & finish • Limitations on location for usage • Larger mechanical structure + seal volume • Leak rate degradation (cycling) • Degradation & seal material (corrosion) • Creep wear/products others • Problems with external loads in plane of cells • Electrical insulation for metallic seals • Stacking issues & assembly • Operational procedure • Stack height dimensional changes & long-term operation • How big of load needed and applied • Need for flexibility to seal YSZ variations • Dimensional tolerance • Compliance vs. spring back	Pros • Allows CTE mismatch • Potential for low leakage • Accommodate irregularities in surface • Low interfacial stresses • Self-healing Cons • Molten glass - voltalization • Molten glass - continuous change in properties • Need for reservoir to replenish • Possible wicking • What liquid? • Reactivity • Possibility of migration and lead formation • Containment stop • Proper viscosity over operational temperature range

Technical Challenges

TABLE 1.2 NOVEL R&D APPROACHES PLUS REQUIREMENTS

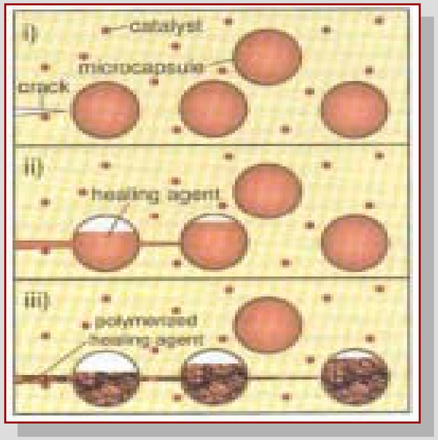
COMPLIANT WET	RIGID	SMART MATERIALS	GRADED SEAL STRUCTURES	FLEXIBLE MECHANICAL SEALS	REQUIREMENTS
• Impregnated materials, e.g., felt, fabric • Self-healing materials • Porous/dense reservoir/hard stop wet seal	• Microcracking toughened glasses • Particle reinforced glasses • Development of organo precursors	• Adaptive • Magneto strictive • Electro rheologic material • Piezo electric • SMA - shape memory alloys • "MEMS" inspired manufacturing approach • Magneto-elastic materials	• Multi-layered/Graded microstructures, e.g., porosity, nested Vs • Chemical modification of mica • Multi- functional layered structure • Engineered materials, e.g., macor	• Zr O-ring • Compliance with rigid tubes 3YSZ • Glass coated bellows • High temperature RTV • Nano ceramic springs	• Voltage effects on seal • Standardized testing protocols • Strain management • Seal design methodology

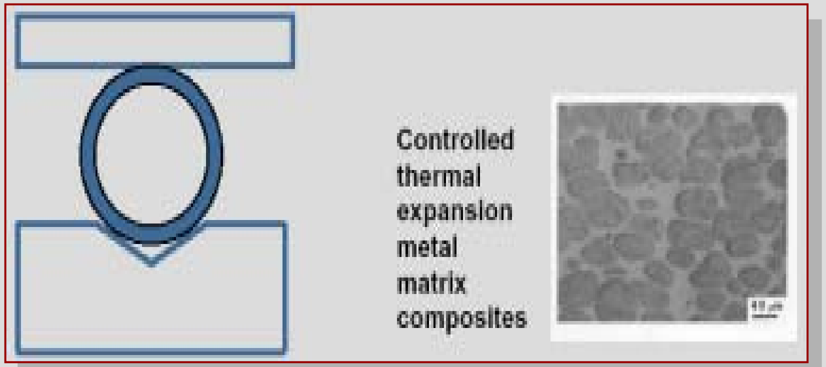
SECA Core Technology Task Force on Sealing
Rating of Sealing Concepts

