Sealing Glasses for Electrochemical Devices

Richard K. Brow
Missouri S&T

IMI Conference on Functional Glasses: Properties and Applications for Energy and Information

January 8, 2013

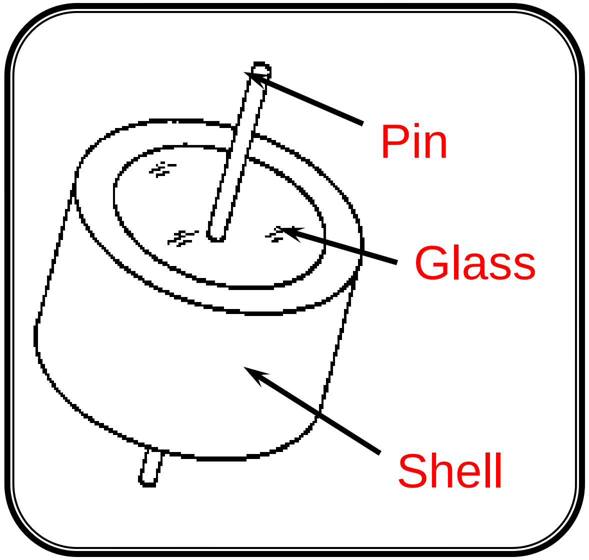
Siracusa, Sicily, Italy

Outline

- Background- and opportunities
  - *Low volume, high value technologically enabling glasses*
- Ambient temperature devices
- Na/β-Al_2O_3 batteries
- Solid oxide fuel cells
- What's next?
  - Research focus areas

Function and requirements of hermetic seals

- Isolate components from environment
- Mechanically bond different components
- Electrically insulate one component from another
- Weak link/strong link functions

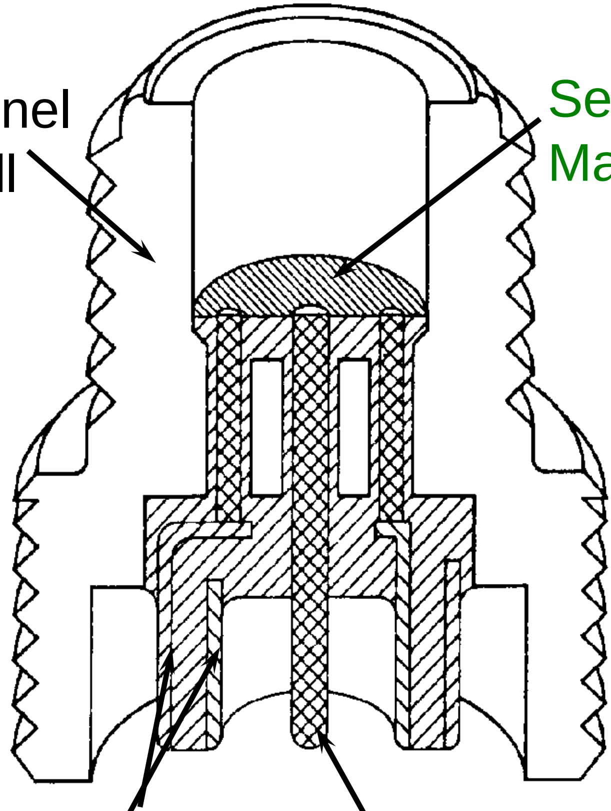


- Thermo-mechanical compatibility
    - CTE requirements (matched vs. compression)
    - Sealing temperature
- Environmental stability (ambient and other component materials)
- Component functionality (dielectric, optical, etc. properties)

Why use glasses for hermetic seals?

- Superior hermeticity
  - $>10^3$ lower permeation rates than polymers
- Compositional flexibility to tailor specific properties
  - E.g., CTE ranges to match fused silica and copper….
- High temperature stability
- Electrically insulating
- Processing flexibility
  - Viscous flow for complex shapes
  - Solid, powder preforms; thin films
  - Glass-ceramic options
- Brittle- CTE mismatches
- Temperature limitations
- Incompatible chemistries

Example: High-strength seals for pyrotechnics

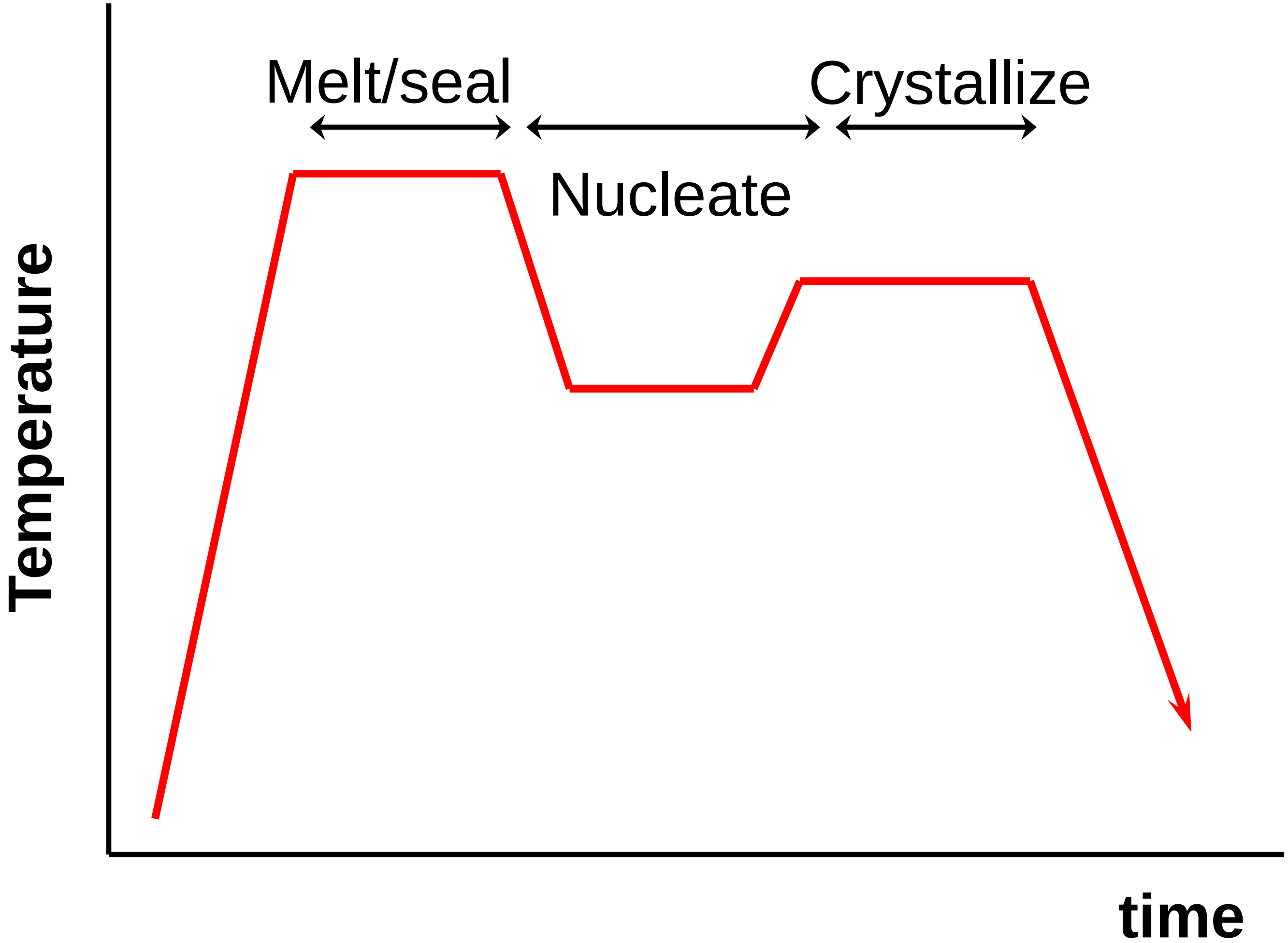


- High yield strengths
  - >100 kpsi
- good fracture toughness
- excellent corrosion resistance

Problem:
Hermetic seals are required to isolate air-sensitive materials.

- Glass-ceramics are the solution
  - good mechanical properties
  - CTE-matches to many alloys
  - good chemical properties
  - convenient manufacturing

Conventional glass-ceramic process profile

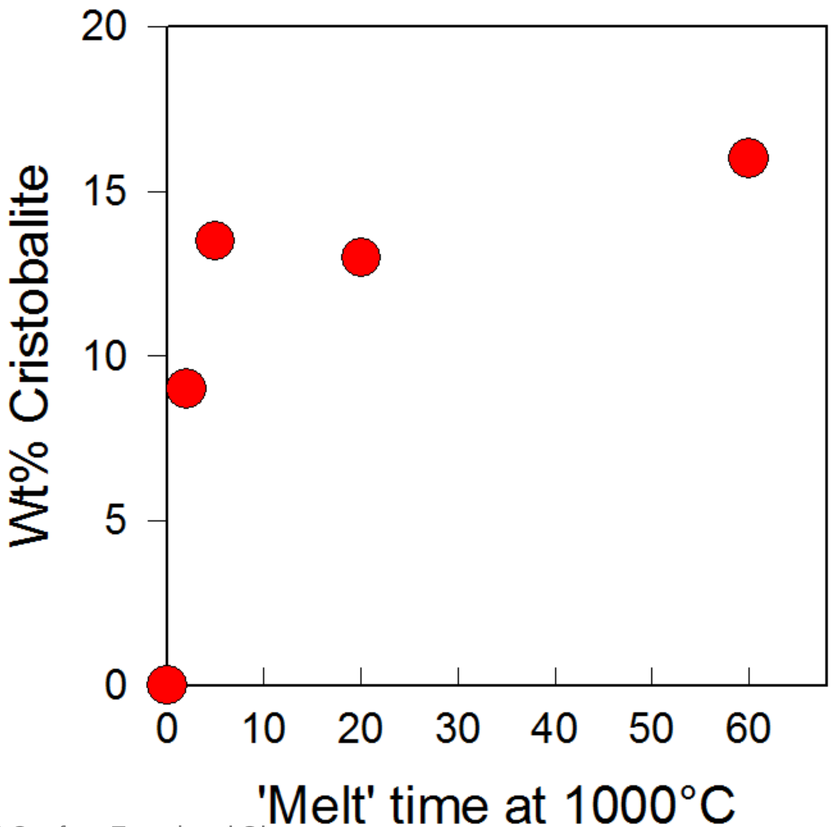


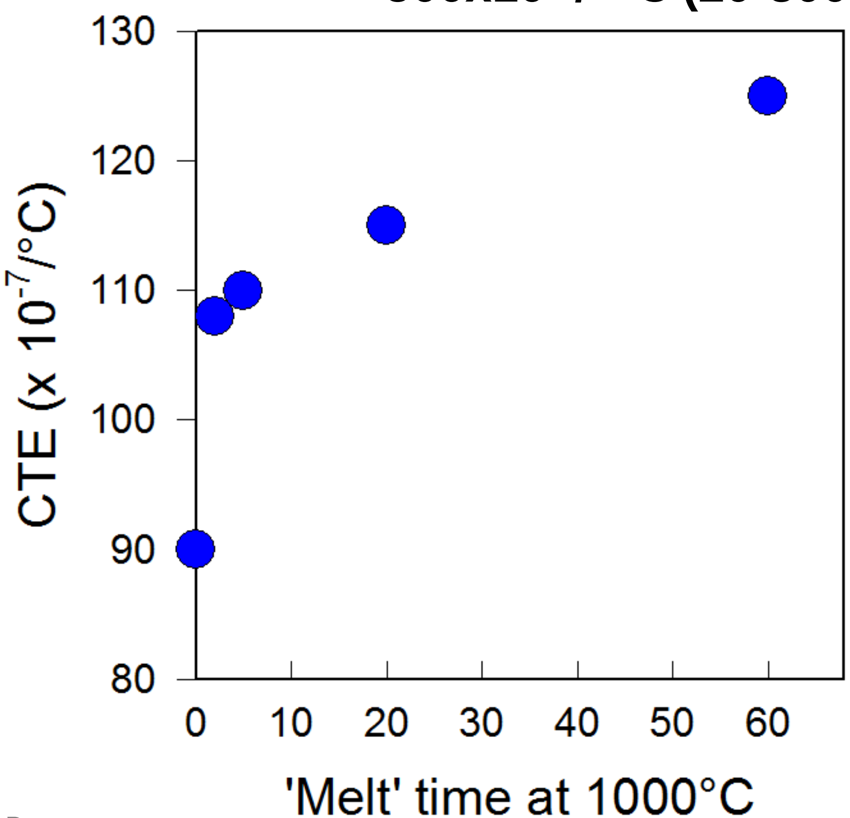
Li-silicate glass ceramics have the requisite CTEs for super-alloy seals

'S-glass' (mole%)
23.7 Li_2O 2.8 K_2O 2.6 Al_2O_3 2.6 B_2O_3 1.0 P_2O_5 67.1 SiO_2

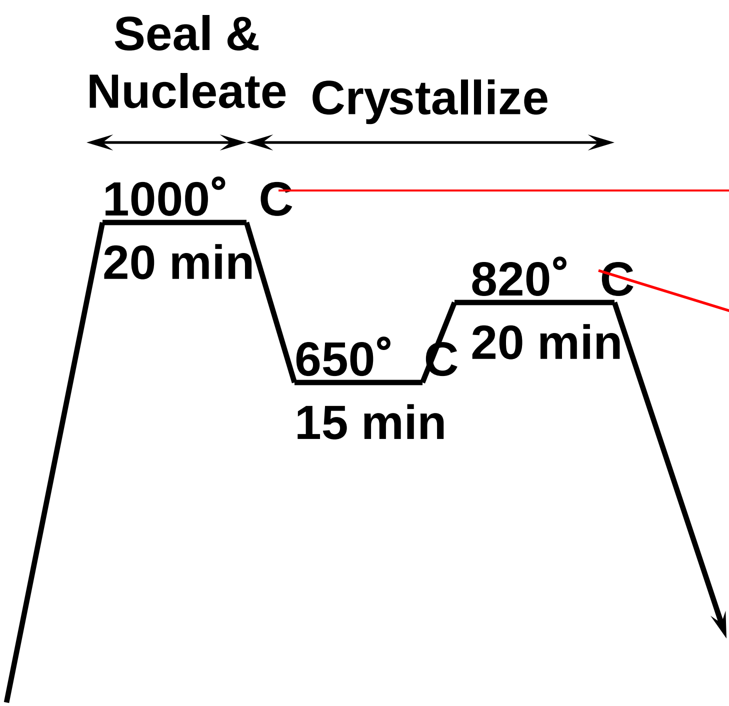
CTE depends on crystalline phases:

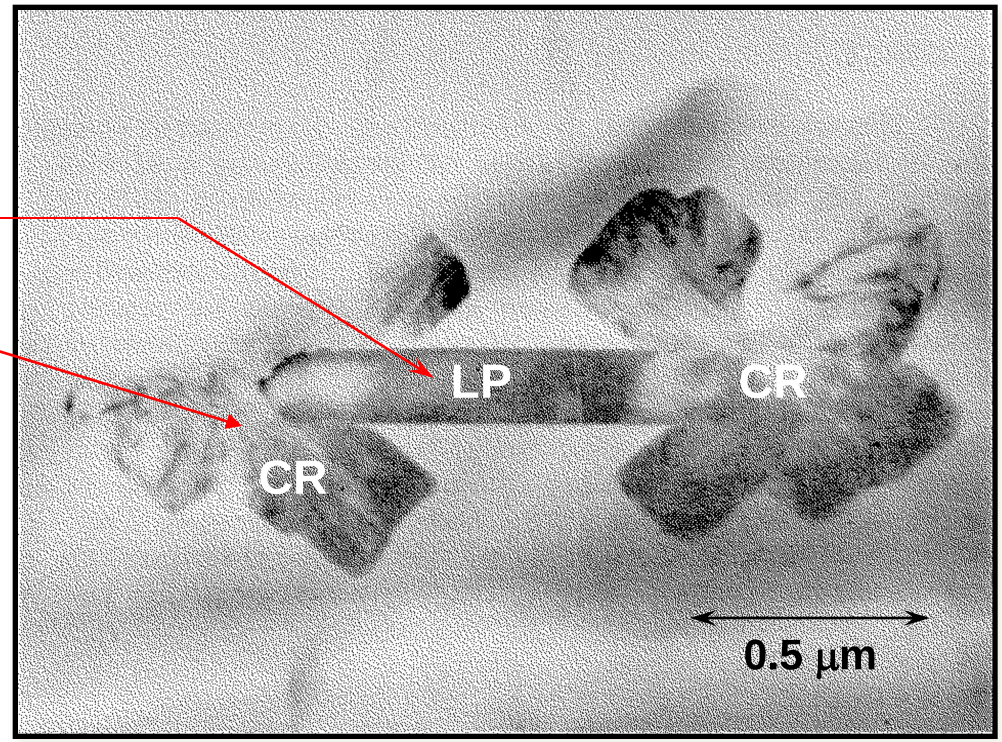
Li-disilicate,	**CTE**	**~110x10^{-7}/° C**
cristobalite,	**CTE**	**~125x10^{-7}/° C (20-100° C)**
		~500x10^{-7}/° C (20-300° C)





High temperature heterogeneous nucleation leads to desirable glass-ceramics

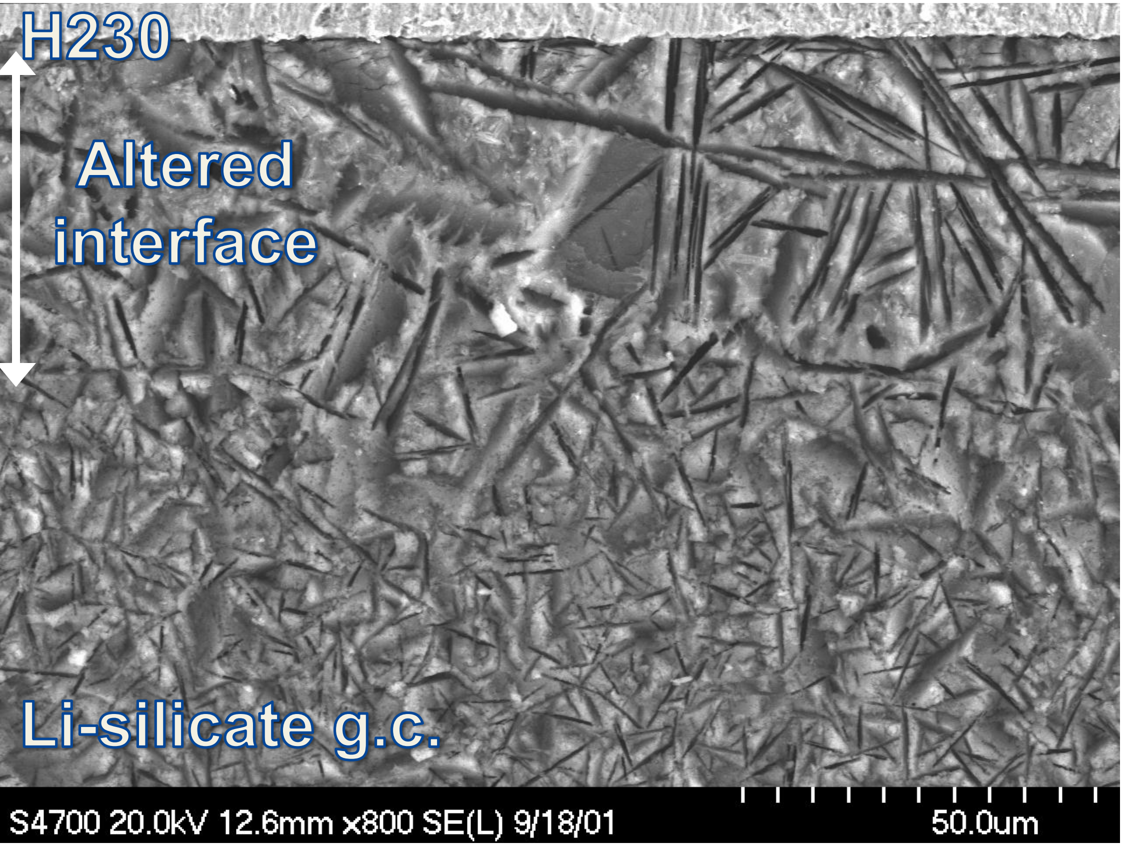




- Li_3PO_4 nuclei form at 1000° C
- Epitaxial growth of cristobalite at 820° C
    - no nuclei: low CTE Li-disilicate

(Headley and Loehman, J. Am. Ceram. Soc., 1984)

The heterogeneous nucleation mechanism has important application ramifications



- poorly crystallized interface
- Cr-phosphide crystallites

$Cr_{(metal)} + Li_3PO_4 \rightarrow Cr_xP_y + Li_2O_{(gl)}$

- 25% lower CTE

detonators, actuators, bolt cutters, high-voltage connectors, etc.

