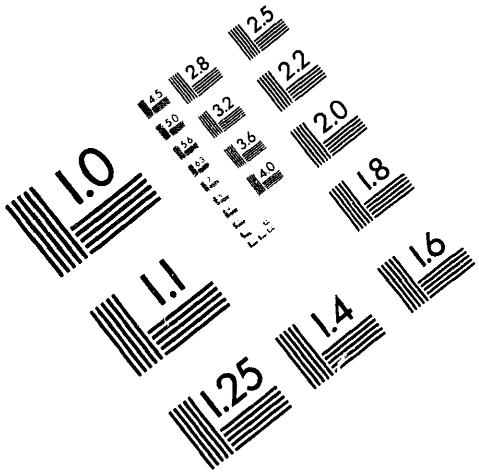

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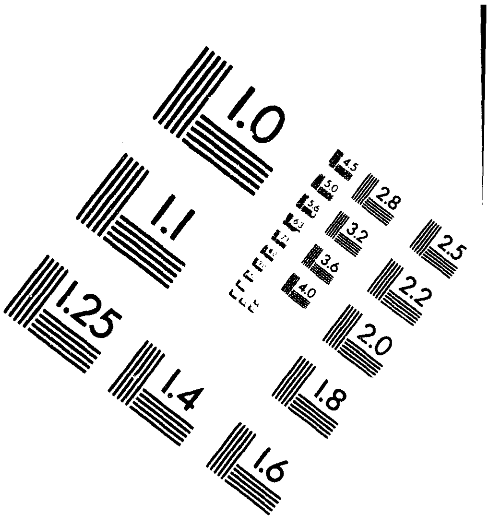

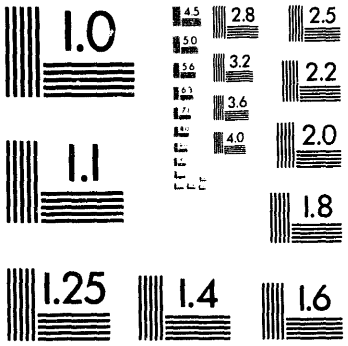

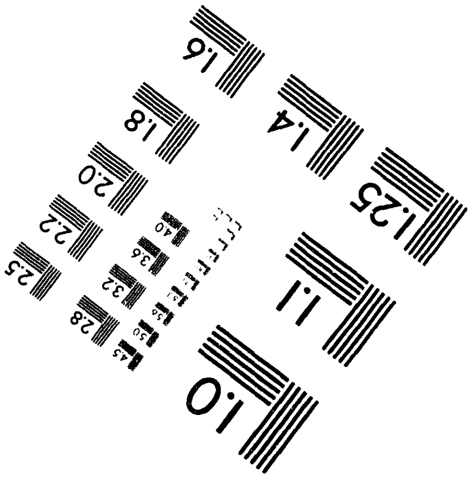

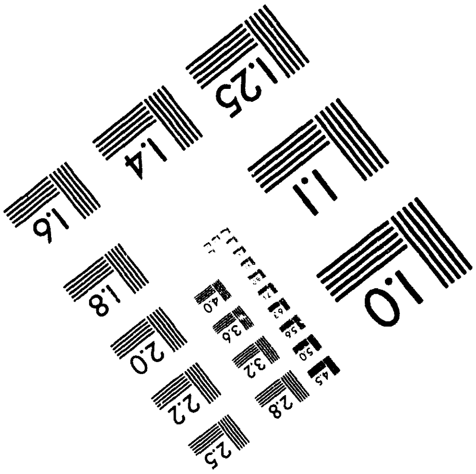

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SEALANT MATERIALS FOR THE SOLID OXIDE FUEL CELL

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Sealant Materials for the Solid Oxide Fuel Cell

CONTRACT INFORMATION

Contract Number	**49638**
Contractor	**Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439 (708) 252-4342**
Contractor Project Manager	**Kevin M. Myles**
Principal Investigators	**Michael Krumpelt and Romesh Kumar**
Co-Investigators	**Ira Bloom and Kevin L. Ley**
METC Project Manager	**William C. Smith**
Period of Performance	**April 1, 1991 to June 30, 1994**

OBJECTIVE

The objective of this work is to develop sealing materials for solid oxide fuel cells (SOFCs). A suitable sealant must form strong, dense bonds with SOFC components, be chemically stable and mechanically compatible with the components at the operating temperature and over the temperature range of interest, be chemically stable in the operating environment of the SOFC (i.e., H_2 and H_2O on the anode side, O_2 on the cathode side), and must be electronically insulating.

