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**Development of Materials
for Open-Cycle
Magnetohydrodynamics
(MHD): Ceramic Electrode,
Final Report**

**J. L. Bates
D. D. Marchant**

September 1986

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
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251-275	A012
276-300	A013

DEVELOPMENT OF MATERIALS FOR OPEN-CYCLE
MAGNETOHYDRODYNAMICS (MHD): CERAMIC
ELECTRODE, FINAL REPORT

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Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

Pacific Northwest Laboratory, supported by the U.S. Department of Energy, developed advanced materials for use in open-cycle, closed cycle magnetohydrodynamics (MHD) power generation, an advanced energy conversion system in which the flow of electrically conducting fluid interacts with an electric field to convert the energy directly into electricity. The purpose of the PNL work was to develop electrodes for the MHD channel. Such electrodes must have: 1) electrical conductivity above $0.01 \text{ (ohm-cm)}^{-1}$ from near room temperature to 1900K, 2) resistance to both electrochemical and chemical corrosion by both slag and potassium seed, 3) resistance to erosion by high-velocity gases and particles, 4) resistance to thermal shock, 5) adequate thermal conductivity, 6) compatibility with other channel components, particularly the electrical insulators, 7) oxidation-reduction stability, and 8) adequate thermionic emission. This report describes the concept and development of high-temperature, graded ceramic composite electrode materials and their electrical and structural properties.

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1.0 INTRODUCTION

Pacific Northwest Laboratory (PNL),^(a) supported by the U.S. Department of Energy (DOE), is developing advanced materials for use in magnetohydrodynamics (MHD) power generation, an advanced energy conversion system in which the flow of an electrically conducting fluid interacts with a magnetic field to convert the energy directly into electricity. In a coal-fired, open-cycle MHD generator, the fluid is a hot combustion gas, seeded with potassium to make it electrically conducting (Bates 1969, 1978c). In the simplest MHD channel, the high-velocity gas at 2800K flows through a rectangular channel where it interacts with a perpendicular magnetic field to create a DC-current flux in the third orthogonal direction. The active elements of this MHD channel are the anode and cathode electrode walls, which transfer the electric current from the gas plasma to an external load.

For a Faraday or linear channel, the electrode wall consists of alternating slabs of electrodes and insulators over which the hot gas passes at velocities near the speed of sound. The electrodes may be "cold" metal that operates near 750K, or "hot" ceramics that operate above 1600K. In a clean fuel, such as natural gas, the potassium may interact with the electrode/insulator materials, including condensation on the walls if a cold electrode is used. In coal-fired systems, layers of coal slag containing potassium may also condense and interact with the channel wall if the electrode temperatures are lower than 1600K. In both electrode systems, the DC-current moves perpendicularly to the electrode wall, passing to and from the electrode/gas interface.

In cold channel walls in clean fuel, the current must pass through a cold, gas boundary layer. In coal-fired channels, the coal slag will condense on the cold electrode, and the current must pass through the slag layer, which also is a poor electrical conductor at low temperatures. Electrical transport across these insulating layers occurs by arcing or other current breakdown processes. This results in ohmic losses and current instabilities with energy loss.

(a) Operated for the DOE by Battelle Memorial Institute.

The high electrode surface temperatures in ceramic electrode channels eliminate the cold gas or coal slag boundary layers so that the current can pass directly across the solid/gas interface free of the arcing and current instabilities that result in ohmic or breakdown losses. In addition, the low thermal conductivity of the ceramic reduces heat loss from the channel.

The hot, ceramic electrode, although both electrically and thermally attractive for MHD channel operation, must also be resistant to the high-temperature interactions between the high-velocity plasma, the coal slag, the potassium seed, and the high electrical DC-current densities (Bowen 1979; Bowen and Rossing 1976a,b). This places stringent requirements on the properties of the electrode materials. These electrodes must have: 1) electrical conductivities above $0.01 \text{ (ohm-cm)}^{-1}$ from near room temperature to 1900K, 2) resistance to both electrochemical and chemical corrosion by both slag and potassium seed, 3) resistance to erosion by high-velocity gases and particles, 4) resistance to thermal shock, 5) adequate thermal conductivity, 6) compatibility with other channel components, particularly the electrical insulators, 7) oxidation-reduction stability, and 8) adequate thermionic emission.

The MHD electrode ceramic materials for hot-walled channels are of two major classes. The first of these are electrically conducting ceramics that exhibit only small variations in electronic conduction with temperature and can conduct at room temperature (e.g., graphite, ZrB_2 , doped LaCrO_3). These materials are generally not compatible with oxygen, combustion gases, and/or seed at high temperatures. The second class of materials are the more chemically resistant oxides, such as stabilized ZrO_2 . These have adequate electrical conductivity at temperatures above 1600K, but unacceptably low electrical conductivity at lower temperatures. These lower electrical conductivities result in high Joule losses and thermal and electrochemical instabilities. In addition, the stabilized ZrO_2 is an ionic conductor, and the current transferred to the cold metal conductor must involve an oxidation-reduction reaction. Large chemical gradients may occur as current densities increase, resulting in the potential for chemical degradation.

The purpose of the work described in this report was to develop high-temperature ceramic electrodes that meet the requirements described above,

especially that of a hot, thermally and chemically stable surface adjacent to the hot plasma, adequate electric conduction at all temperatures, electrochemical stability in seed and coal slag, and an electronically conducting, cold oxide surface that can be attached to the metal current connection. This report describes the concept of a high-temperature, graded ceramic composite electrode and the research directed toward its development. Although a channel was designed and constructed for testing this concept, the scope of the program did not accommodate testing the channel. Details of this research and development can be found in a series of reports,^(a) publications,^(b) and patents.^(c)

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- (a) Bates 1975, 1976a through e, 1977a and b, 1978a and b; Bates and Marchant 1978a, 1979a through c, 1982a and b, 1983a through c; Bates, Griffin and Marchant 1981.
 - (b) Anderson et al. 1978; Bates 1977c; Bates and Garnier 1981; Bates and Marchant 1978; Bates and Mellinger 1975; Bates, Rossing and Bowen 1976; Cadoff et al. 1978; Marchant and Bates 1980a and b; Marchant, Griffin and Bates 1978; Romanov et al. 1976.
 - (c) Bates and Marchant 1980, 1981.

2.0 GRADED CERAMIC COMPOSITE ELECTRODE

2.1 BACKGROUND

A high-temperature ceramic electrode was developed for hot-wall channels of open-cycle, coal-fired MHD power generation systems. This graded ceramic composite electrode was designed to operate at plasma/electrode surface temperatures above 1800K. These high plasma/electrode surface temperatures can improve channel performance and efficiency by: 1) eliminating the arcing between the plasma and the electrode surface, 2) reducing heat losses, and 3) eliminating or minimizing slag deposition on the electrode-insulator surfaces, thereby reducing the interactions of electrochemical corrosion. The high temperatures introduce a number of other electrode requirements that are not relevant to cold electrode systems. The major requirement is for refractory materials (oxides) that exhibit a high electrical conductivity, greater than $0.1 (\text{ohm-cm})^{-1}$, over the wide temperature range and large temperature gradients that exist from the hot ceramic electrode/plasma surface ($>1800\text{K}$) to the cold metal base ($<500\text{K}$). However, these high temperatures enhance the chemical and electrochemical reactions between the plasma, slag, insulators, and other materials and the ceramic electrode; the rates of these reactions increase significantly with temperature. Furthermore, ceramics generally exhibit poor thermomechanical resistance and the mismatch in thermal expansion makes it difficult to bond the ceramic electrode to the metal (Cu) base.

The graded ceramic composite electrode was being developed to address the problems described above. The criteria used in the development effort were that the electrode should be: 1) thermodynamically stable with a high melting point and low vapor pressure; 2) electrically conducting at room temperature and above; 3) electrochemically stable to potassium seed, coal slag and electrical insulators; and 4) easily fabricated with a graded composition.

The graded ceramic composite electrode concept consists of a refractory, thermally stable, electrically conducting oxide, such as cubic stabilized HfO_2 or ZrO_2 , which can be exposed to the high-temperature plasma. This high-temperature, electrically conducting oxide (which does not exhibit high electrical conductivity at lower temperatures) is graded in chemical composition

with other oxide additions into a low-temperature, electrically conducting oxide (which is generally less refractory at high temperatures) that can be attached to the cold metal base. This concept is shown schematically in Figure 1. The example in Figure 1 indicates three compositions; however, only two may be required and more than three could be advantageous. In addition, the gradations may be either as distinct steps or as continuous gradations in composition. As shown, the result is a composite electrode with high electrical conductivity over the large temperature gradient from the plasma surface to the metal base. Furthermore, the electrode surface is thermodynamically stable and corrosion resistant even at the high temperatures of the plasma.

2.2 MATERIALS SELECTION

Two critical areas were addressed in developing this ceramic electrode concept: 1) the refractory oxides, intermediate oxides, and low-temperature, electrically conducting oxides (designated as the oxide current leadout) must be structurally, thermomechanically, and electrochemically compatible with each other under MHD channel operating conditions; 2) the oxide current leadout must be attached to the cold metal base to accommodate the thermomechanical stresses due to the expected mismatch in thermal expansion between the oxide and the metal. At the same time, this attachment must conduct both electricity and heat.