Materials issues for designing a sealing glass

- CTE requirements
- Other desirable physical and chemical properties
- Sealing and operational temperatures
  - Viscosity and process-required properties
  - Long-term stability of properties
  - Interactions with seal components

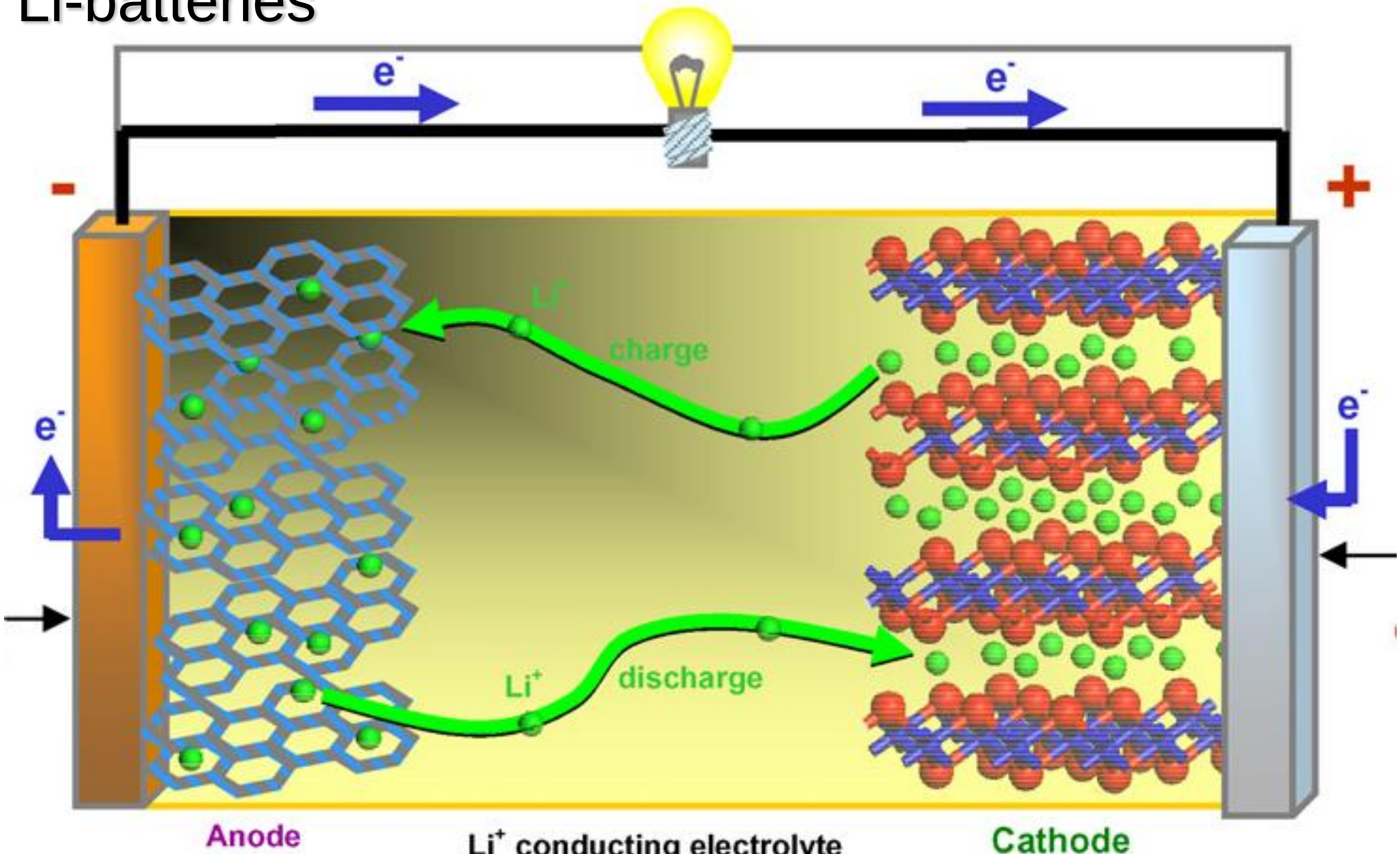
RK Brow
brow@mst.edu

We will consider three types of electrochemical devices

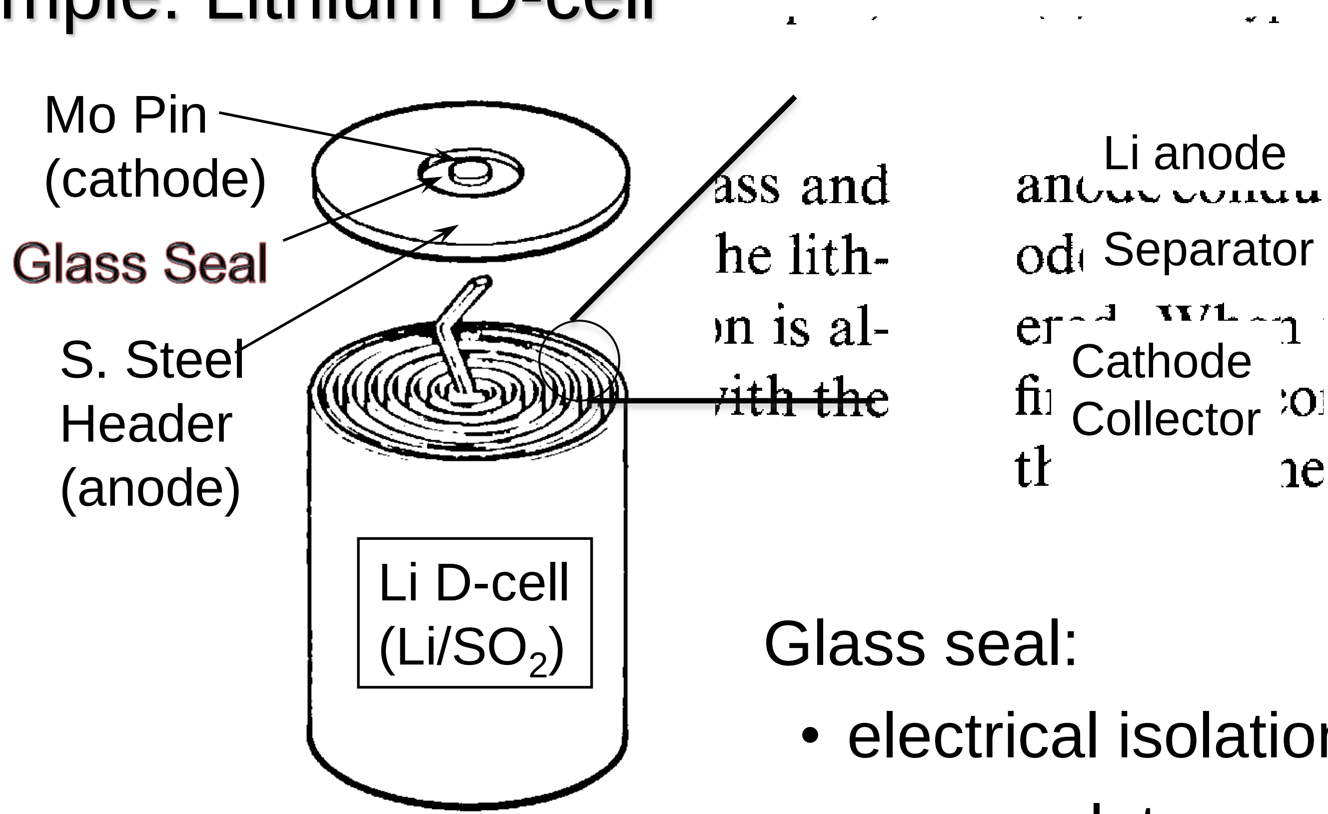
- Lithium batteries (ambient temperatures, liquid electrolyte)
  - Lithium stability
- Alkali storage batteries (intermed. temperatures, 200-400° C)
  - Long-term alkali stability
- Solid oxide fuel cells (high temperatures, 600-900° C)
  - Long-term thermo-chemical stability
  - Failure from thermal cycling

Glass is an enabling technology to produce robust devices

Glasses have been developed as electrolytes for Li-batteries



Example: Lithium D-cell



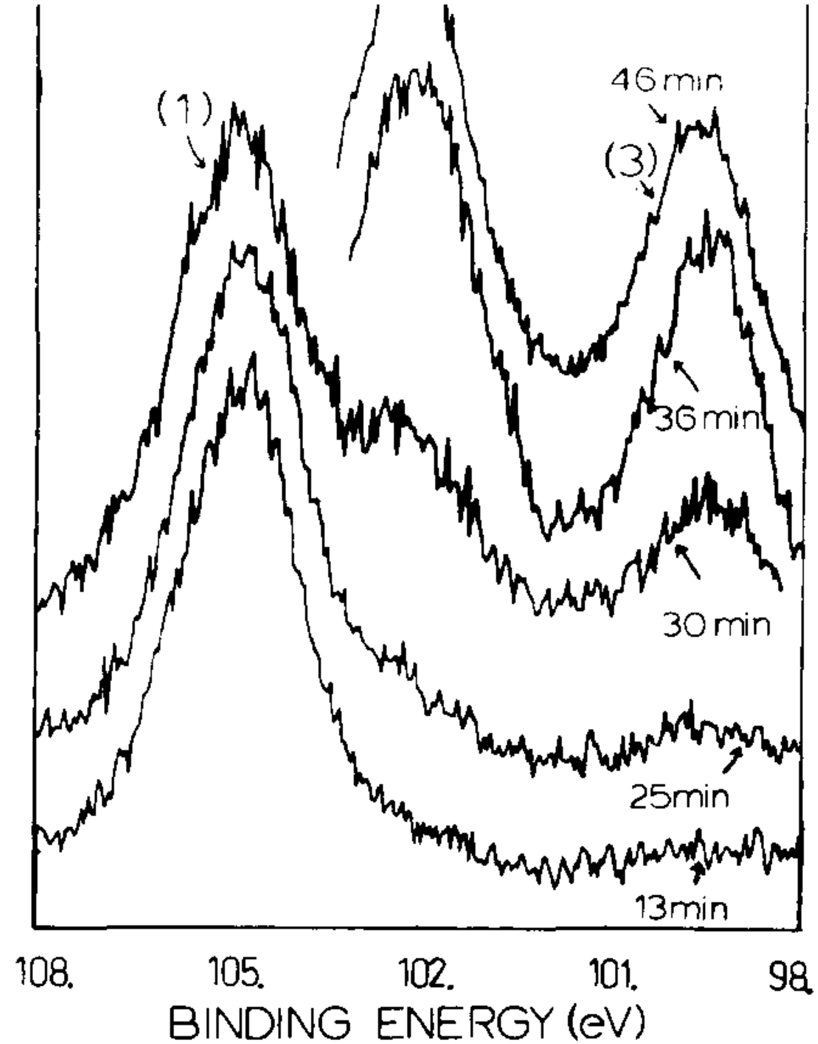
Glass seal:

- electrical isolation
- encapsulates reactive electrolyte

Lithium and other alkali metals react with silicate glasses

Li thin film on silica at 75° C

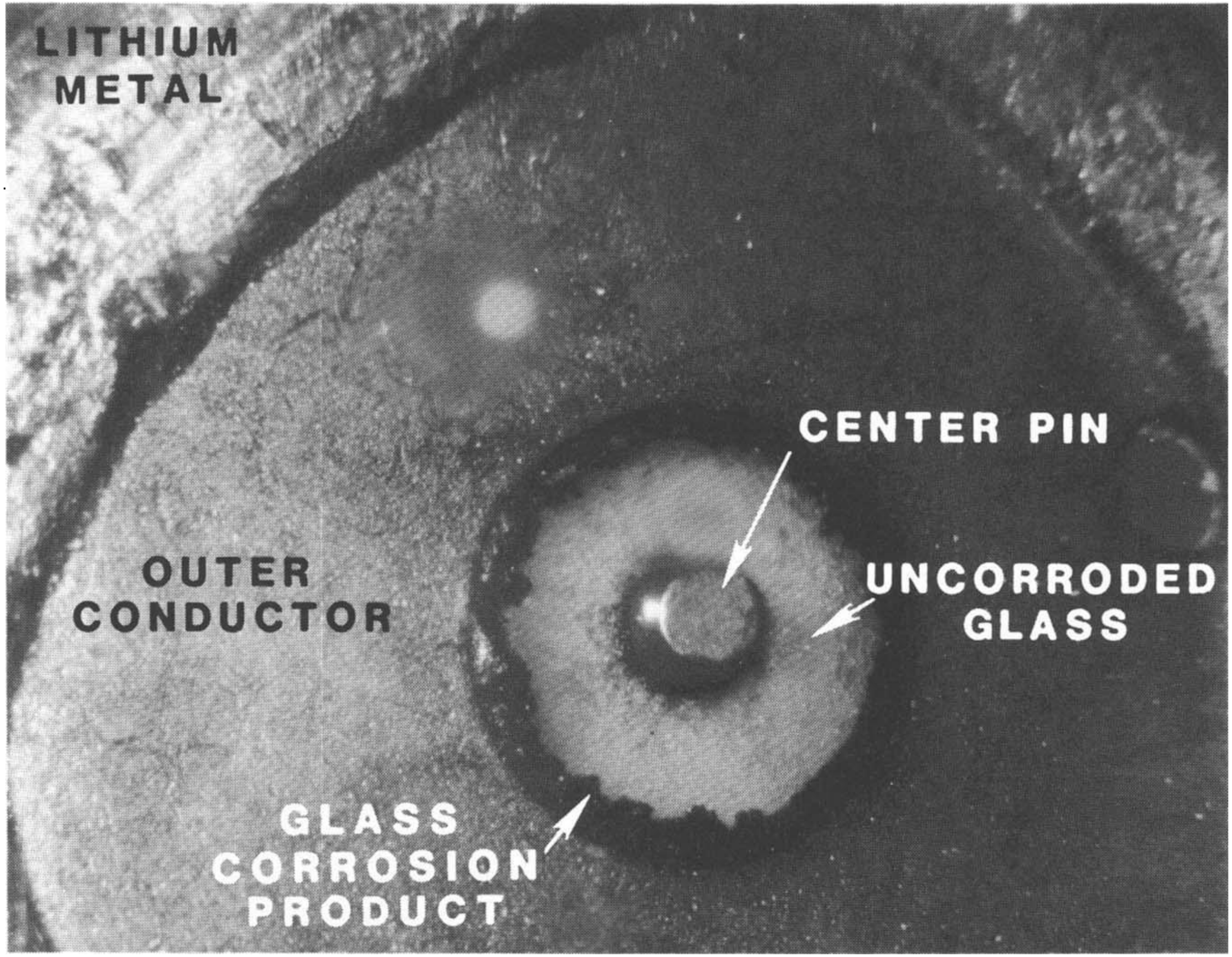
$4Li + SiO_2 \rightarrow 2Li_2O + Si$



Maschoff, et al., Appl. Surf. Sci. 27 (1986)

for Li/SiO_2 heated to 75° C for given times after

Silicate glass seals are attacked by lithium

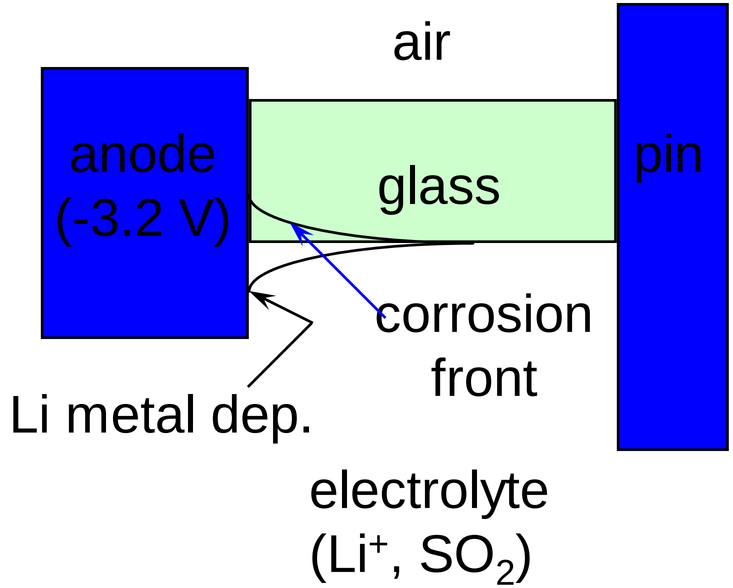


Conventional silicate sealing glass after three months at 70° C, Li/$SOCl_2$ electrolyte-

Bunker et al., J. Mat. Res. 2 (1987)

A mechanism for glass corrosion has been established

Underpotential Deposition



Reaction limits the shelf-life of Li liquid electrolyte cells

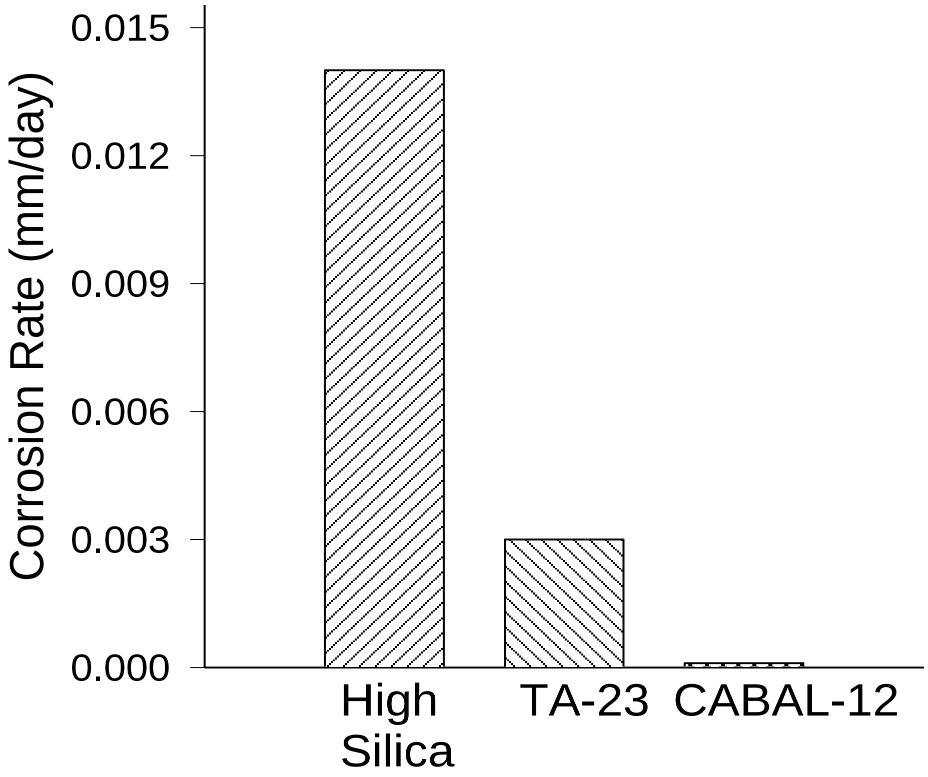
$$4Li + SiO_2 \rightarrow 2Li_2O + Si$$

(Bunker *et al.*, *J. Mater. Res.*, 1987.)

Corrosion resistant glasses have been developed

1. **Low silica compositions**
   - **TA-23** (45 wt% SiO_2)
     - shelf-life > 5 years

2. **Aluminoborate compositions**
   - **CABAL-12** (silica-free)
     - $20MgO \bullet 20CaO \bullet 20Al_2O_3 \bullet 40B_2O_3$
     - shelf-life > 20 years
     - lower sealing temperature
     - less prone to crystallization



Applications include Li-batteries for cameras, computers, and biomedical components.

These glasses are used in designs for long-life Li cells

United States Patent (10) **Patent No.: US 7,803,481 B2**
Howard et al. (45) **Date of Patent: Sep. 28, 2010**

LITHIUM-ION BATTERY

United States Patent (10) **Patent No.: US 7,641,992 B2**
Howard et al. (45) **Date of Patent: Jan. 5, 2010**

MEDICAL DEVICE HAVING LITHIUM-ION BATTERY

4,446,212	A	5/1984	Kaun
4,464,447	A	8/1984	Lazzari et al.

United States Patent (10) **Patent No.: US 6,498,951 B1**
Larson et al. (45) **Date of Patent: Dec. 24, 2002**

IMPLANTABLE MEDICAL DEVICE EMPLOYING INTEGRAL HOUSING FOR A FORMABLE FLAT BATTERY

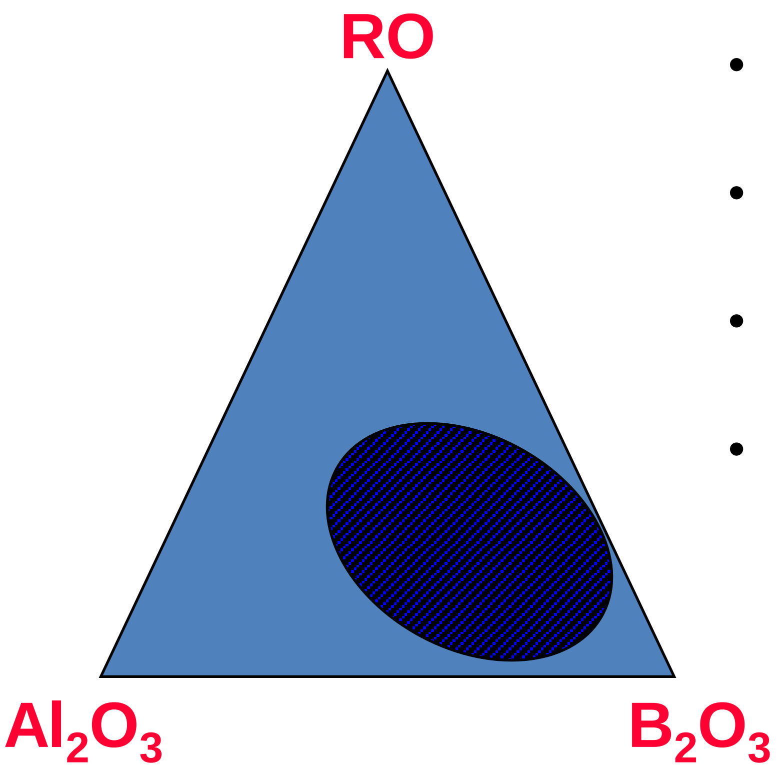
5,199,428	A	4/1993	Obel et al.	128/419 C
5,207,218	A	5/1993	Carpentier et al. ...	128/419 PG
5,312,453	A	5/1994	Shelton et al.	607/19

United States Patent Application Publication (10) **Pub. No.: US 2005/0255380 A1**
Lasater et al. (43) **Pub. Date: Nov. 17, 2005**

LITHIUM-ION BATTERY SEAL

(60) Provisional application No. 60/346,031, filed on Nov. 9, 2001.

Alkaline earth aluminoborate glasses have the requisite properties for lithium battery seals



- Range of CTEs for variety of pin materials
- Relatively low sealing temperatures (<800° C)
- CABAL glasses are used in Na-vapor lamps
- Resist attack by lithium
  - kinetic stability (Li reduces B_2O_3 to boride)
  - >20 year projected battery lifetime

How does structure affect useful properties?

