INNOVATIVE SEALS FOR SOLID OXIDE FUEL CELLS (SOFC): *VISCO-ELASTIC 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, San Antonio, August 7-9, 2007

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 (40,000h) under electrochemical and oxidizing/reducing environments at high temperatures ~600-850°C
  - Low cost

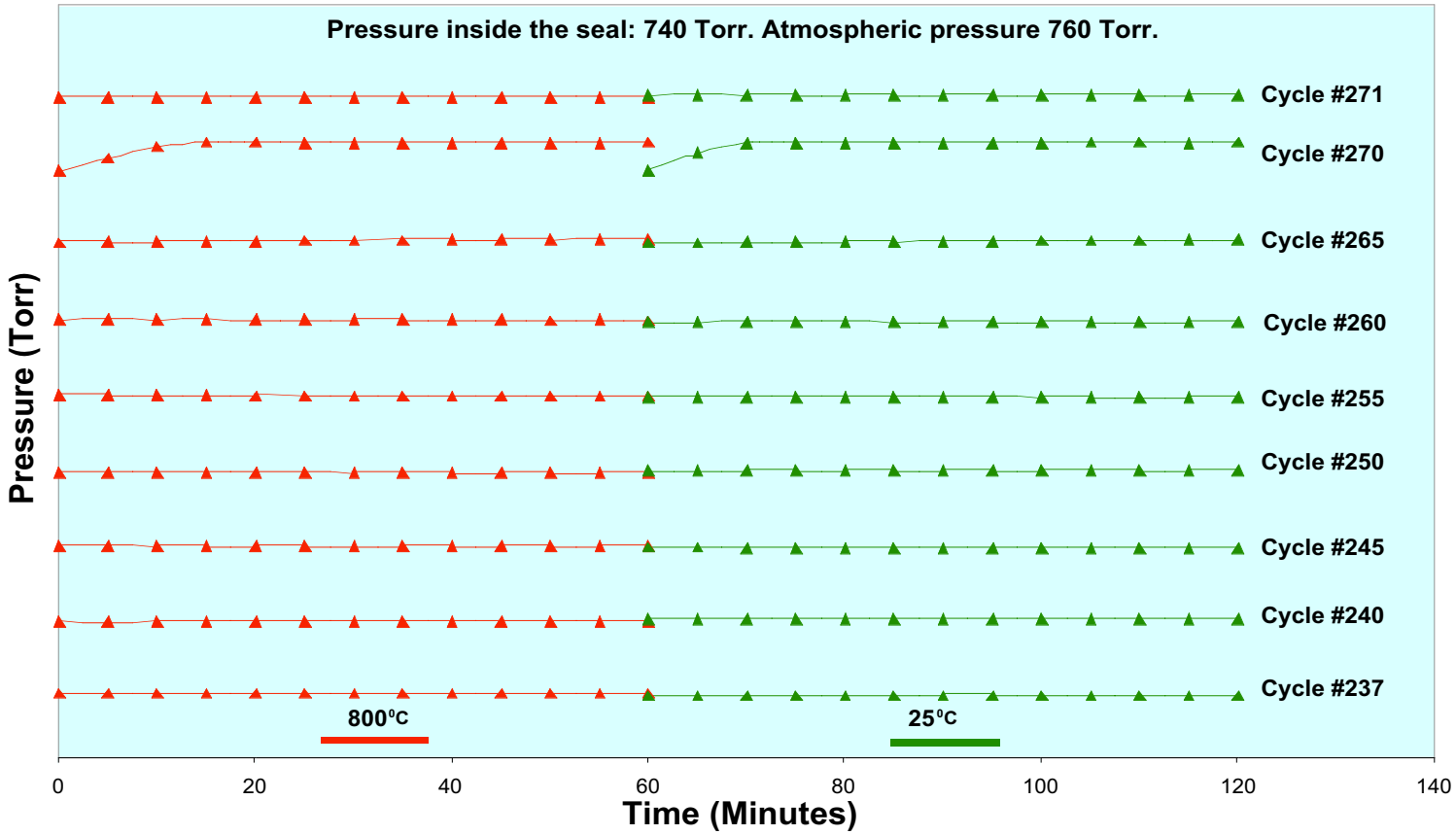
- **Type of Seals**
  - Ceramic-Ceramic (Electrolyte-Ceramic Insulator)
  - Ceramic-Metal
  - Metal-Metal
  - Rigid and/or Compliant
  - Chemical/Mechanical/Liquid

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 a range 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.

