Development of Brazing Technology for Use in High-Temperature Gas Separation Equipment

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Overview of the Joining Program

- **Vision 21 Technical Roadmap:**

  "Develop coal as a potential source of clean hydrogen fuel for use in fuel cells, turbines and various process applications."

- **To realize this goal, we need efficient, low cost gas separation systems to produce :**
  - **Oxygen from air for combustion (avoids N_2 dilution and NO_x formation)**
  - **Hydrogen from the gasified coal stream (produces higher yield product due to water-gas-shift reaction)**
  - **Carbon dioxide for sequestration**

Overview of the Joining Program

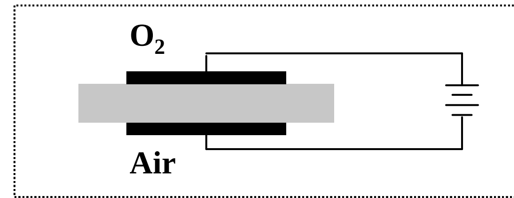
- **The primary enabling materials technologies in manufacturing these gas separation systems:**
  - **Separation membranes (ceramic)**
  - **Gas manifold and support structures (heat resistant metal)**
  - **Membrane-to-support (ceramic to-metal) seals**

Overview of the Joining Program

- O_2 Separation

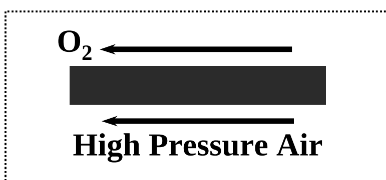
Type	Material
Electrically Driven	YSZ, CeO_2
Pressure Driven	MIEC
Chemical Potential Driven	MIEC

Electrically Driven:



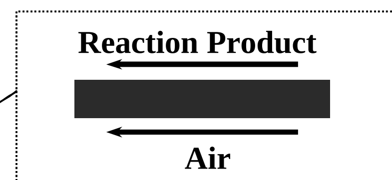
Apps.: Medical O_2
Cutting O_2

Pressure Driven:



Apps.: Tonnage O_2
Co-gen
Syngas with co-gen

Chemical Potential Driven:



Apps.: Syngas
Gas-to-liquid
H_2 production

Direct FE Support

Overview of the Joining Program

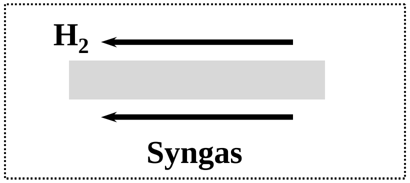
- **H_2 Separation**

Type	Material
Pressure Driven	Porous Al_2O_3
Chemical Potential Driven	$BaCeO_3$

Pressure Driven:

Direct FE Support

Chemical Potential Driven:



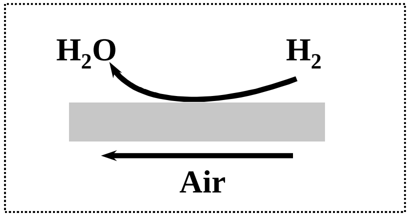
Being considered – wetting studies show feasibility

- **Solid Oxide Fuel Cells**

Material

YSZ

$(La_{0.8}Sr_{0.2})FeO_3$

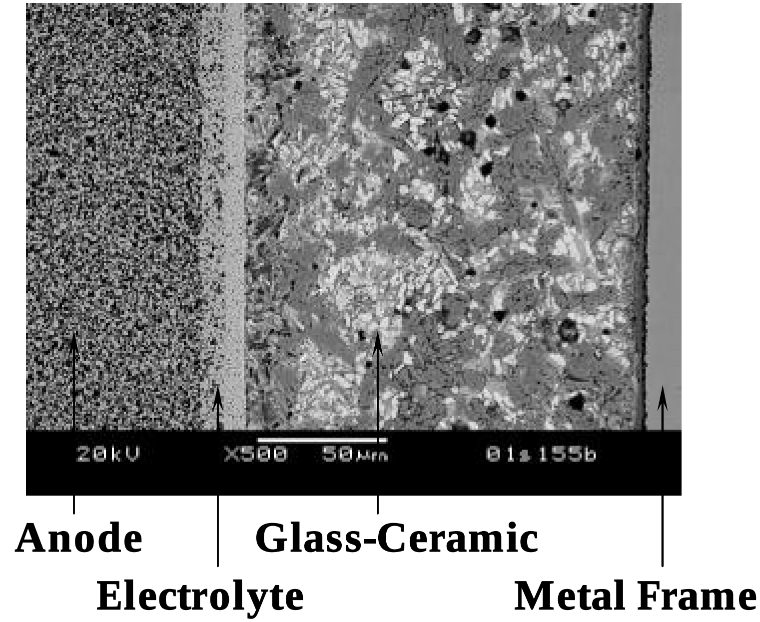


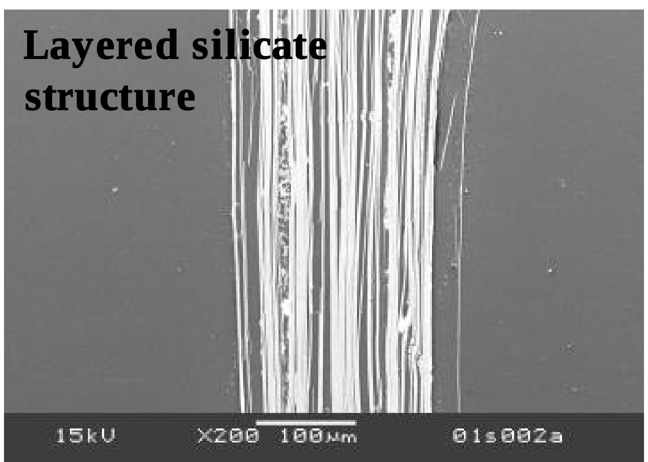
Project Objectives

- Develop joining/sealing technology for high temperature electrochemical devices
- Barriers/Challenges
  - Hermeticity is key
  - Resist degradation at high temperature/extended exposure time
  - CTE mismatch is inherent in joining dissimilar materials
  - Resistance to thermal cycling/thermal shock degradation
  - Retain mechanical robustness in the joint and device
- Options
  - High-temperature glass-ceramics
  - Compressive sealing
  - Brazing
- Scientific Approach
  - Examine the application of a new brazing technology to the various ceramic-metal systems of interest in high-temperature electrochemical devices
  - Understand the materials and processing variables that are key to obtaining high integrity, long-lasting seals

Current Status of Sealing Technology

- **Glass-Ceramic (BAS-based)**
  - Hermetic
  - Good stability in air and H_2 environments
  - Good wetting on stainless steel and ceramics such as Al_2O_3 and YSZ
  - Poor thermal shock characteristics
  - Long-term CTE not stable – problems with thermal cycling





- **Compressive (Mica or Metal)**
  - CTE matching not required
  - Good stability in air and H_2 environments
  - Excessive leak rate even under high compression
  - Load frame required

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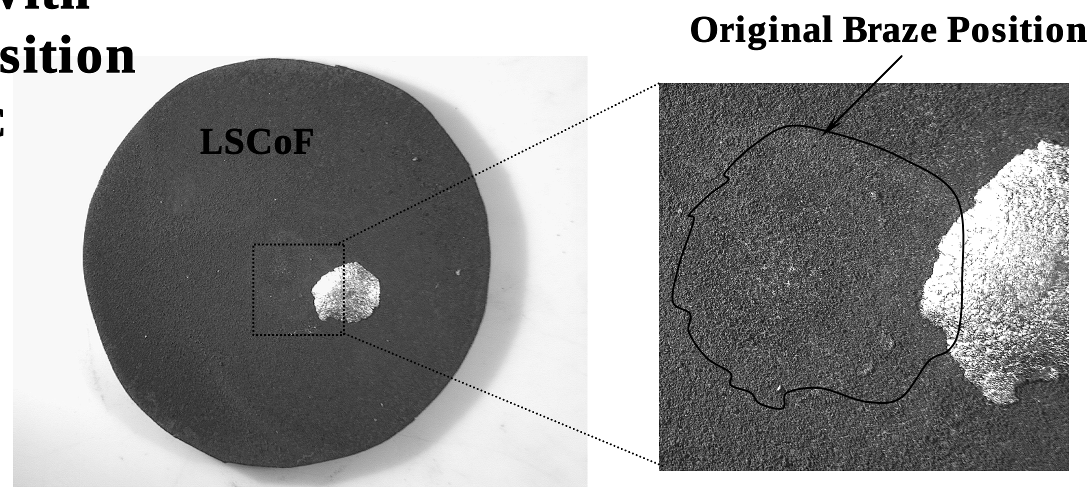
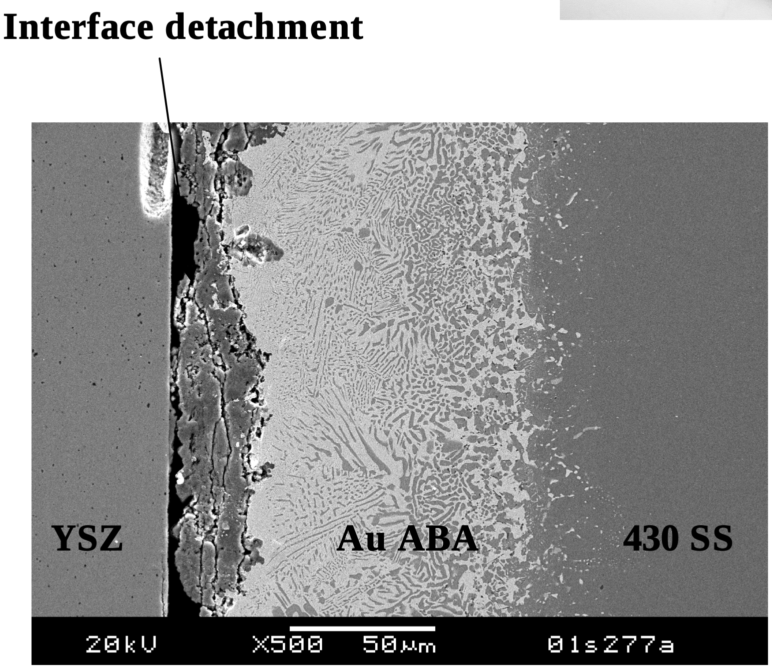
Why Traditional Metal-Ceramic Brazing is not Feasible

