

RECEIVED

JAN 25 1995

OSTI

SEALANT MATERIALS FOR SOLID OXIDE FUEL CELLS*

by

**Timothy W. Kueper
Michael Krumpelt
John Meiser**

**Argonne National Laboratory
Electrochemical Technology Program
9700 South Cass
Argonne, IL 60439**

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

To be presented at the
Fuel Cells '95 Review Meeting
Morgantown Energy Technology Center
Morgantown, WV

August 9-10, 1995

*This research was supported by the U.S. Department of Energy, Morgantown Energy Center, under contract No. W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 85

MASTER

SEALANT MATERIALS FOR SOLID OXIDE FUEL CELLS

CONTRACT INFORMATION

Contract Number	49638
Contractor	Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439
Contractor Project Manager	Kevin M. Myles
Principal Investigator	Michael Krumpelt
Co-Investigators	Timothy W. Kueper and John H. Meiser
METC Project Manager	Bruce Harrington
Period of Performance	October 1, 1994 to July 1, 1995

OBJECTIVES

The objective of this work is to complete the development of soft glass-ceramic sealants for the solid oxide fuel cell (SOFC). Among other requirements, the materials must soften at the operation temperature of the fuel cell (600-1000°C) to relieve stresses between stack components, and their thermal expansions must be tailored to match those of the stack materials. Specific objectives included addressing the needs of industrial fuel cell developers, based on their evaluation of samples we supply, as well as working with commercial glass producers to achieve scaled-up production of the materials without changing their properties.

BACKGROUND INFORMATION

Argonne National Laboratory has been developing soft glass-ceramic sealant materials to meet the requirements of planar solid oxide fuel cells. Depending on the design, sealing may be required at the edges of the cells and at the junction of the stack and manifold. A successful sealant for these purposes must meet several demands in addition to relieving stress and matching the thermal expansion of the stack components. The sealant must be chemically compatible with the cell components and the cell environment, while at the same time forming dense, adherent bonds to the cell components. In addition, the material must have low gas permeability and, in manifold sealing applications, it must be electrically insulating.

In early work, many compositions in the five-component system, B_2O_3 - SiO_2 -

Al_2O_3 - SrO - La_2O_3 , were studied, and several of these were found to have promising characteristics. Bonding behavior with SOFC cell components, interaction zones with the cell components, and thermal cyclability were all investigated, and no problems were detected. Thermal expansion and viscosity-temperature behavior were determined, and two compositions in particular were chosen for further development: a high-temperature sealant, Material K, has appropriate viscosity for use in 1000°C stacks and an expansion coefficient of $11.5 \times 10^{-6}/^\circ\text{C}$, and a low-temperature sealant, Material 43, softens appropriately for use at 800°C and has an expansion coefficient of $9.5 \times 10^{-6}/^\circ\text{C}$.

The sealing ability of Material K was tested by using it to seal the edges of an electrochemical cell, which consisted of a zirconia wafer and platinum electrodes, to a zirconia tube. When this device was operated as a fuel cell, all EMFs were measured to be greater than 99% of the theoretical values, even after thermal cycles between room temperature and 1000°C .

Other properties of the sealants that were tested in previous work included gas permeability and conductivity as a function of temperature and oxygen partial pressure. Material K had low permeabilities and a predominantly ionic conductivity of 10^{-3} S/cm at 1000°C . These values are suitable for fuel-cell sealing materials.

PROJECT DESCRIPTION

This year, we have continued to study sealant compositions in the same five-component system, and have addressed several more issues and potential problems, some of which were suggested by fuel cell manufacturers working with samples of our

materials. These issues included long-term stability under various combinations of conditions. For example, we tested high-humidity reducing atmospheres as well as voltage gradients that were applied by using cell materials as electrodes. Long-term tests in voltage gradients provided information on cation migration between the sealant and interconnect as well as on conductivity changes in the bulk of the sealant and at the interfaces.

A systematic study of mechanical properties (bonding behavior, thermal expansion, and softening) as a function of composition within the five-component system was also performed during this period. Data from these tests were used in a statistical analysis to determine property trends with composition. For the statistics, we used the nominal compositions for each batch, but we also checked for variations from nominal compositions in the actual samples by using ICP-AES (inductively coupled plasma-atomic emission spectroscopy).

We also studied the effect of scaled-up production methods (by commercial glass manufacturers) on the sealant structure and properties. Commercially prepared batches of the sealants differed in composition from those prepared on a laboratory scale. Analytical results (ICP-AES) were used to determine what changes were necessary in the ratios of starting materials to compensate for these variations.

A further element of this project was interaction with industrial fuel cell developers. We have worked with five fuel cell manufacturers and two university research groups to test the performance of the sealants and to study potential problems.