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**

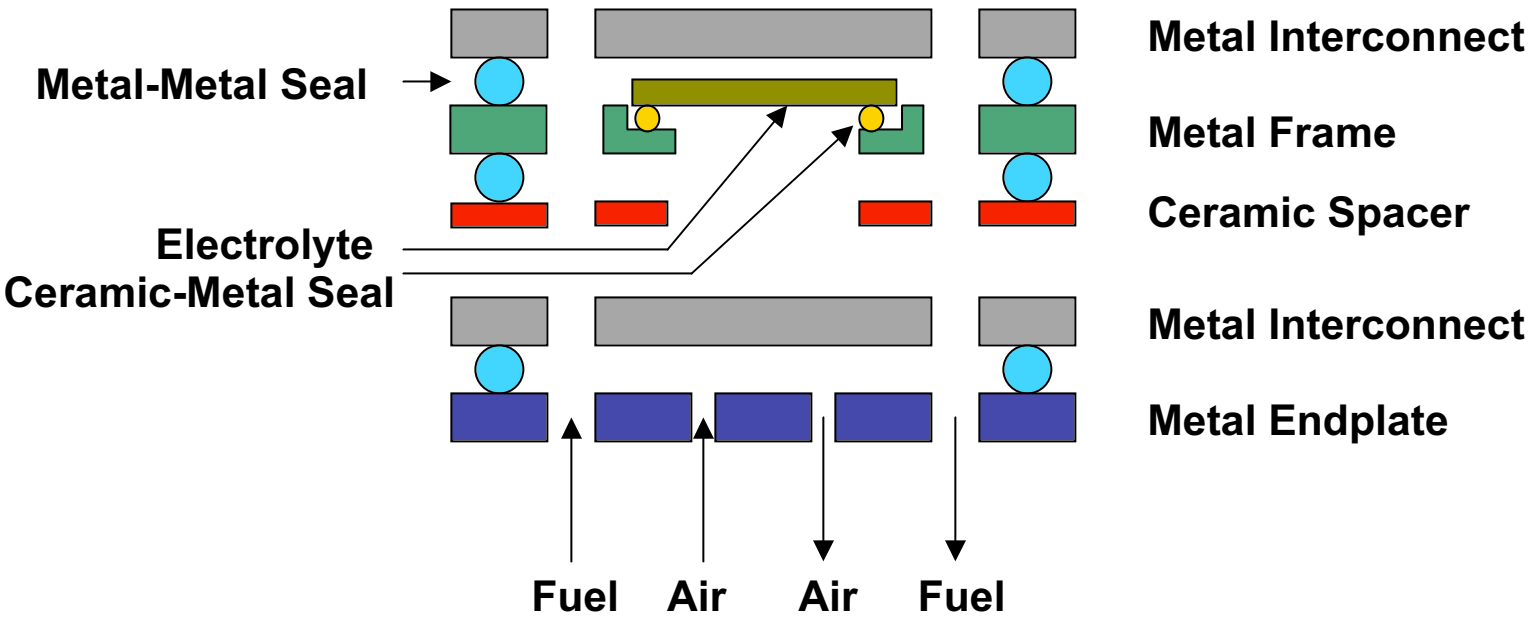
Raj Singh-2007

PROGRAM OBJECTIVES AND ACCOMPLISHMENTS

- **Phase-II**
  - Develop self healing sealing glasses and demonstrate long-term stability
  - Demonstrate toughening of glasses by fiber/filler reinforcement
  - Demonstrate seal durability of self-healing and reinforced-glasses
  - Demonstrate and transition sealing technology to SECA team

- **Accomplishments**
  - Determined stability of the sealing glasses and glasses with fillers
  - Demonstrated ability of reinforced self-healing glasses in sealing components through leak tests at temperatures between 25-800°C
  - Achieved >1500 hours of hermetic seal performance
  - Measured DC electrical resistance/resistivity of sealing glass over 25-800°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

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, wet-sealing 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.