BACKGROUND AND PRIOR WORK

Advanced flat-plate, SOFC stacks under development offer high electrochemical performance because of their short current paths. However, in such a planar SOFC stack, the individual cells must be sealed at the edges, and the stack itself must be sealed to the gas supply and exhaust manifold.

In general, the sealant must be compatible with the cell components and the cell environment. If excessive reactions between the sealant and cell components or gases occur, they can lead to cell failure. This effort seeks to develop materials that are chemically stable toward the cell gases and that form dense, adherent bonds to cell and stack components.

For use in the planar SOFC, the sealant must be electrically insulating. Since it would contact both the anode and cathode, any electronic conductivity in the sealant will produce undesirable shunt current flow.

The thermal properties of the sealant must match its application. At the cell edge, the sealant must be compatible with the thermal expansion behavior of, at most, two ceramics. For example, in the cathode compartment, the sealant must be matched to the behavior of yttria-stabilized ZrO_2 (YSZ) and $La(Sr)MnO_{3-x}$ (LSM). Rigid sealants are appropriate here. Along the stack-to-manifold junction, the thermal requirements are different. Because of the number of different ceramics present (anode, cathode, electrolyte, interconnect, and the manifold) and the long sealing distances, sealants which can tolerate some thermal mismatch may be necessary.

Borate-based sealants were chosen for several reasons: they are electrical insulators, they possess the desired combination of viscosity and expansion coefficient in the temperature region of interest, and they contain no mobile ions. A borate-based material was preferred over a silica-based one since, in addition to eliminating any possible SiO_2 reduction, target viscosities in the desired temperature range (800–1000°C) could be achieved without loss of compositional flexibility.

Last year, the properties of one glass-ceramic sealant, Material K, were reported. Material K was found to produce extremely adherent and durable bonds to coupons of YSZ, NiO/YSZ, and LSM. The glass-ceramic also bonded very well to disks of alumina. No obvious signs of interfacial reactions, such as phase formation, were observed between the glass-ceramic material and any of the bonded substrates. Sealant/substrate composites were thermally cycled twice between room temperature and 1000°C to gauge the thermal compatibility of the sealant with substrate materials. No delamination or cracking was observed.

The sealing ability of the glass-ceramic was tested in an electrochemical cell consisting of a 500-μm-thick YSZ disk with platinum screen electrodes on either side. A 1-mm-thick O-ring gasket of the glass-ceramic was used as the seal. The sealing operation itself consisted of pre-shrinking the gasket at 800°C and then using the gasket to bond a zirconia tube to the disk at 1000°C. The cell was then tested for electrochemical performance. Flowing, humidified 5% H_2 in helium served as the fuel gas, and the stagnant furnace air as the oxidant. The cell EMF was measured at 800, 900, and 1000°C. All EMF values were 99% of theoretical. During the test, the cell was thermally cycled between 400 and 1000°C five times and between room temperature and 1000°C once. The EMFs after thermal cycling were within 1–2 mV of previous values.

PROJECT DESCRIPTION

Argonne is continuing development of a family of glass- and glass-ceramic sealants. The advantage of using these glass-based materials over rigid ceramics as seals is that expansion-mismatch-induced stresses between components occur over only a fraction of the cooling cycle, hence reducing the stresses produced. The temperature at which stresses start to build corresponds to the temperature at which the viscosity exceeds 10^{12}–10^{13} Pa-s and the glass becomes essentially a solid. This temperature is approximately the same as the glass-transition temperature and should be as low as possible. At the same time, the viscosity of the sealant at the fuel cell operating temperature should be greater than 10^3 Pa-s (below which glass flows readily) and, hence, should not be excessively fluid.

The first test of a sealant is its ability to bond to the fuel cell components: YSZ electrolyte, porous NiO/YSZ anode, and LSM cathode. The next step is to determine the interactions between the fuel cell components and the sealants as a function of time at 1000°C and under humidified-hydrogen atmospheres. The bonding ability of various candidate sealing materials to these components is determined qualitatively. Sealant materials that form strong bonds are subsequently examined by microscopy to determine porosity and extent of chemical interaction.