RK Brow
brow@mst.edu

Glass properties depend structure

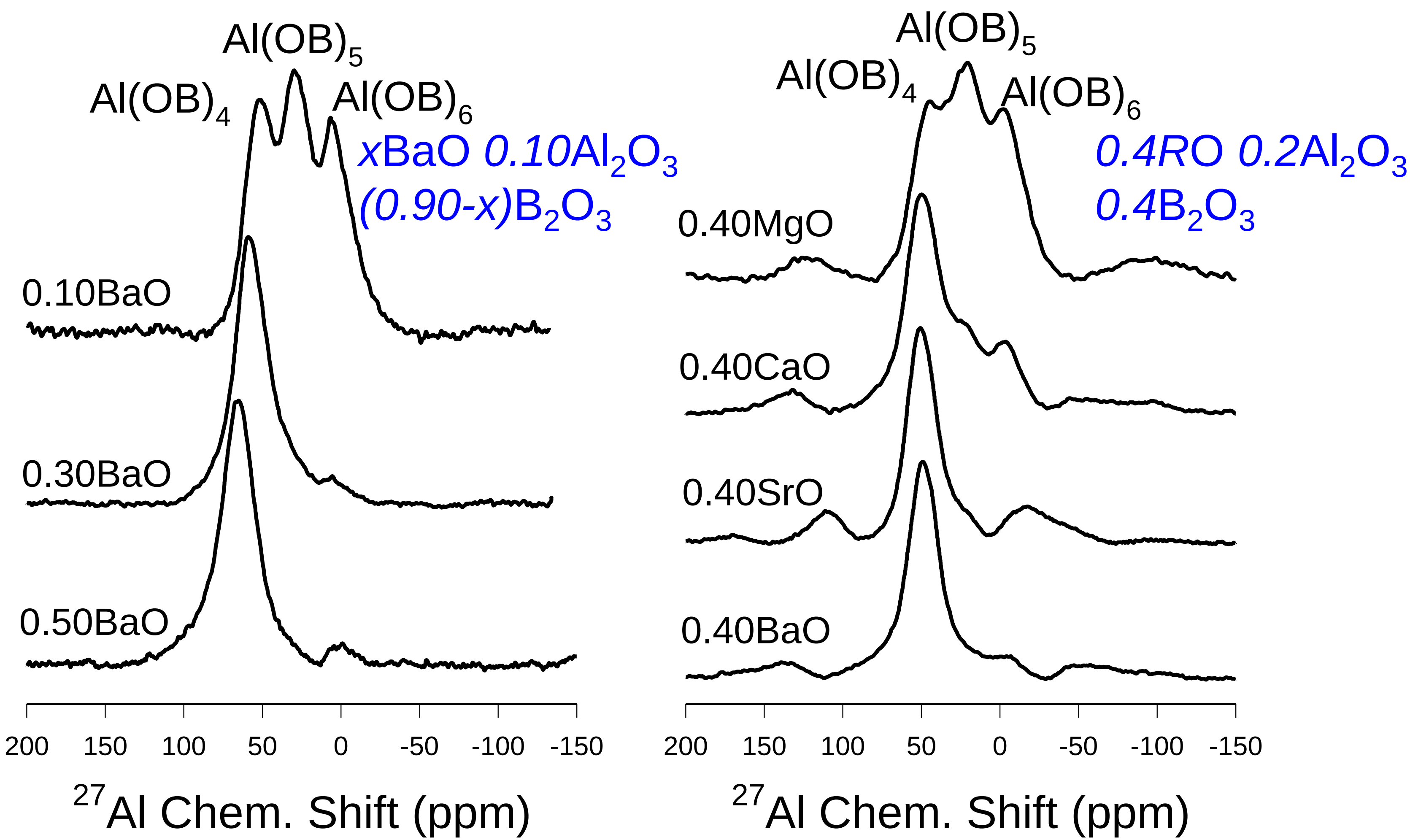
xRO 0.10Al$_2$O$_3$ $(0.90\text{-}x)$B$_2$O$_3$

This image cannot currently be displayed.

This image cannot currently be displayed.

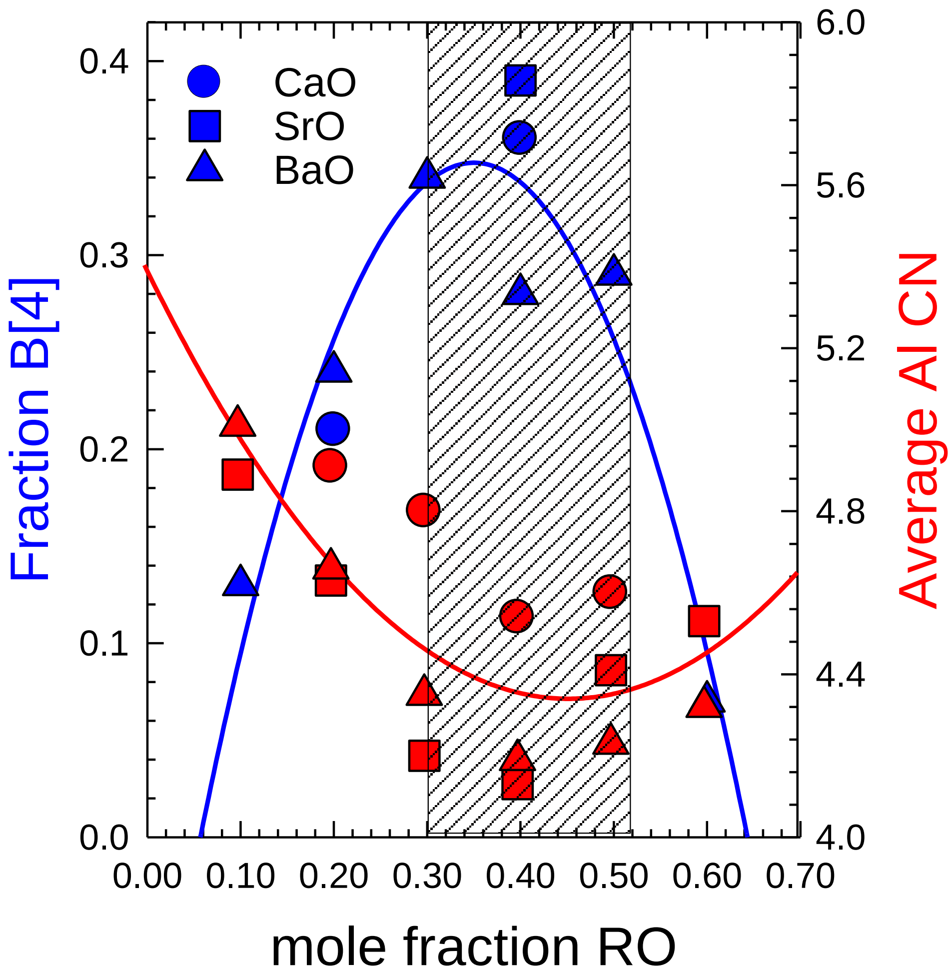
Brow and Tallant, 1997

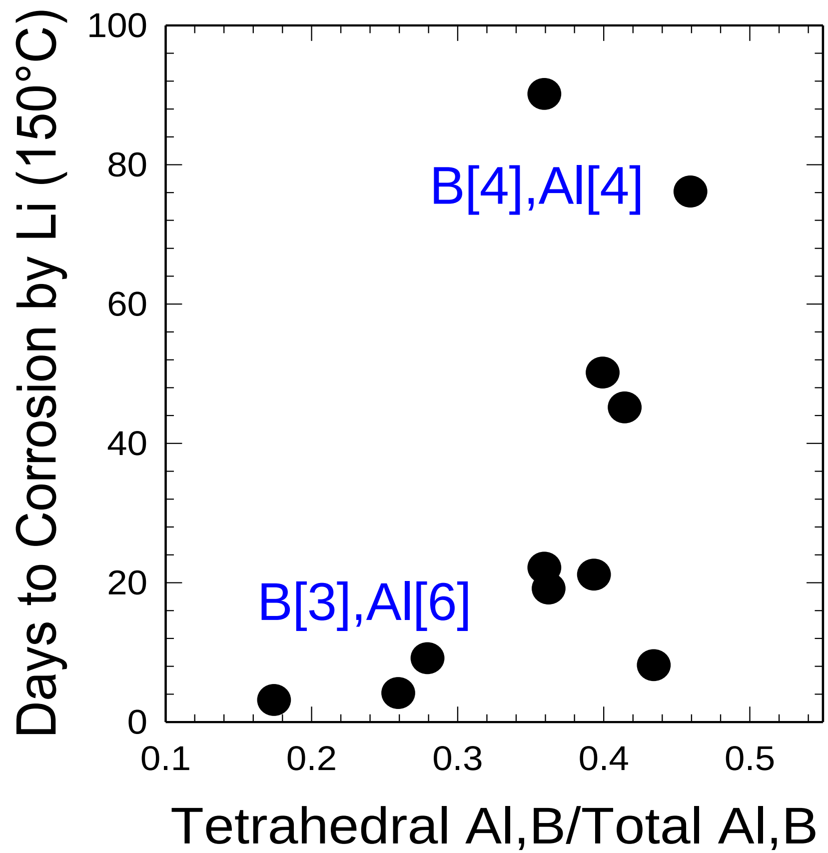
Alumina coordination also depends on composition



Brow and Tallant, 1997

The most durable glasses have tetrahedral networks

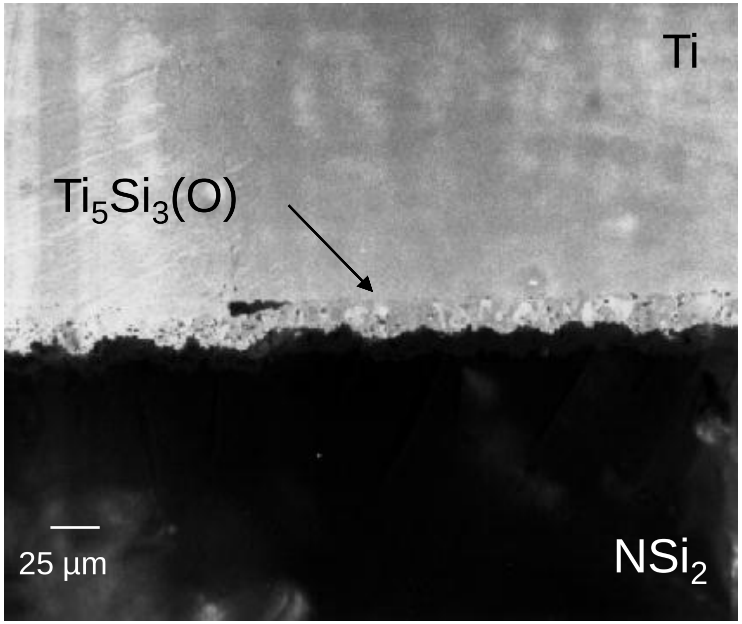




Aqueous durability exhibits similar structural dependencies

Spin-Off Development: Titanium Sealing Glasses

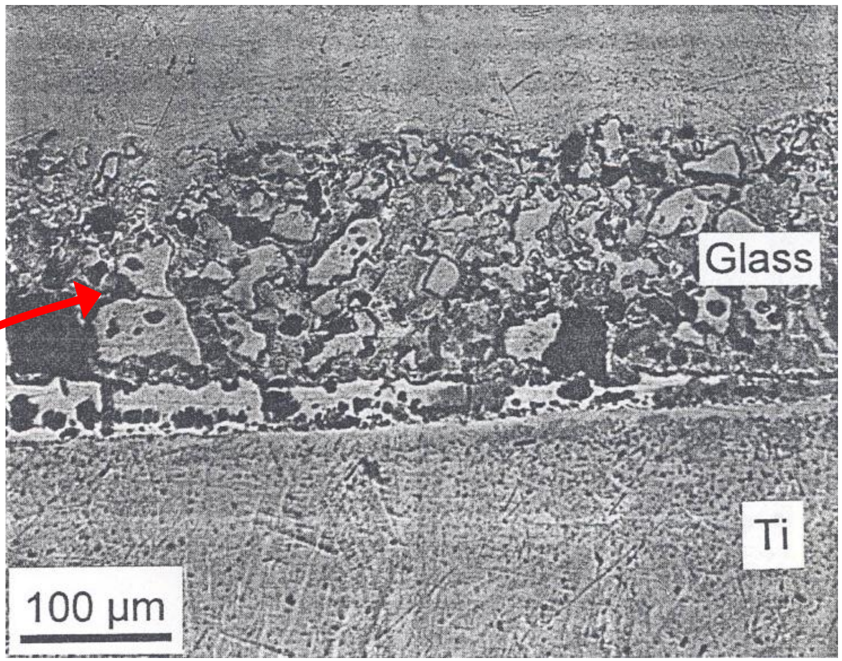
- Titanium alloys have a variety of useful properties
  - High strength-to-weight ratio
  - Superior corrosion resistance
  - Reasonable weldability
- Potential Sealing Applications:
  - Satellite connectors, actuators
  - Implanted biomedical components (pacemakers, insulin pumps, etc.)
  - Biocompatible coatings on prosthetic alloys



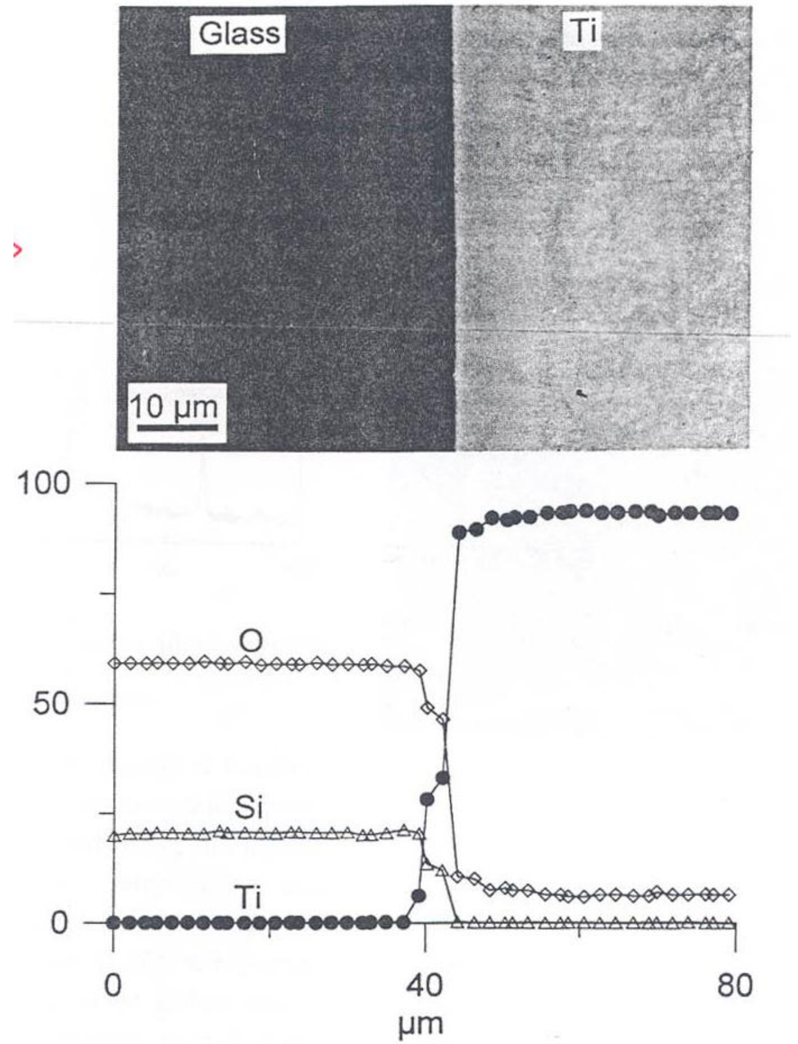
Limitation: Reliable, commercial hermetic sealing technology
- conventional silicate sealing glasses are reduced by titanium
  - silicide formation leads to weak glass/Ti interfaces

Silicate bio-glass coatings for titanium require very short processing times

800°C/1 minute: no deleterious reactions between silicate glass and Ti.

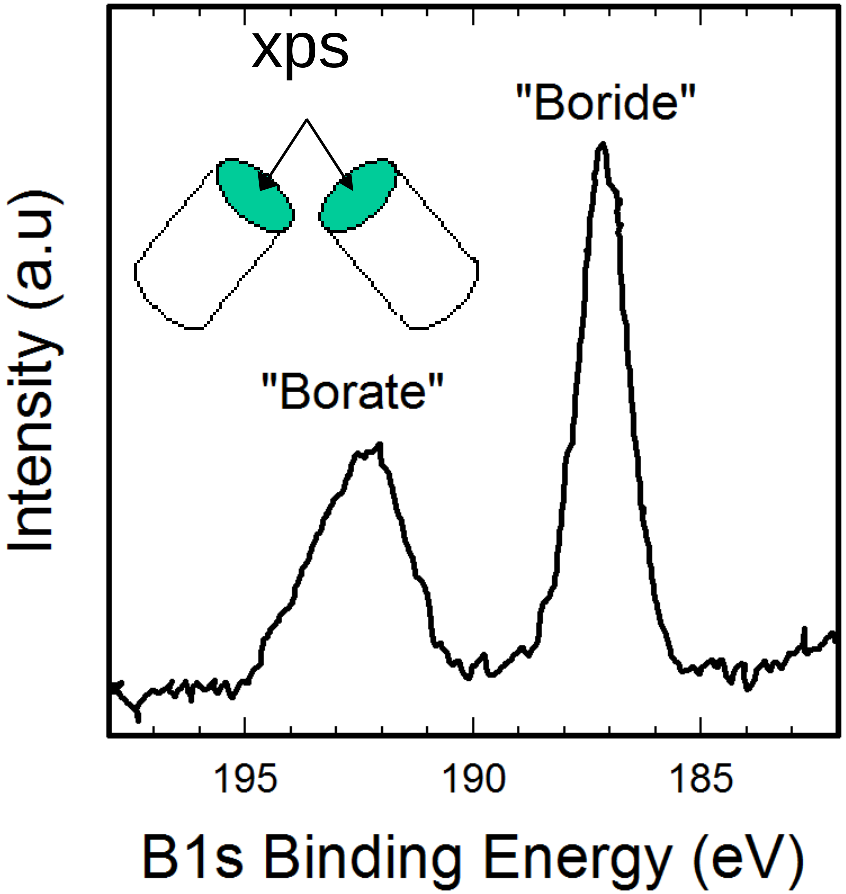


900°C/1 minute: excessive interfacial reactivity between Bioglass and Ti.

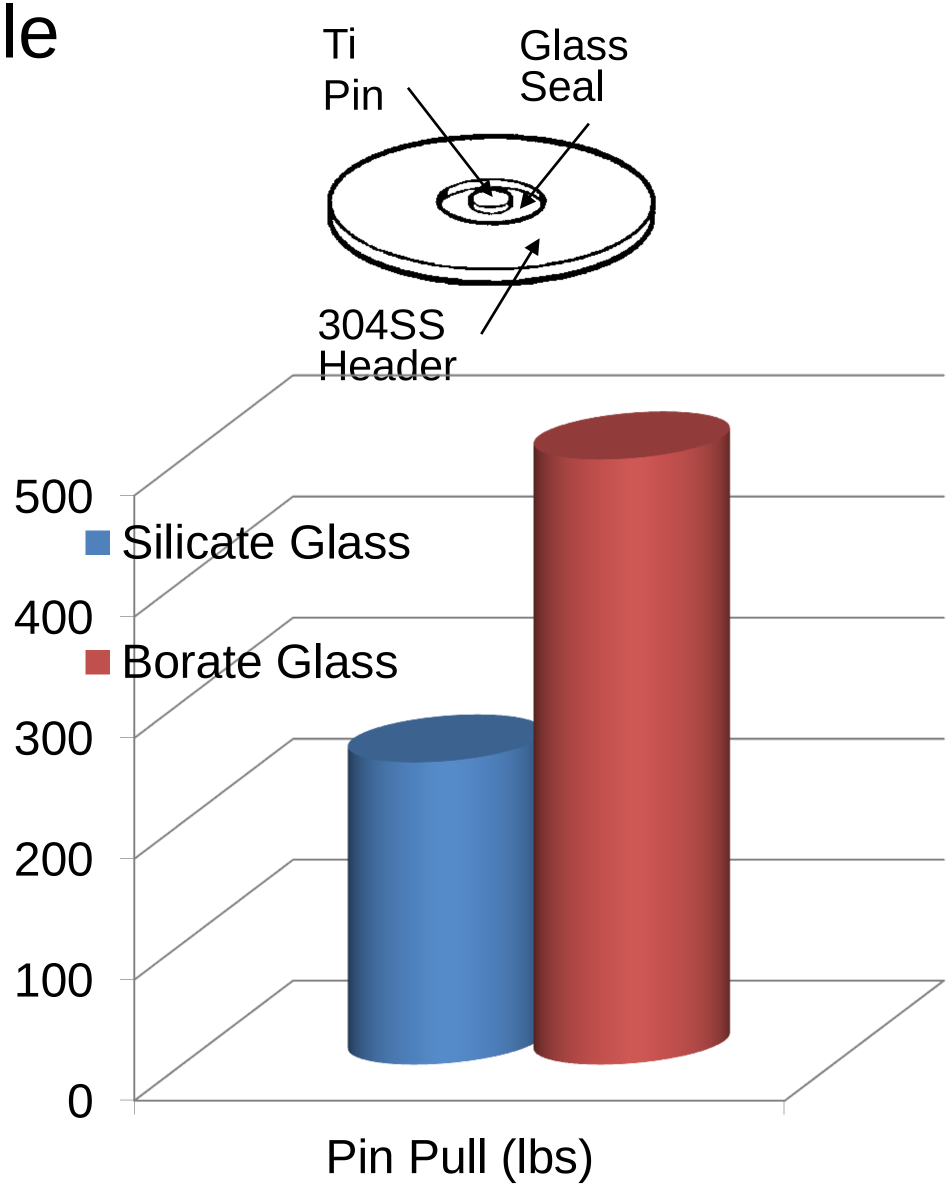


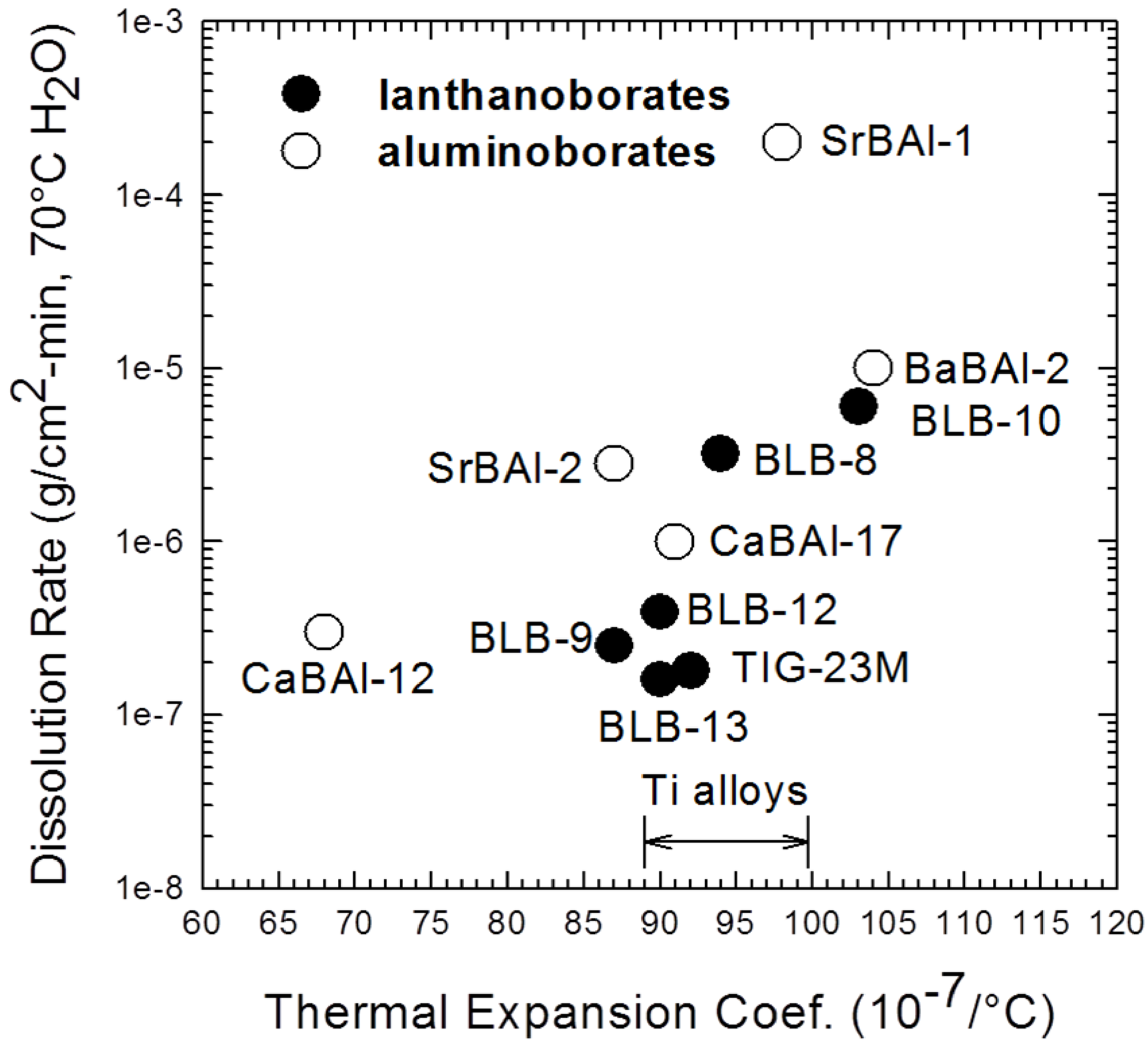
Pazo et al (1998)