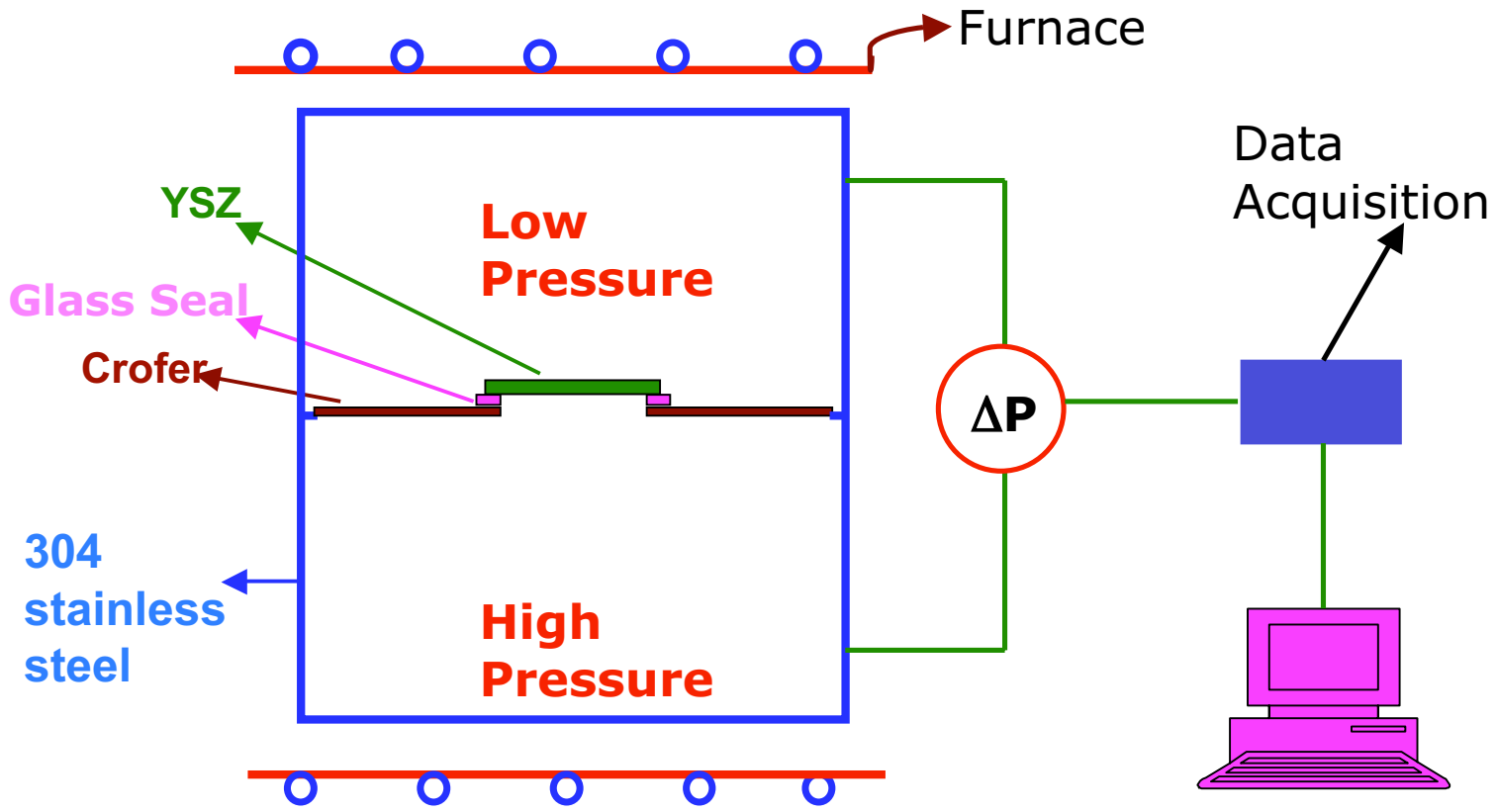
OBJECTIVES

- Demonstrate Stability of the Self-Healing Glasses under SOFC Environment
- Fabricate Glasses with Fillers and Fibers and Demonstrate Stability and Sealing Behaviors
- Describe Performance of Reinforced Glass Seals and Electrical Properties of Glasses

EXPERIMENTAL

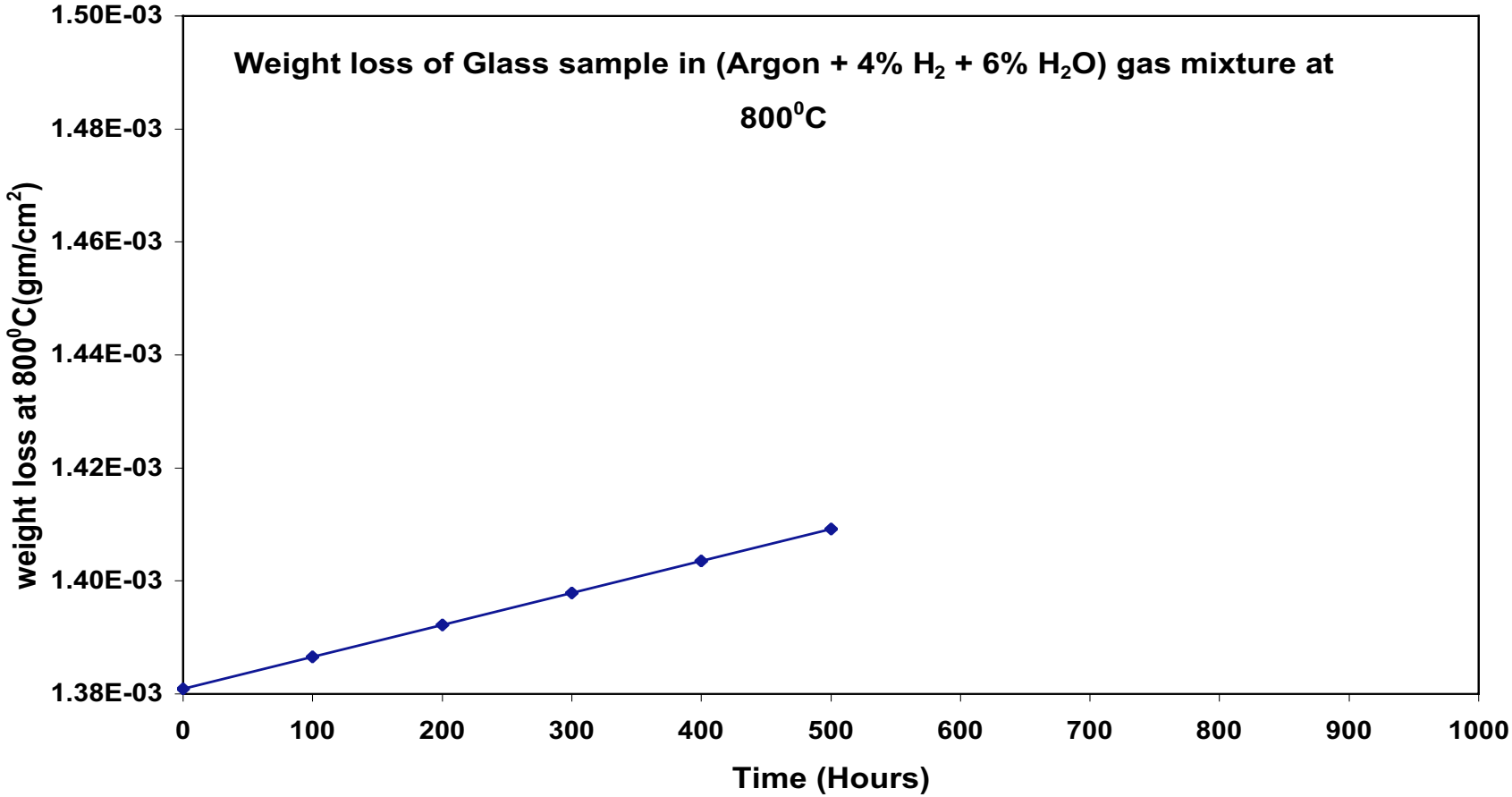
- **Materials**
  - Electrolyte YSZ (Tape Casting and Sintering)
  - Metal (Crofer22 APU)
  - Sealant-Silicate Glass
- **Fabricate Seals Displaying Self-Healing Behavior**
  - Self-healing Behavior in situ
- **Durability of the Self-Healing Glass and Performance of Seals**
  - Testing at RT and High 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