Promising materials are characterized further to evaluate both the thermal expansion behavior and viscous properties over the temperature regimes of interest. Since candidate sealing materials have to be electronically insulating, electrical properties are also evaluated using standard four-point dc techniques.

The final stage of the sealant development is evaluation by external companies. Presently, two glass-ceramic materials are in this stage of evaluation.

RESULTS

Several additional sealants from the borate-based family have been made to determine the feasible range of coefficients of thermal expansion (CTEs) and viscosity versus temperature. The developed sealant materials have CTEs in the range of about 8–12 × 10^{-6}/°C, which spans the CTE values needed for SOFC applications. To illustrate the behavior and flexibility of these materials, a dilatometric curve of Material K (a glass-ceramic) is given in Fig. 1 along with that obtained from commercial YSZ. As can be seen from the figure, there is excellent thermal matching up to temperatures where the sealant exhibits viscous flow.

The viscosity vs. temperature profiles for four sealant compositions (the glass-ceramic K and the glasses 42, 43, 47) were determined by a sagging beam method [1, 2]. These profiles are given in Fig. 2 and show the range of viscosities feasible by changing composition and microstructure. From the figure, the glass-ceramic material (Material K) is much more viscous and its viscosities are not as sensitive to temperature as glass (Materials 42, 43, and 47). The viscosity curves for the three glasses illustrate the range feasible by changing composition only. Adding the crystalline phase makes the slope of the curve less steep.

These sealants were found to form bonds at temperatures where their viscosity is 10^6 Pa-s or less. From Fig. 2, such temperatures are 1000 and 675°C for Materials K and 43, respectively.

Four-point dc measurements were used to determine the electrical properties of the glass-ceramic at three different oxygen partial pressures (0.21, ~10^{-10}, and ~10^{-19} atm), in the temperature range of 800 to 1000°C (see Fig. 3). The electrical conductivity at a given temperature was found to be independent of oxygen partial pressure in the range studied, confirming that the conductivity is ionic and not electronic.

Structures similar to the cell edge and stack-to-manifold junction were bonded using these sealants to verify their usefulness. Two types of cell edge structures were assembled. One consisted of ceramic interconnect, anode, and electrolyte. The other was made up of interconnect, cathode, and electrolyte. Both types were thermally cycled 7–10 times in air. In addition, the anode-containing structures were thermally cycled 10 times in humidified 5% H_2 in helium. No cracking was observed in either structure type.

The stack-to-manifold seal was found to be strongly affected by geometry. In the electrolyte-edge-sealed-to-interconnect configuration (A), cracking reproducibly occurred in the electrolyte. In the interconnect-edge-sealed-to-electrolyte configuration (B), structures could be sealed without cracking. Since the electrolyte is the less expansive and stronger material present, the first observation is contrary to expectation; the interconnect should crack first.

Finite-element analyses employing macro- and micro-models were used to aid understanding of the results. In configuration (A), the electrolyte component invariably cracked in a characteristic mode. Modeling indicated that tensile stresses exceeding the fracture strength of the electrolyte developed through the full thickness of the electrolyte normal to the sealant line, leading to crack propagation. In configuration (B), modeling revealed that the tensile stresses present were localized at the corners of the interconnect and in the sealant line. The analyses also showed that the angle between the plates has a minor influence on the overall stress patterns developed at stack-to-manifold junctions.

FUTURE WORK

Testing of glass- and glass-ceramic sealants by industrial fuel cell developers is underway. Preliminary results are encouraging. Argonne is working with these developers to tailor sealant materials to their specific SOFC materials and cell geometries and is determining materials interactions under cell operating conditions.