Borate glasses are compatible with titanium alloys



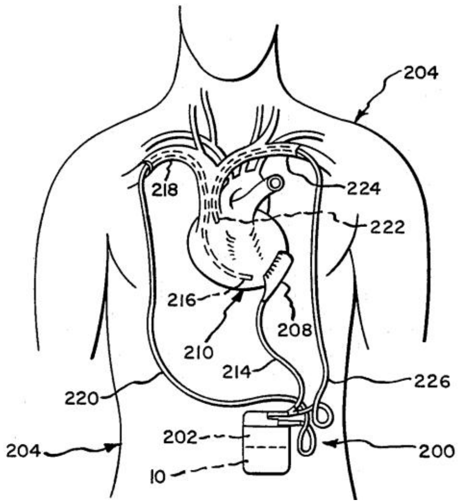
$Ti + B_2O_3 \rightarrow TiB_x + TiO_y$



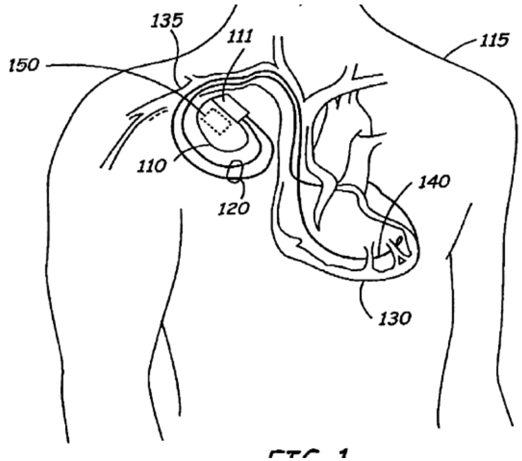


RK Brow
brow@mst.edu

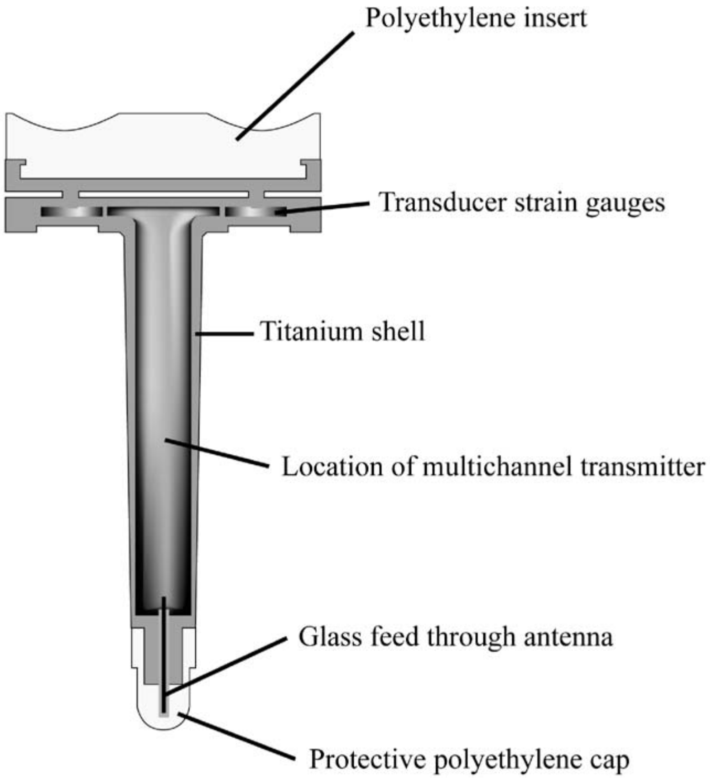
Borate glasses are now being used in a variety of titanium biomedical applications



Pacemakers and defibrillators

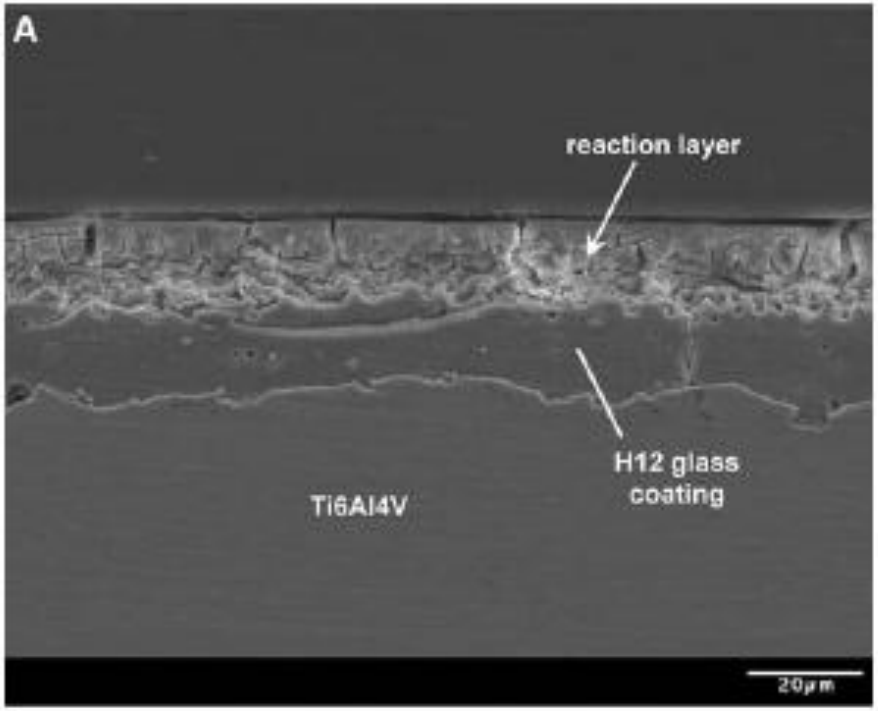


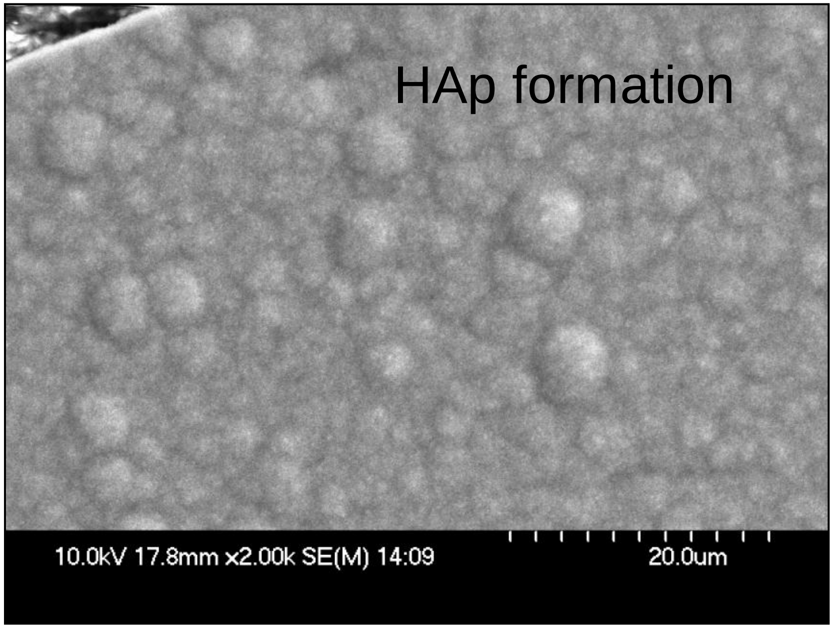
Insulin pumps



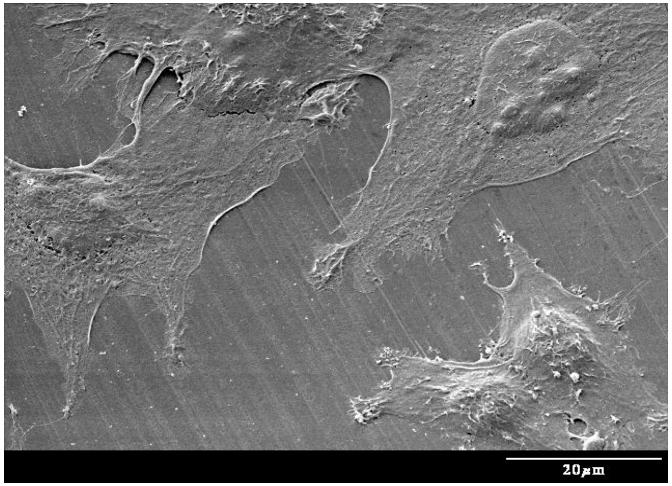
Orthopedic pressure sensors

Bioactive borate glass coatings have been developed for titanium





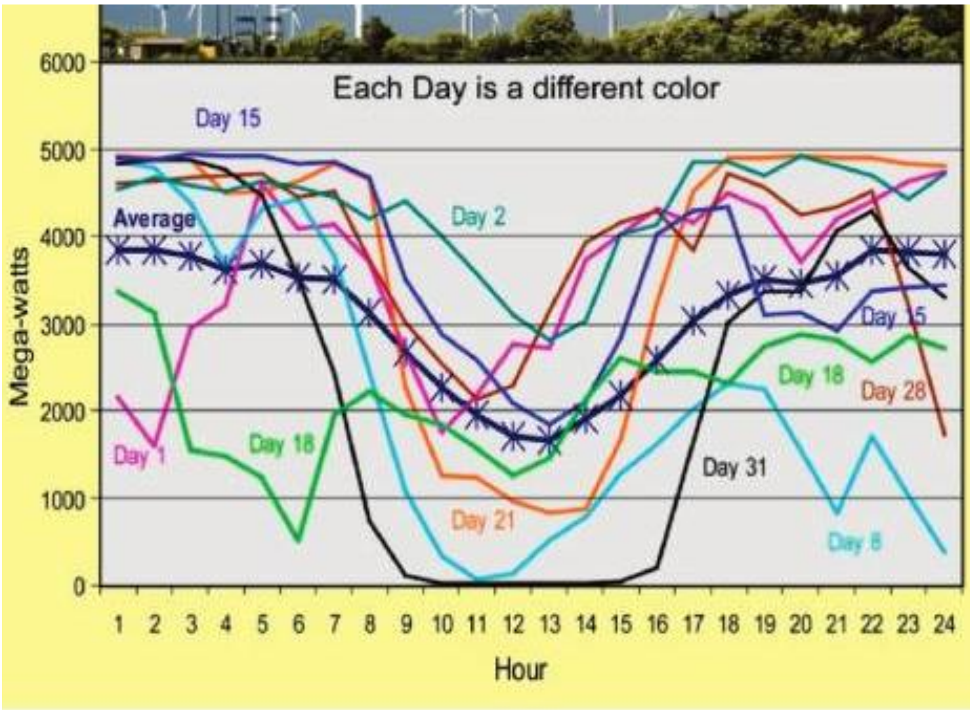
L. Peddi, RK Brow and RF Brown, J. Mater. Sci. Mater Med (2008) 19, 3145



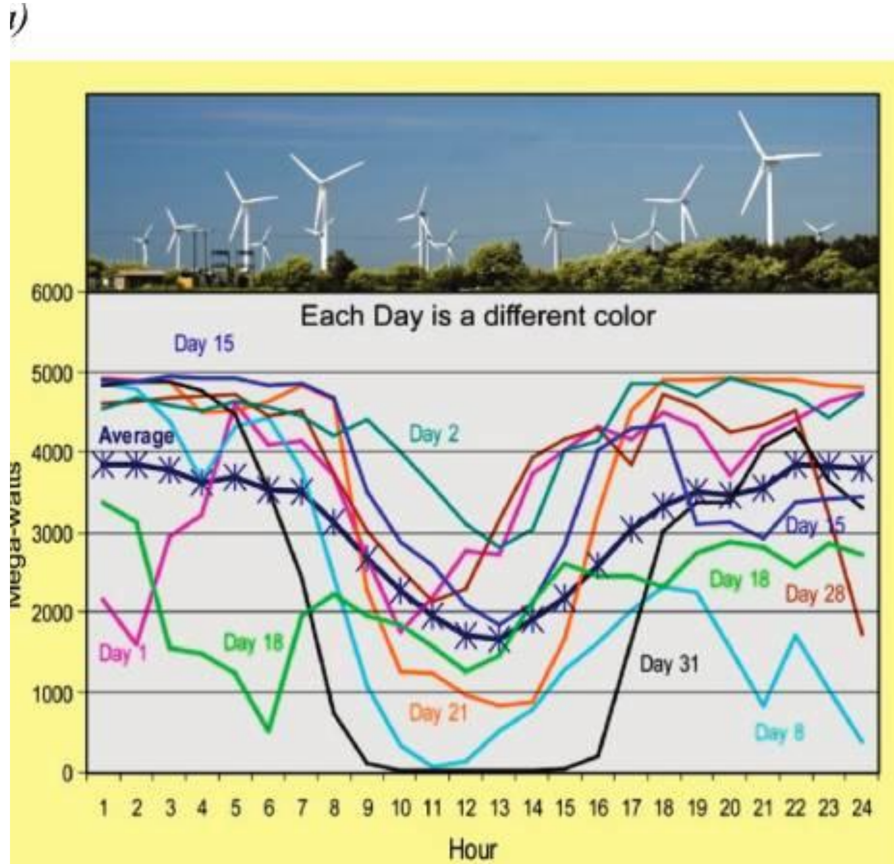
Saos-2 cell compatibility

Alkali Thermal Battery Seals

Electrochemical energy storage for the green energy grid

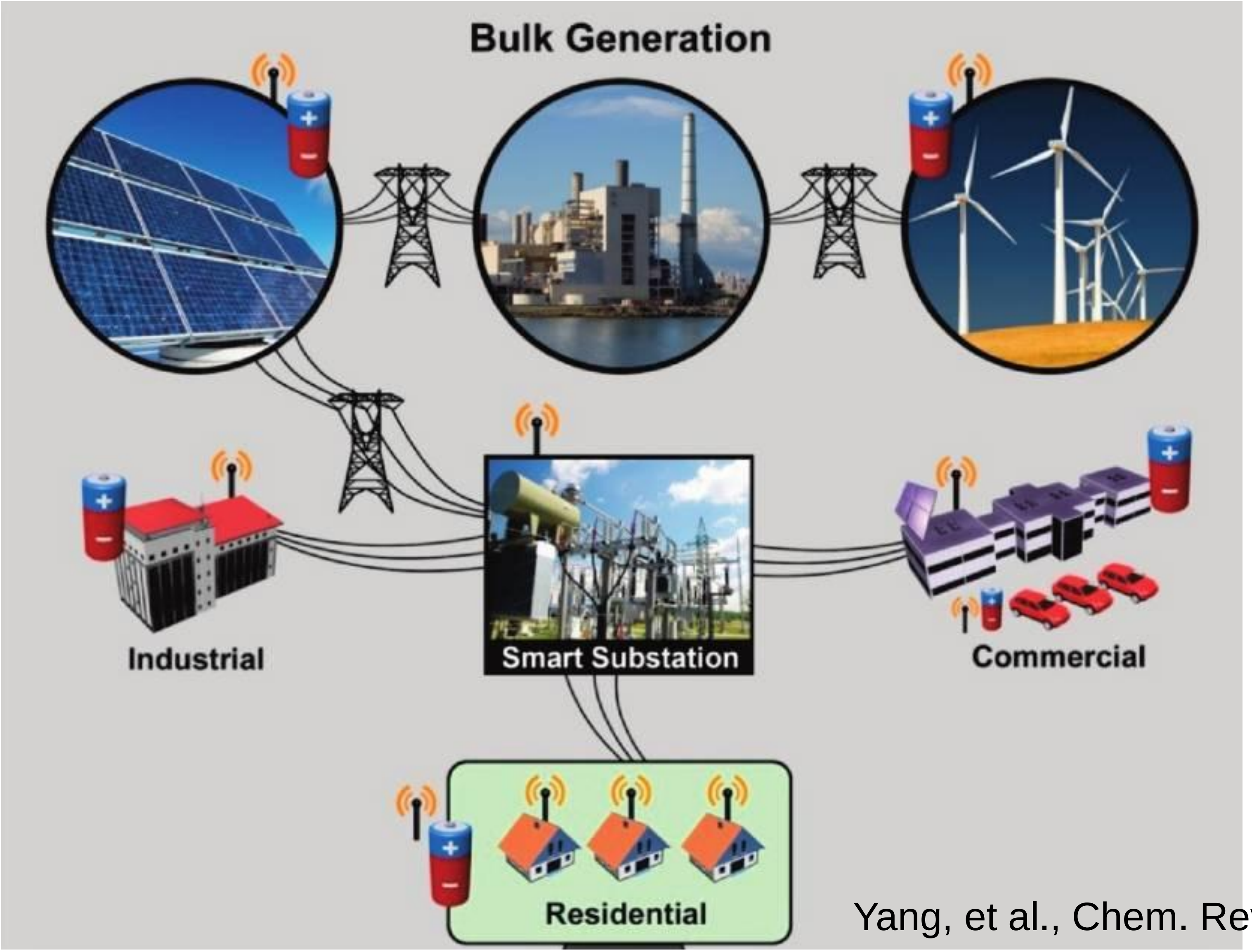


b)

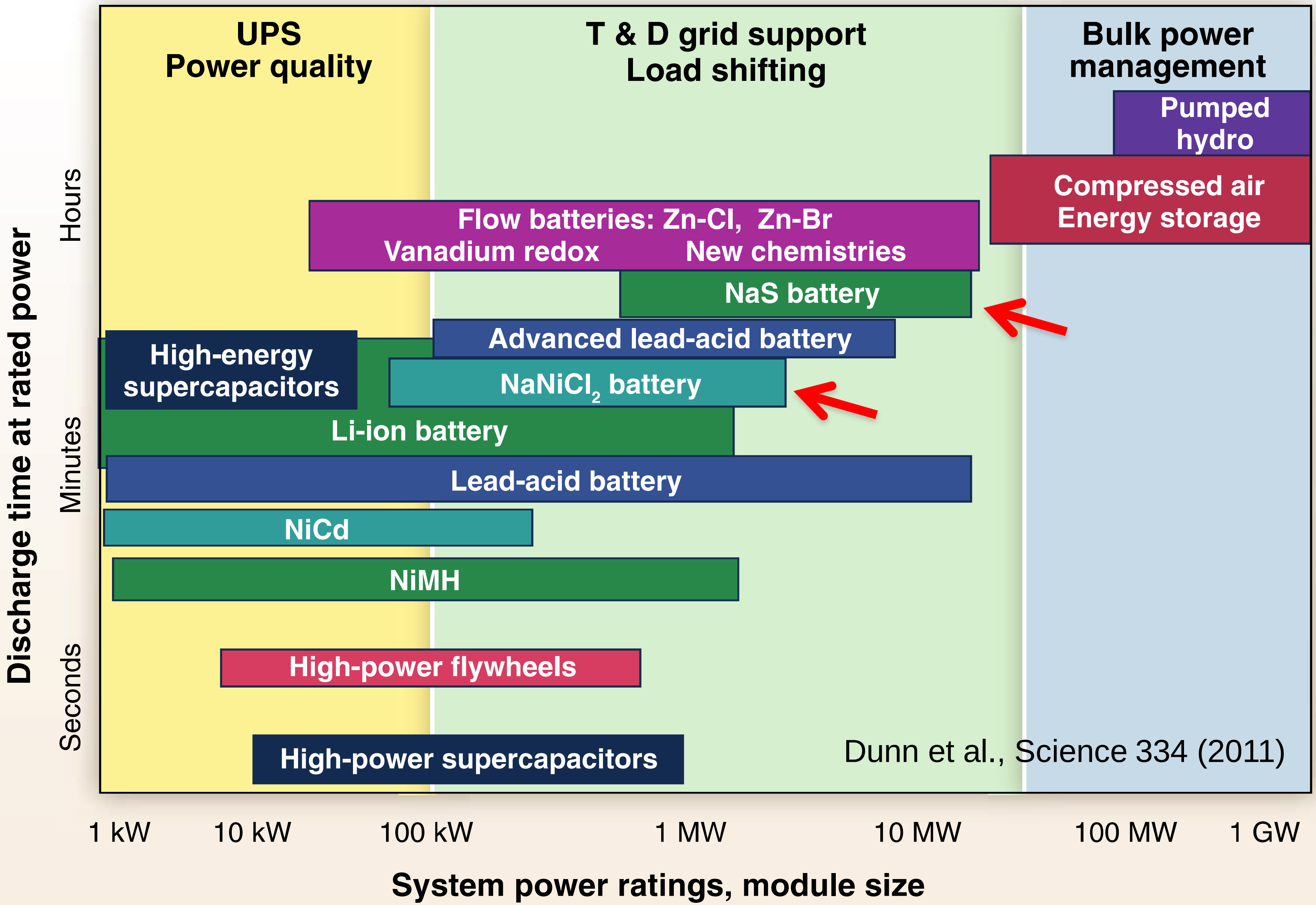


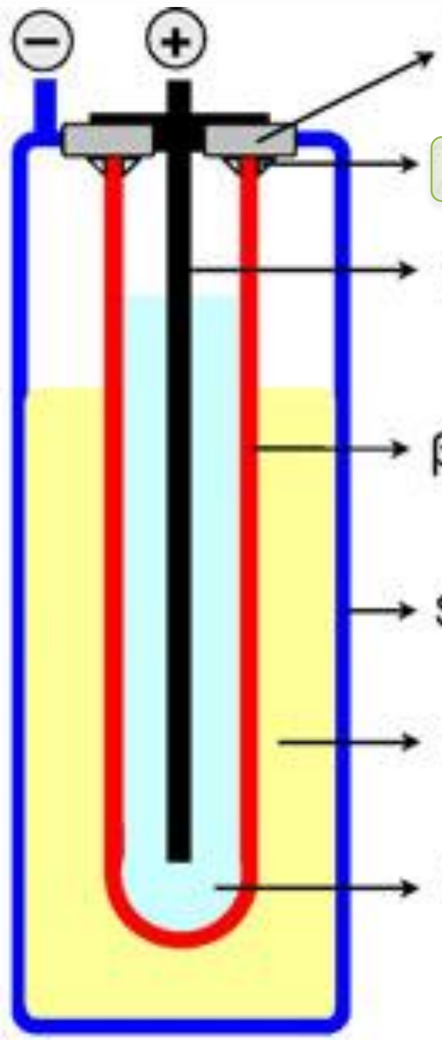
Yang, et al., Chem. Rev. (2011)