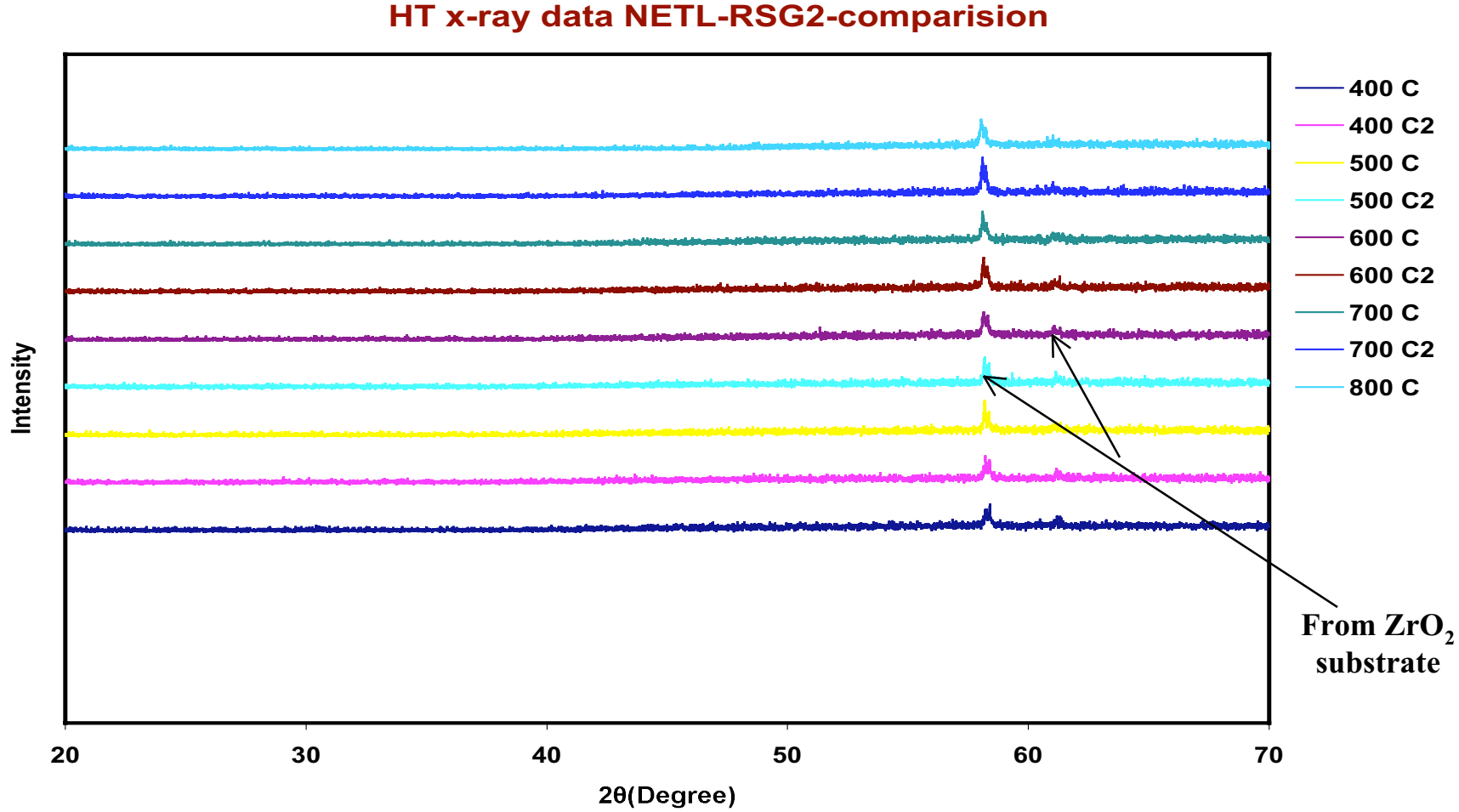
STABILITY OF THE GLASS IN MOIST FUEL ENVIRONMENT AT 800°C