- **Potential problems with membrane decomposition**
  - T_{soak}: 1000°C – 1100°C
  - t_{soak}: 15 – 30min
  - P_{O_2}: 10^{-6} atm





- **Problems with braze oxidation**
  - T_{oxid} = 700°C
  - t_{oxid} = 50hrs
  - P_{O_2}: 0.2 atm

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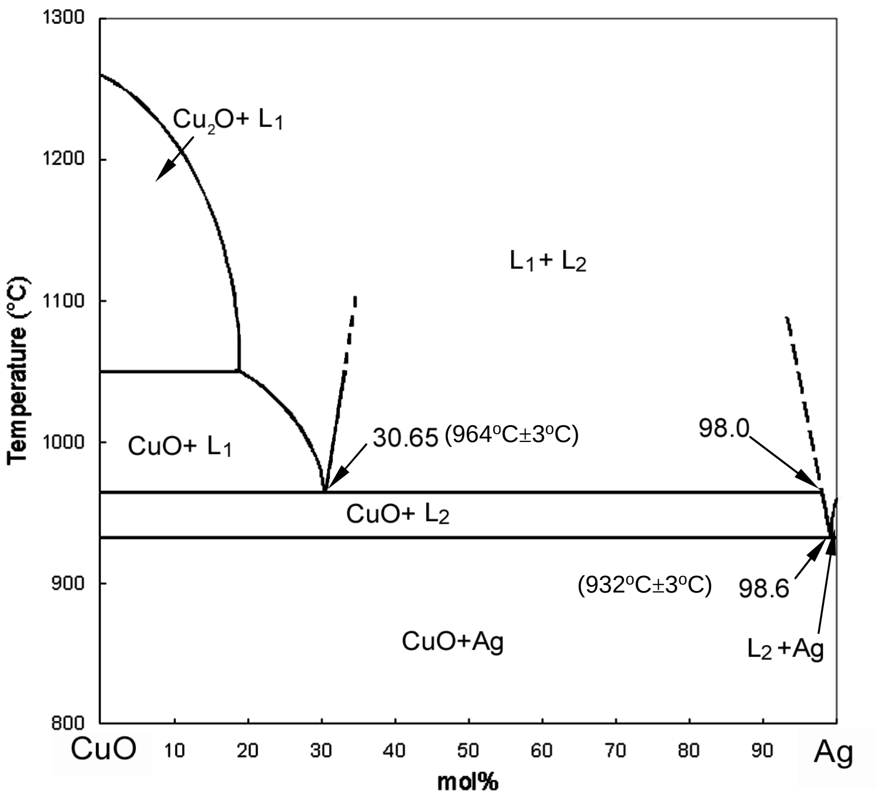
New joining Technique: Reactive Air Brazing

- **Concept: reactive/wetting compound dissolved in a noble metal solvent**
  - **Compound can react with or wet the MIEC and/or metal oxide scale**
  - **Examples: Ag-CuO, Ag-TeO_3, and Pt-Nb_2O_5**
  - **Noble metal filler offers a compliant medium**

- **Joining in air**
  - **Simplifies processing**
  - **More cost effective**
  - **Joint should be oxidation resistant**

New joining Technique: Reactive Air Brazing

The CuO-Ag System



Shao et al, *J. Am. Ceram. Soc*. [1993] 2663

- The CuO-Ag system displays a monotectic point and a eutectic point)
- CuO known to react with Al_2O_3
  - Can form $CuAlO_2$ ~900 – 1000°C
  - CuO-Ag melts wet Al_2O_3 (Meier et al, *J. Mat. Sci.* [1995] 4781)
  - Cu-Ag melts wet YSZ (Hao et al, *J. Am. Cer. Soc.* [1995] 2157)
- Al_2O_3 scale forming steels - top candidates for balance of plant in electrochemical devices

Experimental Methodology

- **Wetting Studies**
  - Wetting angle measured as a function of braze and substrate composition, joining temperature, and time at temperature
  - Braze/substrate interfaces evaluated by SEM and EDX
- **Adhesion and Joint Strength**
  - Joint strength/adhesion measured by a number of techniques, including: 4-pt bend, tension, torsion, rupture, and peel testing
  - Measured as a function of braze and substrate composition, joining temperature, and time at temperature
- **Exposure Testing**
  - Joints are aged at expected operating temperature in the appropriate atmosphere(s): air, wet H_2, or dual atmosphere
  - Joint strength measured as a function of exposure
- **Thermal Cycling and Thermal Shock**
  - Joints are cycled between room and operating temperature. Testing can be heating rate dependent
- **Other Testing**
  - Electrical resistivity measurements
  - Electrochemical stability testing

Oxygen Separation

Wetting Studies

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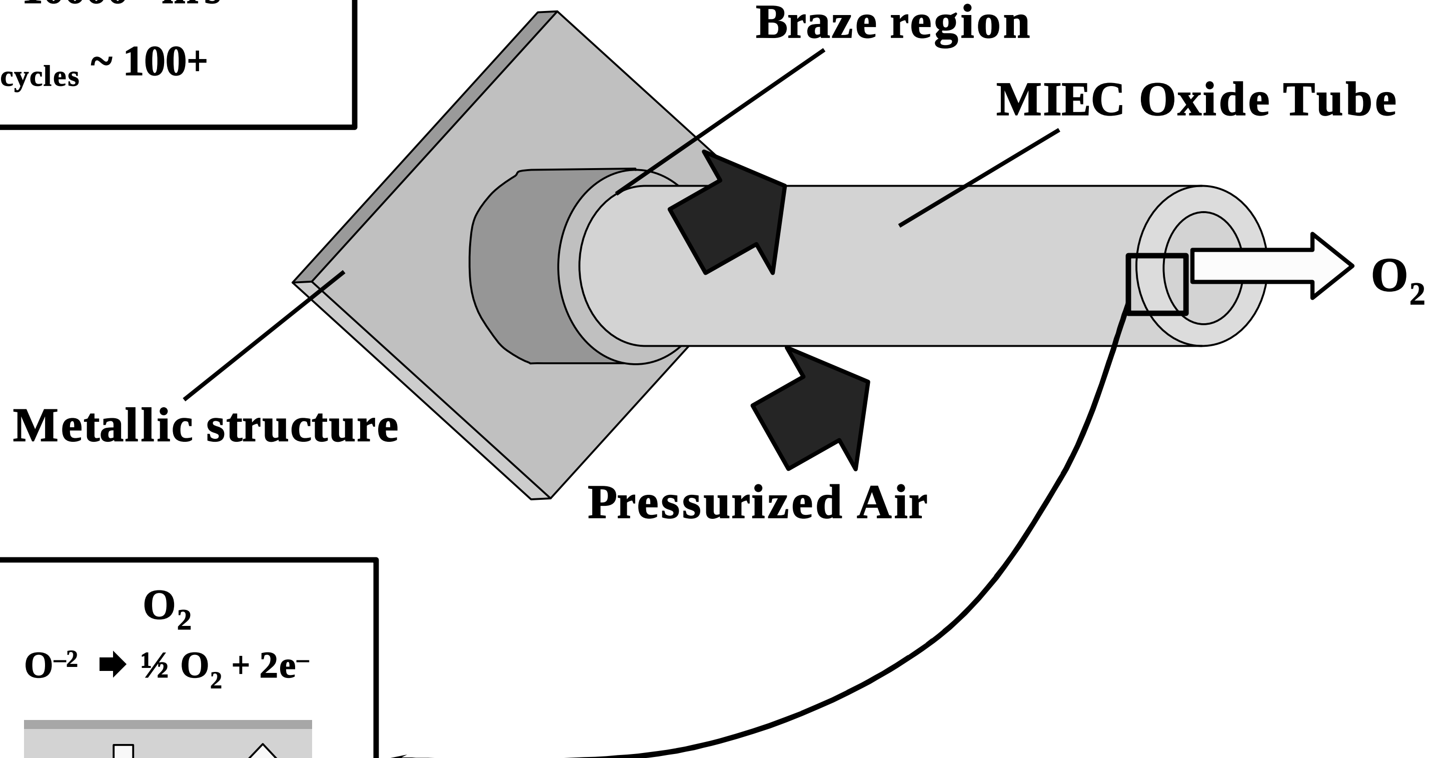
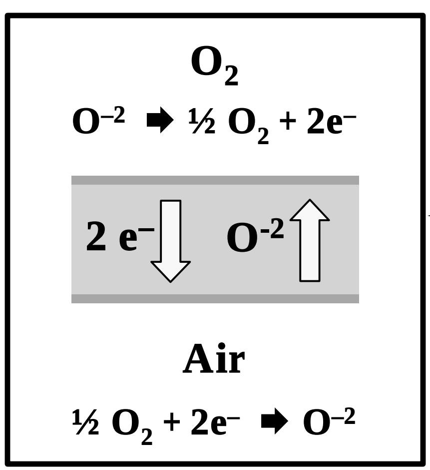
Application: Solid State Oxygen Separation Devices