RESULTS

Long-Term Stability Testing

Tests in high humidity (40% H₂O in helium) and in high-humidity hydrogen were done to determine the long-term stability of our materials. In high-humidity reducing atmospheres, we found slight boric acid volatility in the sealant materials, which could be controlled with compositional changes. Volatility was determined by three methods, namely, measurements of weight loss of the sample, weight of material recovered from the furnace exhaust, and void formation within the sample. Weights lost and recovered tended to agree fairly well, whereas void formation often led to a higher porosity fraction than the associated percentage weight loss. This discrepancy was due to plastic deformation of the sample under internal gas pressure.

Volatility reductions were seen in several cases: volatility always decreased in subsequent 1000°C treatments after an initial high-temperature hold. Reduced volatility was also observed for low-silica compositions, with a minimum at 1 mol% SiO₂. Samples high in lanthanum borate were clearly the most stable. These samples showed some weight loss in an initial 1000°C hold in 40% humidity, but had no measurable weight loss during an additional 62 hours under the same conditions.

Stability in Voltage Gradients

In a manifold-sealing application, the sealant will experience voltage gradients during stack operation. Thus, mobile ions (e.g., chromium ions) from stack materials may be driven into the sealant and may affect its conductivity. To simulate these conditions, Material K was bonded between two

lanthanum chromite interconnect pellets, with platinum current collectors attached to the chromite and reference platinum wires at the sealant interfaces. This structure was held in air at 1000°C while a 1-V gradient was established across the sealant. The conductivity of the sealant during a 113-h test is shown in Figure 1. The conductivity decrease in the first 20 h was probably due to the formation of an interfacial phase: in post-test analyses using scanning electron microscopy (SEM), it was found that the positive-biased sealant interface was high in strontium and calcium. In addition, some chromium had migrated into the sealant, which may account for the gradual increase in conductivity toward the end of the test. In general, the conductivity values ($< 10^{-3}$ S/cm) are sufficiently insulating for the application.

Thermal Expansion and Softening

Thermal expansion and dilatometric softening data was gathered for a number of sealant compositions that are variations on Material K within the five-component system, B₂O₃-SiO₂-Al₂O₃-SrO-La₂O₃. Materials studied included those low in either silica or borate, and two series in which strontia and lanthana concentrations were varied independently. Data for these nominal compositions were combined with data from previous studies by our group and with data from the literature (for example, on the B₂O₃-Al₂O₃-SrO glass system) to create a database for linear regression analysis.

The thermal expansion data were fit reasonably well by an expression in which the sealant composition was described by four mole fractions: lanthanum borate, alumina, silica, and boron oxide. The intercept value in this case is associated with pure strontia. With an R² value of 0.86 and a standard error

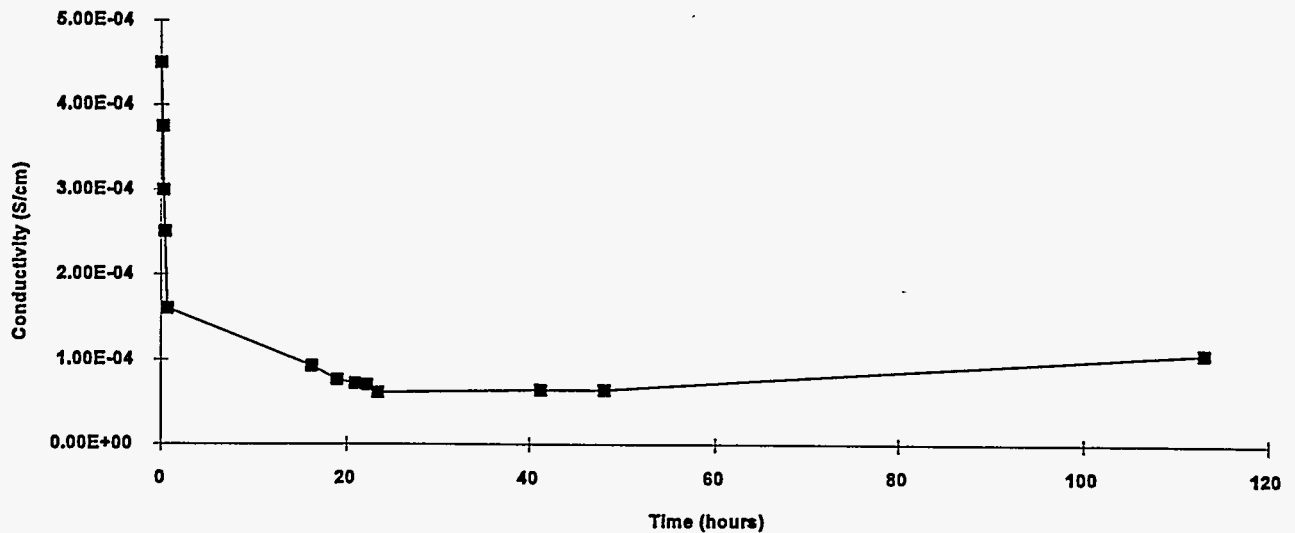


Figure 1. Conductivity of Sealant Material in 1-V Applied Gradient.

of 1.00, the coefficient of thermal expansion, CTE, is given by:

$$\text{CTE} = 18.6 - 3.7[\text{LaBO}_3] - 11.6[\text{Al}_2\text{O}_3] - 13.6[\text{SiO}_2] - 16.4[\text{B}_2\text{O}_3]$$

This equation allows us to predict with some accuracy the expansion coefficient of a material whose composition falls within the range that we have studied (although this linear expression will probably not be useful for dramatic compositional changes). Linear regression analysis was also used to study the softening behavior of our materials, but no reliable expression was found. In general, materials that were lower in boron oxide, and higher in lanthana and strontia, had higher softening points.