Advanced batteries will be part of the green energy grid



Yang, et al., Chem. Rev. (2011)


UPS
Power quality
T & D grid support
Load shifting
Bulk power
management
Pumped
hydro
Compressed air
Energy storage
Flow batteries: Zn-Cl, Zn-Br
Vanadium redox
New chemistries
NaS battery
Advanced lead-acid battery
High-energy
supercapacitors
NaNiCl2 battery
Li-ion battery
Lead-acid battery
NiCd
NiMH
High-power flywheels
High-power supercapacitors
Dunn et al., Science 334 (2011)
Hours
Minutes
Seconds
Discharge time at rated power
1 kW
10 kW
100 kW
1 MW
10 MW
100 MW
1 GW
System power ratings, module size



$Na/NiCl_2$ Cell

Glass seal requirements

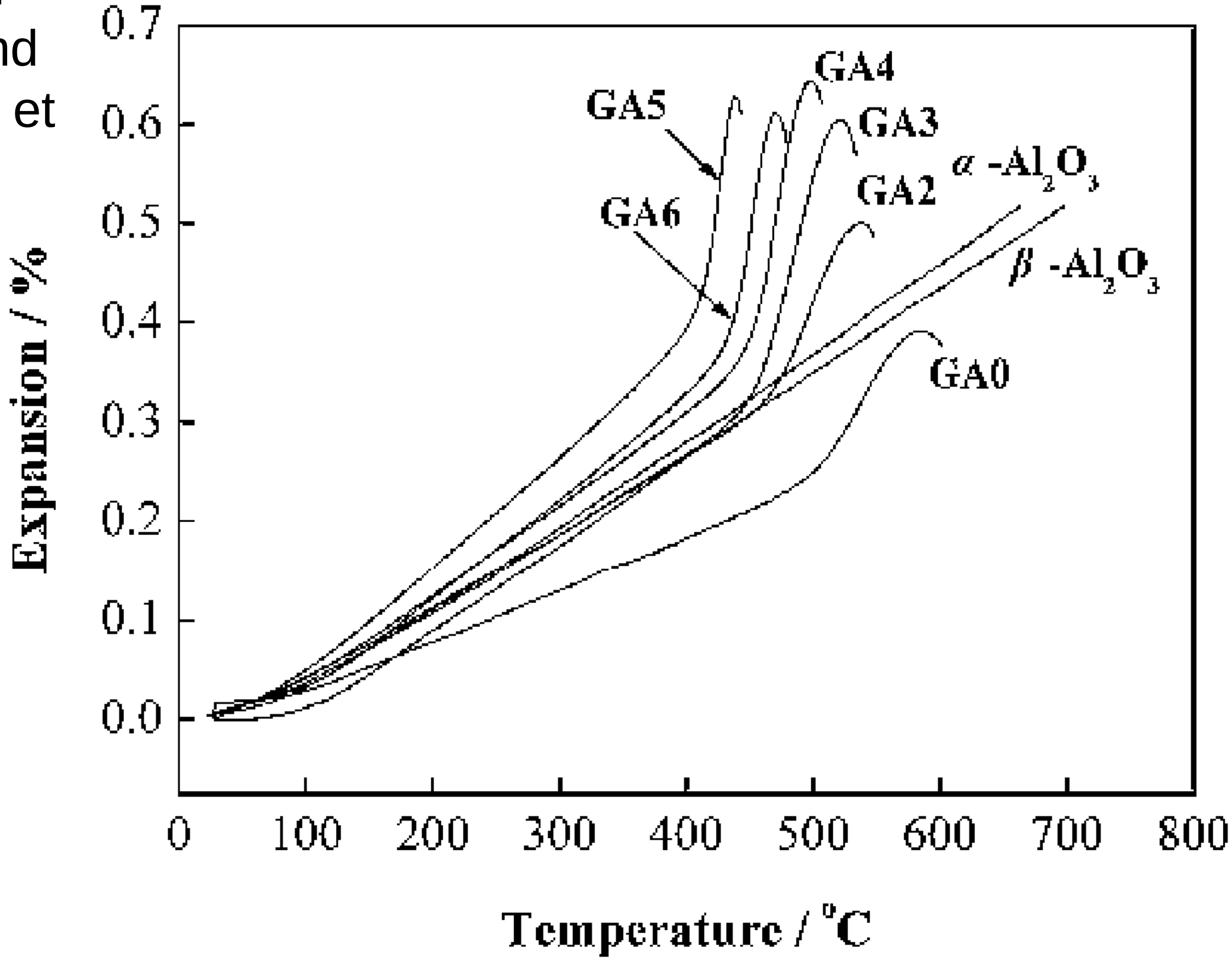
- α-Al_2O_3-to-β–Al_2O_3
- Chemical compatibility
  - molten, gaseous Na and halides (electrolyte)
  - No 'poisoning' ions for β–Al_2O_3 (sealing reactions)
- Operate at 300-400° C for up to 20 years

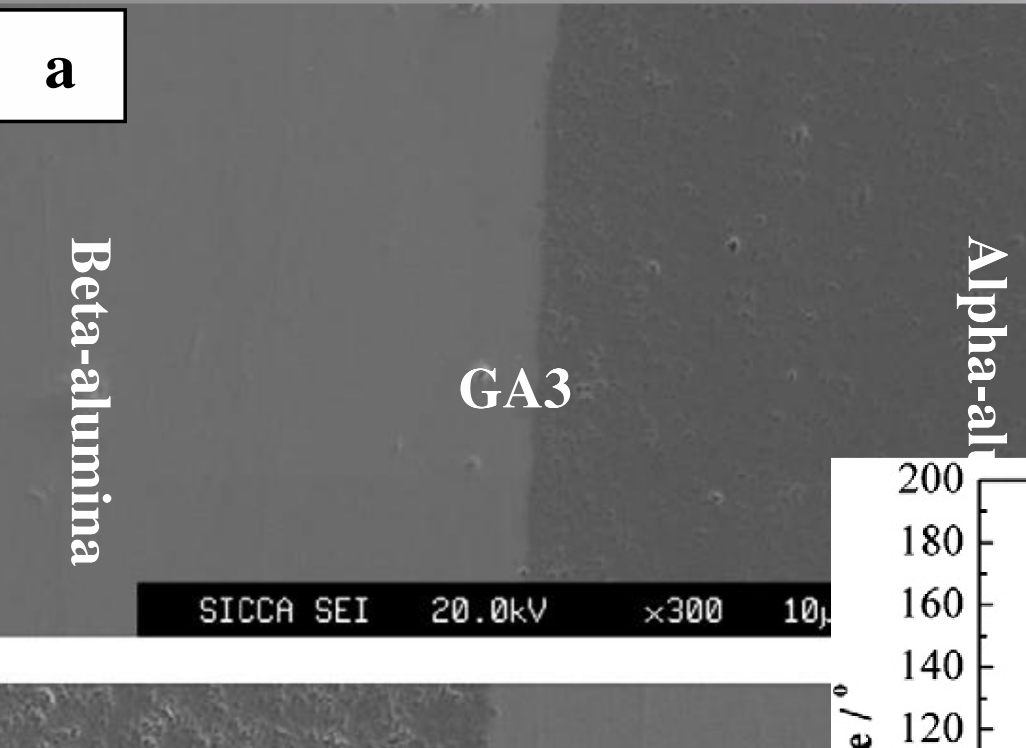
$$NiCl_2 + 2Na \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2NaCl + Ni \quad \text{e.m.f.} = 2.58\ V \quad \text{at } 300^{o}C$$

RK Brow
brow@mst.edu

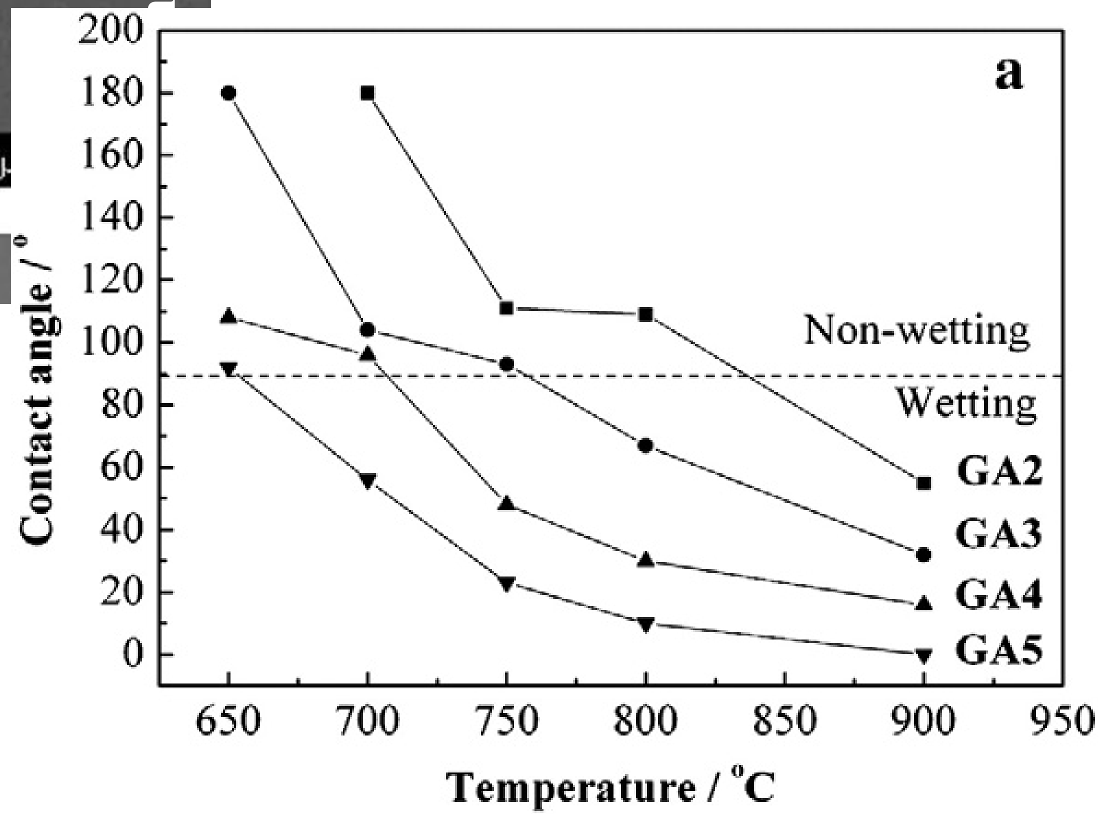
Example: Low alkali Bi-borosilicate glasses and glass-ceramics (Song, et al., JNCS (2011))

0-62 Bi_2O_3 replacing SiO_2





Example: Low alkali Bi-borosilicate glasses and glass-ceramics (Song, et al., JNCS (2011))



Wetting behavior on β-Al_2O_3

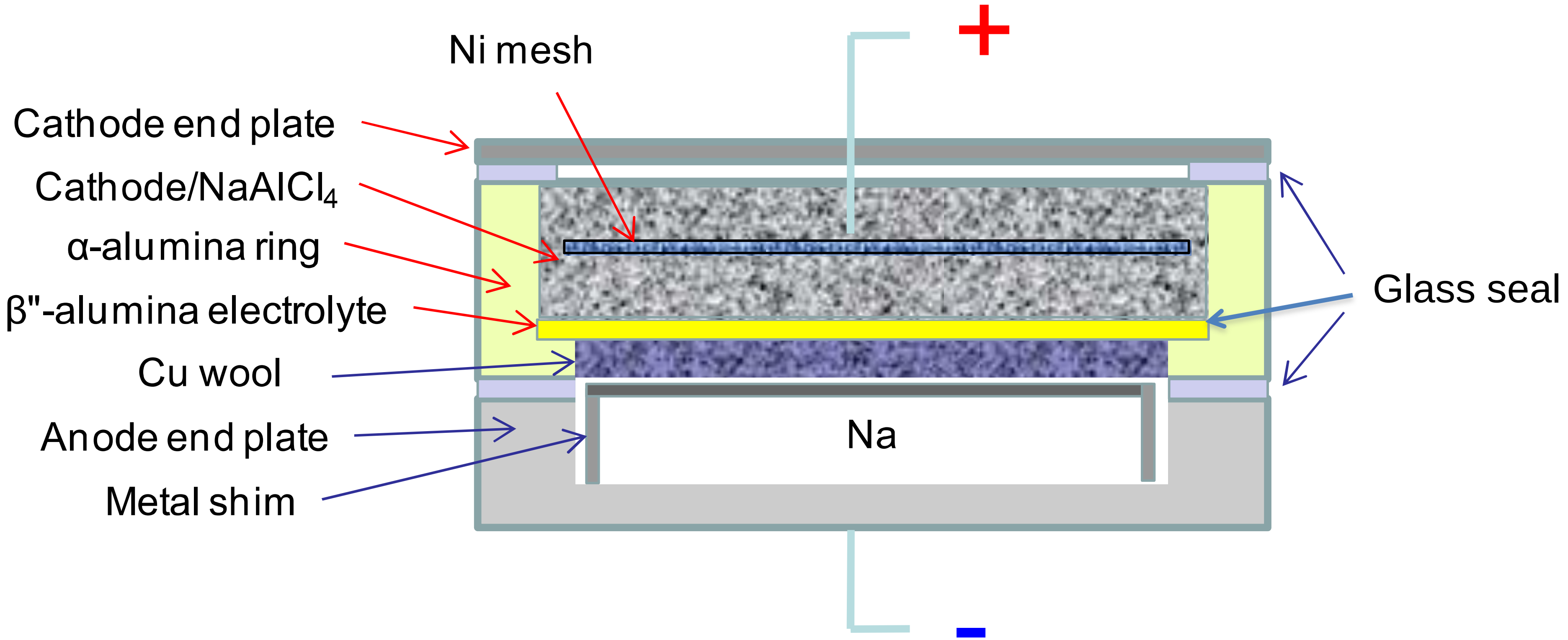
Still, there is an opportunity for new sealing materials

“Major obstacles to demonstrating long-life liquid metal batteries center on … the engineering of robust, high temperature, insulating seals.”- Kim et al., Liquid Metal Batteries: Past, Present, and Future, Chemical Reviews (2013)

“Chemically stable sealants” are one of the outstanding materials problems remaining for Na/S batteries- Cheng et al. Advanced Materials (2011)

New designs face more complex sealing challenges

Planar $Na/NiCl_2$ stack for load-leveling applications: same α-to-β alumina seal, but added alumina-steel seal



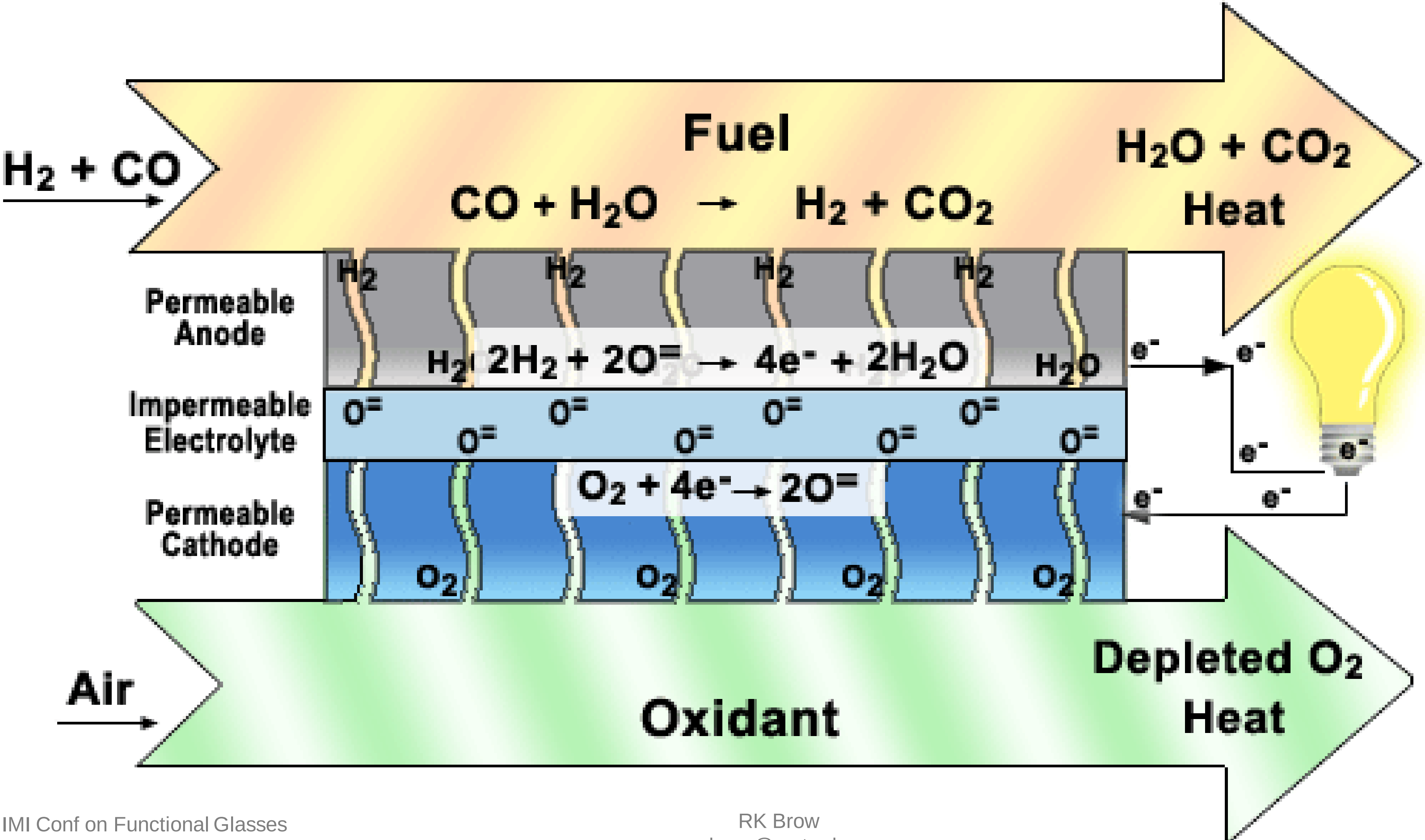
Lu et al., High Power Planar Sodium-Nickel Chloride Battery, ECS Trans. 28(22) 7 (2010)

Solid Oxide Fuel Cells

From I. Donald, et al., J Mater Sci (2011) 46:1975–2000

Fig. 6 SOFCs. Experimental unit. Julich Research Centre 13.3 kW

Solid Oxide Fuel Cell



RK Brow
brow@mst.edu

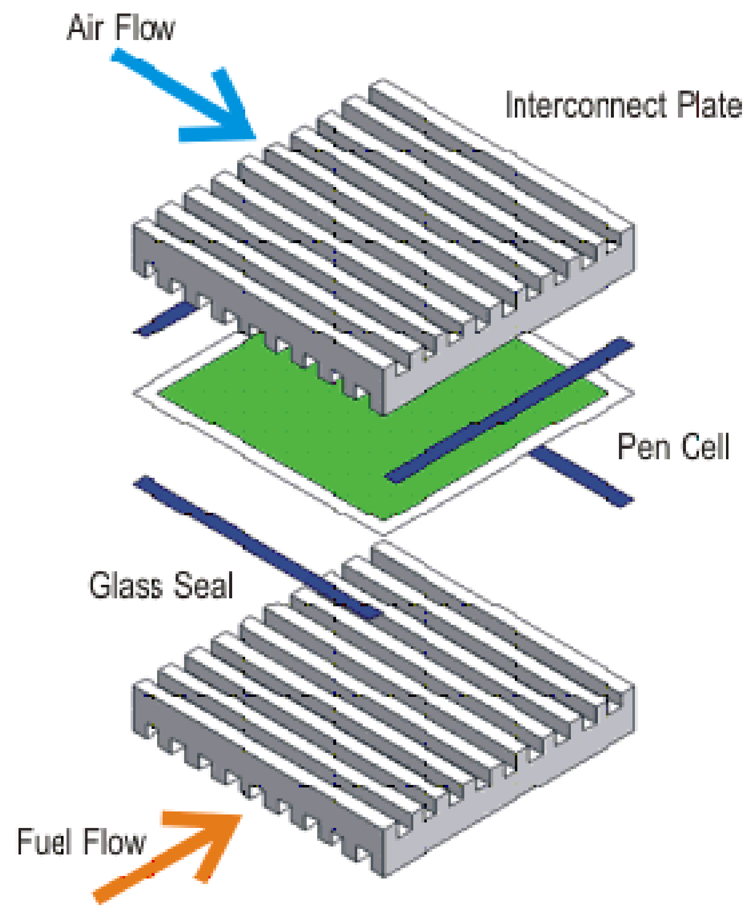
Designing glasses for SOFC seals is a significant challenge