- Calculated insignificant weight loss of 0.53% in 40,000 hours

Raj Singh-2007

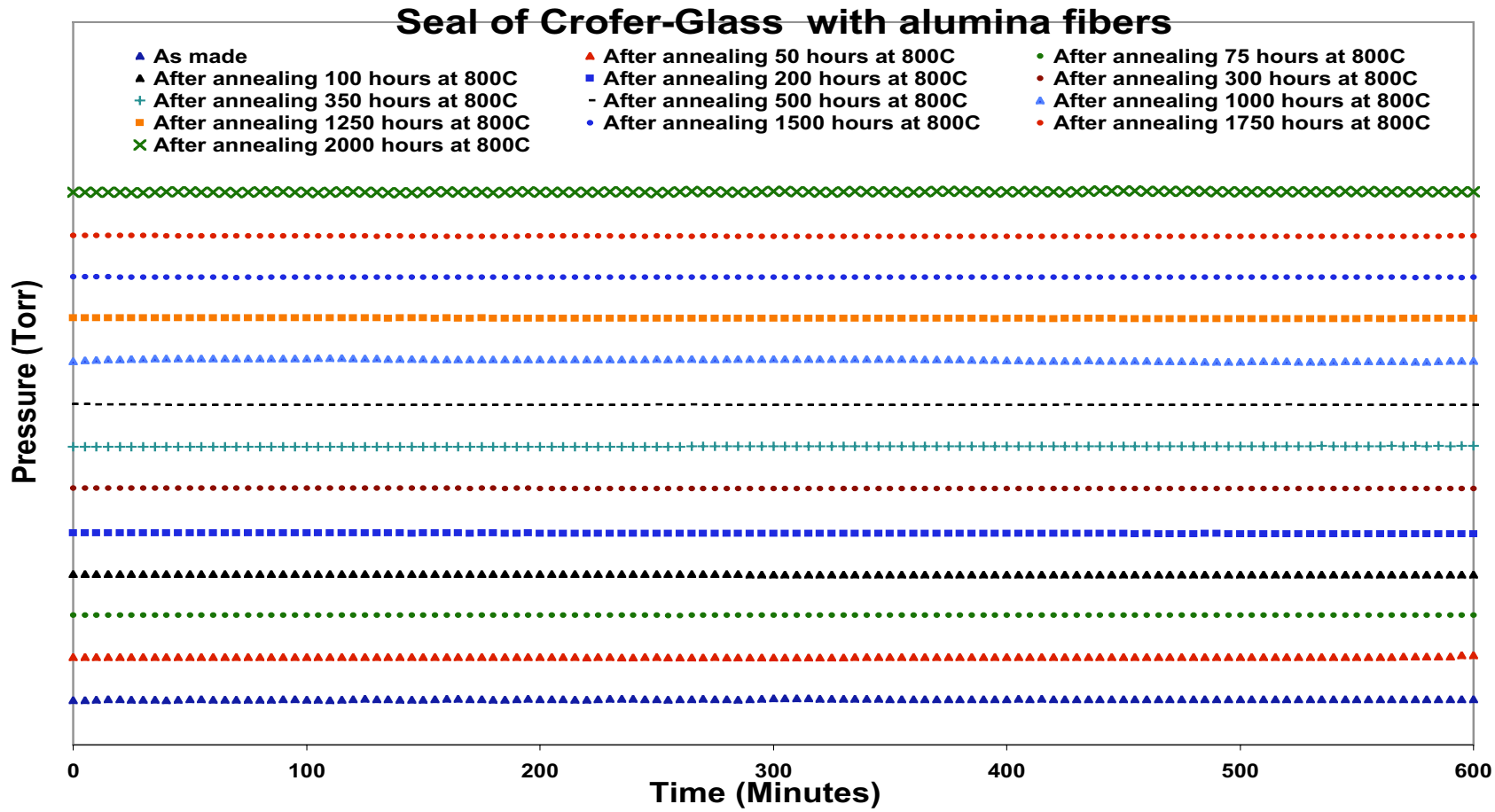
STABILITY OF THE GLASS TO 800°C IN AIR
In Situ X-Ray Diffraction at NETL (Dr. C. Johnson)



- Stability against crystallization between 25-800°C

Raj Singh-2007

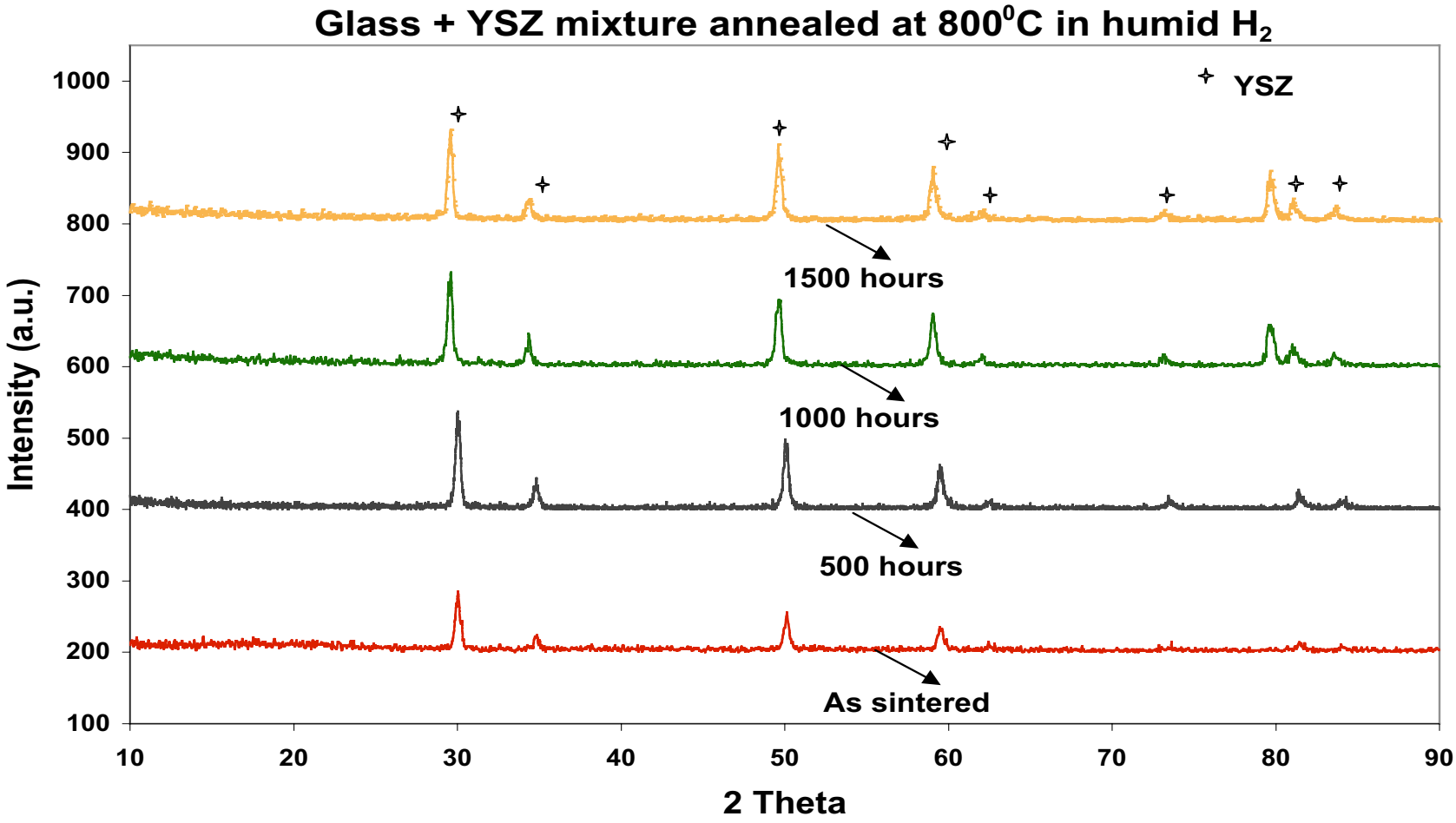
PERFORMANCE OF THE GLASS COMPOSITE SEAL AT 800°C