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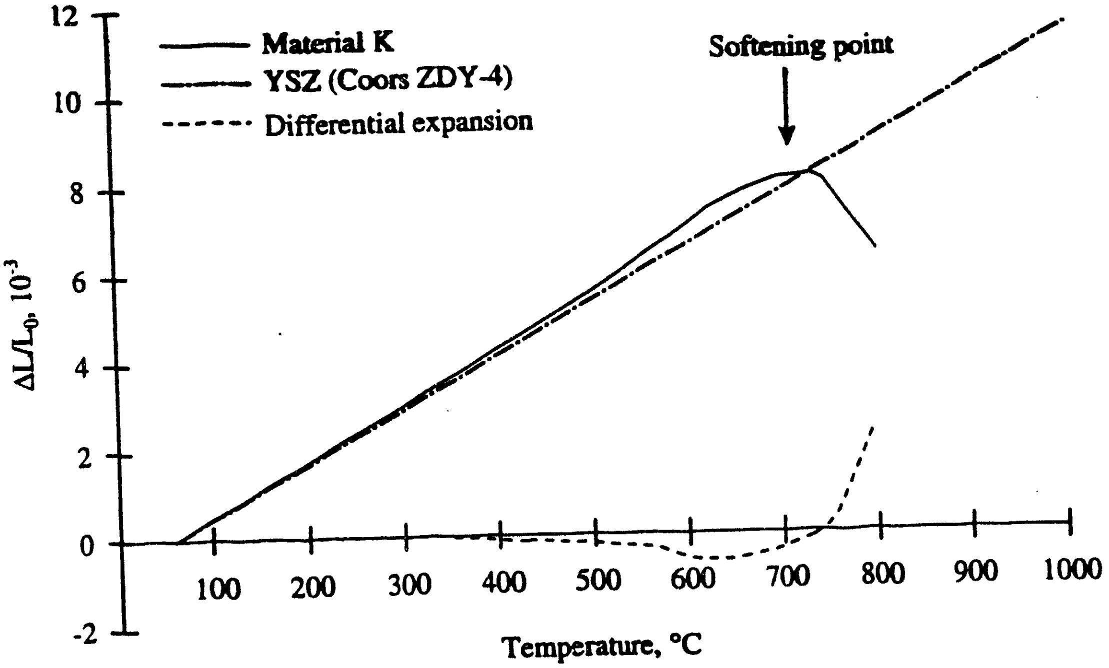

