# **INNOVATIVE SEALS FOR SOLID OXIDE FUEL CELLS (SOFC)-SOFT SEALS**

#### Raj N. Singh

#### Department of Chemical and Materials Engineering University of Cincinnati, Cincinnati OH 45221-0012

Supported by DOE-SECA Program (Drs. Mani Mannvanan and Travis Shultz, Project Managers) and University of Cincinnati

SECA Workshop, Philadelphia, September 12-14, 2006





# **INTRODUCTION**

#### • **Requirements of Seals for SOFC**

- Electrochemical-insulating to avoid shorting
- Lowest possible thermomechanical stresses upon processing, during heatup, cooldown, and in steady state/transient operations
- Long life (5,000-40,000h) under electrochemical and oxidizing/reducing environments at high temperatures ~600-850°C

✦ Low cost

#### • Type of Seals

- Ceramic-Ceramic (Electrolyte-Ceramic Insulator)
- Ceramic-Metal
- Metal-Metal
- Rigid and/or Compliant
- Chemical/Mechanical/Liquid







# PROGRAM OBJECTIVES AND ACCOMPLISHMENTS

#### • Phase-I

Select self-healing glasses for functionality as seals for SOFCs

- ✦ Demonstrate functionality of the self-healing seals by leak tests
- ✦ Measure stability of the self-healing glass in SOFC environments
- ✦ Develop approaches to toughening self-healing glasses as seals for SOFs
- Survey commercial glasses suitable for making seals for SOFCs

#### • Accomplishments

- Developed glasses displaying self-healing ability
- Demonstrated ability of self-healing glasses in sealing components through leak tests over arange of temperatures between 25-800°C
- Achieved 300 thermal cycles between 25-800°C without leak of seals and accumulated 3000 hours of hermetic seal performance at 800°C
- These results provide great promise towards meeting SECA goals of seals for SOFC.





### **SEALS FOR PLANAR SOFC**



Metal-Ceramic and Metal-Metal Seals Must Work at 650-850°C in Corrosive Environments of Fuel and Air





# **MATERIALS FOR CELL COMPONENTS**

- Electrolyte: YSZ, 10-30 μm, dense
- Anode: Ni-YSZ Cermet, 25-600 μm, porous
- Cathode: Doped La-Perovskite, 25-2000 µm, porous
- IC (Interconnect): Doped Chromites/Alloys, 30 µm -5 mils, dense
- Seals: Insulating Ceramics/Glasses, dense
- Manifolds: Heat Resistant Alloys
- Operating Temperature: 650-850°C
- Fuels: Reformed PNG, Propane, Diesel etc.

### • Highly incompatible materials require seals





### **POSSIBLE APPROACHES TO SEALS FOR SOFC**

#### • Rigid Seals

- Glass-Metal, Ceramic Polymer-Ceramic/Metal, Brazes: require stable glasses, brazes, preceramic polymers
- ✤ Low leak rates but susceptible to failures due to stresses
- Feedback to materials and seal concept modifications to reduce stress buildup and avoid failure

#### Compliant Seals

 Bellows, Viscous Glass, Wet-Seals (MCFC): require flexible seal designs, stable glasses with appropriate viscosity over a range of temperature, wetsealing materials and their containment

✦ Moderate leak rate, some concepts may require pressure

- Our Approaches for Seals
  - Self-Healing Glass Seals
  - Reinforced-Glass Seals
  - Layered Composite Seals



# A SELF-HEALING SEALING CONCEPT FOR SOFC

- **Rationale:** A glass of appropriate characteristics can self-heal the cracks created upon thermal cycling and/or stresses created during SOFC operation. In addition, thermomechnical incompatibilities between ceramic and metallic materials requiring seals/joining can be alleviated using a self-healing glass seal.
- Advantages: Materials with dramatically different expansions can potentially be used for seals because this approach can alleviate/minimize thermomechanical stresses and chemical reactions. The leaks developed upon SOFC operation and thermal cycling can be repaired in situ by the self-healing concept.
- **Challenges:** Develop appropriate glasses which satisfy thermomechanical and thermochemical compatibilities, remain stable for long-time, and maintain self-healing capability.
- Approach: Thermophysical and thermochemical property measurements and optimization, self-healing ability, and leak testing to demonstrate self-healing seals.