- T_{oper} = 600 - 750°C
- t ~ 10000+ hrs
- N_{cycles} ~ 100+





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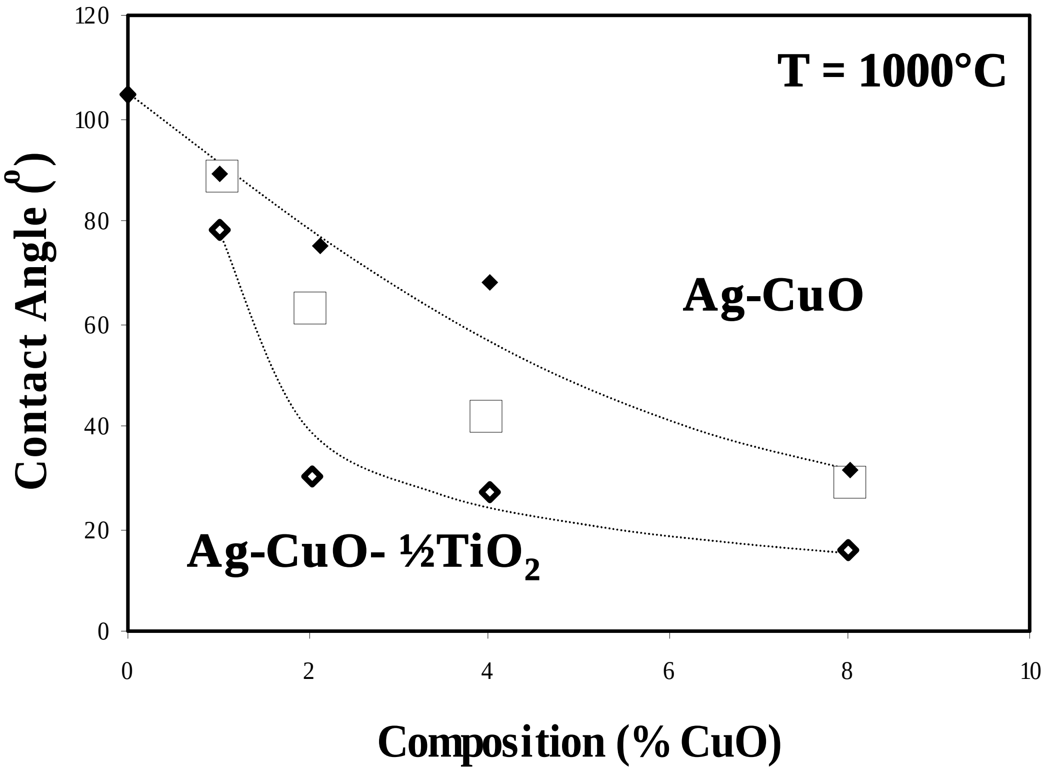
Wetting of $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ (LSCoF) by Ag-CuO and Ag-CuO-TiO_2

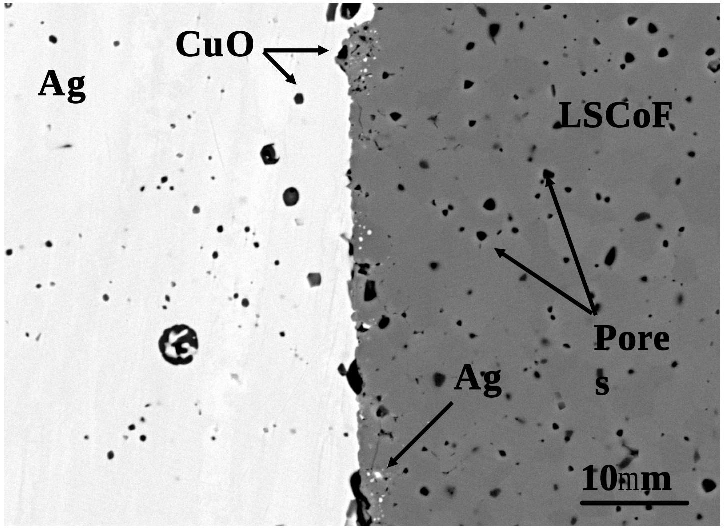
- **Wetting improves with increased CuO content.**
- **The improvement is accentuated by the addition of TiO_2.**



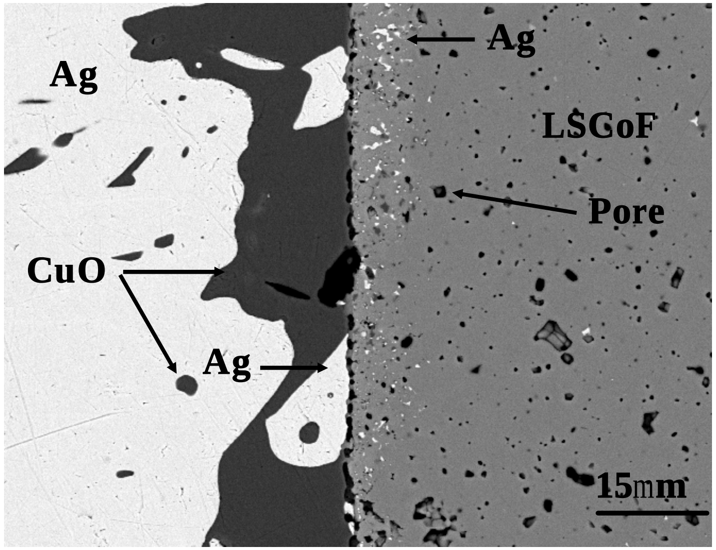
Wetting of LSCoF by Ag-CuO: Microstructures

- **Low CuO content: discrete droplets of CuO precipitate onto the surface of the LSCoF**
  - No reaction between CuO and LSCoF observed
  - Ag infiltrates micron scale porosity within the LSCoF

1 w/oCuO



8 w/oCuO



- **High CuO content:**
  - CuO forms a continuous layer on the faying surface
  - More Ag infiltration apparent

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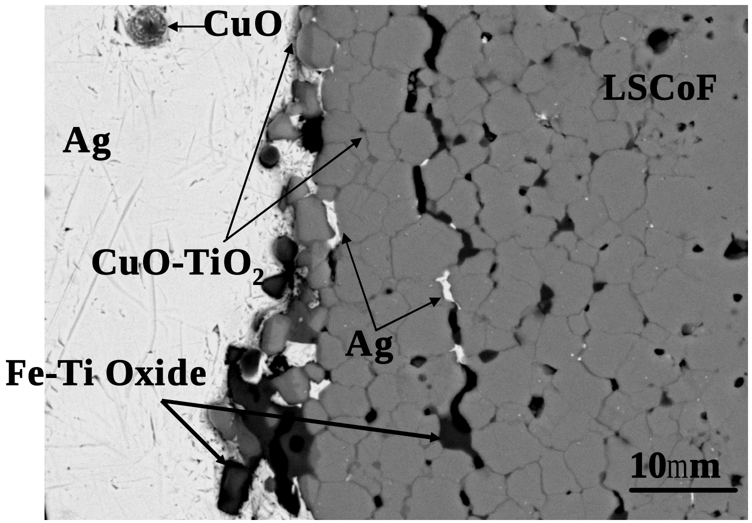
Wetting of LSCoF by Ag-CuO-TiO_2 : Microstructures

- **A reaction zone forms on the LSCoF faying surface**
  - **Reaction occurs along LSCoF grain boundaries**
  - **Formation of an obvious iron-titanium oxide phase**

2 w/oCuO - ½w/o Ti



- **Grain boundary reaction can be mitigated by reducing TiO_2 content**
  - **Study underway to examine the effect of TiO_2 content on wetting, adhesion, and joint strength**