Fig. 1. Thermal Expansion Behavior of Material K

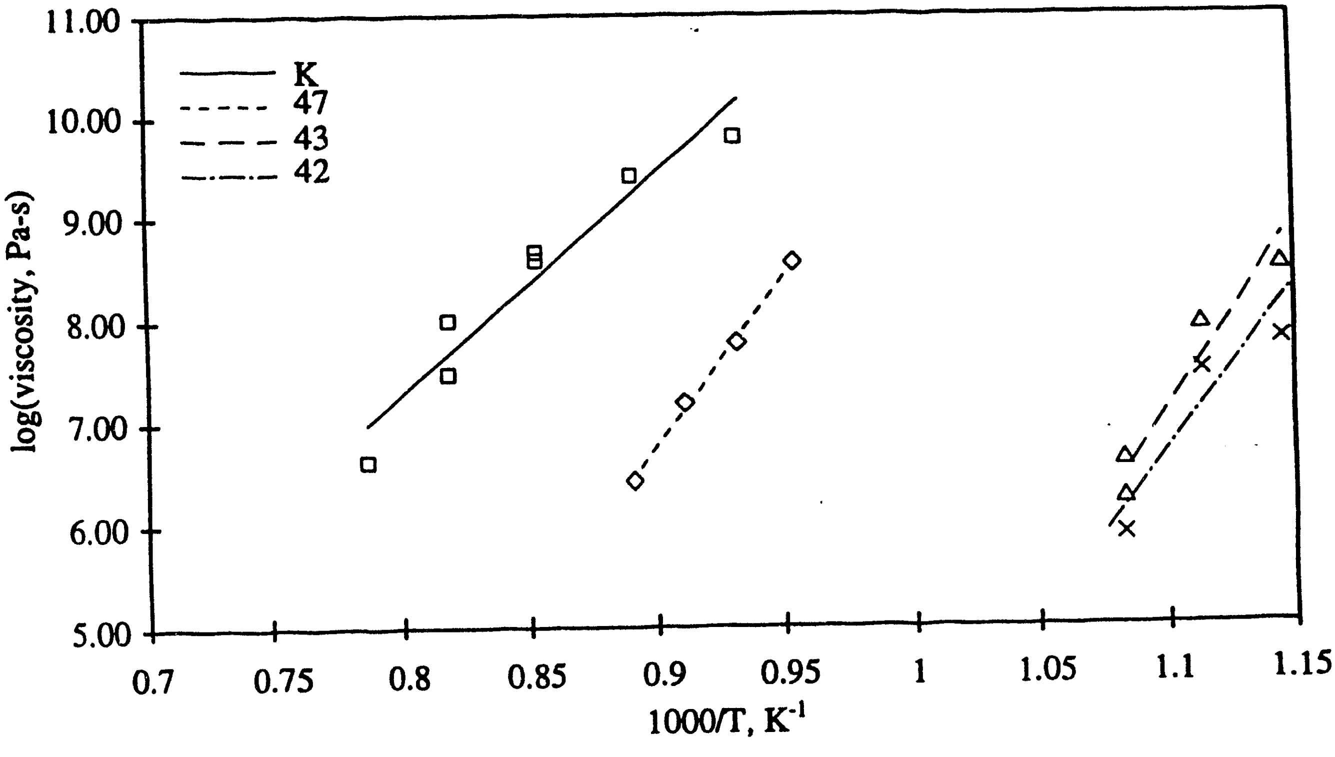

Fig. 2. Arrhenius Plot of Viscosity vs. Temperature for some Sealant Materials.

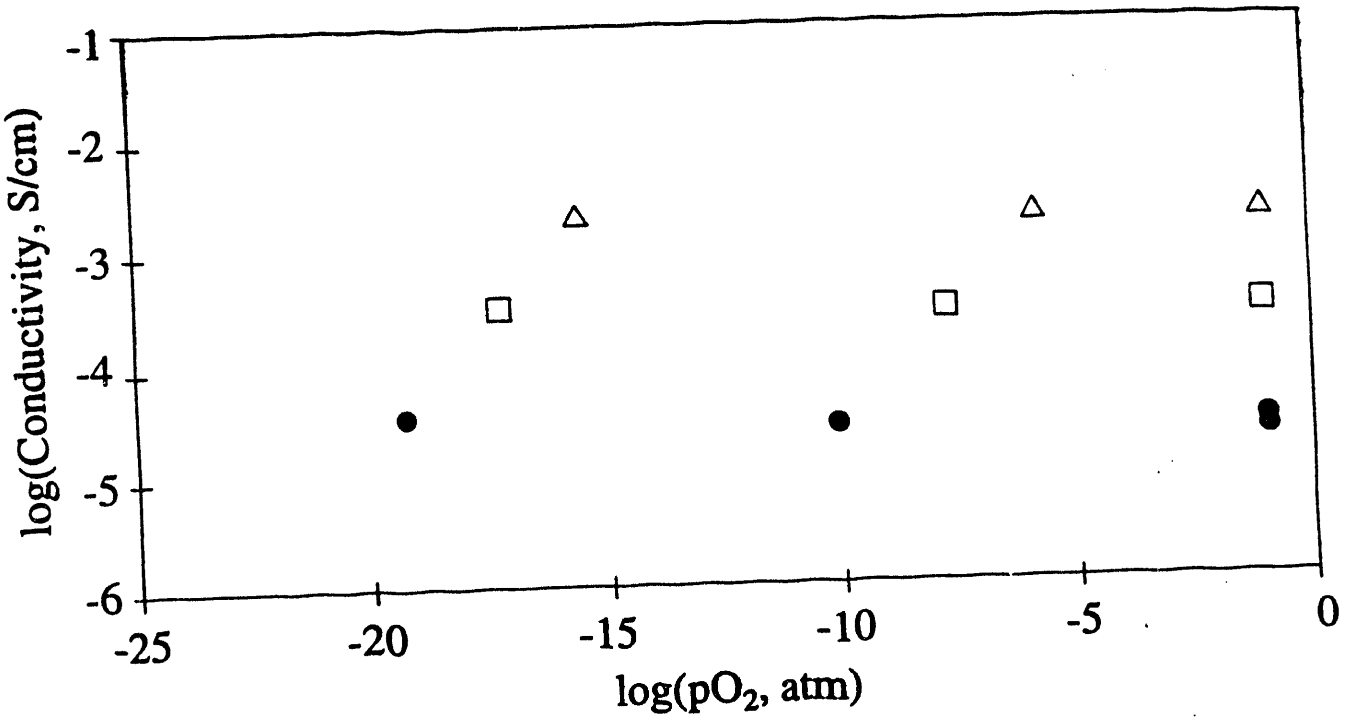

Fig. 3. Dependence of Conductivity of Material K on Oxygen Partial Pressure.

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