- **Hermetic seal performance after 1750 hours**

Raj Singh-2007

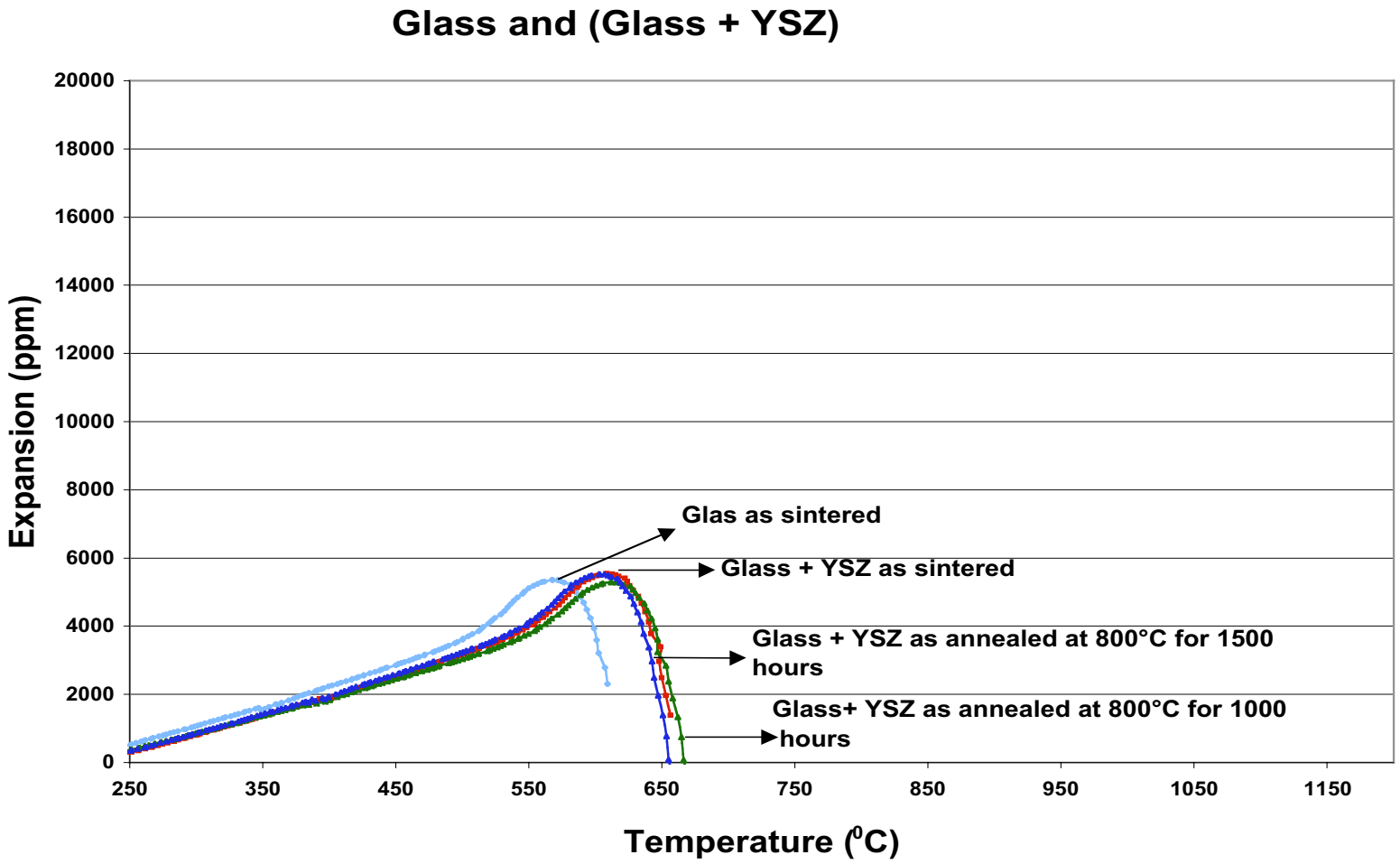
STABILITY OF THE GLASS+5%YSZ AT 800°C IN HUMID FUEL ENVIRONMENT