Hydrogen Separation

Wetting Studies

Exposure Testing

Joint Strength Testing

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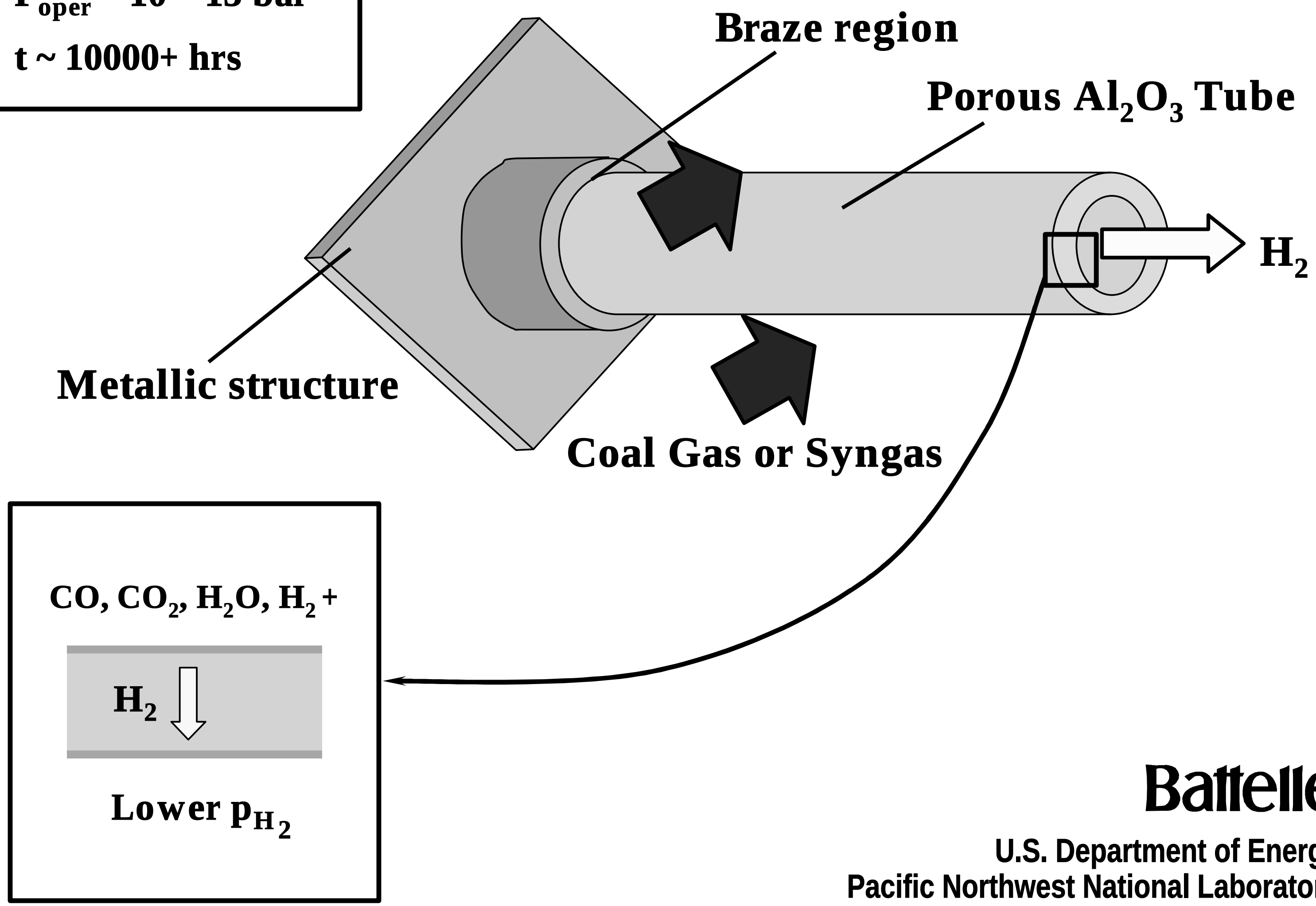
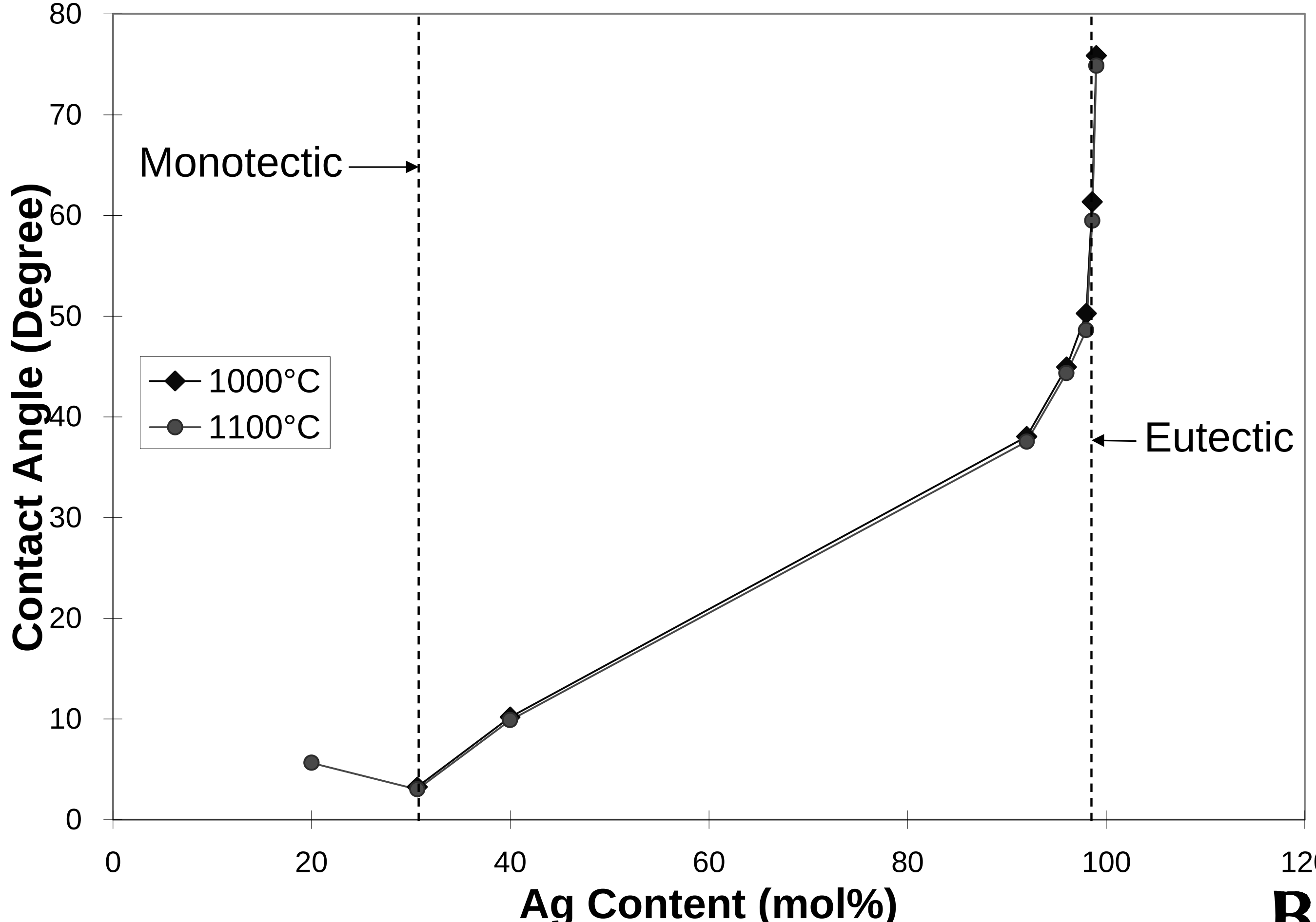
Application: Hydrogen Separation Device

- T_{oper} = 650 - 700°C
- P_{oper} = 10 – 15 bar
- t ~ 10000+ hrs



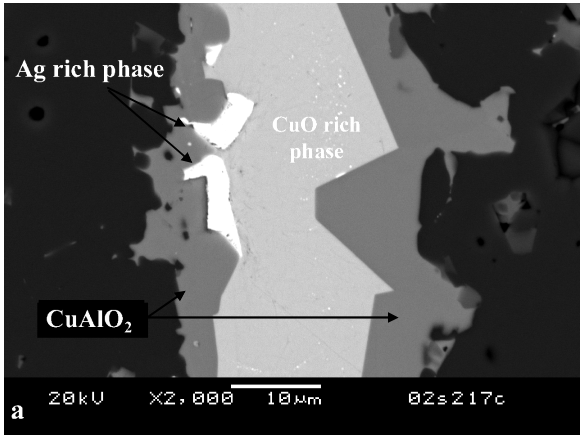
Wetting of Al_2O_3 by Ag-CuO

Contact angle is minimized at the monotectic composition:

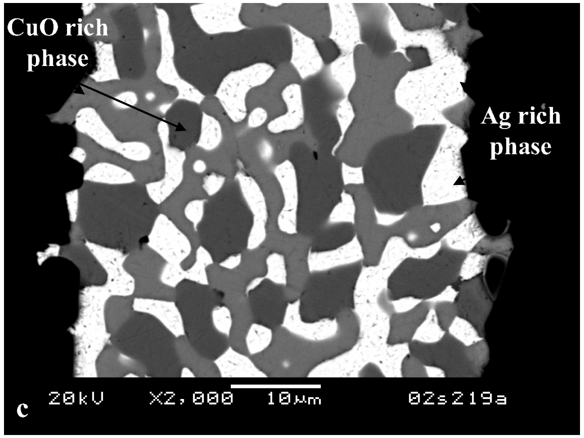


Microstructural Analysis of RAB Al_2O_3 in As-Joined Condition

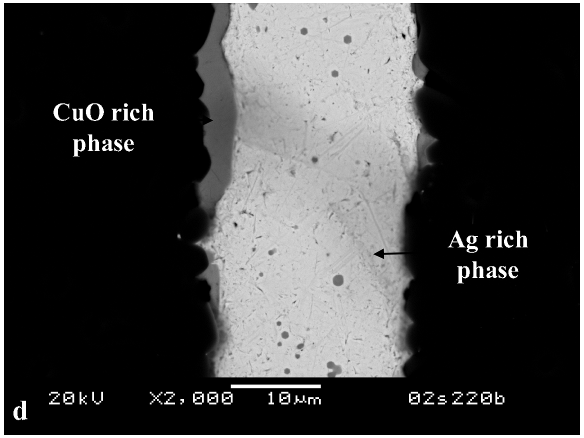
CA8020 (joined at 1100ºC)