The materials selected for use in this electrode were centered around HfO_2 stabilized into the face-centered-cubic (fcc), fluorite phase with RE_xO_y (RE = rare earth) as the high-temperature electrode composition. Using this same $\text{HfO}_2\text{-RE}_x\text{O}_y$ base, other metal oxides were added to make the oxide electrically conducting at low temperatures while retaining its original thermal mechanical properties. The development was centered around $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ as the oxide current leadout composition. HfO_2 was selected over ZrO_2 because of its higher thermodynamic and chemical stability and because the monoclinic to tetragonal to cubic phase transition temperatures are 500 to 800K higher for HfO_2 than for ZrO_2 . The rare-earth-stabilized HfO_2 had exhibited significant resistance to electrochemical corrosion in molten coal slags and alkali salts (Cadoff et al. 1978; Marchant and Bates 1980a and b; Marchant, Griffin and

FIGURE 1. Concept of Graded Composite Electrode with Refractory Oxide and High Conducting Current Leadout

Bates 1978). Indium oxide has also demonstrated the ability to substantially increase the electrical conductivity of the rare-earth-stabilized HfO_2 and to make the oxide electronically conducting with only small changes in the thermal expansion properties (Marchant and Bates 1980a and b; Marchant, Griffin and Bates 1978).

Preliminary studies were conducted on a number of other rare-earth and hafnium-oxide systems to determine which binary and ternary systems might exhibit the best electrochemical corrosion resistance with the potential for adequate electrical conductivity at low temperatures. This investigation included praseodymium, neodymium, samarium, europium, terbium, erbium, ytterbium, and yttrium oxides combined with hafnium oxide. In the range of 10 to 20 mol% rare-earth of the stabilized HfO_2 , the electrochemical corrosion resistance, determined using a simple immersion method at 1675K in molten "Rosebud" coal slag containing 5% potassium carbonate, showed the relative reactivity as oxide additions to be $\text{Eu} > \text{Sm} > \text{Yb} > \text{Pr} > \text{Y} > \text{Tb}$. All were more reactive than pure HfO_2 . Preliminary electrical conductivity studies using these same oxides showed that Pr and Yb oxide additions gave the highest electrical conduction in

the $\text{PrO}_{1.83}\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ systems. Thus, research centered on the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ with Yb_2O_3 added in smaller amounts.

The $\text{In}_2\text{O}_3\text{-SnO}_2$ system was studied as a possible substitute for In_2O_3 to increase the thermal and electrochemical stability of the In_2O_3 -stabilized HfO_2 while retaining high electronic conductivity. $\text{In}_2\text{O}_3\text{-SnO}_2$ might also have been selected as one of the compositions in the graded composite ceramic electrode if the thermal expansion were found to match that of the other graded compositions.

3.0 FABRICATION

Methods for synthesizing and processing the $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ were developed to fabricate samples for physical property, phase equilibria, and electrochemical studies and for MHD electrode testing. Ceramic bodies with reproducible properties, controlled density, and similar structures were required. Because these materials were not available commercially and the techniques for synthesizing and processing the ceramic powders into ceramic shapes were not available, it was necessary to develop methods for fabricating powders from starting materials and for sintering them into compacts. In addition, the sintering rates for the different oxides must be the same to fabricate the different compositions into an integral electrode during the same sintering process.

Simple techniques of mixing, pressing, and sintering the individual oxides were not successful and resulted in low-density, multiphase compacts, and reproducibility was difficult. Some high-density, single-phase compositions could be prepared by sintering above 2150K; however, it was necessary to lower the sintering temperatures below 1875K so that the lower-temperature, hafnium-base current leadout materials containing In_2O_3 could be prepared with, and as an integral part of, the highly refractory oxide.

A coprecipitation synthesis process was developed for fabricating $\text{HfO}_2\text{-RE}_x\text{O}_y$ and $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ with reproducible, high-density sintered bodies having uniform microstructures and properties. The technique was flexible, in that a wide selection of $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ compositions could be prepared by this technique. The technique involved the dissolution of rare-earth oxide powder in nitric acid (although some rare earths could be purchased in nitrate form). These salt solutions were then mixed with hafnium salts (oxychloride, nitrates, or sulfates) and indium salt solutions, coprecipitated with ammonium hydroxide, filtered, washed, and dried. The precipitate was calcined to form the oxide. These powders were comminuted, cold pressed, and sintered. The typical process for fabricating these $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ compositions into high-quality, sintered compacts is outlined in the flowsheet in Table 1; the various steps are described in more detail in the paragraphs that follow.

TABLE 1. Fabrication Process and Properties of Ceramic Electrodes

Coprecipitation. The rare-earth-oxide powders were dissolved in concentrated nitric acid; the hafnium oxychloride, in water. The solutions were diluted and mixed and the mixed oxide powders were coprecipitated from the solution by using an ammonium hydroxide solution. The precipitate was filtered and washed sequentially with water, acetone, toluene, and again acetone before air drying. The resultant granular powder was a hydroxide salt that was calcined in air for four hours between 1073K and 1273K. X-ray diffraction (XRD) analyses of the post-calcined powders show that, for most compositions, the rare-earth stabilization of the hafnium powders occurred during calcination and resulted in the fluorite, pyrochlore, and monoclinic phases as predicted from the phase diagram.

Ball Milling. The powders were ball milled to break up the agglomerates that formed during calcination before pressing and sintering. Ball milling was performed in a Neoprene-lined mill with CaO-stabilized ZrO₂ grinding balls in a Freon TF wet grinding medium. The ball milling increased the surface area.

For example, the $0.29 \text{ PrO}_{1.83}0.5\text{Yb}_2\text{O}_3 \cdot 0.66\text{HfO}_2$ powder milled for 0, 10, and 960 minutes had surface areas of 12.4, 14.4, and $16.1 \text{ m}^2/\text{g}$, respectively. Ball milling also improved the flow properties of the powders and the uniformity of the sintered material.

Pressing. The powders were slugged at 69 MPa (10,000 psi) before passing through a -145 Tyler mesh screen. The slugged and granulated powder was pressed uniaxially in steel dies at 152 MPa (22,000 psi) into right parallelepipeds. For graded compositions, the high-temperature electrode composition (e.g., the stabilized HfO_2) was placed in the steel die and very lightly pressed to form a smooth surface; a uniform layer of the lower-temperature, electronically conducting oxide was then added and again lightly pressed in the die. Another uniform layer of the stabilized HfO_2 was added and pressed at high pressure. Humidity from the air provided an adequate binder. For final compaction, the green bars were isostatically pressed in double-rubber (plastic) evacuated containers in a water-soluble oil at 228 MPa (33,000 psi).

Sintering. The bars or cylinders were sintered between 1850K and 1875K in air. Sintering times varied from 8 to 20 hours, with 5-hour heatup and cool-down cycles. Sintering times and temperatures were selected according to the desired final density, powder characteristics and oxide compositions. Each bar or cylinder was then sectioned near the center to produce two electrodes. This multiple fabrication method was employed to eliminate fracture and bending of the bar during sintering due to slight mismatches in sintering rates between the two materials.

Since an integral electrode composed of more than one ceramic material was required for the graded ceramic composite electrode, it was necessary to prepare powders of the various compositions that could be sintered simultaneously into a single electrode bar. By controlling the coprecipitation, calcination, and ball milling, the sintering rates of the various oxides could be controlled. The powders of both the refractory oxide and the low-temperature, electrically conducting oxide were activated and deactivated by altering the calcining conditions. This provided approximately the same sintering rates and shrinkage during sintering so that the compact would not fracture during sintering and intimate contact could be obtained between the different ceramic materials.

For example, the 0.52 p.p.m. 0.52 p.p.m. powder milled for 0, 10, and 30 minutes had surface areas of 1.4, 1.4, and 1.1 m², respectively. Milling also improved the flow properties of the powder and the uniformity of the electrode material.

Preparation. The powders were milled at 60 MPa (10,000 psi) before passing through a 140-mesh screen. The milled and granulated powder was pressed uniformly in a steel die at 52 MPa (52,000 psi) into right circular pellets. For pressed compositions, the high-temperature electrode composition (e.g., the stabilized H₂) was placed in the center die and very lightly pressed to form a smooth surface. A uniform layer of the lower-temperature electrode composition was then added and again lightly pressed in the die. Another uniform layer of the stabilized H₂ was added and pressed at the pressure. Finally, from the air provided an electrode binder, which, in solution, the green bars were mechanically pressed in a rubber glass (c) evacuated container in a water-cooled oil at 52 MPa (52,000 psi).

Stacking. The sets of cylinders were stacked between 1850K and 1875K in air. Stacking times varied from 8 to 20 hours, with 8-hour intervals and cooling cycles. Stacking times and temperatures were selected according to the electrode finish density, power characteristics and oxide composition. Each bar or cylinder was then sectioned and the center to produce two electrodes. This multiple fabrication method was used to eliminate fracture and bending of the bar during stacking due to slight misalignment in stacking times between the two materials.

Since an integral electrode composed of more than one ceramic material was required for the various current composition electrodes, it was necessary to pre-heat powder of the various compositions that could be sintered simultaneously into a single electrode bar, by controlling the composition, as a function of the sintering rate of the various oxides could be controlled. The powder of both the electrolyte oxide and the low-temperature, electrode composition oxides were activated and activated by sintering the cathode composition. This provided a satisfactory sintering rate and shrinkage during sintering so that the cathode would not fracture during sintering and the contact could be obtained between the different ceramic materials.

4.0 PHASE EQUILIBRIA

A ternary phase diagram was developed for the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ system at 1823K in air to identify structures that might provide the highest electrical conductivity, best electrochemical corrosion resistance in molten coal slag and potassium seed, good thermal stability, and compatibility with stabilized HfO_2 . The diagram was developed with air-cooled samples using quantitative energy-dispersive x-ray analysis (EDAX) to identify the phase compositions and XRD to determine the crystallographic structures. The binary phase relationships were determined for the $\text{HfO}_2\text{-In}_2\text{O}_3$ and $\text{PrO}_{1.83}\text{-In}_2\text{O}_3$ systems; the $\text{HfO}_2\text{-PrO}_{1.83}$ had been determined previously (Kravchinskaya et al. 1973). The structures and compositions of samples inside the ternary were coupled with these binary-phase diagram data to generate the ternary diagram shown in Figure 2.