Function:

- Prevent mixing of fuel/oxidant within stack
- Prevent leaking of fuel/oxidant from stack
- Electrically isolate cells in stack
- Provide mechanical bonding of components

Challenges:

- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures (>700ºC)
  - Long lifetimes (>10000's hrs)
  - Maintain stability over range of P_{O2}, P_{H2O}
- Relatively low sealing temperatures (<900ºC)
  - Avoid altering other SOFC materials



For some designs, glass-ceramics may be suitable, others may require viscous seals

There have been a number of recent reviews of SOFC sealing glasses

J Mater Sci (2007) 42:3465–3476
DOI 10.1007/s10853-006-0409-9

J. Mat. Sci. (2007)

A review of sealing technologies applicable to solid oxide electrolysis cells

Journal of Power Sources 147 (2005) 46–57

J. Power Sources, (2005)

Review

Sealants for solid oxide fuel cells

Jeffrey W. Fergus *

Contents lists available at ScienceDirect

Materials Science and Engineering R

journal homepage: www.elsevier.com/locate/mser

Glass-based seals for solid oxide fuel and electrolyzer cells – A review

M.K. Mahapatra, K. Lu *

Mat Sci Eng B (2010)

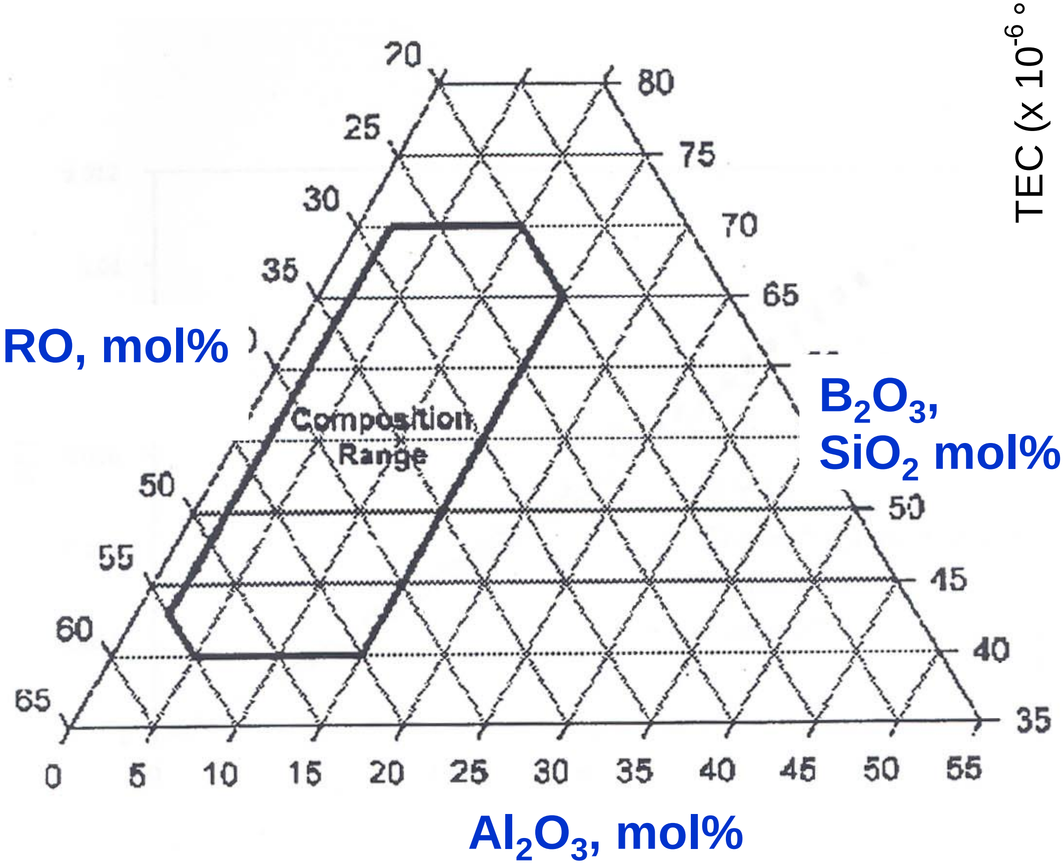
The State-of-the-Art in Sealing Technology for Solid Oxide Fuel Cells

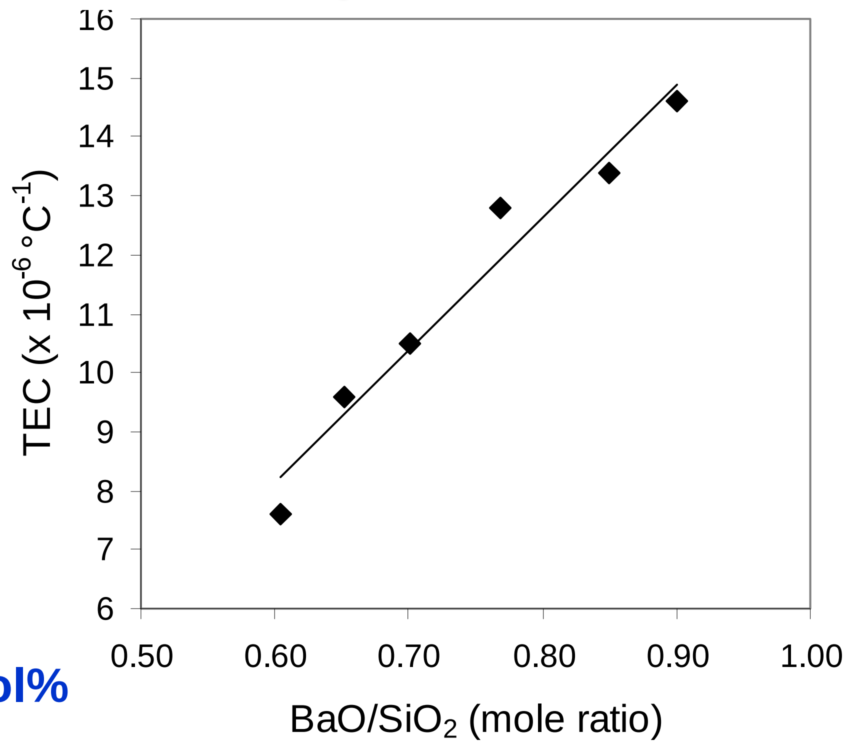
K. Scott Weil

JOM, August 2006

Ba-silicate glass-ceramics have shown promise

Meinhardt, et al., USP 6,532,769
Mar. 18, 2003

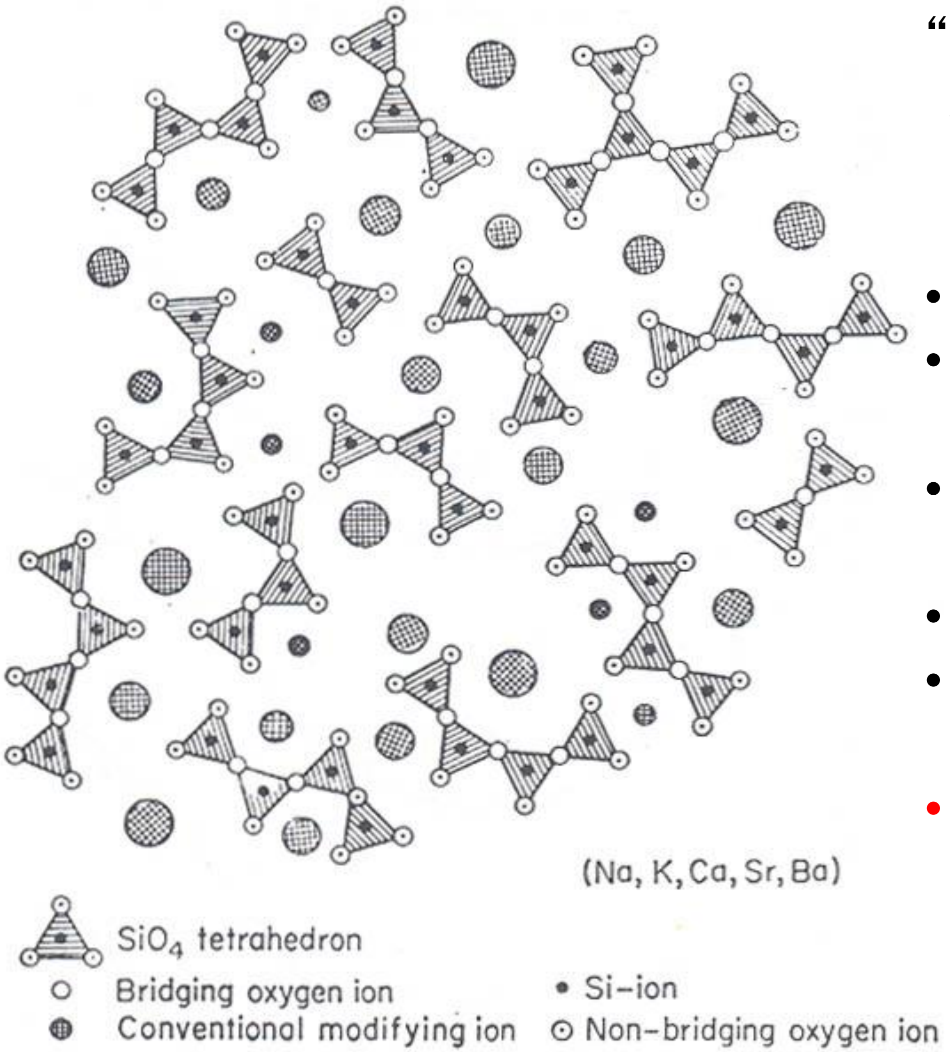




Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases; e.g., $BaO{\cdot}2SiO_2$, $2BaO{\cdot}3SiO_2$

RK Brow
brow@mst.edu

Candidate sealing glasses have ‘invert’ structures

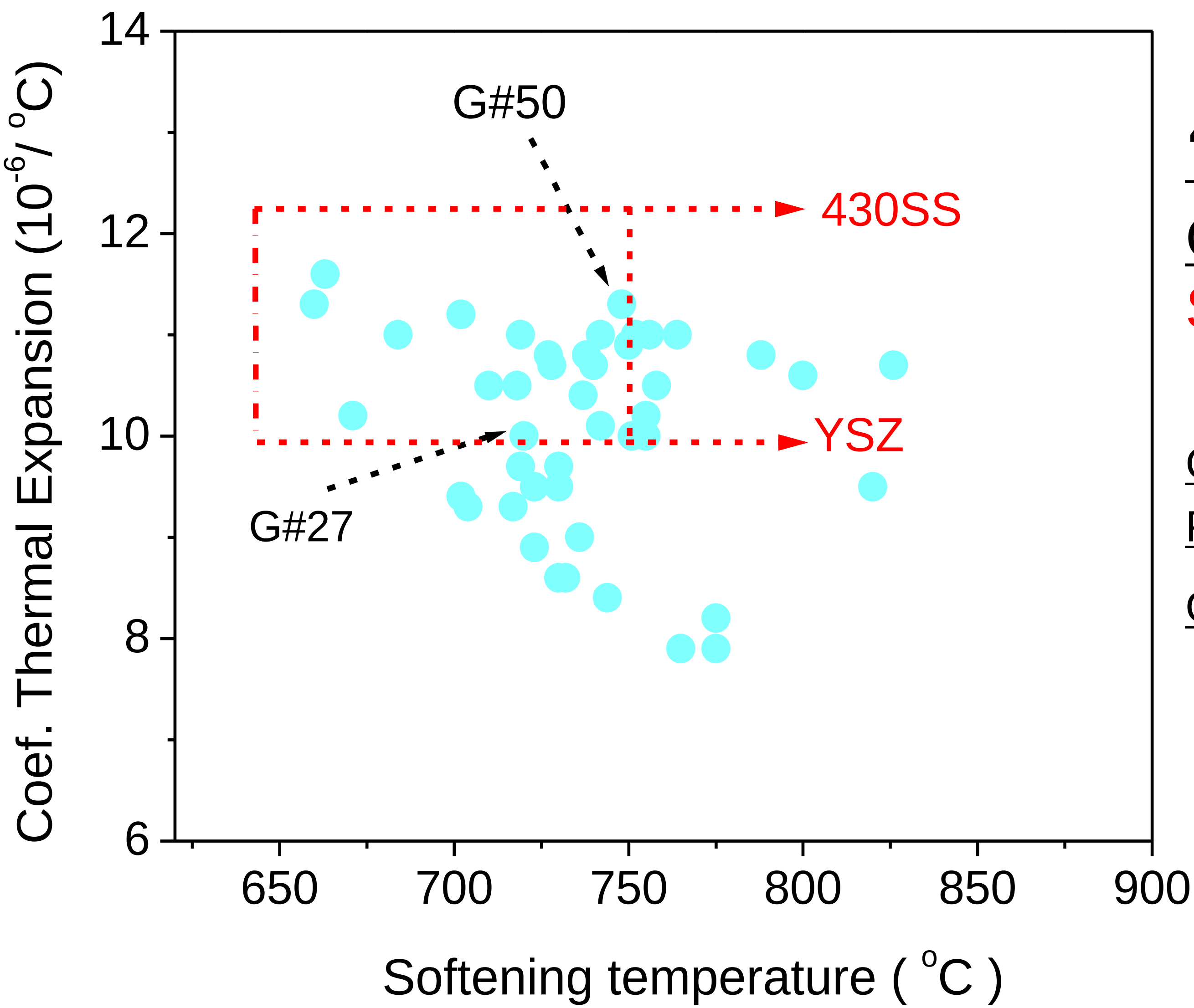


“**Invert Glasses**”: discontinuous silicate anions tied-together through modifying cations.

- Greater CTE’s
- More fragile viscosity behavior
    - ‘shorter’ glasses
- More ‘basic’ reaction chemistries

- Metasilicates (chains): [O]/[Si]~3.0
- Polysilicates (short chains): [O]/[Si]>3.0

- Greater CTEs from polysilicate crystalline phases



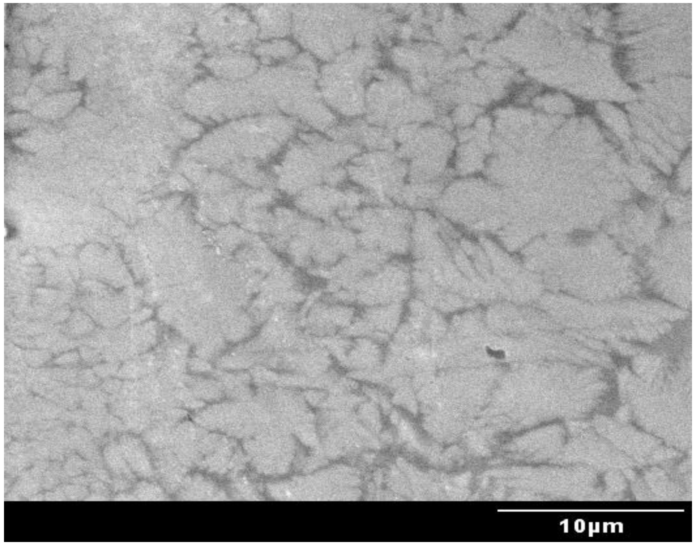
"Invert" silicate: Glasses with SiO_2<45 mole%

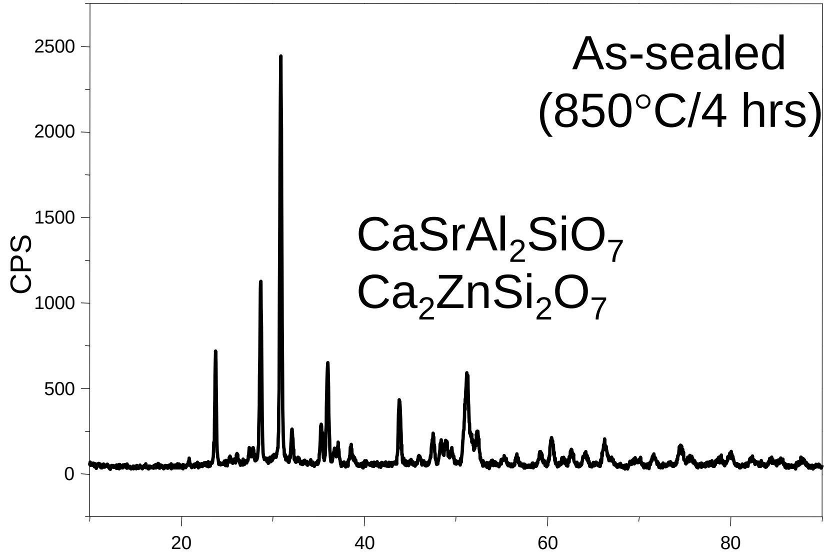
Compositions based on:

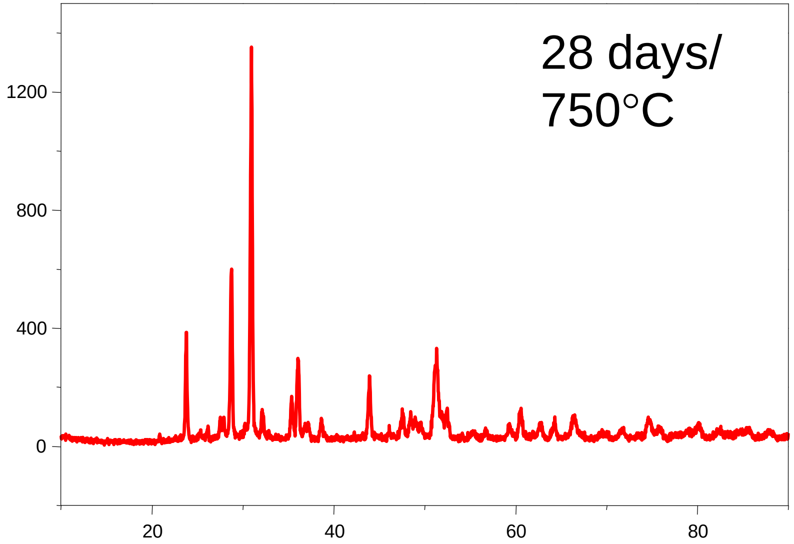
Pyrosilicate and

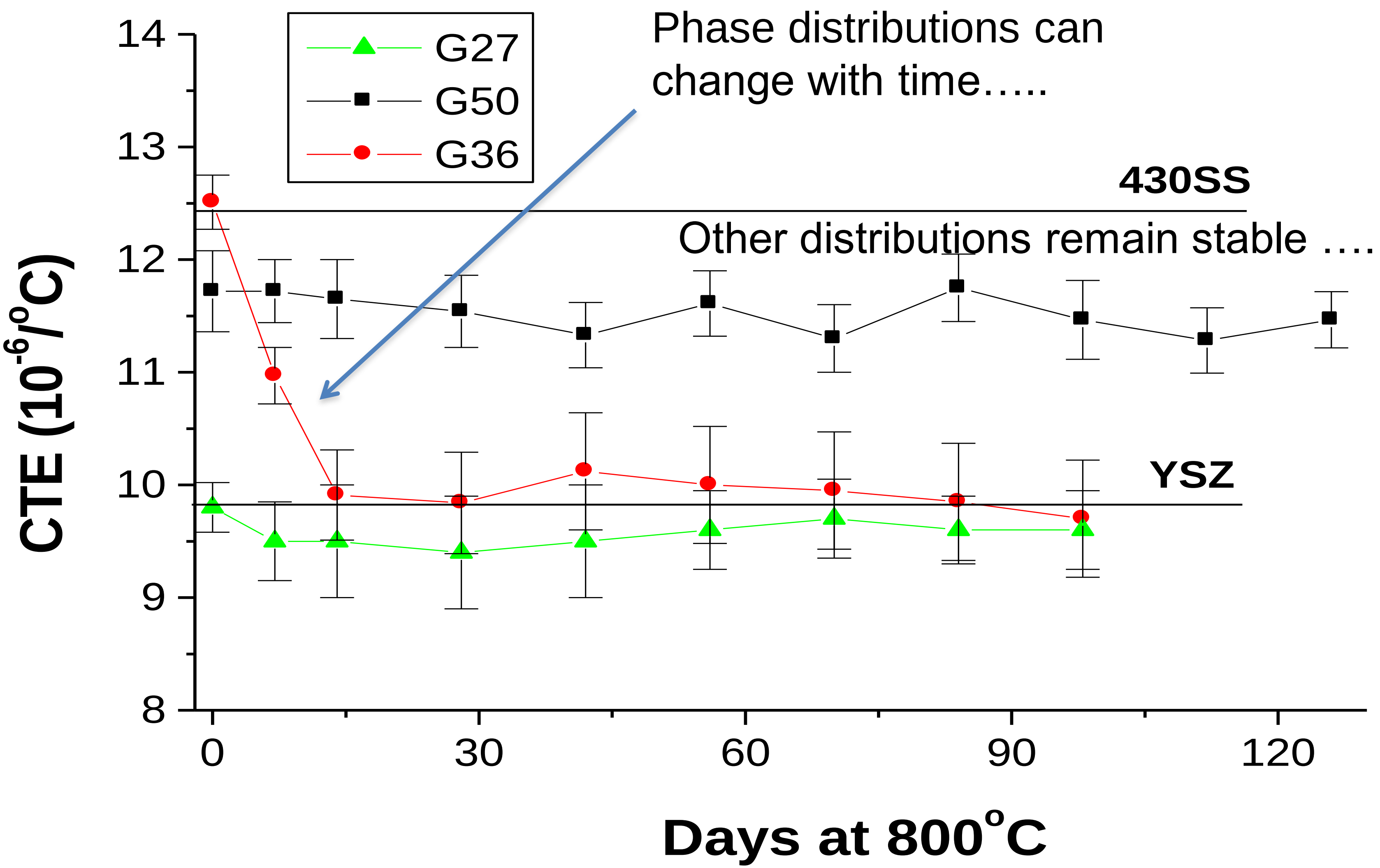
Orthosilicate phases

- **Pyrosilicates**
  - $CaSrAl_2SiO_7$, $Ca_2ZnSi_2O_7$
- **Orthosilicates**
  - Sr_2SiO_4, Zn_2SiO_4
- The crystalline phases appear to be thermally stable.