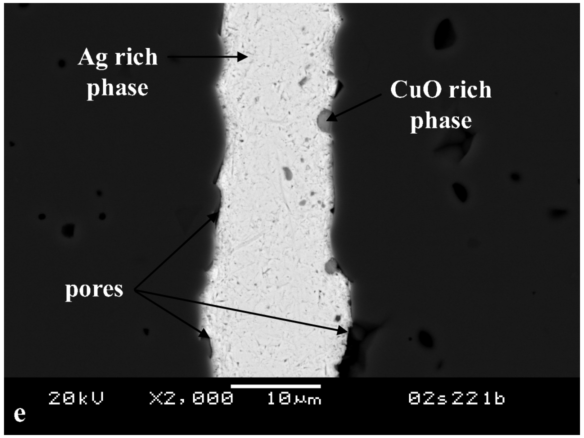
CA6931 (joined at 1000ºC)



CA7030 (joined at 1000ºC)



CA0199 (joined at 1000ºC)



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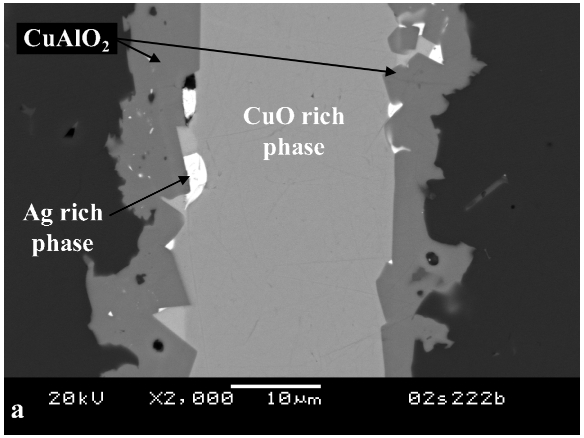
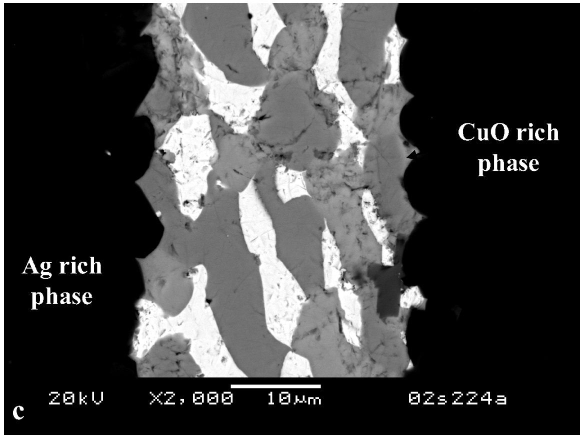
Microstructural Analysis of RAB Al_2O_3 in As-Aged Condition (500hrs, 800°C H_2)

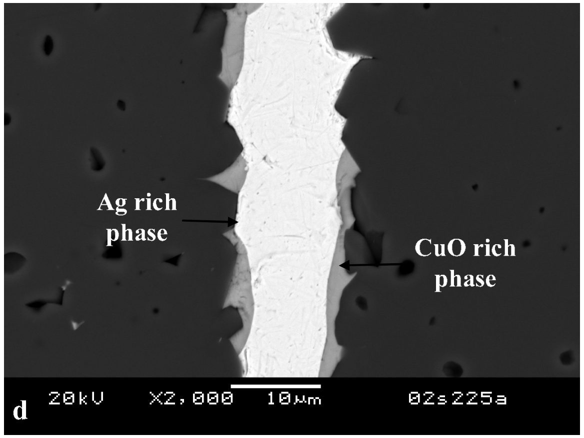
CA8020 (joined at 1100ºC)



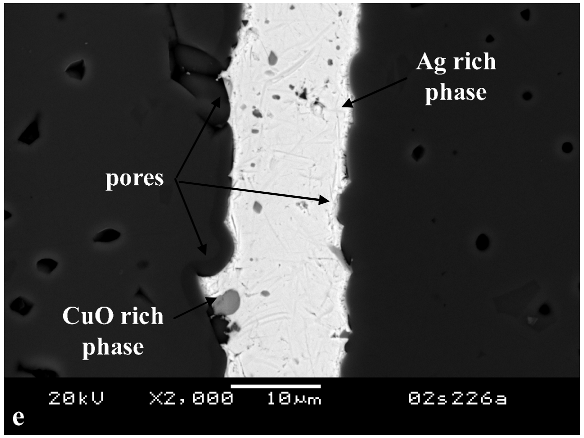
CA6931 (joined at 1000ºC)



CA7030 (joined at 1000ºC)



CA0199 (joined at 1000ºC)



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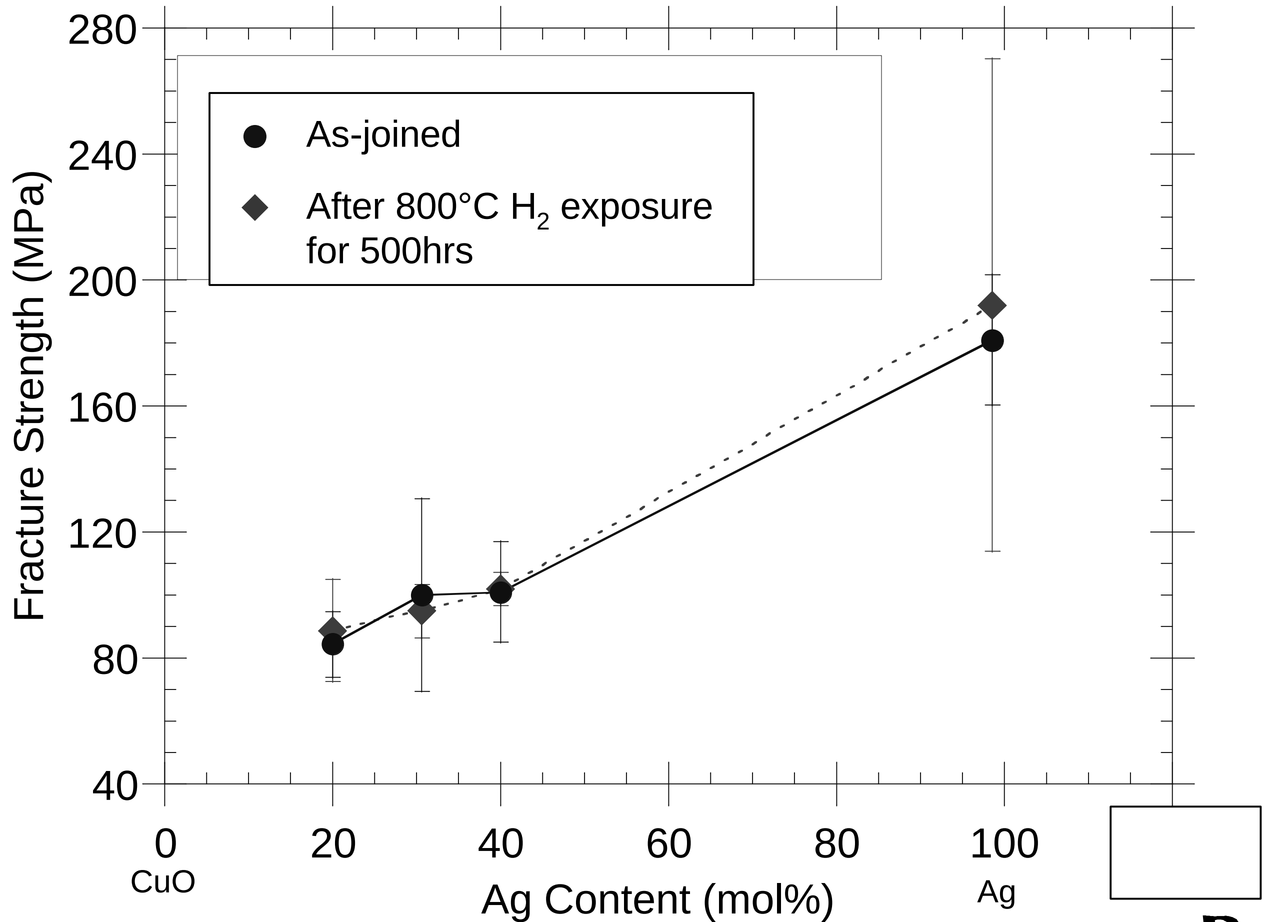
Four-Point Bend Strength Testing of Al_2O_3/Ag-CuO/Al_2O_3 Joints

Fracture strength increases with lower CuO content:



Fuel Cells

Joint Strength Testing

Thermal Shock/Cycle Testing

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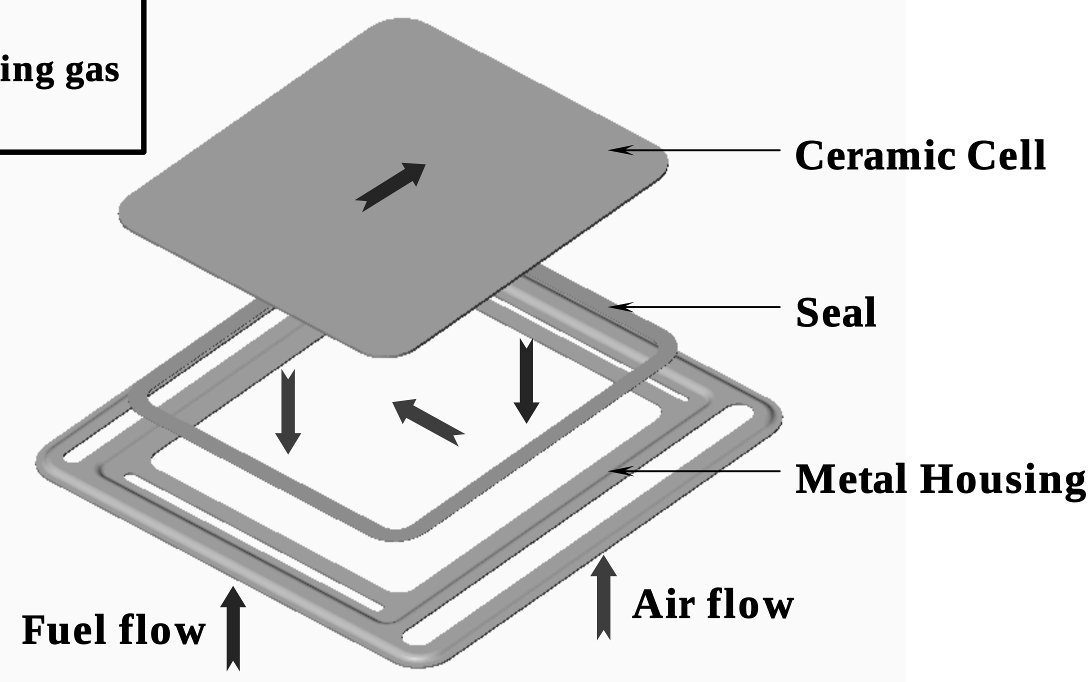
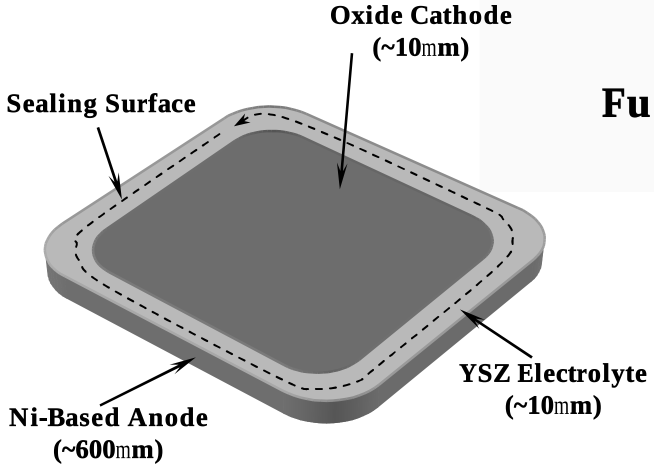
Application: Solid Oxide Fuel Cell

Typical Operating Conditions:

- $T = 750°C$
- $t_{(at\ 750°C)} \sim 5000+$ hrs
- Exposed to air and reducing gas simultaneously





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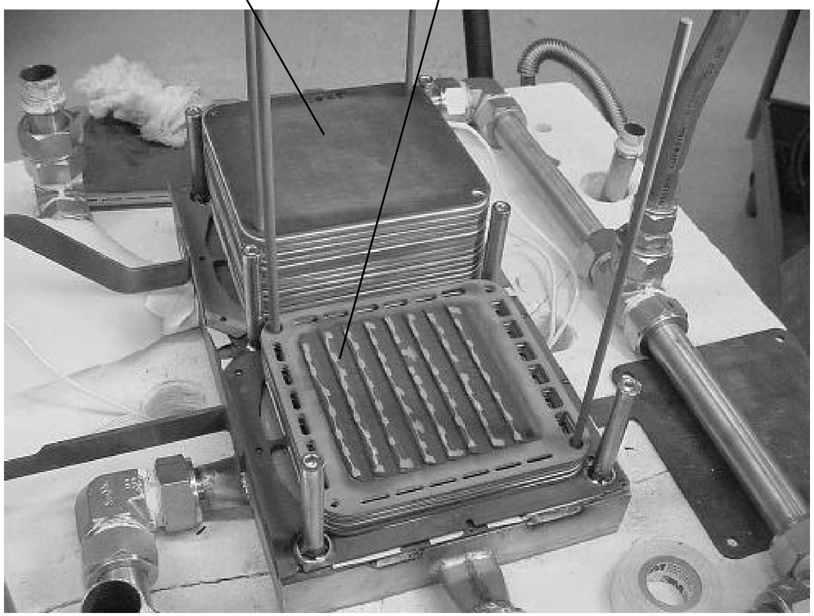
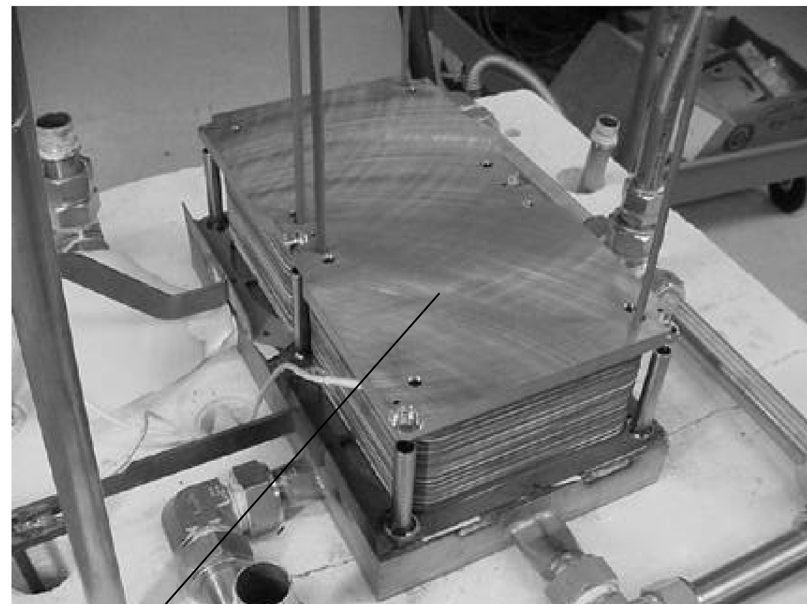
SOFC Stack Manufacture

Stack

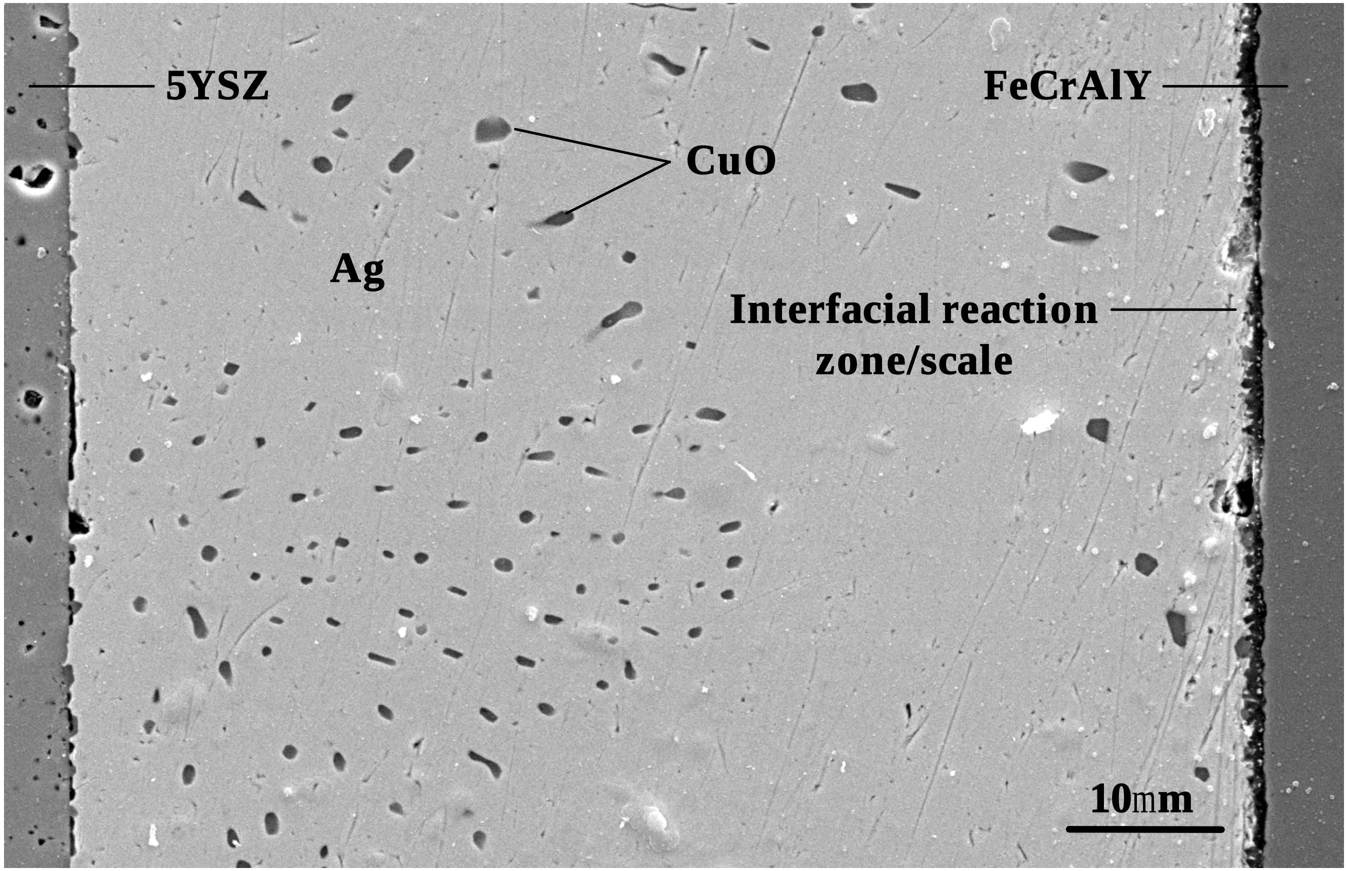
PEN – sealed to SS window frame using Ag-CuO