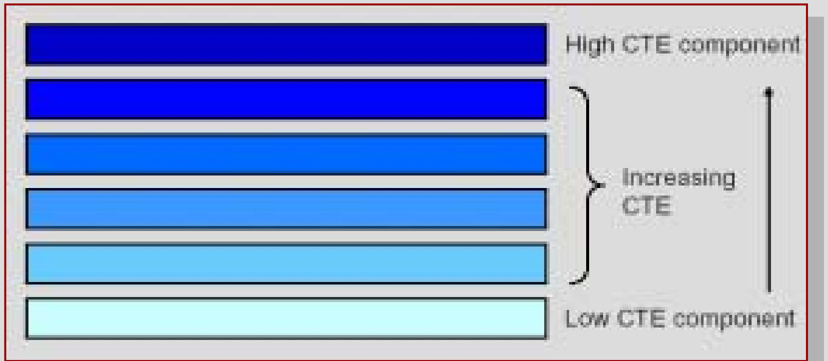
Sealing Concepts	Leak Tightness	Stability - Mechanical	Stability - Chemical	Manufactur ability	Cyclic Ability	Afford ability	Rating	Technology Readiness E/D/R
Particle Reinforced Glasses	7.0	5.9	5.8	7.2	4.6	7.2	**37.7**	**D**
Impreganted Materials Felt/Fabric	6.0	6.6	5.6	6.5	5.9	5.5	**36.1**	**R-D**
Micro-Crack Toughened Glasses	6.6	5.2	6.2	6.7	4.4	6.8	**35.9**	**D**
Organo-precursors	7.4	5.9	5.3	6.8	4.2	5.4	**34.9**	**R-D**
ZR O-ring	3.8	6.7	7.8	5.1	6.2	4.6	**34.2**	**R-D**
Porous-Dense Reservoir Wet Seal	6.1	5.6	4.1	5.6	6.5	6.1	**33.9**	**R-D**
Glass Coated Bellows	7.0	6.5	6.0	4.2	6.3	3.3	**33.3**	**R-D**
Multi-Layered/ Graded Materials	6.4	6.8	5.1	4.2	6.3	4.4	**33.2**	**R-D**
Self-Healing Materials	6.4	6.4	4.9	4.0	6.8	4.7	**33.2**	**R**
Chemical Mods to Mica	4.8	5.4	5.9	5.0	5.6	5.5	**32.3**	**R-D**
Engineered Materials	6.0	5.6	5.4	4.3	5.4	4.5	**31.3**	**R-D**
Multi-Functional Layered Structures	6.2	6.2	5.6	3.9	5.1	3.4	**30.4**	**R**
Shape Memory Materials	5.0	5.0	5.1	5.0	6.0	3.7	**29.8**	**R**
Complaince w/Rigid Tubes	4.1	5.8	5.8	4.1	5.3	4.1	**29.1**	**R-D**
Hi-Temp RTV	7.4	6.4	4.1	3.1	5.2	2.6	**28.8**	**R**
Adaptive Materials	6.3	4.6	4.0	2.9	5.0	3.5	**26.4**	**R**
Nano Ceramic Spring	4.5	5.3	6.3	2.8	5.5	2.0	**26.4**	**R**
Piezo Electric Materials	3.8	5.2	4.0	4.2	5.0	3.4	**25.6**	**R**
MEMS	4.5	5.3	4.5	3.1	5.4	2.3	**25.1**	**R**
Magneto-Elastic Materials	3.8	4.5	4.7	4.0	5.0	2.8	**24.7**	**R**
Electro-Rheologic Materials	4.6	5.0	3.2	3.4	4.4	3.4	**24.1**	**R**
Magneto-Restrictive Materials	3.1	2.3	1.8	1.7	1.9	1.6	**12.5**	**R**

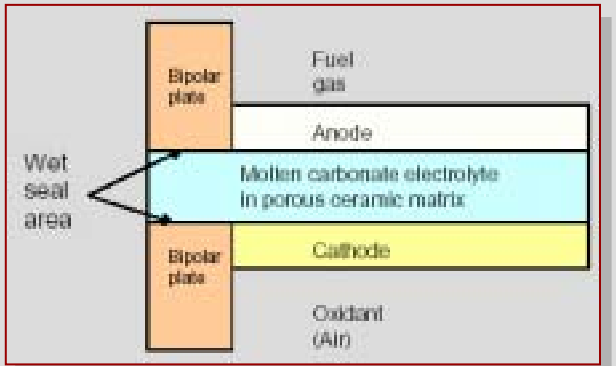
Next generation concepts

- *Self healing*
- *Functionally graded*
- *Compliant wet seal*
- *High temperature spring*