We used ICP-AES analysis to check for variations from nominal compositions in the actual samples. Figure 2 gives the deviations from nominal composition (in

percent of the nominal amount of each component) for six different materials. Materials G42, G43, G45 and G47 have low-lanthana, high-silica compositions compared with the two versions of Material K on the left. The general trend is for the low-silica materials to be deficient in strontium and aluminum, while those high in silica are deficient in boron oxide. These trends are probably the result of segregation in the melt, which is likely to occur during small-scale, unstirred melt processing.

Scaled-Up Production Methods

Two commercial glass manufacturers produced scaled-up batches of Material K, and the resulting powders were analyzed for compositional and microstructural changes. The ICP-AES analyses are given in Table 1 for two batches, one from each manufacturer, along with the composition of Argonne-

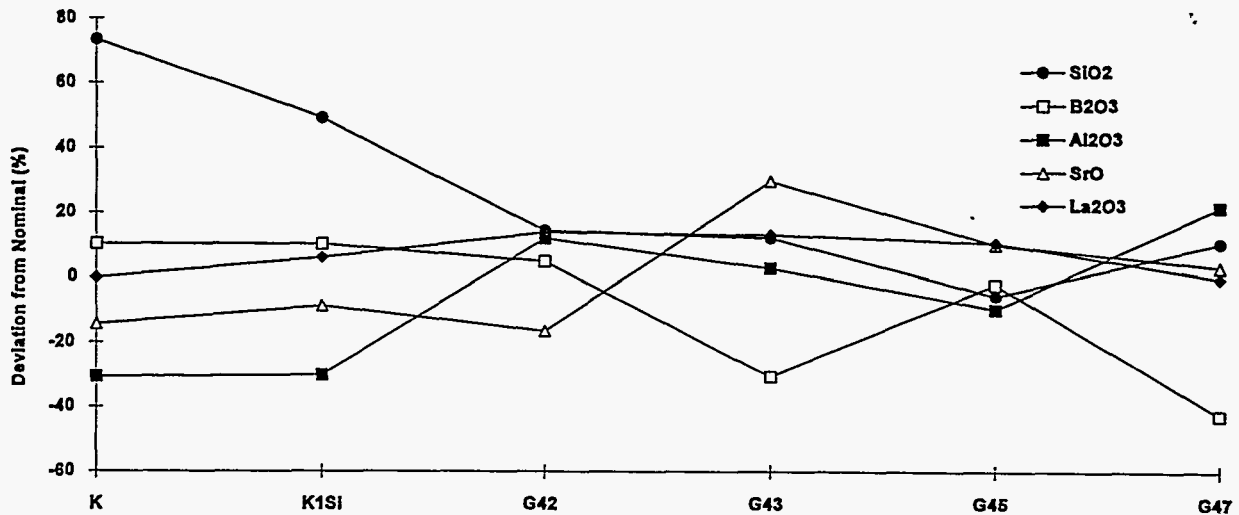


Figure 2. Deviation from Nominal Composition for Six Materials.

produced material. The nominal composition is included for comparison.

The low values for strontia and alumina in the Argonne sample suggest segregation of these oxides during the process. Segregation of strontium-aluminum compounds was confirmed by using X-ray diffraction on an unstirred test melt produced by one manufacturer. Segregation is not expected in full-scale, stirred melt processing.

According to the manufacturer, the large deviation from the nominal strontia amount was due to the raw material: the strontium nitrate was contaminated with sodium. This problem has since been corrected, but is an example of problems that may be encountered during scale-up. The composition of Batch 2 matched the nominal composition fairly well, and with further fine-tuning of the starting composition based on these results, the manufacturer expects to achieve the desired final composition.

FUTURE WORK

Several fuel cell manufacturers have made successful seals with Argonne-produced materials and wish to license the technology for the production of these sealants. Future work will include the analysis of commercial batches now scheduled to be poured, and further modification of the raw material amounts if necessary. Sealants with modified properties for specialized applications may also need to be developed.

This work is supported by the U.S. Department of Energy under contract no. W-31-109-Eng-38.

Table 1. Compositions of Material K Batches Produced by Different Methods

Oxide	Nominal mol%	Argonne mol%	Batch 1 mol%	Batch 2 mol%
SiO ₂	4.6	8.11	9.06	4.99
B ₂ O ₃	36.6	40.3	42.6	35.2
Al ₂ O ₃	10	6.92	8.73	7.51
SrO	28.7	24.6	13.6	30.9
La ₂ O ₃	20.2	20.1	22.5	21.4
Na ₂ O	0	0	3.51	0