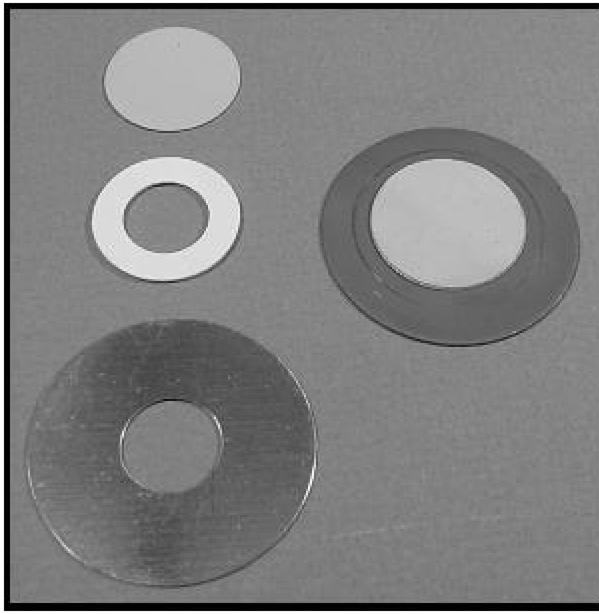


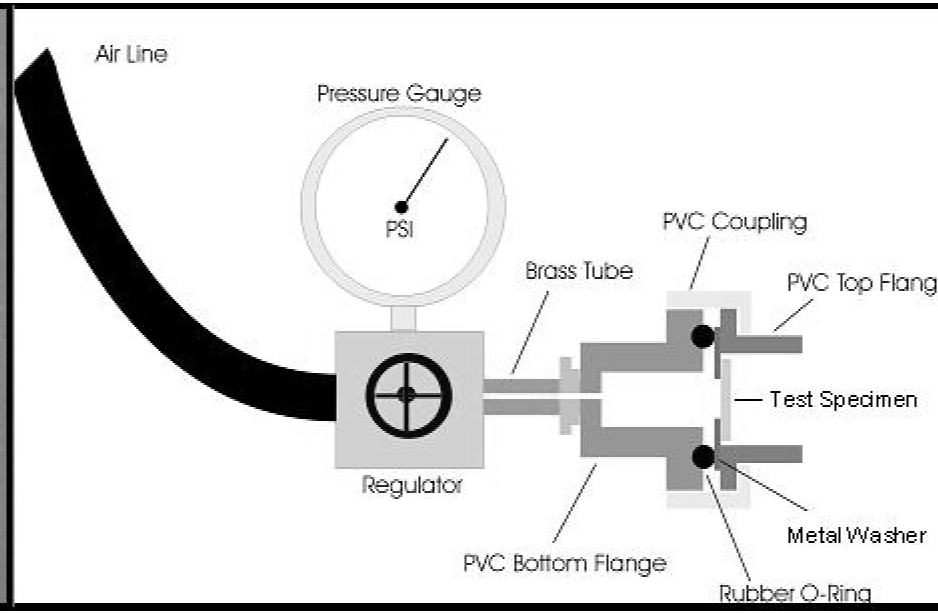
Dual 30 cell Stack APU

As-Brazed 5YSZ/FeCrAlY Joint



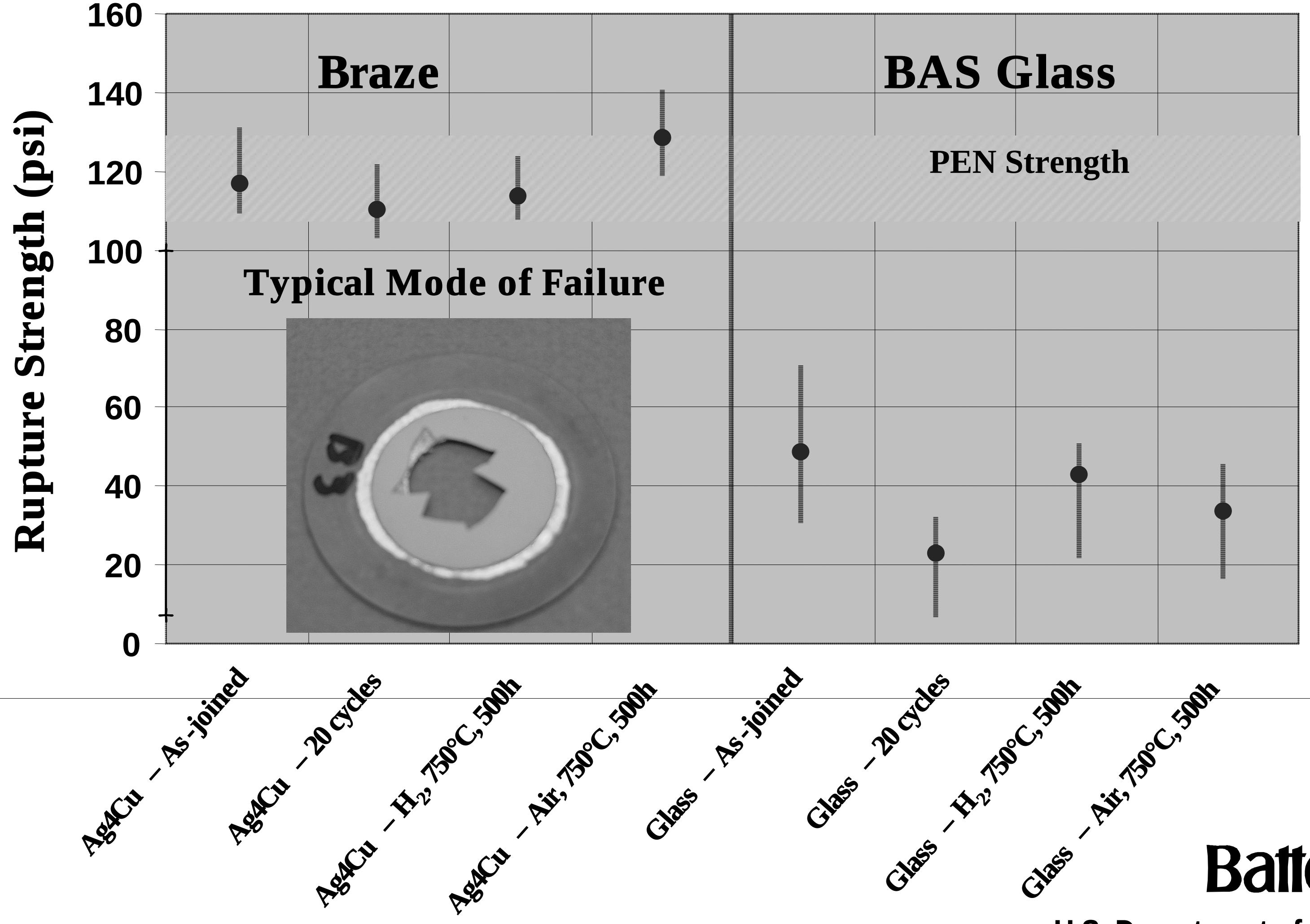
Rupture Strength Testing





- **Measured rupture strength of Ag-4CuO brazed bilayer/FeCrAlY joints**
  - **In the as-brazed condition**
  - **After aging in wet H_2 or ambient air at 750°C**
  - **After thermal cycling in ambient air from RT to 750°C to RT at 5°C/min**