FIGURE 2. Proposed $\text{HfO}_2\text{-In}_2\text{O}_3$ Phase Diagram at 1823K

The $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ phase diagram revealed characteristics significant to the development of the current leadouts for the graded ceramic composite electrode. Two new phases were identified:

- An orthorhombic PrInO_3 phase was found in the $\text{PrO}_2\text{-In}_2\text{O}_3$ binary. This orthorhombic phase (with lattice parameters of $a, b, c = 0.567, 0.593, 0.818$ nm, respectively) has solubility limits from 30 to 36 mol% In_2O_3 . The higher indium solubility is found at the phase boundary next to the two-phase region consisting of the orthorhombic PrInO_3 and body-centered-cubic (bcc) In_2O_3 solid solution. The solubility limit of $\text{PrO}_{1.83}$ in the solid solution is about 2 mol%. The solubility of In_2O_3 in $\text{PrO}_{1.83}$ is between 7 and 10 mol% with a lattice parameter of 0.546 nm at maximum solubility compared to 54.7 nm for $\text{PrO}_{1.83}$.
- A rhombohedral $\text{Hf}_2\text{Pr}_2\text{O}_7$ compound was formed in the $\text{HfO}_2\text{-In}_2\text{O}_3$ binary. This structure may result from the anisotropic ordering of the fcc In_2O_3 -stabilized ZrO_2 , since this phase is only a few tenths of a degree from a cubic phase with $a = 2.35$ nm and $\alpha = 90.4^\circ$. The nominal composition of $\text{Hf}_2\text{In}_2\text{O}_7$ under microprobe analysis was 35 mol% In_2O_3 and 65 mol% HfO_2 . The HfO_2 is stabilized as fcc with 10 to 24 mol% In_2O_3 . These results differ from those of Saito, Maruyama and Kato (1983), who have reported that the solid solution decomposes to a mixture of monoclinic HfO_2 and cubic In_2O_3 below 1623K.

The In_2O_3 forms a solid solution with both HfO_2 and $\text{PrO}_{1.83}$ with a combined solubility near 10 mol%. The exact solubility limits were not determined. This bcc In_2O_3 solid solution exhibits a rare-earth, B-type, sesquioxide structure.

The $\text{PrO}_{1.83}\text{-HfO}_2$ binary reported by Kravchinskaya et al. (1973) was confirmed. The HfO_2 is stabilized into a fcc fluorite structure at high temperature up to about 36 mol% $\text{PrO}_{1.83}$ (24 mol% Pr_2O_3). The pyrochlore compound $\text{Hf}_2\text{Pr}_2\text{O}_7$ lies within the limits of 42 to 57 mol% $\text{PrO}_{1.83}$. The reported lattice parameter of the $\text{Hf}_2\text{Pr}_2\text{O}_7$ phase is 1.0662 nm.

The major portion in the center of the phase diagram most important to the high-electrical conducting oxides is made up of a phase field containing two or three phases of the structures detailed above. Using the above binary systems coupled with the examinations of ternary compositions with XRD and EDAX, a preliminary $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary phase diagram was developed. The ternary compositions were concentrated between the compositions between $\text{Hf}_2\text{Pr}_2\text{O}_7$, $\text{Hf}_2\text{In}_2\text{O}_7$, and the In_2O_3 -stabilized HfO_2 . Two large three-phase regions were identified: the orthorhombic, pyrochlore, and bcc solid solution and the pyrochlore, rhombohedral, and bcc solid solution. Two significant two-phase regions of pyrochlore/bcc solid solution and rhombohedral/bcc solid solution were also found in the phase diagram. Regions high in $\text{PrO}_{1.83}$ and HfO_2 remain to be defined. However, the results suggest that a compound may exist near $0.65\text{HfO}_2 \cdot 0.18\text{PrO}_{1.83} \cdot 0.17\text{In}_2\text{O}_3$. As will be discussed later, the highest electrical conduction is associated with these two- and three-phase compositions, while the highest corrosion resistance is associated with the phase highest in HfO_2 . The phase field is not complete, but it provided the direction for developing electronically conducting current leadout materials.

The major portion in the center of the phase diagram was important to the
physicists' conclusion which is made up of a phase field containing two or
three phases of the structure detailed above. Using the above phase diagram
coupled with the examination of ternary compositions with XRD and EPR, a phase
diagram (Fig. 1) for the ternary system was developed. The ternary
compositions were concentrated between the compositions between $\text{Hf}_{0.5}\text{Ti}_{0.5}$
and $\text{Hf}_{0.2}\text{Ti}_{0.8}$ and the $\text{Hf}_{0.5}\text{Zr}_{0.5}$ and $\text{Hf}_{0.2}\text{Zr}_{0.8}$ compositions were
identified. The orthorhombic, pyrochlore, and hexagonal phases and the
pyrochlore, rhombohedral, and hexagonal phases. Two significant two-phase
regions of pyrochlore/hexagonal and rhombohedral/hexagonal solid solution
were also found in the phase diagram. Regions with $\text{Hf}_{0.5}\text{Ti}_{0.5}$ and $\text{Hf}_{0.2}\text{Ti}_{0.8}$
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electrical conductivity is associated with these two- and three-phase composi-
tions, while the highest conduction resistance is associated with the phase
highest in HfO_2 . The phase fields are not complete, but it provides the direc-
tion for developing electrically conducting ceramic materials.

5.0 ELECTRICAL CONDUCTIVITY

An understanding of the electrical conductivity of the oxides is critical for selecting compositions, improving properties and structures and evaluating the performance of materials for use in the graded ceramic composite electrode. Electrical conductivities were determined in air as a function of temperature to identify the compositions, structures and phases relating to the phase diagram and to high electrical (electronic) conductivities.

Initial electrical conductivity studies were given to those HfO_2 rare-earth oxide systems that would provide the highest electrical conductivity and the best electrochemical corrosion resistance to molten coal slag containing potassium seed. Those systems with the highest potential were evaluated further; additions of In_2O_3 were made to increase the low-temperature electrical conductivity. The HfO_2 - In_2O_3 systems with $\text{PrO}_{1.83}$, Y_2O_3 , and Yb_2O_3 additions were selected for further studies of phase equilibria and electrical conductivity. The HfO_2 - $\text{PrO}_{1.83}$ - In_2O_3 system was eventually selected for the most in-depth research and development.

5.1 HfO_2 - RE_xO_y

The rare-earth stabilized hafnium oxides have demonstrated electrochemical stability in the potassium seed and coal slag environments (Marchant and Bates 1980a) and also are a critical part of the hot, graded composite ceramic MHD electrode. The selection of compositions for electrical conductivity studies was based upon electrochemical stability, fabricability, and rare-earth oxide additives that were thought to provide the highest electrical conductivities. Since only limited phase data have been reported for the HfO_2 - RE_xO_y systems, potential compositions and structures were often based on the better known and analogous ZrO_2 - RE_xO_y systems.

A four-contact technique was used to measure the electrical conductivity in air from 544 to 1704K. The oxide samples were prepared from coprecipitated powders which had been calcined at 1275K and ball milled to break agglomerates. The powders were uniaxially pressed followed by isostatic pressing. The samples were sintered in two ways: 1) in 2.67×10^{-2} Pa (2×10^{-4} torr) vacuum

at 2225 to 2275K for 4 to 5 hours followed by an air anneal at 1475K for 8 hours, or 2) in air at 1825K for 20 hours. The microstructures for all compositions (Table 2) were similar, with small, 1- to 2- μ m closed pores. Sample D had larger, irregularly shaped pores with a second phase present. Samples Q and O contained microcracks after measurements were completed. All others were single phase.

TABLE 2. Composition and Density of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

Electrode		Composition, mol%						Density, g/cm ³
		HfO_2	Er_2O_3	$\text{PrO}_{1.83}$	Tb_4O_7	Y_2O_3	Yb_2O_3	CeO_2
O	a,b	91.4		8.6				8.44
Q	a,b	80		20				8.94
A-17	a,b	66		29			5	8.80
A-273-1	c	66		29			5	8.34
A-273-2	c	66		29			5	8.39
F	a,b	77.6		17.5			2.9	8.54
V	a,b	89.5		5.3			9.2	9.14
120-3	c	80	10	10				8.59
C-4	a,b	80	10		10			8.36
100-2	c	90			10			7.02
101-2	c	85		5	5		5	6.73
P	a,b	94.5			5.5			8.05
P-202	a,b	94.5			5.5			8.37
B-1	a,b	88			6	6		8.97
B-273-1	c	88			6	6		8.13
R	a,b	80				20		6.24
I	a,b	82				8		7.93
B	a	89					11	9.43
D	a,b	80					20	7.43

- (a) Sintered in 2.67×10^{-2} Pa vacuum at 2225 to 2275K for 4 to 5 hours.
 (b) Annealed in air between 1375 and 1475K for 8 hours.
 (c) Sintered in air at 1875 to 1925K for 20 hours.

The electrical conductivities for most compositions could be represented by one or two straight ($\log_{10}\sigma$ versus K^{-1}) lines, one for the high-temperature and one for the low-temperature data (see Figure 3 and Table 3). The break in the curves generally occurred below 1000K. Some data exhibited a change in slope at lower temperatures, but it was either nonreproducible or could not be resolved into two linear relationships. The data for D, R, P, 100-2 did not exhibit breaks in the $\log_{10}\sigma$ versus K^{-1} curves even though measurements were made to temperatures as low as 625K. However, these oxides were approaching the lower conductivity value limit, which can be measured using the four-contact technique.