# **OBJECTIVES**

- Demonstrate Self-Healing Behavior of Glass
- Fabricate Seals Displaying Self-Healing Response
- Describe Performance and Durability of the Self-Healing Seals Under SOFC Conditions
  - Fuel Environment
  - Dual Fuel-Air Environments
  - Thermal Cycles and Time





# **EXPERIMENTAL**

#### • Materials

- Electrolyte YSZ (Tape Casting and Sintering)
- Metal (Crofer22 APU)
- Sealant-Silicate Glass

#### • Fabricate Seals Displaying Self-Healing Behavior

Self-healing Behavior by Video Imaging

#### • Performance and Durability of the Self-Healing Seals

- Testing at RT and High Temperatures
- Effect of Pressure Drop Across The Seal
- ✦ Effect of Thermal Cycling Between 25-800°C
- Effect of Test Atmosphere Typical of SOFC
- ✦ Effect of Time at 800°C on Seal Durability



### A SEAL PERFORMANCE TEST SYSTEM



• Continuous monitoring of leak test conditions





### STUDY OF CRACK-HEALING BEHAVIOR OF GLASS



#### • Demonstration of self-healing of crack





### LEAK PERFORMANCE OF SELF-HEALING SEAL At 25°C





**ل** 

### LEAK PERFORMANCE OF SELF-HEALING SEAL At High Temperatures



#### • Hermetic behavior upon heating and cooling





### DEMONSTRATION OF SELF-HEALING BEHAVIOR OF SEAL AT HIGH TEMPERATURES



#### • Hermetic behavior after self-healing





### DEMONSTRATION OF SEAL DURABILITY UPON THERMAL CYCLING BETWEEN 25-800°C IN DRY FUEL



#### • Hermetic behavior after 217 cycles/1700 h





### DEMONSTRATION OF SEAL DURABILITY UPON THERMAL CYCLING BETWEEN 25-800°C IN WET FUEL







### DEMONSTRATION OF SELF-HEALING ABILITY AND SEAL DURABILITY BETWEEN 25-800°C IN DUAL ATMOSPHERE



• Self-healing in 271 cycle of leak in 270 cycle/2900 h





# SUMMARY

- A self-healing sealing concept is developed for SOFC to satisfy significant thermochemical and thermomechanical incompatibilities among materials requiring hermetic seals.
- Seals incorporating self-healing concept were fabricated and tested under conditions prototypical of a SOFC.
- Performance of the self-healing seals for ~3000 hours and ~300 thermal cycles was demonstrated via leak tests as functions of temperature, pressure, thermal cycling, environment, and in situ self-healing.
- Long term leak test results demonstrated promise of the selfhealing seals for potential applications in SOFC.



# **PROGRAM OBJECTIVES-Phase II**

- Develop additional sealing glasses and demonstrate long-term stability
- Demonstrate toughening of glasses by fiber reinforcement
- Demonstrate seal durability of self-healing and reinforcedglasses
- Demonstrate and transition sealing technology to SECA team





# ACKNOWLEDGMENTS

- SECA Core Technology for Program Support
  Mani Mannvanan and Travis Shultz for Program Management and Guidance on Project
   Wayne Surdoval, Don Collins, and Lance Wilson for Discussions on Seals
- S. Parihar for help with experiments
- PNNL, Ceramatec, and University of Utah for Electrolyte Samples Matt Chou, Jeff Stevenson, P. Singh, S. Elangovan and Anil Virkar
- GE Power Systems, FuelCell Energy, and Delphi for Guidance and Industry Perspective

N. Minh, Pinakin Patel, and Diane England



# **Thank You !**