- Stability against crystallization to 1500 hours

Raj Singh-2007

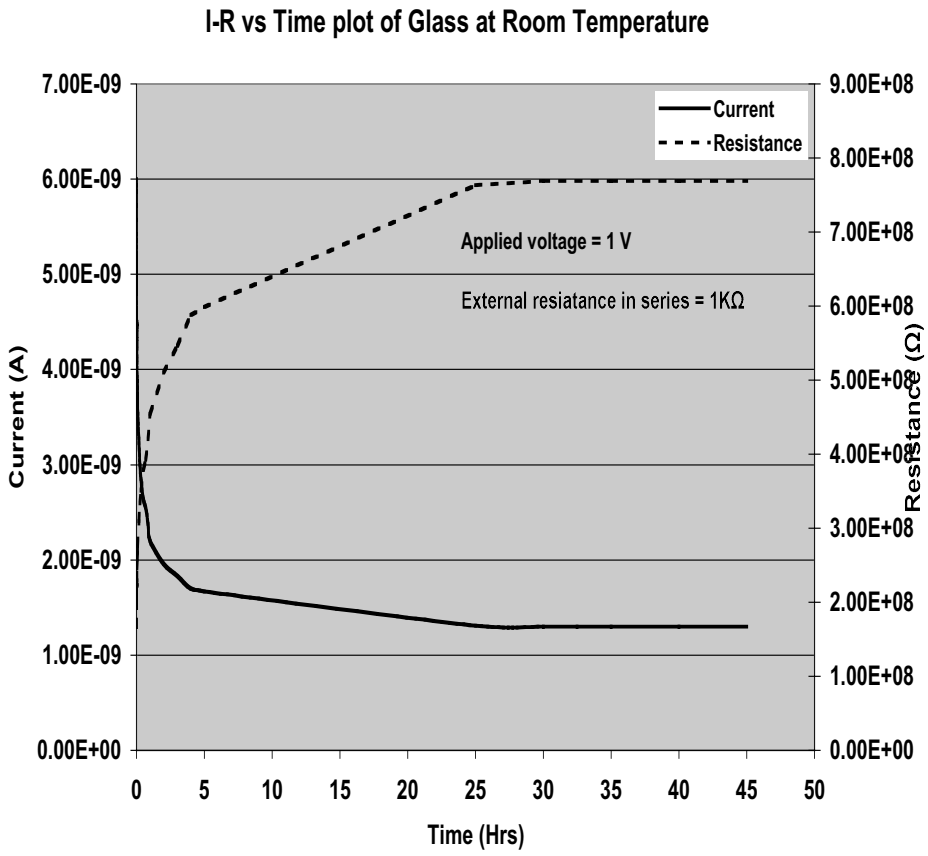
STABILITY OF THE GLASS+5%YSZ AT 800°C IN HUMID FUEL ENVIRONMENT