Two oxides, Q and V, exhibited a reproducible decrease in electrical conductivity above ~1620K. The cause of this decrease was not known. The lowest conductivity values for O and Q could possibly be attributed to sample cracking during the electrical conductivity measurements.

The activation energies for the high-temperature and low-temperature conductivities varied between 0.85 and 1.38 eV and 0.24 and 0.98 eV, respectively. Some compositional factors appear to have influenced the high-temperature activation energy. Generally, the results suggest that an increase in HfO_2 content and a decrease in $PrO_{1.83}$ content result in an increase in the activation energy. Those samples, A-17, A-273-1, and A-272-2, that had high $PrO_{1.83}$ concentrations exhibited higher high-temperature activation energies than that expected simply by reducing the HfO_2 concentration. There appears to have been a slight increase in activation energy with decreasing Yb_2O_3 . No patterns could be resolved for the effects of Tb_4O_7 , Er_2O_3 , or Y_2O_3 . Those high- HfO_2 oxides without $PrO_{1.83}$ (B, P-202, P, and I) exhibited the lowest activation energies (0.83 to 0.86 eV).

A comparison of the magnitudes of the conductivities at 1000K suggests that the conductivity increases with increasing HfO_2 content above 80 mol%, increases with increasing Yb_2O_3 content, and decreases slightly with increasing Y_2O_3 and $PrO_{1.83}$ content. The effects of Tb_4O_7 and Er_2O_3 could not be defined with any certainty.

The electrical conductivities of 0.028 and 0.0043 (ohm-cm) $^{-1}$ and activation energies of 1.12 and 1.4 eV for these rare-earth stabilized HfO_2 oxides

FIGURE 3. Electrical Conductivities of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

TABLE 3. Electrical Conductivity of $\text{HfO}_2\text{-RE}_x\text{O}_y$ Electrode Materials

Electrode Material	High Temperatures					Low Temperatures			
	Log ₁₀ ^σ = A-B/K, S/m)		Energy, Temperatures,			Log ₁₀ ^σ = A-B/K, S/m)		Energy, Temperatures,	
	A	B(10 ³)	eV	K		A	B(10 ³)	eV	K
O	2.211	4.954	0.98	1019-1411		-1.438	1.205	0.24	800-1019
Q	3.184	6.073	1.21	1316-1620	(a)	-	-	-	-
A-17	5.300	6.912	1.37	1080-1451		3.550	4.918	0.98	806-1080
A-273-1	4.896	6.497	1.29	986-1532		1.587	3.220	0.64	813-986
A-273-2	4.644	6.087	1.21	1110-1493		2.775	3.973	0.79	834-1110
F	4.472	5.745	1.14	1007-1514		3.235	4.415	0.88	816-1007
V	4.625	5.266	1.05	863-1680	(a)	-	-	-	-
120-3	5.001	6.146	1.22	929-1665		-	-	-	(b)
C-4	3.822	5.011	1.00	1023-1539		0.160	1.458	0.29	544-911 (c)
100-2	4.631	5.460	1.08	753-1657		-	-	-	(d)
101-2	4.493	5.210	1.03	860-1664		-	-	-	-
P	3.557	4.328	0.86	619-1609		-	-	-	-
P-202	4.084	4.303	0.85	1149-1520		-	-	-	-
B-1	5.454	6.946	1.38	1000-1491		2.938	4.380	0.87	777-1000
B-273-1	4.625	5.891	1.17	1020-1553		3.305	4.191	0.83	862-1020
R	4.106	5.562	1.10	909-1705		-	-	-	-
I	4.048	4.345	0.86	807-1467		-	-	-	(b)
B	4.230	4.156	0.83	910-1515		0.284	1.996	0.40	794-910
D	4.789	6.585	1.31	808-1499	(e)	-	-	-	-

(a) Reproducible decrease in $\text{log}_{10}\sigma$ above 1620 K.

(b) A low temperature $\text{log}_{10}\sigma$ which could not be analyzed.

(c) Decreasing temperature data only. Some variations on heating.

(d) Indications of change in slope at lower temperatures.

(e) Some irregularities on heating.

Note: Some data are not illustrated on Figure 3.

were very near the reported values for $0.08\text{Y}_2\text{O}_3 \cdot 0.92\text{HfO}_2$ and $0.20\text{Y}_2\text{O}_3 \cdot 0.80\text{HfO}_2$, respectively, at 1275K (Besson, Deportes and Robert 1966). The sample of $0.2\text{Y}_2\text{O}_3 \cdot 0.8\text{HfO}_2$ had values of $0.006 \text{ (ohm-cm)}^{-1}$ and 1.1 eV at 1275K. The reported values at 1275K for $0.125\text{CaO} \cdot 0.875\text{ZrO}_2$ were $0.005 \text{ (ohm-cm)}^{-1}$ and 1.83 eV (Johansen and Cleary 1964).

Compositions similar to $0.29\text{PrO}_{1.83} \cdot 0.05\text{Yb}_2\text{O}_3 \cdot 0.66\text{HfO}_2$ (A-273-1) and $0.06\text{Tb}_4\text{O}_7 \cdot 0.06\text{Y}_2\text{O}_3 \cdot 0.88 \text{HfO}_2$ (B-272-1) were to be tested in MHD facilities. The phases present in these two compositions have been studied in detail using XRD and scanning electron microscopy (SEM)-EDX. These results indicate that the A-273-1 was mainly a pyrochlore fcc structure (possibly $\text{Pr}_2\text{Hf}_2\text{O}_7$) with a fcc fluorite second phase. The unit cell values of 1.032 nm (10.32 Å) were consistent with the 1.061 to 1.0068 nm for low-temperature reacted $\text{Pr}_2\text{Hf}_2\text{O}_7$. B-273-1 is a single-phase fcc fluorite with a unit cell of 0.517 nm. This is very close to values reported for $\text{Tb}_2\text{Hf}_2\text{O}_7$ (0.5205 to 0.5216 nm) and $\text{Yb}_2\text{Hf}_2\text{O}_7$ (0.5141 to 0.5143 nm) (Portnoi et al. 1970).

The compositions from 29 to 39 mol% $\text{PrO}_{1.83}$ are expected to be predominantly a pyrochlore structure (Kravchinskaya et al. 1973) with an anticipated lower electrical conductivity as the $\text{PrO}_{1.83}$ increases. Conversely, the additions of Er_2O_3 , Tb_4O_7 , Yb_2O_3 and Y_2O_3 were reported to stabilize the fluorite cubic phase (Portnoi et al. 1970; Glushkova and Krzhizkanovskaya 1973), resulting in a higher electrical conductivity. However, the conductivity of the pyrochlore is expected to be mainly electronic, while the fluorite phases will possibly be predominantly ionic or mixed; however, this has yet to be demonstrated.

5.2 $\text{HfO}_2\text{-In}_2\text{O}_3$

The $\text{HfO}_2\text{-In}_2\text{O}_3$ was studied initially because of the high conductivity of the bcc In_2O_3 solid solution (ss), the similarity of the In_2O_3 -stabilized HfO_2 to the Y_2O_3 -stabilized HfO_2 considered as the high-temperature, refractory cap of the graded electrode, and because it is an essential binary system of the $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ ternary system. The electrical conductivity between 17 and 40 mol% In_2O_3 (Table 4) decreased with increasing In_2O_3 and reached a minimum near near 40%, which corresponds in general to the $\text{Hf}_2\text{In}_2\text{O}_7$ rhombohedral

TABLE 4. Compositions of $\text{HfO}_2\text{-In}_2\text{O}_3$, mol%

Sample	HfO_2	In_2O_3
FC-13-3	0	100
FC-53	69	31
FC-14-1	60	40
FC-52	50	50
FC-54-1	83	17

composition (Figures 4 and 5 and Table 5). The conductivity then increased rapidly between 40 and 50 mol%, which is attributed to the increasing presence of the bcc In_2O_3 (ss) phase. The conductivity should continue to increase with increasing In_2O_3 content as the bcc In_2O_3 (ss) increases in this two-phase region, reaching values near that for In_2O_3 , $<10^2$ (ohm-cm) $^{-1}$. The electrical

FIGURE 4. Electrical Conductivity of $\text{HfO}_2\text{-In}_2\text{O}_3$, $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ Single Crystal and $\text{HfO}_2(\text{Y}_2\text{O}_3)$. Percentages are mol% In_2O_3 .

FIGURE 5. Electrical Conductivity - Activation Energy $\text{HfO}_2\text{-In}_2\text{O}_3$

conductivity of the 17 mol% In_2O_3 with the fcc structure is only slightly lower than the conductivity for the 10 mol% Y_2O_3 HfO_2 or ZrO_2 , which exhibits the highest electrical conductivity of the fcc-stabilized systems. The extrapolation of the electrical conductivity data for a 10 mol% In_2O_3 in HfO_2 suggests conductivity values near that for Y_2O_3 -stabilized HfO_2 and ZrO_2 . Thus In_2O_3 appears to be effective in the fcc stabilization of HfO_2 .