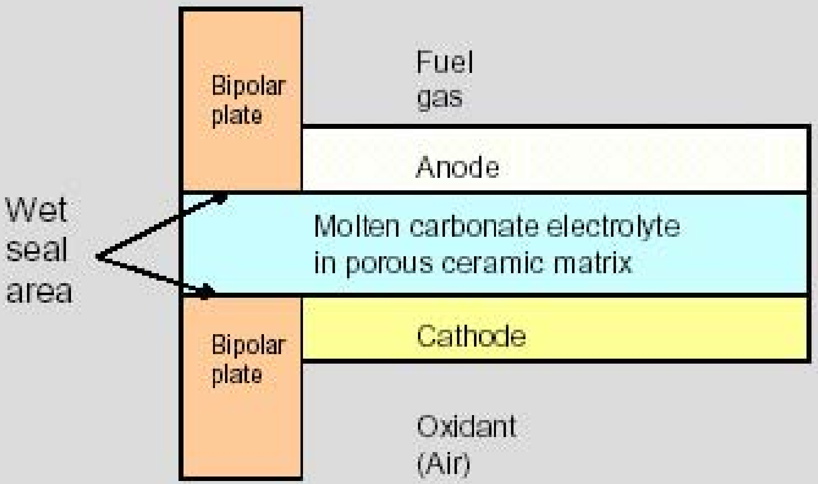








Compliant Molten Seals



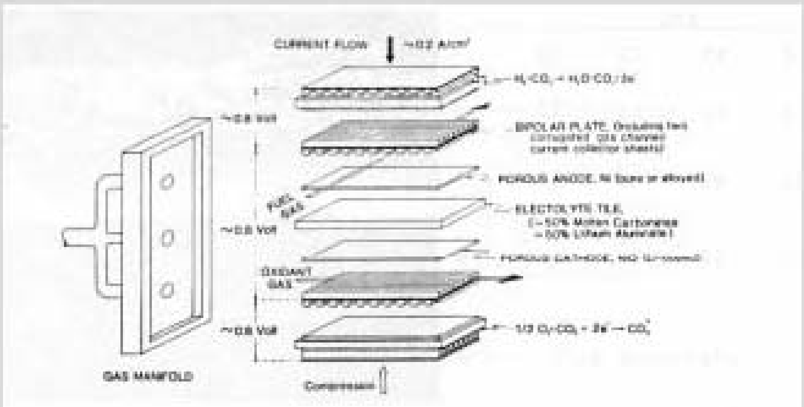


FIGURE 1 EXPLODED VIEW OF A MOLTEN CARBONATE FUEL CELL STACK (Reference 7)

At operating temperature, seal is liquid (highly viscous or contained in porous matrix by surface tension).

At low temperatures, seal solidifies, but is non-bonding, allowing for sliding to prevent stress buildup

Utilized in Molten Carbonate Fuel Cells (600-700°C)

- Singh et al., Corrosion 87, NACE (1987).

Technical Challenges

- **Development Needs**
  - Identify or develop suitable liquids
  - Determine surface energies
  - Temp/ viscosity relationships
  - Evaporation rates
  - Reservoir microstructure
  - Manufacturability – method of surface treatment – control microstructure
  - Identify surface treatments – wetability
  - Dielectric properties

- Development Approach
  - Microstructure
  - Surface Treatments
  - Temp/ viscosity relations
  - Evaporation rates

Summary

Based on the findings from the CTP seal meeting, we initiated:

- **Seal development program at Sandia National Laboratory**
- **Collaboration with NASA**
- **More emphasis on seal development activities within PNNL-Core Technology Program**

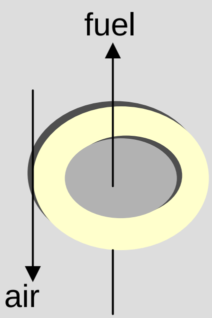
Summary

- Based on the availability of funds , we plan to initiate seal development projects through solicitations .

- We seek specific ideas and white papers on broad areas identified in workshop report.

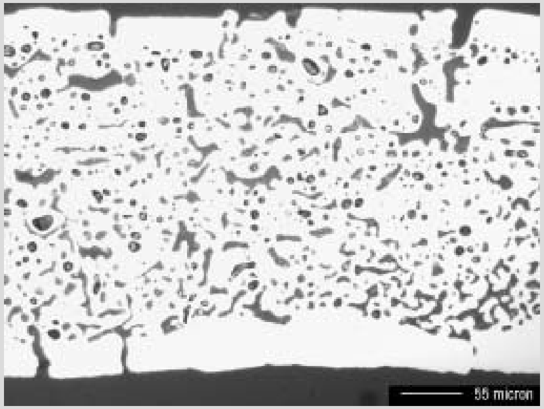
- We encourage you to review results from the web site

Compressive seals



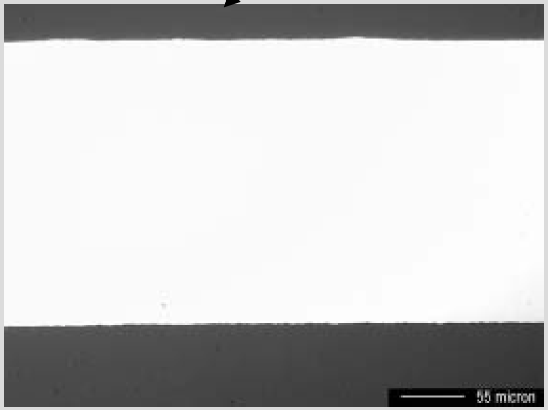
O-ring Gasket

Fuel//Air



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

Air//Air



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

Silver metal shows porosity formation and cracking under seal exposure conditions

Seal Development Approach