Rupture Strength Results



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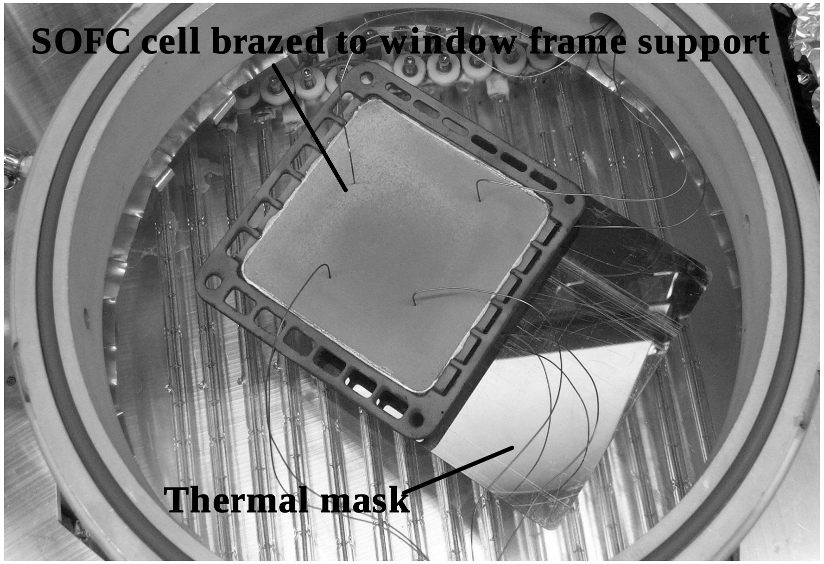
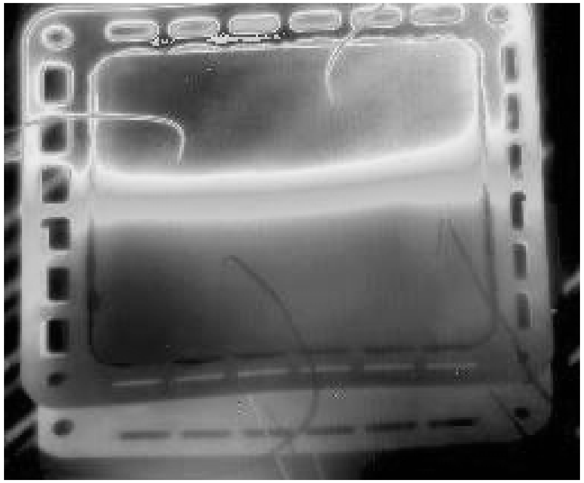
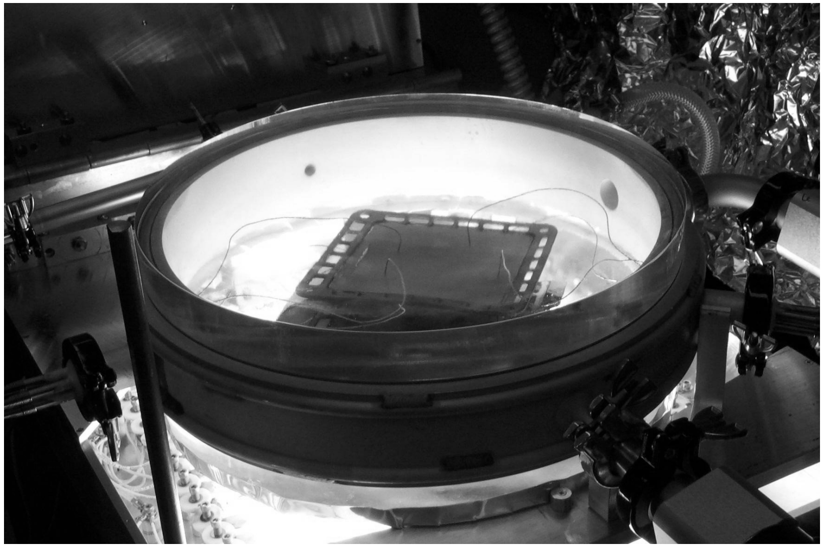
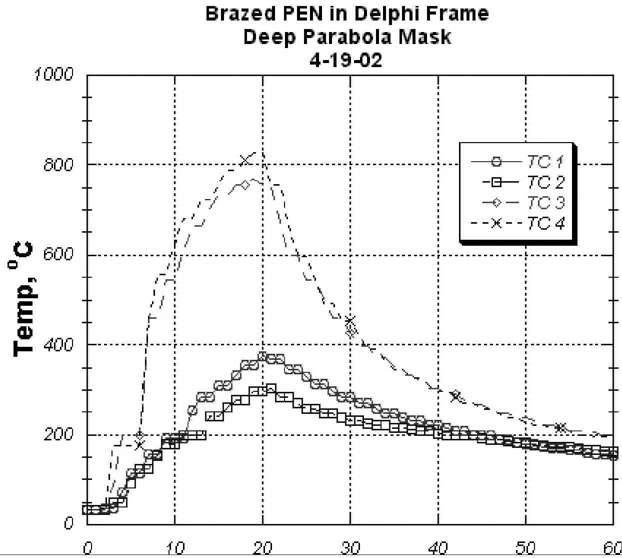
Thermal Shock Testing









Seal remains hermetic after testing through five thermal cycles

Technology Transfer

- O_2 Generation
  - Litton Corporation
  - Battelle Memorial Institute

  Small-scale devices for medical and military applications

- SOFCs
  - Delphi
  - BMW
  - Elring Klinger

  SOFC APUs for transportation applications

Potential New Functional Material Application for Ag-CuO

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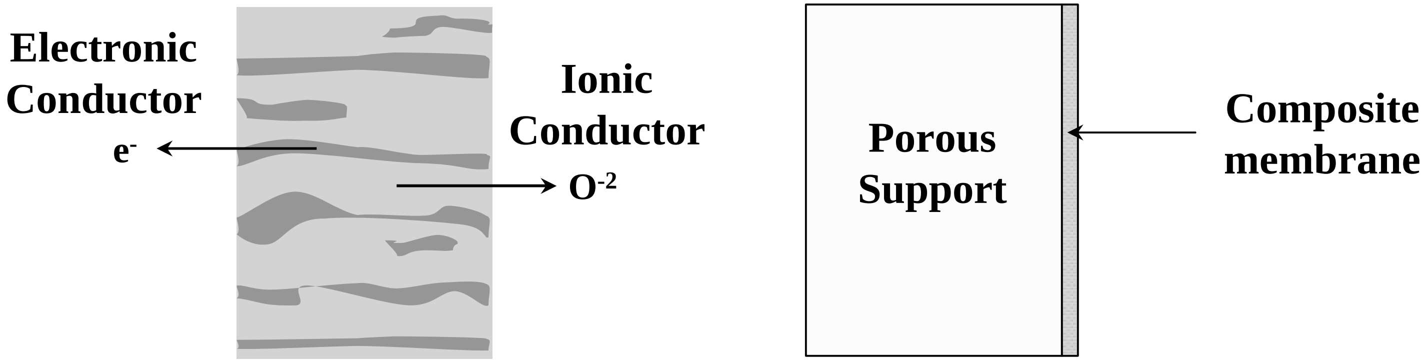
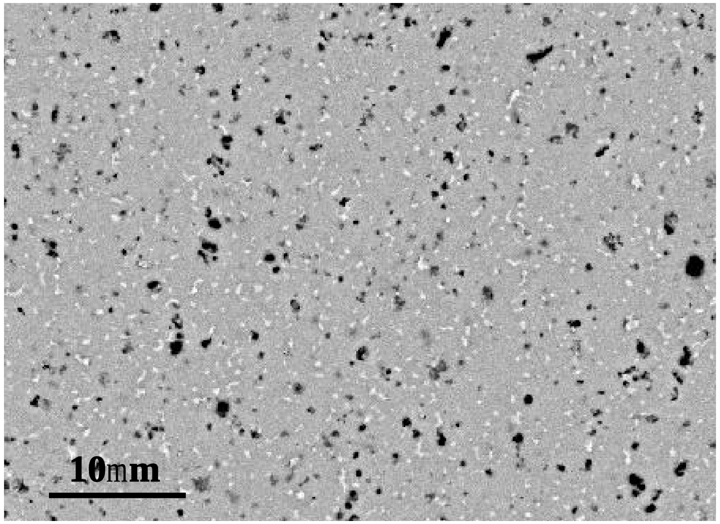
Exploratory Study: Composite Separation Membranes

- **Investigation of a dual phase membrane for oxygen ion transport:**



J. Kim, Y. S. Lin, AIChE J. 46 (2000)

15 vol% AgCuO-4 in CeO_2



- **The RAB braze and an appropriate electrolyte can be simultaneously processed into a nanoscale composite:**
  - **Intimate mixing and better phase adhesion and contact, potentially improving transport characteristics**
  - **Potentially offers improved chemical stability**
  - **Mechanical properties can be optimized**

Summary

- Developed a new joining technique specifically for high temperature electrochemical applications: Reactive Air Brazing
  - Exploits liquid-liquid solubility between noble metals and low melting oxides
  - Can be conducted in air
  - Offers good wetting with YSZ, MIECs, and Al_2O_3
  - Braze is stable under high temperature oxidizing conditions
  - Offers good joining strength which is retained after oxidation
- Have examined RAB for use in O_2 separation devices, H_2 separation devices, and SOFCs
  - Wetting and adhesion properties of the braze can apparently be optimized for a given materials system (i.e. ceramic membrane/metal support combination)
  - RAB appears to offer very good joints strengths in the as-brazed condition and withstands exposure to high temperature air and wet H_2 environments for up to ~1000hrs
  - RAB sealing can be thermally cycled and rapidly heated and cooled without adverse effects

Acknowledgements

- Nat Saenz and Shelly Carlson - metallography
- Jim Coleman – scanning electron microscopy
- Support: U. S. DOE, Office of Fossil Energy