Saito, Maruyama and Kato (1983) reported electrical conductivity values for 20 to 30 mol% In_2O_3 in HfO_2 that show a decrease in conductivity with increasing mol% In_2O_3 ; however, these values are 5 to 50 times higher than those in the present study. The activation energy was reported to be nearly constant (~ 1.7 eV) over this composition range, while those of this study varied from 1.2 to 2.3 eV (Figure 5). These differences are attributed to the

TABLE 5. Compositions and Electrical Conductivity of $\text{HfO}_2\text{-In}_2\text{O}_3$

Sample	Composition, mol%		$\text{Log}_{10}\sigma^{(a)} = A-BK^{-1}$		Temp. Range, K	Activation Energy, eV	Coefficient Determination, R^2
	HfO_2	In_2O_3	A	B			
FC-13-3	0	10	1.752	-0.1560 ^(b)	397-1631	--	0.890
FC-53	69	31	4.238	9.423	994-1719	1.87	0.980
FC-14-1	60	40	5.465	11.54	986-1655	2.29	0.999
FC-52	50	50	2.521	5970	668-1731	1.19	0.980
FC-54-1	83	17	3.422	6419	657-1726	1.27	0.985

(a) $(\text{ohm-cm})^{-1}$.

(b) Slope is positive.

differences in the fabrication methods. Saito, Maruyama and Kato sintered admixtures of HfO_2 and In_2O_3 powders; this could have resulted in inhomogeneous structures, the inability to form the rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ phase during sintering and the presence of the bcc In_2O_3 (ss) phase at lower In_2O_3 content, which results in higher electrical conductivity.

5.3 $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$

The electrical conductivities of compositions in the $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ were measured to determine the phase fields and phases that exhibit the highest electrical conductivity. Results for compositions listed in Table 6 in the center of the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary were emphasized; these results are summarized in Table 7 and in Figures 6 and 7, and also include samples with similar compositions containing a few percent Yb_2O_3 or other rare-earth oxides.

The electrical conductivity of the major phases in the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ system were determined as a base for further study of the two- and three-phase structures in this system. The results for $\text{Hf}_2\text{In}_2\text{O}_7$ were discussed

TABLE 6. Composition and Density of Oxide Current Leadouts

	Composition, mol%						Density, g/cm ³
	HfO_2	In_2O_3	$\text{PrO}_{1.83}$	Y_2O_3	Yb_2O_3	Tb_4O_7	
BB	25	45	30	--	--	--	7.056
B-4	25	55	20	--	--	--	8.818
B-5	25	55	20	--	--	--	9.022
LLL-40	47	30	20	--	3	--	7.537
LLL-44	47	30	20	--	3	--	7.618
KKK	41	39	17	--	3	--	5.975
Z	25	55	--	20	--	--	7.557
Y	25	55	--	20	--	--	6.649
MMM	49	43	--	4	--	4	7.330
AA	25	45	--	--	30	--	7.207
EE	89	05	--	--	05	--	7.970
CC	96	01.5	--	--	2.5	--	0.998

TABLE 7. Electrical Conductivity of Oxide Current Leadouts

Electrical Conductivity (S/M) $\text{Log}_{10}\sigma = A - B(K^{-1})$

	High Temperature				Low Temperature			
	A	B	eV	K	A	B	eV	K
BB	5.462	1.970×10^3	0.391	800-1434	4.1278	8.811×10^2	0.175	562-763
					3.005	2.498×10^3	0.050	299-562
B-4	5.160	1.904×10^3	0.378	895-1651(a)	4.188	1.051×10^3	0.209	697-895
					2.8052	8.240×10^2	0.164	398-697
8-5	5.206	1.927×10^3	0.383	898-1649(a)	--	--		(b)
LLL-40	5.273	2.840×10^3	0.564	997-1508	3.516	9.953×10^2	0.198	646-997(a)
LLL-44	5.530	3.325×10^3	0.660	1151-1551	3.758	1.375×10^3	0.273	851-1052
KKK	6.496	3.120×10^3	0.620	950-1491	4.045	7.773×10^2	0.154	612-950(a)
Z	7.289	7.616×10^3	1.51	940-1450	--	--		(b)
Y	7.289	5.798×10^3	1.15	940-1350	2.1517	8.410×10^3	0.167	720-940
MMM	5.275	2.038×10^3	0.405	829-1556	--	--		(b)
AA	7.207	9.034×10^3	1.79	900-1452	4.855	1.758×10^3	0.173	665-900
EE	4.908	5.060×10^3	1.00	697-1415	--	--		
CC	4.346	4.644×10^3	0.912	770-1538				
AF-1	4.378	9.695×10^3	1.925	1324-1503	-0.5501	-3.596×10^3	0.71	791-1242
AG-1	1.958	3.178×10^3	0.63	930-1725	-0.449	8.118×10^2	0.16	643-930
AB-1	3.878	2.783×10^3	0.55	987-1647	1.138	2.544×10^2	0.05	335-930

(a) Difference on heating and cooling.

(b) Data irregular at low temperatures; e.g., higher scatter at room temperature.

FIGURE 6. Electrical Conductivity of Oxide Current Leadouts

previously. The electrical conductivity of the orthorhombic PrInO_3 and the pyrochlore $\text{Hf}_2\text{Pr}_2\text{O}_7$ is low, with values between 10^{-3} and $10^{-4} (\text{ohm-cm})^{-1}$ at 1273K and a high temperature dependence. The electrical conductivity of the monoclinic HfO_2 is even lower, 10^{-4} to $10^{-5} (\text{ohm-cm})^{-1}$.

5.4 $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$

The single-phase bcc In_2O_3 (ss) containing HfO_2 and/or $\text{PrO}_{1.83}$ exhibits the highest electrical conductivity, $<10^2 (\text{ohm-cm})^{-1}$, and a very small temperature dependence. Those phases fields associated with this bcc In_2O_3 (ss) also have high electrical conductivities. This includes the two-phase fields containing either the $\text{Hf}_2\text{Pr}_2\text{O}_7$ or $\text{Hf}_2\text{In}_2\text{O}_7$ phases or the two three-phase fields that border on them. Using the preliminary phase diagram for the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ system shown in Figure 2, the concentration of the bcc In_2O_3 (ss) was estimated from each of the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ compositions. The bcc In_2O_3 (ss)

FIGURE 7. Electrical Conductivities of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ at 923K, 1273K, and 1667K as a Function of In_2O_3 Content

was assumed to be the major contributor to the overall conductivity. The logarithm of the electrical conductivities as a function of bcc In_2O_3 (ss) content at 923K, 1273K, and 1667K shows a nearly linear increase up to 30 mol% (Figure 7). At higher concentrations, the data exhibit more scatter but appear to reach a near-constant value at each temperature, up to 60 mol% bcc solid solution. It should be noted that all of the compositions above 30 mol% in Figure 7 contain some Yb_2O_3 , with one exception. These data confirm that the major conducting phase in the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary is the In_2O_3 (ss) and that the maximum conductivity value would be near 100 mol% In_2O_3 , measured previously to be near $100 (\text{ohm-cm})^{-1}$.

The activation energies for these compositions also exhibit significant scatter. However, there appears to be a general decrease in both the high- and low-temperature activation energies with increasing In_2O_3 (ss) concentrations.

Conductivities of compositions containing higher concentrations (6 to 3 mol%) of Yb_2O_3 (LLL and KKK) in $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ are also shown in Figure 7. These compositions exhibit larger electrical conductivities than those containing less Yb_2O_3 or those with no Yb_2O_3 . These compositions, as determined by XRD and SEM-EDX, are two-phase and do not contain the bcc In_2O_3 (ss) phase and the $\text{Hf}_2\text{In}_2\text{O}_7$ phase that contains some $\text{PrO}_{1.83}$. This suggests that other rare-earth oxides besides $\text{PrO}_{1.83}$ may: 1) form conducting phases free of the In_2O_3 (ss) and/or 2) stabilize high-temperature structures that revert on cooling to the In_2O_3 (ss).

In addition, the data also show the conductivity of a two-phase sample (AC) to be lower than that for the other oxides. This composition is in a two-phase sample region containing $\text{Hf}_2\text{In}_2\text{O}_7$ and In_2O_3 (ss) near the boundary of the three-phase pyrochlore, rhombohedral, and sesquioxide phase field. The lower conductivities are consistent with the previously reported electrical conductivities of the $\text{HfO}_2\text{-In}_2\text{O}_3$ rhombohedral phase. The lower conductivity values also suggest that $\text{PrO}_{1.83}$ may be requisite for higher electrical conductivity.

It has been observed in this study that samples with compositions in or near the two-phase $\text{Hf}_2\text{Pr}_2\text{O}_7$ region may exhibit a hysteresis on heating and cooling during the electrical conductivity measurements (see FC-54-1 in Table 5). Although the oxides were sintered at 1823K in air and measurements were made in air, some conductivity changes did occur for some samples. The magnitude of these changes varied among samples.

Generally, the conductivity on cooling was higher than that on heating. For some samples, the two straight lines in the $\log \sigma$ versus K^{-1} were eliminated and the cooling curve was linear over the entire temperature range. The cause of these changes was not determined; it is possible that some vapor loss of the more volatile In_2O_3 may have resulted in a compositional change,

especially near the sample surface. In addition, as suggested for the Yb_2O_3 -containing oxides, phase changes may occur during the measurements that change the conductivity values.

5.5 $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$

As was observed in Figure 7, the addition of small amounts of Yb_2O_3 to the $\text{HfO}_2\text{-PrO}_2\text{-In}_2\text{O}_3$ system increased the electrical conduction. To investigate this effect, the electrical conductivity was measured on a nominal $0.63\text{HfO}_2 \cdot 0.27\text{PrO}_{1.83} \cdot 0.10\text{YbO}_{1.5}$ base composition containing varied amounts of In_2O_3 . These compositions had also exhibited good corrosion to molten coal slag and alkali seed. These structures contain both the fluorite and pyrochlore phases in addition to the bcc In_2O_3 (ss). The electrical conductivities of the compositions listed in Table 8 are shown in Figure 8 and Table 7.