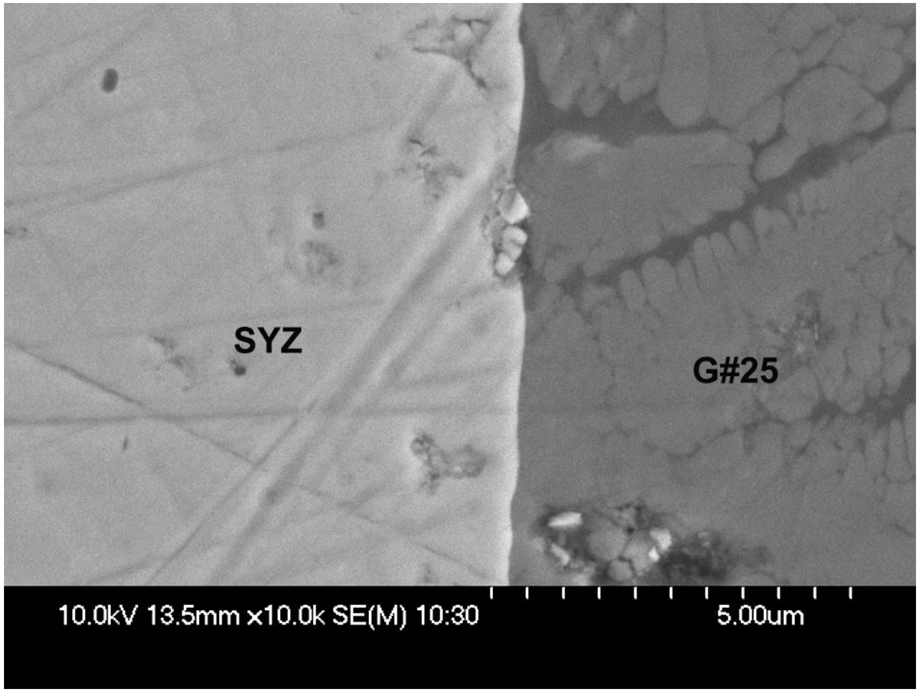


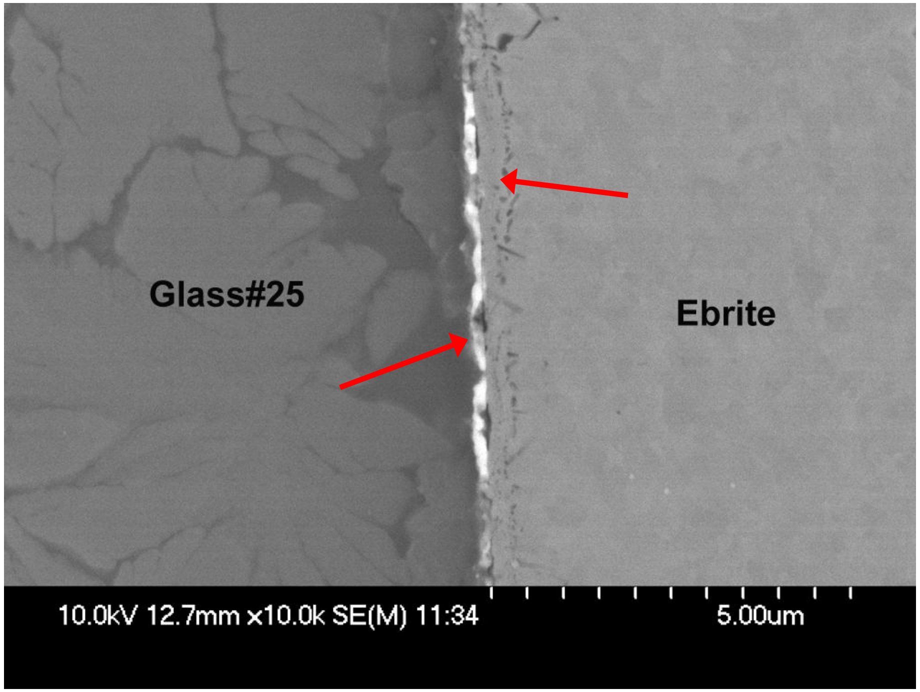





G27
G50
G36
Phase distributions can change with time…..
430SS
Other distributions remain stable …..
YSZ
CTE (10^{-6}/°C)
14
13
12
11
10
9
8
0
30
60
90
120
Days at 800°C

Thermo-mechanically robust seals can be made to SOFC component materials

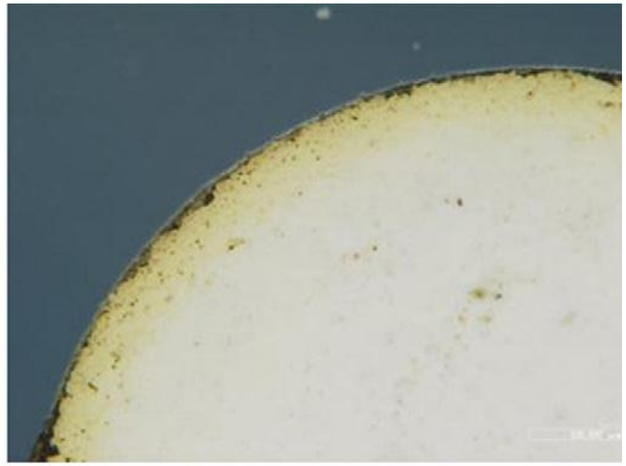




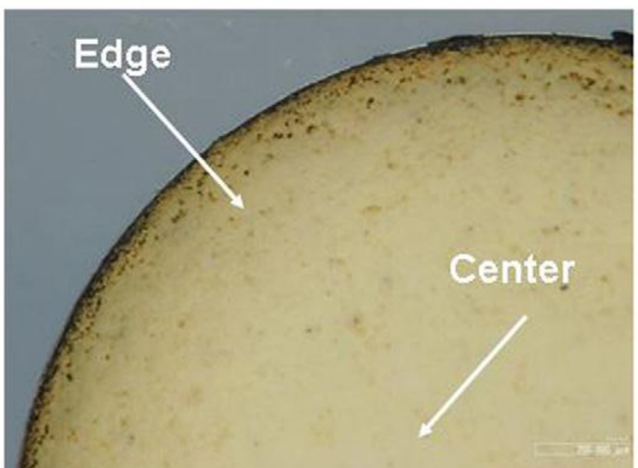
750° C/two weeks in air

One potential problem is deleterious reactions with chromia

As sealed



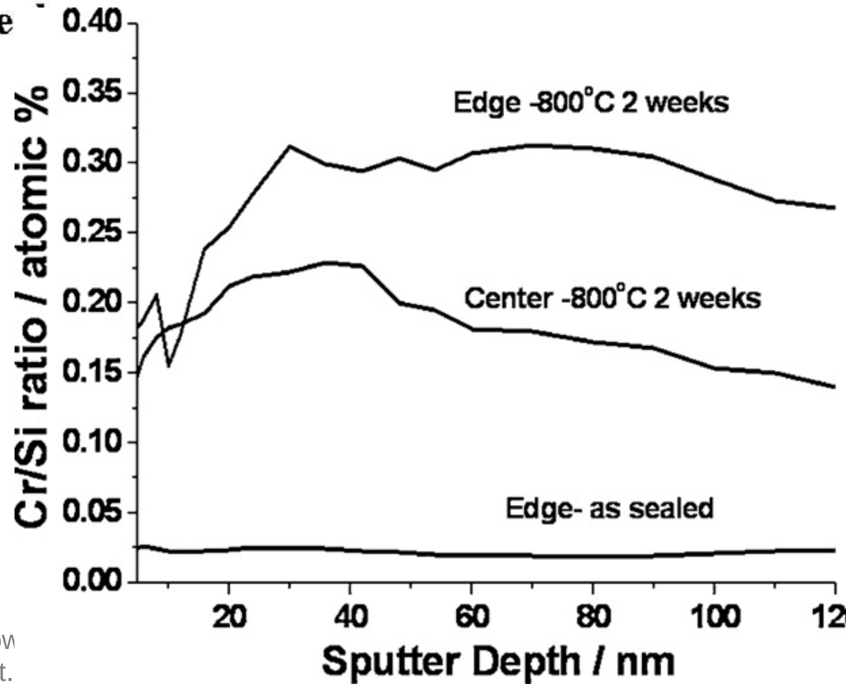
800°C for 1 we



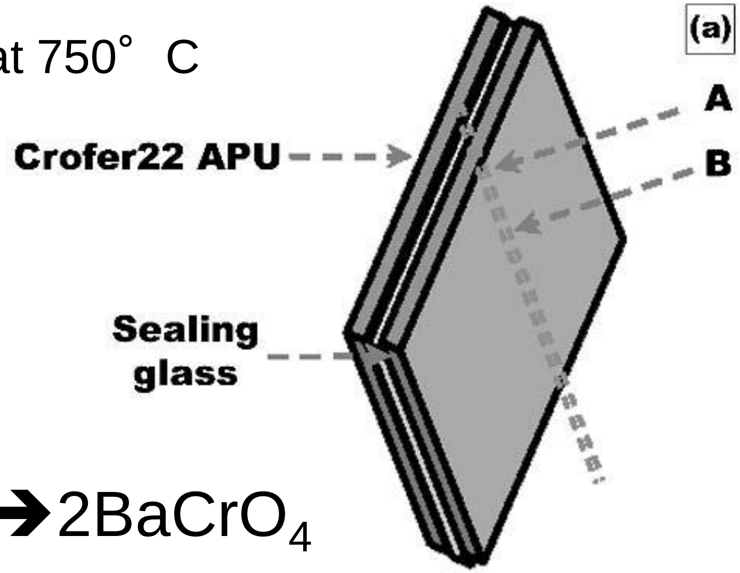
800°C for 2 weeks

CTE mismatches occur at the glass-metal interface:

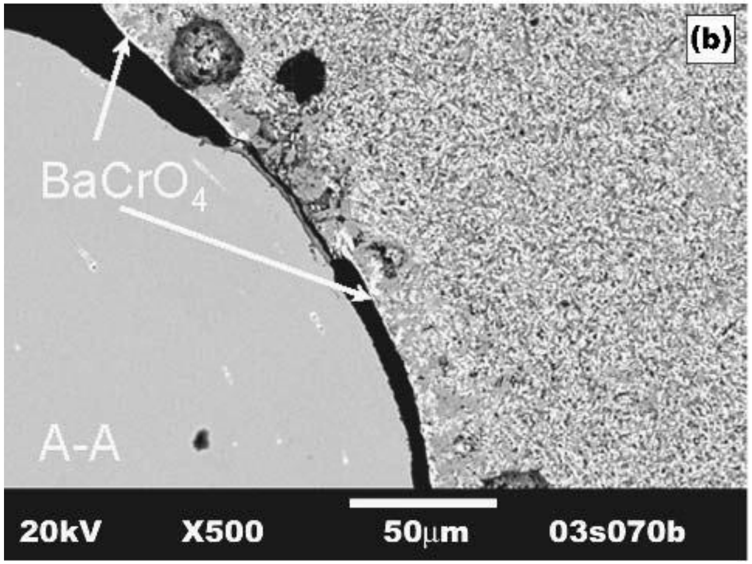
$BaCrO_4$: 18 ppm/K
Steel/Glass: 12ppm/K

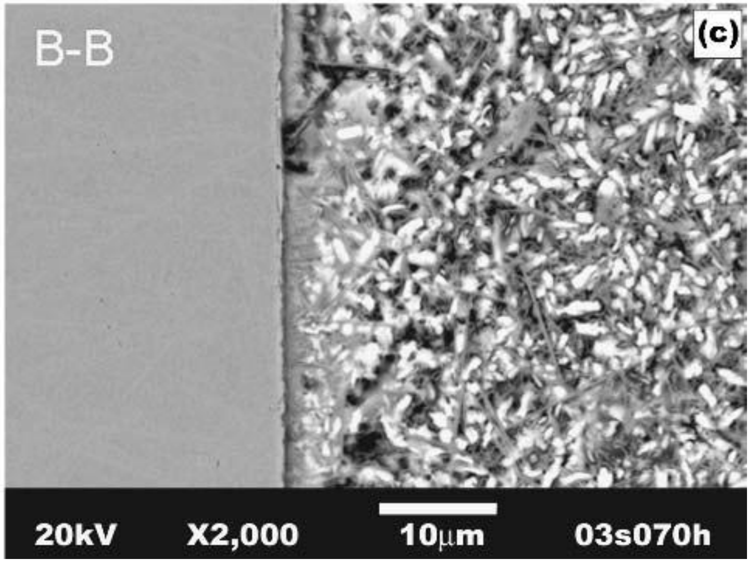


G18/Crofer after 1 week at 750° C



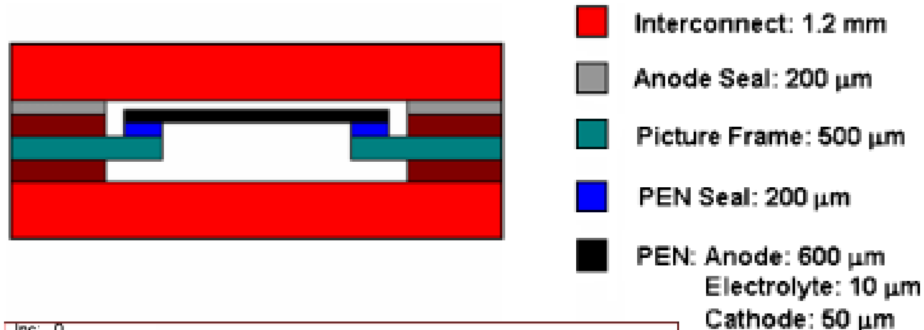
$$2BaO + Cr_2O_3 + \frac{1}{2}O_2 \rightarrow 2BaCrO_4$$

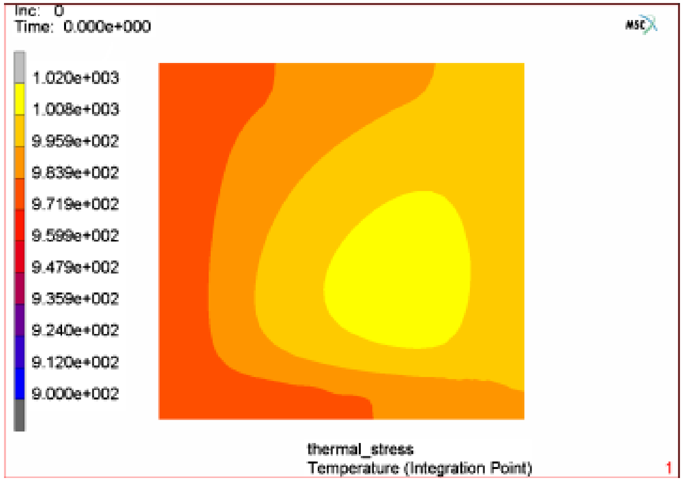


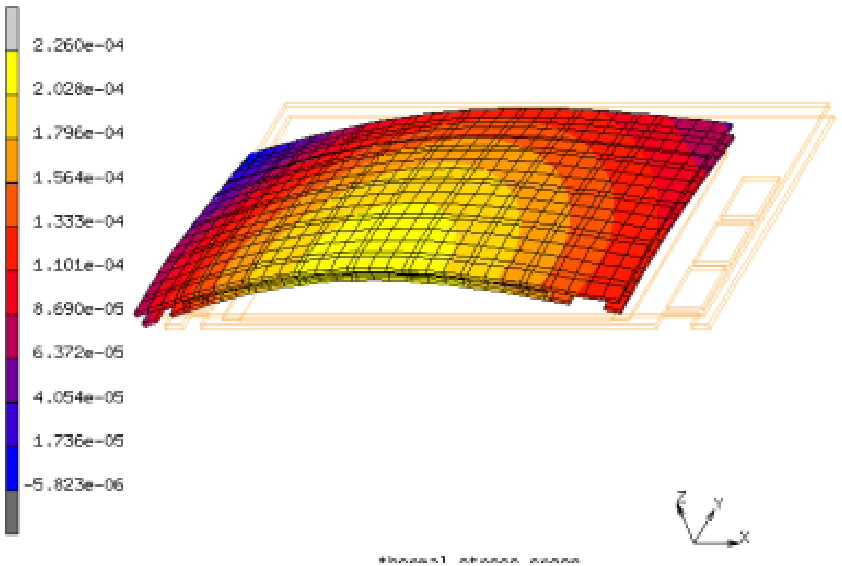


Yang et al., JMEPEG 13, 327 (2004)

A second problem with ‘rigid’ glass-ceramic seals involves the thermal stresses associated with slight CTE mismatches







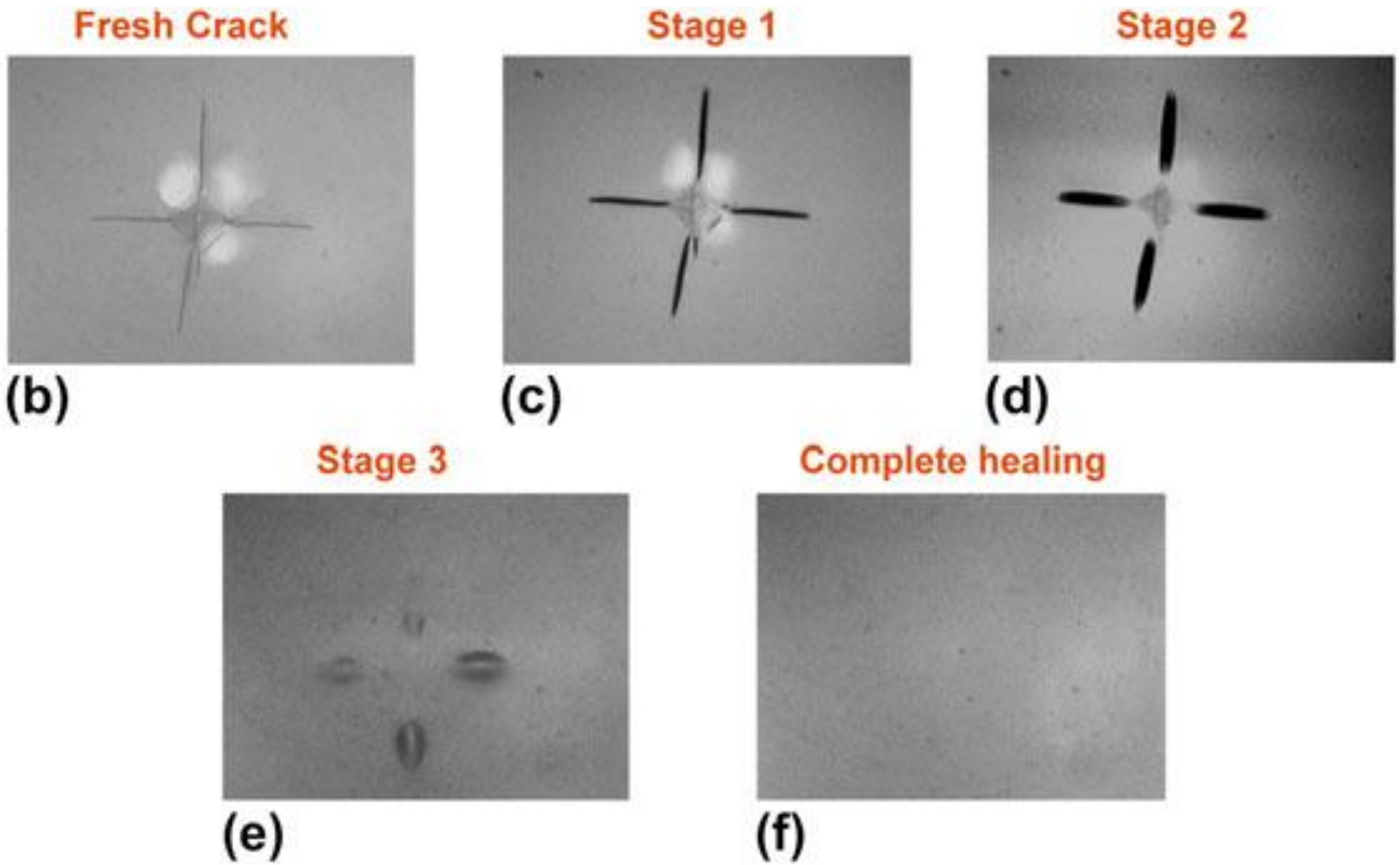
Liu, et al., Int. J. Appl. Cer. Tech., 8[1], 49 (2011)

One solution may be to use a ‘viscous’ seal that will ‘re-heal’ on heating

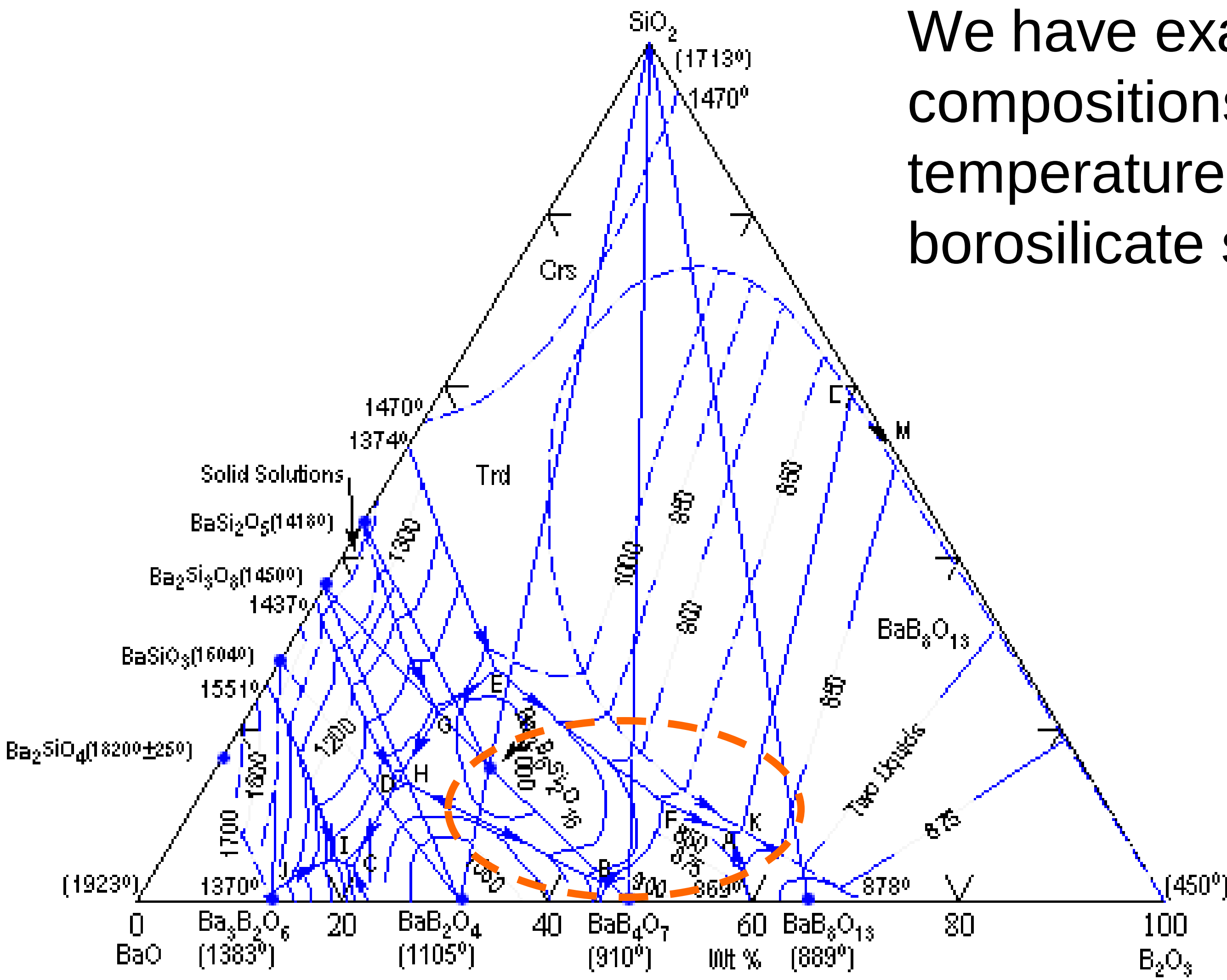
RK Brow
brow@mst.edu

Self-repairable glass seals for solid oxide fuel cells

Raj N. Singh[a)]
School of Materials Science and Engineering, Oklahoma State University, Tulsa, Oklahoma 74106-0700