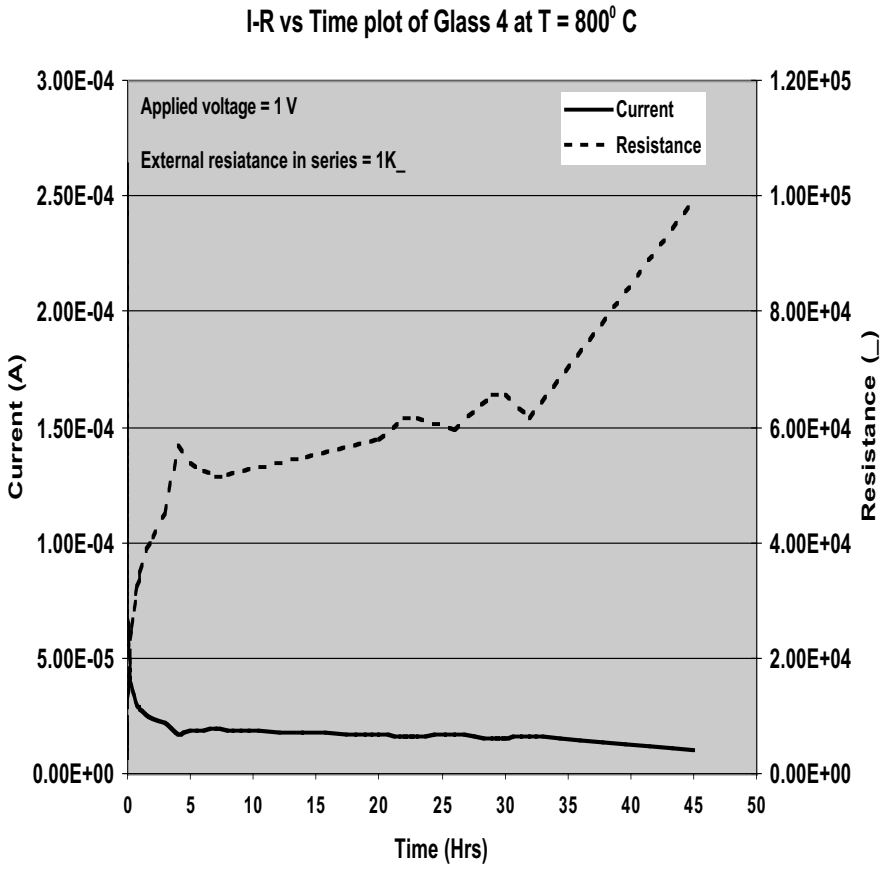


- **Stable expansion behavior for 1500 hours**

Raj Singh-2007

DC RESISTANCE MEASUREMENTS OF GLASS BETWEEN 25-800°C

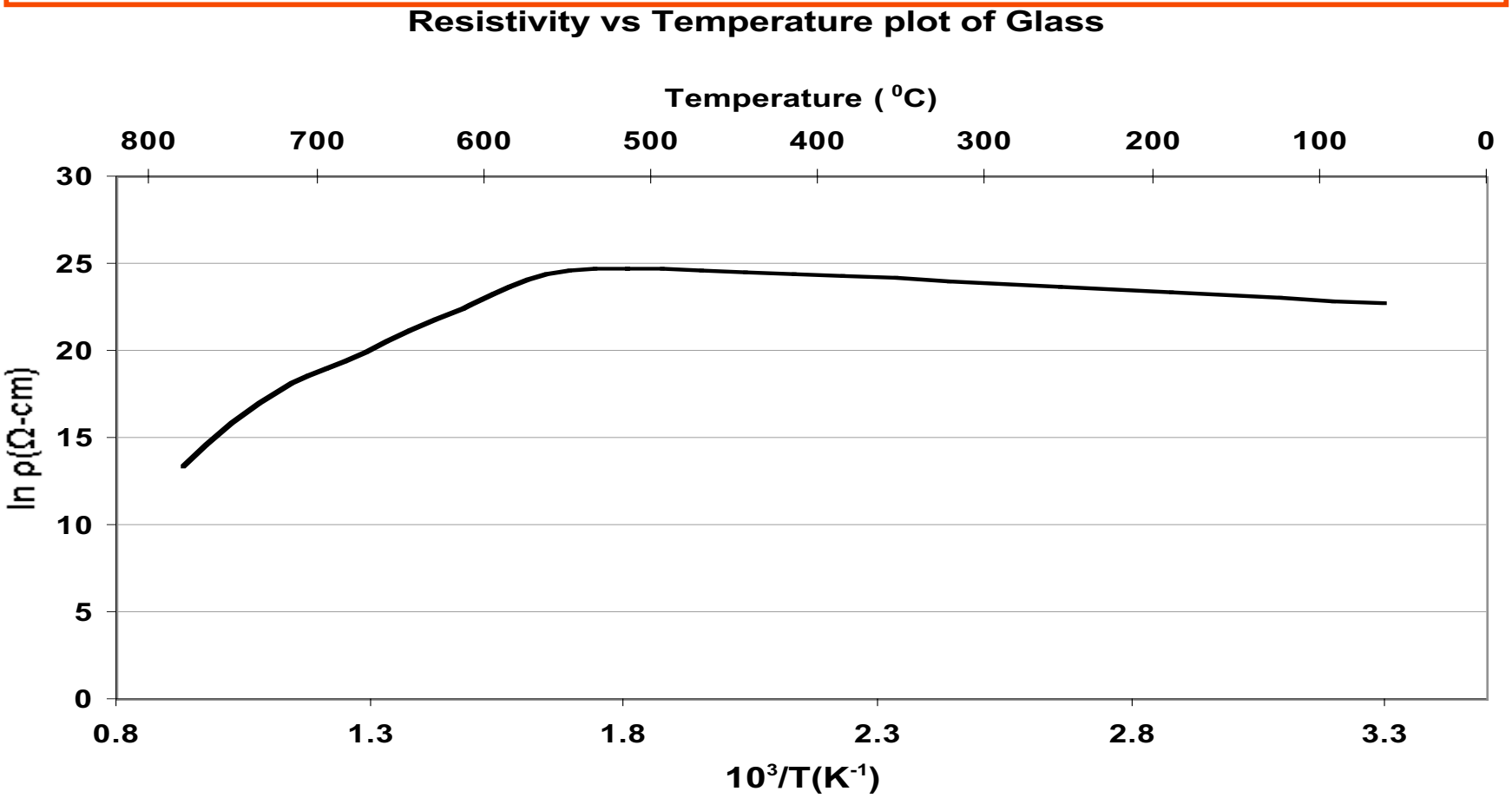




- **High DC Resistance to 800°C**

Raj Singh-2007

DC RESISTIVITY OF GLASS BETWEEN 25-800°C



- **High DC Resistivity to 800°C**

Raj Singh-2007

SUMMARY

- A self-healing sealing concept is further developed for SOFC to satisfy significant thermochemical and thermomechanical incompatibilities among materials requiring hermetic seals.
- Stability of the self-healing and reinforced glasses were measured by x-situ experiments at 800°C for times >1500 hours and demonstrated stability.
- Performance of the self-healing seals with fibers for ~1750 hours was demonstrated via leak tests as a function of temperature.
- Long term stability and leak test results demonstrated promise of the self-healing 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 reinforced-glasses in SOFC tests
- 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 the Project

  Wayne Surdoval, Don Collins, and Lane Wilson for Discussions on Seals

  Chris Johnson of NETL for help with in situ x-ray diffraction at high temperature.

- **S. Parihar, S. Singh, and S. Chavan 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 !