The results suggest a sharp increase in electrical conductivity near 25 mol% In_2O_3 , with smaller increases above 30 mol%. The range of compositions for the $\text{Hf}_2\text{Pr}_2\text{O}_7$ single-phase pyrochlore structure was 0.42 to 0.58 mol% HfO_2 . The above compositions were high in HfO_2 where both the fluorite and pyrochlore phases were present. The addition of In_2O_3 resulted in the formation of a three-phase structure containing the bcc In_2O_3 (ss).

To determine the effect of In_2O_3 and the bcc In_2O_3 (ss) on the pyrochlore structure containing Yb_2O_3 without the fluorite phase, a series of compositions containing equal amounts of HfO_2 and $\text{PrO}_{1.83}$ and 6 mol% Yb_2O_3 with varying amounts of In_2O_3 were studied in air to 1820K (Table 9). The five compositions were $(0.94 - x)[0.5\text{HfO}_2 \cdot 0.5\text{PrO}_{1.83}] \cdot x\text{In}_2\text{O}_3 \cdot 0.06\text{Yb}_2\text{O}_3$ with x between 20 and 40 mol%; see Table 10. The weight ratio of the bcc In_2O_3 (ss) and pyrochlore

TABLE 8. Compositions of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ Containing Yb_2O_3

AF-1	$0.85(0.27\text{PrO}_2 \cdot 0.63\text{HfO}_2 \cdot 0.10\text{YbO}_{1.5}) \cdot 0.15\text{In}_2\text{O}_3$
AG-1	$0.75(0.27\text{PrO}_2 \cdot 0.63\text{HfO}_2 \cdot 0.10\text{YbO}_{1.5}) \cdot 0.25\text{In}_2\text{O}_3$
LLL	$0.70(0.27\text{PrO}_2 \cdot 0.64\text{HfO}_2 \cdot 0.09\text{YbO}_{1.5}) \cdot 0.30\text{In}_2\text{O}_3$
AB-1	$0.43(0.27\text{PrO}_2 \cdot 0.63\text{HfO}_2 \cdot 0.10\text{YbO}_{1.5}) \cdot 0.57\text{In}_2\text{O}_3$
BB	$0.55(0.55\text{PrO}_2 \cdot 0.45\text{HfO}_2) \cdot 0.45\text{In}_2\text{O}_3$
KKK	$0.61(0.27\text{PrO}_2 \cdot 0.64\text{HfO}_2 \cdot 0.09\text{YbO}_{1.5}) \cdot 0.39\text{In}_2\text{O}_3$

FIGURE 8. Electrical Conductivity of Current Leadout Materials

TABLE 9. Compositions of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$

Sample	Composition, mol%				Phases, wt%	
	HfO_2	$\text{PrO}_{1.83}$	In_2O_3	Yb_2O_3	Pyrochlore	bcc
FC-157	27	27	40	6	50	50
FC-153	29.5	29.5	35	6	55	45
FC-154	32	32	30	6	65	35
FC-155	34.5	34.5	25	6	60	40
FC-156	37	37	20	6	67	33

TABLE 10. Electrical Conductivity of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$

Sample	Log $\sigma = A-B/K$		Temperature Range, K	Activation Energy, eV	Coefficient of Determination
	A	B(10^3)			
FC-157	4.268	4.253	1109 - 1576	0.84	0.992
	1.094	0.777	578 - 1109	0.15	0.922
FC-157 HT ^(a)	4.841	5.376	879 - 1579	1.07	0.994
	1.551	2.482	503 - 879	0.49	0.984
FC-153	5.020	5.892	890 - 1588	1.17	0.998
	2.035	3.259	503 - 890	0.65	0.992
FC-153 HT	4.968	5.960	888 - 1580	1.18	0.996
	2.335	3.577	518 - 888	0.71	0.997
FC-154	4.657	5.910	885 - 1597	1.17	0.994
	1.771	3.377	510 - 885	0.66	0.995
FC-154 HT	4.944	6.404	104 - 1575	1.27	0.995
FC-155	3.524	5.517	878 - 1599	1.10	0.984
	-0.656	1.841	500 - 878	0.37	0.874
FC-156	2.969	4.163	1101 - 1564	0.95	0.990
	1.367	3.313	552 - 1101	0.66	0.996
FC-156 HT	2.972	4.798	868 - 1578	0.95	0.986
	-0.139	2.084	534 - 868	0.41	0.962

(a) HT = Heat treated in air at 1820K for 48 h.

$\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$ phases was determined by XRD. The electrical conductivities were determined from 500 to 1600K in air (Table 10 and Figure 9) and after heat treatment in air at 1820K for 48 hours (Figure 10).

The electrical conductivity data were fitted to $\log \sigma$ versus K^{-1} with two straight lines intercepting near 900K. The electrical conductivities were changed by heat treatment. A large decrease in conductivity was noted for the composition with the highest In_2O_3 content, FC-157 (40 mol%). In contrast, the composition with the lowest indium content--FC-156 with 20 mol%--exhibited little change at high temperatures. Below 900K, the conductivity of the heat-treated sample was higher than the as-fabricated sample. These changes may

FIGURE 9. Electrical Conductivity of $(0.96-x) \cdot [0.5\text{HfO}_2 \cdot 0.5\text{PrO}_2] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$ in Air

relate to the loss of In_2O_3 or PrO_2 during heat treatment. All heat-treated samples experienced some small weight loss. The greatest loss was observed for the higher- In_2O_3 oxides. However, XRD before and after heat treatment exhibited the same bcc and pyrochlore structures with only a slight increase in the bcc In_2O_3 (ss) phase.

The electrical conductivity increased with both increasing In_2O_3 content and bcc phase content. At 1270K, a plot of $\log \sigma$ versus mol% in In_2O_3 was nearly linear. The 25 mol% In_2O_3 composition deviated from this general pattern. This composition exhibited a higher bcc phase concentration, a lower electrical conductivity, and an activation energy different from that expected from other trends in the data.

Thus, a number of compositions in the $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ system, especially those with $\text{HfO}_2\text{-PrO}_2\text{-In}_2\text{O}_3$ containing Yb_2O_3 , have electrical properties suitable as electrode current interconnectors for use in the graded ceramic

FIGURE 10. Electrical Conductivity of $(0.94-x) \cdot [0.5\text{HfO}_2 \cdot 0.5\text{PrO}_2] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$ Before and After Heat Treatment to 1820K for 48 h (HT)

composite electrode system. The compositions that appear most promising are those two- and three-phase structures that contain between 30 and 45 mol% of the bcc In_2O_3 (ss) phase.

5.6 In_2O_3 - SnO_2

Indium oxide-tin oxide compositions were considered as a substitute for In_2O_3 in MHD current interconnectors to increase the electrical conductivity of HfO_2 - RE_xO_y - In_2O_3 . The results of this study have been published (Bates et al. 1986); the data and conclusions are summarized here.

The In_2O_3 - SnO_2 compositions were made from coprecipitated powders that were cold pressed into rectangular bars and sintered in air between 1800K and 1850K. The final densities varied between 60% and 80% of the theoretical density.

Three stable crystalline phases were observed in the In_2O_3 - SnO_2 system:

1) an In_2O_3 bcc solid solution containing up to 20 mol% SnO_2 ; 2) a rhombohedral phase of $\text{In}_4\text{Sn}_3\text{O}_{12}$; and 3) a SnO_2 tetragonal phase (Figure 11). In_2O_3 and SnO_2 formed a solid solution between 80% and 100% with a maximum solubility of 20 mol% SnO_2 in In_2O_3 .

A single-phase rhombohedral structure occurred at 40 mol%. This rhombohedral phase had lattice parameters (a_0) of 80.43 ± 0.01 nm, and the alpha angle was 72.12° .^(a) The lattice parameters increased slightly with increasing In_2O_3 at both higher and lower In_2O_3 concentrations adjacent to $\text{In}_4\text{Sn}_3\text{O}_{12}$, suggesting some solubility of SnO_2 or bcc solid solution into the rhombohedral phase.

A single-phase, $\text{In}_4\text{Sn}_3\text{O}_{12}$ rhombohedral phase that had not been reported previously occurred at 40 mol% In_2O_3 . The rhombohedral phase appeared to be developed from a fluorite structure with a close-packed, $\text{M}'_m\text{M}''_n\text{O}_{3m}$ complex.

FIGURE 11. Phases at 1123K in Air for In_2O_3 - SnO_2 as a Function of In_2O_3 Content Determined by XRD

- (a) For simplification in the analysis, a rhombohedral phase is generally expressed as an equivalent hexagonal cell using the hexagonal nomenclature (a_0 and c_0) to describe the lattice parameters. The lattice parameters for an equivalent hexagonal cell are $a_0 = 94.77$ nm and $c_0 = 117.96$ nm.

Prolonged heating of the single-phase oxide at temperatures between 1173K and 1873K in air did not produce any observable compositional or structural changes, suggesting that the rhombohedral phase was thermally stable in air to these temperatures. However, as discussed later, electrical transport data do suggest a possible phase change near 1000K to 1200K.

At compositions below 40%, a two-phase structure of tetragonal SnO_2 and rhombohedral $\text{In}_4\text{Sn}_3\text{O}_{12}$ occurred. The relative amounts of these two phases, determined by XRD, suggest little solubility of one in the other. However, the microstructures and the EDX analyses show two distinct phases with no detectable In_2O_3 in the SnO_2 phase. The small decreases in lattice parameters for the rhombohedral phase with decreasing In_2O_3 content suggested some solubility of SnO_2 in the $\text{In}_4\text{Sn}_3\text{O}_{12}$.