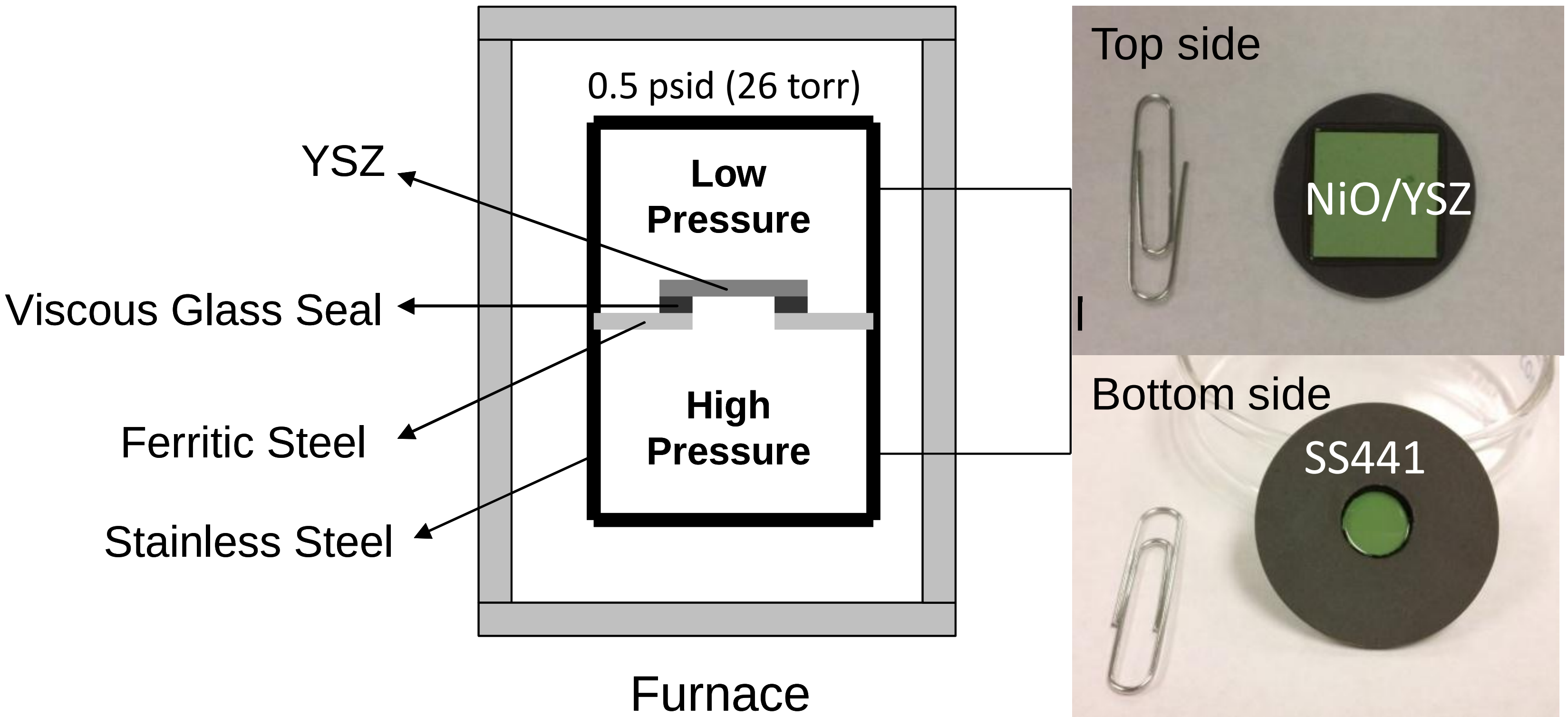


Singh, J. Mater. Res., 27[15] 2055 (2012)



We have examined compositions with low liquidus temperatures in the Ba-borosilicate system

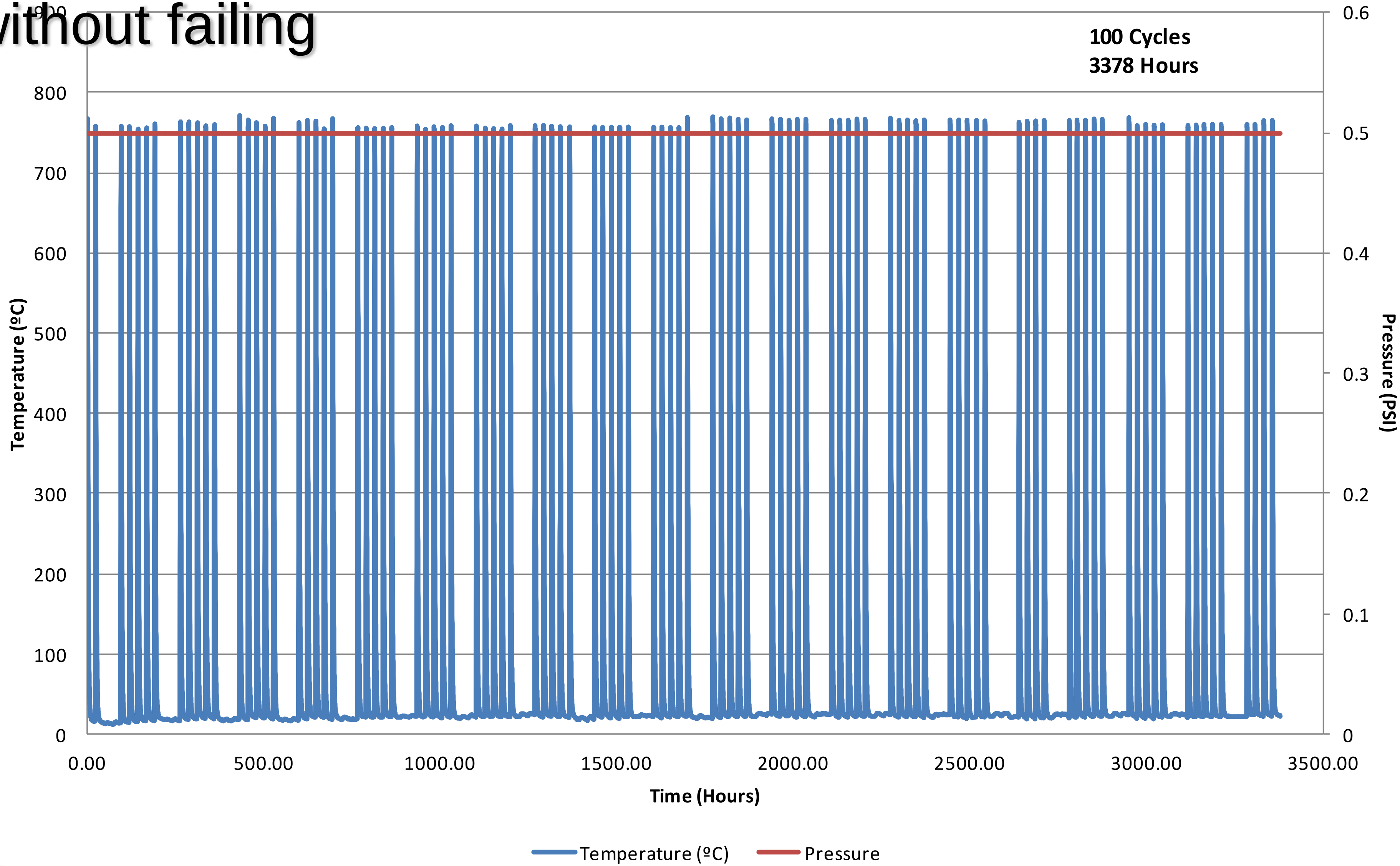
Hermetic Sealing Tests



- Glass pastes were made from powders (-45 µm) mixed with PVB binder and acetone, and used to bond NiO/YSZ bi-layer to aluminized steel (SS441) substrate (materials from PNNL)
- Sandwich seals fired in air at 850° C for 8 hours

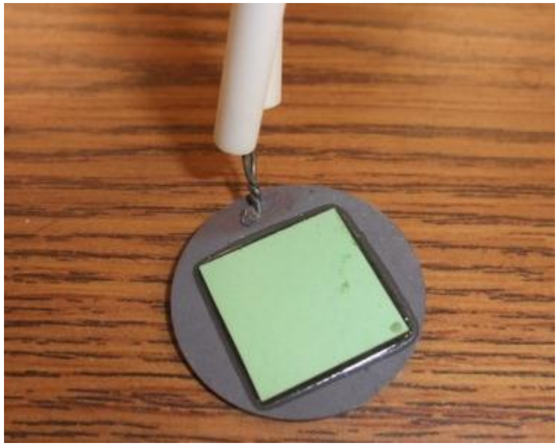
RK Brow
brow@mst.edu

Viscous seals survey >100 thermal cycles from 750° C without failing

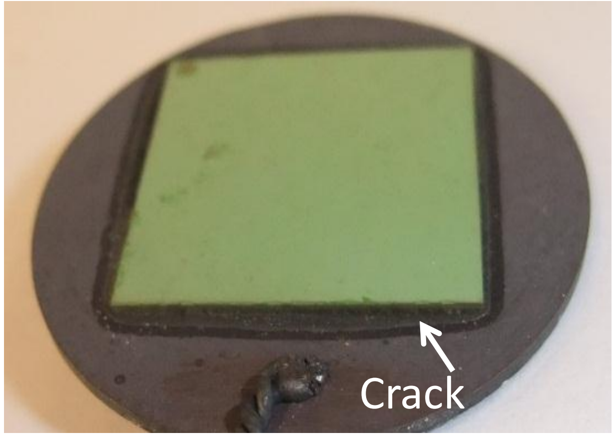


Thermally shocked sample "re-seals" when re-heated

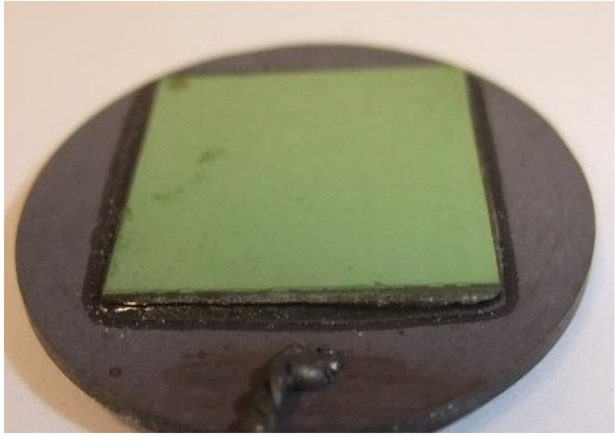
Original hermetic seal



Cracked on quenching (>25° C/s)



Resealed (2 hrs at 725° C)

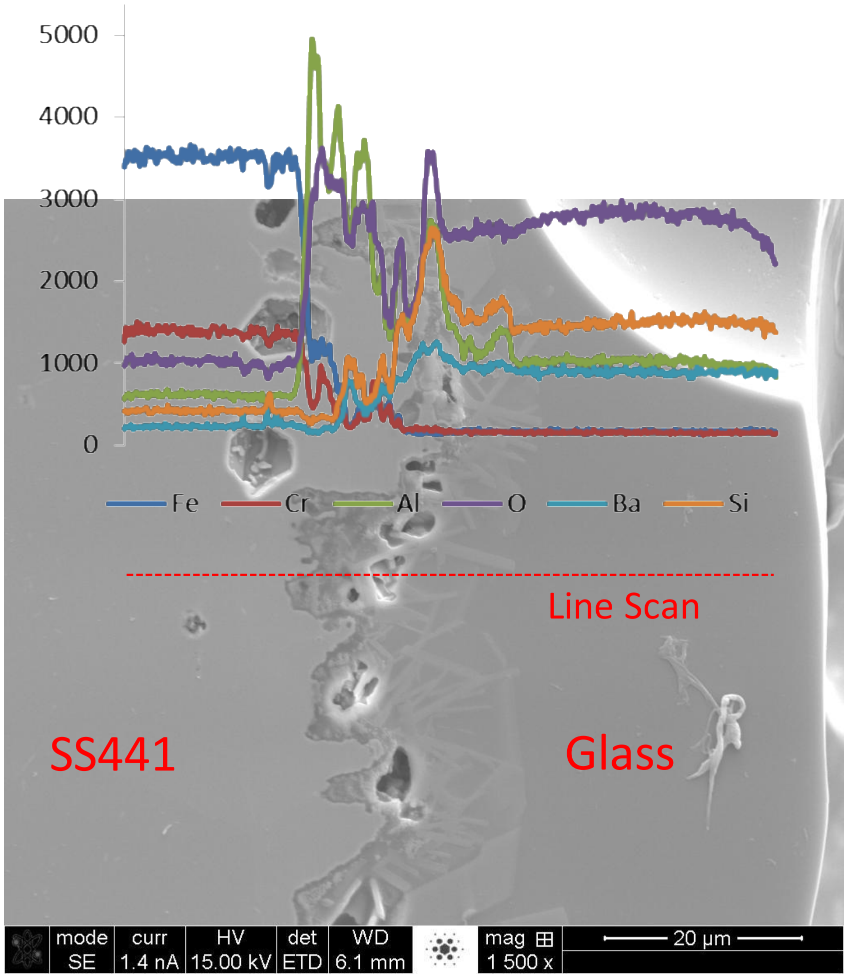


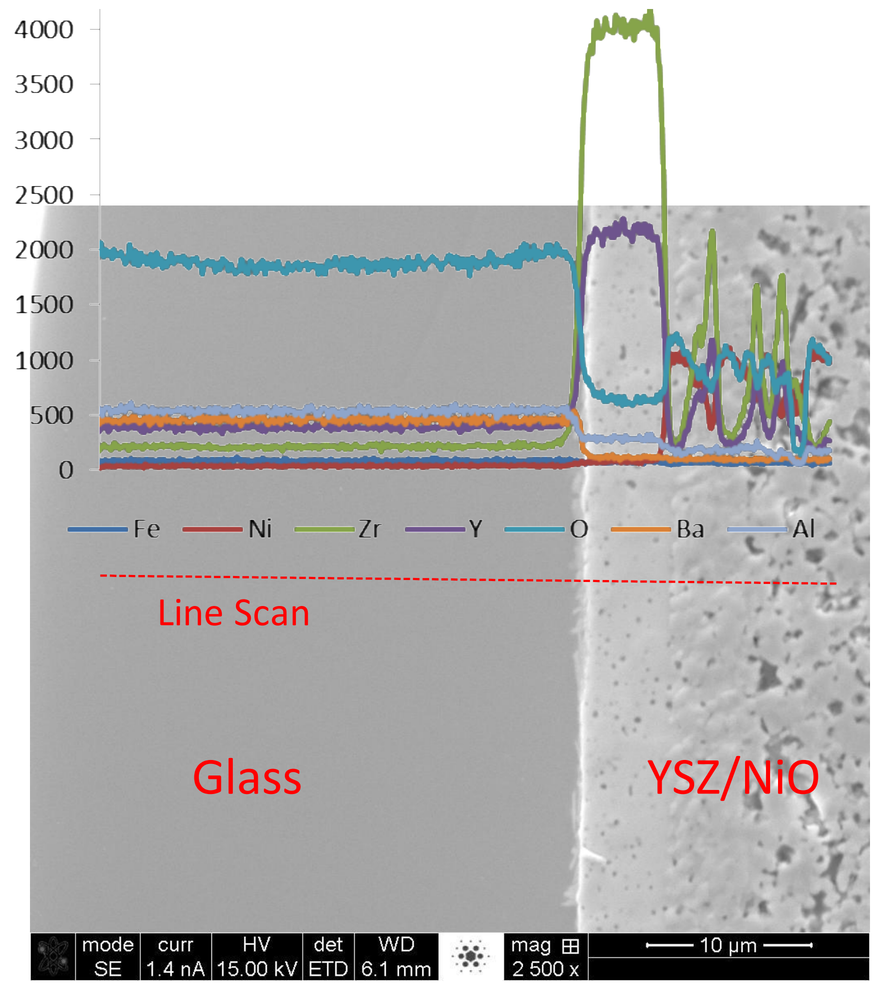
Foaming in soapy water

Samples re-seal in two hours with viscosities of 10^6 Pa-s

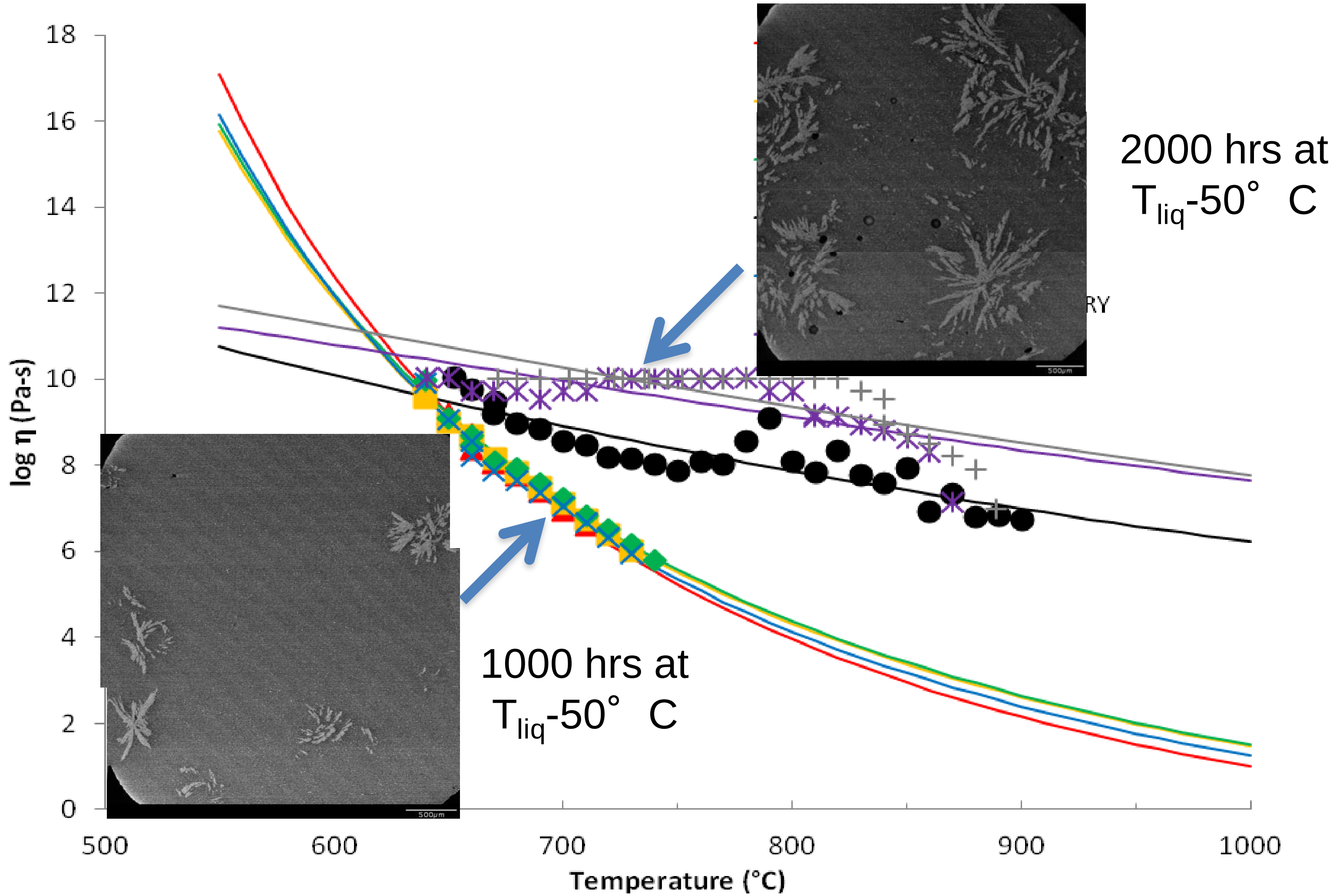
RK Brow
brow@mst.edu

Viscous seals may be more reactive that the glass-ceramics





Long-term crystallization will affect glass viscosity- and so the self-sealing properties



Summary

- As a materials science platform, sealing glasses offer opportunities to explore new compositions and to study glass phenomena
  - Chemically stable non-silicate compositions
  - Crystallization around the liquidus temperature
  - High temperature compatibility with metals

- Glass seals are enabling materials for many technologies
  - Reliable Li-batteries➔biomedical devices
  - Optimization still required for Na/S, Na/$NiCl_2$ and SOFC systems

- The ability to model sealing processes may be the key to ’scaling up’ technologies to useful products
  - Accurate viscoelastic properties
  - Well-controlled manufacturing process parameters
  - Well-understood ‘application’ conditions

Acknowledgments

- Department of Energy/SECA
  - Mo-Sci Corp. (Rolla)- CW Kim
  - Signo Reis, Teng Zhang, Rick Hsu
- National Institutes of Health
  - Laxikanth Peddi, Heather Teitlebaum, Roger Brown
- Sandia National Labs


Grazie!