At compositions between 40% and 80%, both the bcc and rhombohedral phases and possibly a noncrystalline phase were present. The nonlinear distribution of the rhombohedral and bcc phases, with a sharp change near 60%, suggested a more complex structure than just the two crystalline phases.

The electrical conductivities varied as a function of the In_2O_3 content. Conductivities increased rapidly with increasing indium concentrations and reached a plateau between 30% and 50% (Figure 12 and Table 11). The conductivities increased more slowly at higher indium concentrations, reaching a maximum near 80%. This maximum conductivity was about 25 times larger than that for pure In_2O_3 , and 6 to 10 times larger than that for $\text{In}_4\text{Sn}_3\text{O}_{12}$ (Figure 13).

Below 40% In_2O_3 , the $\log \sigma$ versus K^{-1} curve for each composition could be represented by two or three straight lines, with different conductivity values measured during heating and cooling. Near 16% In_2O_3 and between 1000K and 1400K, the curves were nonlinear during heating. Between 30% and 70%, the temperature dependencies were less and differences observed during heating and cooling were less than those at the lower indium concentrations. The electrical conductivities obtained on subsequent heating and cooling cycles reproduced the initial measurements and continued to show the same hysteresis. Above 1480K, the electrical conductivity became nearly temperature independent, with the same values both on heating and cooling.

FIGURE 12. Electrical Conductivity of $\text{In}_2\text{O}_3\text{-SnO}_2$

Above 80 mol% In_2O_3 , for the bcc solid solutions, conductivities were nearly temperature independent over the entire temperature range with the same values for heating and cooling. A single $\log \sigma$ versus K^{-1} curve describes the electrical conductivity over the entire temperature range; the electrical conductivity decreases with decreasing tin content. However, one 95 mol% In_2O_3 sample had electrical conductivities substantially greater than all other compositions. No explanation for this anomaly could be derived from the x-ray or microstructural data.

The activation energies also varied with composition. At low temperatures, the activation energies decreased rapidly with indium content, reaching

TABLE 11. Electrical Conductivity Values of $\text{In}_2\text{O}_3\text{-SnO}_2$

Composition, mol%		Electrical Conductivity, (a) (ohm-cm) ⁻¹		Activation Energy, eV	Temperature Range, K	R ²	Comments
In_2O_3	SnO_2	A	B				
7	93	6.814	1.109×10^4	2.20	1111-1726	0.99	
11	89	8.498	1.265×10^4	2.51	1088-1478	0.71	
		3.659	4.573×10^3	0.91	1478-1726	0.99	
					1726-1111	--	d
		1.476	8.231×10^2	0.16	1111-613	0.98	b
16	84	-0.55	--	--	740-1000	--	c
					1000-1470	--	d
		1.50	--	--	1470-1736	--	c
					1736-961	--	b, d
		1.409	1.555×10^3	0.23	961-606		b
23	77	-0.45	--	--	600-880		c
					800-1480		d
		1.95	--	--	1480-1735		c
		3.977	3.121×10^3	0.62	1550-962	0.97	b
		1.945	1.232×10^3	0.24	962-308	0.999	b
31	69	1.40	--	--	705-990	--	c
		3.103	1.589×10^3	0.32	994-1270	0.99	
		--	--	--	1270-1480	--	d
		2.142	-2.715×10^2	--	1731-1331	0.98	b
		2.751	8.670×10^2	0.17	1148-708	0.94	b
38	62	2.030	--	--	625-1000	--	c
		3.111	1.116×10^3	0.22	1000-1738	0.99	
		2.771	4.980×10^2	0.10	1738-613	0.98	b
50	50(e)	2.086	-5.214×10^1	--	678-1059	0.36	e
		2.916	9.253×10^2	0.18	1059-1626	0.99	e
		2.457	2.156×10^2	0.04	1626-711	0.90	b, e
54	46	2.05	--	--	750-750	--	c
		4.273	2.147×10^3	0.43	950-1725	0.99	
		2.930	2.460×10^2	0.49	1395-761	0.98	b
60	40(e)	2.212	-1.908×10^2	--	678-971	0.99	e
		3.262	8.760×10^2	0.17	971-1625	0.99	e
		3.054	5.427×10^2	0.11	1625-1281	0.98	b, e
		2.619	--	--	1281-625	--	b, c, e
70	30	2.663	-1.521×10^2	--	597-1100	0.85	c
		3.291	5.307×10^2	0.11	1100-1541	0.96	
80	20	3.040	-7.582×10^1	--	585-1578	0.50	c, e
85	15	2.091	-3.133×10^2	--	558-1535	0.62	c
90	10	2.675	-1.250×10^{-2}	--	746-1720	--	c
95	5	3.203	-2.041×10^2	--	400-1538	0.94	c, e
100	0	1.752	-1.551×10^1	--	401-1631	0.89	c

(a) $\text{Log}_{10} \sigma = A - BK^{-1}$.

(b) During cooling.

(c) Temperature independent.

(d) Nonlinear with increasing or decreasing temperature.

(e) Remeasurements reproduce the same σ values and hysteresis.

FIGURE 13. Electrical Conductivity of $\text{In}_2\text{O}_3\text{-SnO}_2$ as a Function of In_2O_3 Concentration During Heating and Cooling

a minimum of approximately 0.2 eV near 11%. The activation energies then increased slightly at higher concentrations to a maximum of approximately 0.3 eV near 23%. The energies decreased further and approached zero as the indium content increased. At temperatures above 1200K, there was a rapid and continual decrease in activation energy with increased In_2O_3 . Between 80% and 100%, the high- and low-temperature activation energies became the same.

The plateau in the electrical conductivity near 30% and 50%, the maximum in conductivity near 80%, and the decrease in hysteresis effects during cooling and heating above 60% appear to be related to the formation and presence of the noncrystalline phase or a phase change above room temperature.

The electrical properties are consistent with the formation of the rhombohedral $\text{In}_4\text{Sn}_3\text{O}_{12}$ phase in air at 1873K. The data also suggest the presence of a noncrystalline phase between 11% and 80% and/or a phase change in this same compositional range between 1000K and 1400K. Stoichiometry changes might also be expected with reduced oxygen pressures, producing changes in electrical transport property and structure. Both tin and indium oxides exhibited changes in electrical transport properties under reducing conditions.

Therefore, a rhombohedral $\text{In}_4\text{Sn}_3\text{O}_{12}$ phase forms in air and is stable to 1873K. The electrical conductivity of this phase is 2 to 5 times greater than that for pure In_2O_3 , but is 20% to 25% less than for the 80% In_2O_3 (ss), which exhibits the highest electrical conductivity, near $1000 (\text{ohm-cm})^{-1}$.

5.7 $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-(In}_2\text{O}_3\text{-SnO}_2\text{)}$

The electrical conductivities (σ) of some $\text{HfO}_2\text{-PrO}_2\text{-In}_2\text{O}_3\text{-SnO}_2$ compositions were measured in air to determine the effects of $(\text{In}_2\text{O}_3\text{-SnO}_2)$ additions as a substitute for In_2O_3 alone to increase the electrical conductivity. The electrical conductivities from near room temperature to 1665K for three compositions (Table 12) are shown in Figure 14. Significant differences in σ were observed among these compositions, making it difficult to compare directly the substitutional effects of $(\text{In}_2\text{O}_3\text{-SnO}_2)$ relative to In_2O_3 . FC-99, with a total $(\text{In}_2\text{O}_3\text{-SnO}_2)$ content of 12.5 mol%, had an electrical conductivity lower than that anticipated for a content of 12.5 mol% In_2O_3 but about the same as that for 9 mol% In_2O_3 base (see Figure 5). The conductivity and activation energies were, however, comparable to that of $0.266\text{HfO}_2\cdot0.52\text{PrO}_2\cdot0.172\text{In}_2\text{O}_3$ (FC-50-3). In addition, both FC-50-3 and FC-99 compositions showed the same electrical conductivities on heating and cooling, indicating good thermal stability.

TABLE 12. Composition of $\text{HfO}_2\text{-PrO}_2\text{-(In}_2\text{O}_3\text{-SnO}_2\text{)}$

	Composition, mol%			
	<u>HfO_2</u>	<u>PrO_2</u>	<u>In_2O_3</u>	<u>SnO_2</u>
FC-99	35.3	52.2	9.1	3.4
FC-100	36.8	33.3	21.7	8.2
FCCP-80	21.6	32.0	11.8	34.6

FIGURE 14. Electrical Conductivity of $\text{HfO}_2\text{-PrO}_{1.83}\text{-(In}_2\text{O}_3\text{-SnO}_2\text{)}$

The compositions FC-100 and FCCP-80, which were higher in SnO_2 and In_2O_3 than FC-99, exhibited large changes in conductivity on heating and cooling. These large changes in conductivity at higher temperatures suggest phase transformations. For FCCP-80, the transition above 1250K was reversible, but irreversible below 1250K with lower values on cooling. For FC-100, the change was irreversible, with a significantly higher electrical conductivity on cooling. The electrical conductivity values for FC-100 on cooling were about 10 times smaller than for a SnO_2 -free oxide containing 30 mol% In_2O_3 but essentially the same as that for 22 mol% In_2O_3 (see Figure 6). The conductivities were also about 10 times smaller than for a $0.351\text{HfO}_2 \cdot 0.213\text{PrO}_{1.83} \cdot 0.036\text{Yb}_2\text{O}_3 \cdot 0.40\text{In}_2\text{O}_3$ (AS-1) containing similar amounts of $\text{PrO}_{1.83}$ and HfO_2 .

The introduction of SnO_2 appears to have caused hysteresis on heating and cooling. The substitution of $(\text{In}_2\text{O}_3\text{-SnO}_2)$ for In_2O_3 in $\text{HfO}_2\text{-RE}_x\text{O}_y$ did increase the electrical conductivity in a manner similar to that of In_2O_3 alone, but significantly more measurements would be needed to understand the effects of SnO_2 addition.

The introduction of Sn^{2+} appears to have caused a decrease in the conductivity of the solution. The substitution of Sn^{2+} for Fe^{2+} in the FeSO_4 and increase the electrical conductivity in a manner similar to that of Fe^{2+} , but a different set of measurements would be needed to understand the effects of this addition.

6.0 MHD TEST CHANNEL

An MHD test channel based on the graded ceramic component electrode was designed and assembled at PNL for testing in the Westinghouse Test Facility (WESTF) at Pittsburgh, Pennsylvania. The channel was delivered for testing but was never tested because of funding limitations. The design and assembly of the test channel is described in this section. The test incorporated materials described previously in this report.

The purpose of the MHD channel test was to determine the electrical and thermal characteristics of ceramic "superhot" electrodes based on the graded ceramic concept. Specifically, the test would: evaluate ceramic superhot electrodes surrounded by a metal fin; verify the electrode design parameters; and determine the thermomechanical performance and the extent of corrosion/erosion of the electrodes in an electric field when exposed to the slag, potassium seed, and sulfur-containing MHD environment. A simpler, preliminary test had been run previously using induced current and graded ceramic electrodes (Marchant and Bates 1980a).

The test channel consisted of eight electrodes (four anodes and four cathodes) with interelectrode refractory ceramic oxide insulators and refractory ceramic oxide side walls (Figure 16). The channel electrodes were instrumented with thermocouples to better define the thermal characteristics and determine the heat flow. The outside of the channel consisted of a stainless steel jacket, supplied by Westinghouse, which contained water passages for cooling during the test. The jacket was of one-piece construction, with holes in two opposite sides for inserting the electrodes. The inside dimensions of the jacket were 7.6 cm by 6 cm. The length was 37.8 cm. The diameter of the holes used to insert the electrodes was 3.2 cm.

Because the channel was designed for hot wall operation, the jacket was lined on the inside with refractory ceramic oxide, which allows the inside surfaces to operate at temperatures above 1475K (Figure 16). The high temperatures are necessary to minimize the amount of slag that might condense from the plasma. Previous hot ceramic electrode tests generally used hot electrodes in a channel with colder side walls or other areas; consequently,

slag condensed on colder walls, then flowed over the hot electrodes and increased the corrosion of these electrodes.

The refractory ceramic oxide used to line the jacket was a fused cast magnesium oxide/magnesium oxide-aluminum oxide spinel (MMAS). The spinel, which was an experimental composition, was supplied by Applied Technology Laboratories^(a) (Butte, Montana) and manufactured by Cohart (Louisville, Kentucky). The Cohart designation is X-317. The density of the MMAS is 3.37 g/cm^3 with an open porosity of 2 vol%. The microstructure consists of magnesium oxide crystals within a matrix of spinel solid solution. The average thickness of the spinel was 12.1 mm, covering both the electrode and side walls. The dimensions of the channel after lining were 3.6 cm by 52.1 cm; 3.6 cm was the distance between the electrodes.

Originally in the form of bricks approximately 7.6 cm x 7.6 cm x 43 cm, the MMAS was cut to shapes required for the channel. The centers of the bricks were porous due to the fuse casting process, so only the material near the outside of the brick could be used for the channel. The spinel lengths required to line each wall varied between 10 and 18 cm. The joints between the pieces were rabbited to eliminate direct pathways between the plasma and the stainless steel jacket. The rabbiting also helped to produce interlocking joints to mechanically hold the MMAS pieces together.

The spinel was attached to the stainless steel walls by a heat-curable, silicone rubber adhesive (75 U, Dow Corning, Midland, Michigan). Before the adhesive was applied, the ceramic and stainless steel surfaces were cleaned with successive washes of trichlorethylene and acetone, then coated with a primer (1300, Dow Corning, Midland, Michigan). The adhesive was flattened into sheets about 0.018 cm thick and placed between the spinel and the channel. The adhesive was cured by heating to 427K for 30 minutes in an oven. The post-cure treatment consisted of heating to 449K for 4 hours. A silicone rubber insert placed inside the lined channel helped to hold the ceramic in place during curing. Since the jacket was one piece, the ceramic linings had to be slipped in

(a) Use of manufacturer names does not imply PNL endorsement.

from the ends. The silicone adhesive was placed on the spinel, and the spinel was slipped into the channel.

The eight electrodes (four anodes and four cathodes) were mounted in the channel by inserting the electrode/insulator/water-cooling assembly (Figure 15) through holes in the jacket. The electrodes consisted of a cylindrical sintered ceramic body surrounded by a copper sleeve (Figures 15 and 16). The back face of the ceramic was in contact with copper metal mesh with a theoretical density near 50%, which is attached to a copper water-cooling assembly. The copper sleeves were brazed to the cooling assembly with a braze containing 30 wt% Ag, 20 wt% Cd, 27 wt% Cu, and 23 wt% Zn (Easy-Flo 30, Handy and Harmon, New York). The braze liquidus was 983K and the solidus 878K. The brazing flux was WELCO Flux 250 (Welco Alloys, Madison Heights, Michigan). The brazing was done in air using a propane and air flame. An RTV silicone rubber

FIGURE 15. Cross Section of Electrode/Insulator and Water-Cooling Assembly

(RTV 106, General Electric, Waterford, New York), containing 5 wt% natural flake graphite, was used as the electrically conducting, flexible adhesive connecting the copper sleeve, copper mesh, and ceramic. This rubber has a maximum useful temperature of 573K.

The electrode compositions are listed in Table 13. The two electrodes based on hafnium oxide (positions 1 and 4) were composites containing a cap and a current leadout. The cap, in contact with the hot MHD plasma, was refractory and was of a composition to resist high-temperature corrosion. The electrical conductivity of the cap was only adequate at elevated temperatures. The current leadout was located between the cap and the copper mesh. The leadout was not as refractory or as corrosion resistant as the cap but had adequate electrical conductivity at room temperature. The cap and current leadout were of monolithic construction and were fabricated by sintering from reactive powders.

The two electrodes based on yttrium chromite (Table 13) were of one composition throughout, since the electrical conductivity was adequate over the temperature range of operation. Because the chromite materials are not as corrosion resistant at high temperatures as the hafnium oxide materials, the yttrium chromite electrodes were designed to operate at an electrode/plasma interface temperature about 150K lower than for the hafnium-based materials. The chromites were used as a reference because these materials had been tested previously.

Several electrodes contained alumel-chromel thermocouples that were ungrounded to an Inconel 600 sheath (SCAIN-040U-6, Omega Engineering, Inc., Stamford, Connecticut). The Inconel sheath limited the useful temperature of the thermocouple to 1422K. The center of the thermocouple hole was 0.76 cm from the electrode-channel surface. The depth of the thermocouple hole was designed so that the thermocouple tip was at the centerline of the electrode. The hole diameter was about 0.002 cm greater than the thermocouple (0.1 cm) to minimize the temperature difference between the electrode and thermocouple.

Inside the channel, the electrodes were electrically isolated by the spinel insulator (see Figure 16). An alumina-silica machinable ceramic was used between the copper cooling assembly and the stainless steel. The cooling

TABLE 13. Electrodes for WESTF Test

Electrode Position	Electrode Composition, mol%	Material Thickness, cm	Thermocouple		Copper Ring Thickness, cm
			Anode	Cathode	
1 (Cap)	$6.8\text{Y}_2\text{O}_3 \cdot 93.2\text{HfO}_2$	0.28	Yes	No	0.10
(Leadout)	$62.5\text{In}_2\text{O}_3 \cdot 2.1\text{Pr}_6\text{O}_{11} \cdot 2.9\text{Yb}_2\text{O}_3 \cdot 32.3\text{HfO}_2$	1.14			
2	$\text{Y}(\text{Ca}_{0.05}\text{Cr}_{0.95})\text{O}_3$	1.42	No	Yes	0.10
3	$\text{Y}(\text{Mg}_{0.05}\text{Cr}_{0.95})\text{O}_3$	1.42	Yes	No	0.14
4 (Cap)	$7.9\text{Pr}_6\text{O}_{11} \cdot 3.8\text{Yb}_2\text{O}_3 \cdot 88.3\text{HfO}_2$	0.28	Yes	No (a)	0.10
(Leadout)	$62.5\text{In}_2\text{O}_3 \cdot 2.3\text{Pr}_6\text{O}_{11} \cdot 2.9\text{Yb}_2\text{O}_3 \cdot 32.3\text{HfO}_2$	1.14			

(a) Optical sight port.

copper flange was separated from the stainless steel by a fiberglass-filled epoxy. The brass bolts used to attach the stainless steel to the copper were surrounded by heat shrinkable tubing, with fiberglass-filled epoxy washers placed under the head. The hole in the copper used for the thermocouple and alumina tube was sealed with epoxy (Epoxi-Patch).

A thermal profile based on two-dimensional heat flow and anticipated available heat flux was developed for a graded ceramic composite MHD electrode with a copper fin. The results for one test electrode are shown in Figure 16. The analysis was based on thermal properties developed and reported previously (Bates and Marchant 1978; Marchant and Bates 1980a,b).

FIGURE 16. Thermal Profile for MHD Test Electrode

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