Development of Materials for Open-Cycle MHD

**Quarterly Report for the Period
Ending March 1983**

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

July 1983

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

**Pacific Northwest Laboratory
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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
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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Pacific Northwest Laboratory (PNL) is conducting an ongoing study of channel components for open-cycle, coal-fired magnetohydrodynamic (MHD) generators. Specifically, electrodes and insulators are being developed. The electrical conductivity has been measured on several compositions based on hafnium oxide, rare earth oxides, and indium oxide. Indium oxide at present appears to be the main constituent required for high conductivity. As part of the development, materials are being corrosion tested in both Montana Rosebud coal slag and potassium sulfate (K_2SO_4). The results from three coal slag tests and one K_2SO_4 test are discussed in this document.

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INTRODUCTION

Pacific Northwest Laboratory (PNL)^(a) is developing and testing ceramic electrodes and insulators and other channel components for open-cycle, coal-fired magnetohydrodynamic (MHD) generators as part of the U.S. Department of Energy's (DOE) Power Generation Program. The PNL program is divided into four tasks:

- development and fabrication of electrodes/insulators
- design and testing of electrodes/insulators
- characterization and evaluation of electrode/insulator materials
- measurement of thermal, electrical, and mechanical properties

The objectives of the program are to develop:

- electrodes that can withstand the severe corrosive and erosive environment of an MHD channel and that will transfer electrical current efficiently during long channel operation
- insulators that can withstand the corrosive and erosive environment and maintain adequate electrical resistivity during long channel operation
- electrode and insulator designs that are compatible with the demands of channel assembly, operation, and disassembly.

Because the tasks are interrelated, the quarterly reports for this program are organized by activities and not necessarily by specific tasks. This report summarizes two activities: corrosion testing of several current leadout materials and measurement of the electrical conductivity of several ceramic compositions.

(a) Operated for DOE by Battelle Memorial Institute.

TECHNICAL PROGRESS

Adding indium oxide (In_2O_3) to refractory cap compositions has resulted in increases in the electrical conductivity, especially at temperatures below 1300K. Because of the higher electrical conductivity, some compositions can be used as current leadouts between the refractory cap and the water-cooled copper supports. Tin oxide (SnO_2) is another material that is potentially capable of increasing the electrical conductivity. SnO_2 is more refractory and probably less reactive (especially in the corrosive slag and molten salt environments) than In_2O_3 because its melting point is 1903K (Weast and Astle 1979). Several compositions were prepared and fabricated using SnO_2 as the additive, and one of these was corrosion tested in Montana Rosebud coal slag. Two compositions containing In_2O_3 were also tested in the slag and examined using the scanning electron microscope (SEM). The results of these tests are presented in this quarterly. The electrical conductivity of six compositions is also presented.

FABRICATION AND CORROSION TESTING OF MATERIALS CONTAINING TIN OXIDE AND INDIUM OXIDE

A sample of 50 mol% SnO_2 + 50 mol% hafnium oxide (HfO_2) was prepared by mixing SnO_2 powder (-200 mesh, Cerac, Inc.)^(a) and HfO_2 powder (-60 +170 mesh, Teledyne, Wah Chang, Inc.) using a SPEX mixer/mill (SPEX Industries, Inc.). The mixing container was a polypropylene vial containing a Teflon® mixing ball. The mixed powder was preslugged at 2.8×10^7 Pa (4000 psi), uniaxially pressed at 3.5×10^7 Pa (5000 psi), and finally isopressed at 1.4×10^8 Pa (20,000 psi). The pressed compact was placed in an aluminum oxide crucible, surrounded with SnO_2 powder, and sintered in air at 1873K for 5 h. The final density was 5.28 g/cm^3 . X-ray diffraction analysis showed that the compact consisted of two granular phases: 1) a tetragonal SnO_2 phase and 2) a cubic phase, possibly $\text{Sn}_2\text{Hf}_2\text{O}_7$. The SEM with energy dispersive x-ray analysis (SEM/EDX) showed the nominal chemical composition of the phases to be:

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

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Wilmington, Delaware.

1) 68 mol% SnO_2 + 32 mol% HfO_2 and 2) 38 mol% SnO_2 + 62 mol% HfO_2 . Since the overall composition was 50 mol% SnO_2 + 50 mol% HfO_2 , the sample contained about 40% of the phase with the higher SnO_2 concentration. The material was corrosion tested by immersing a rectangular sample in Montana Rosebud coal slag at 1723K for 48.5 h, then cooling to room temperature. Pieces of the sample and slag were then mounted, polished, and examined using both the optical and scanning electron microscopes. Both phases remained after the test. Greater amounts of silicon and aluminum were found in the phase containing the lower SnO_2 content. Measurements of the polished section showed the loss rate for the sample was 6.1×10^{-4} cm/h (a weight loss of 3.2×10^{-3} g/cm²h based on the density of 5.28 g/cm³). The low density of the sample, which resulted in slag penetration, was partially responsible for the high corrosion rate. In future tests, powders will be prepared by coprecipitation instead of mixing; higher density, more uniform samples are expected. The corrosion along the exterior surface appeared uniform, i.e., both grains and grain boundaries appeared to corrode evenly. Composition of the reaction product found at the corrosion interface was 5 mol% SnO_2 + 95 mol% HfO_2 . At the immediate reaction interface, the phase with the high concentration of SnO_2 had dissolved. Consequently, part of the corrosion process appears to be dissolution of the high SnO_2 phase and selective leaching of SnO_2 from the low SnO_2 phase.

A sample of the 39 mol% In_2O_3 + 61 mol% HfO_2 composition was prepared by pressing and sintering coprecipitated powder. This powder was prepared by dissolving In_2O_3 in nitric acid and hafnium oxychloride in water. The two solutions were mixed; and dilute ammonium hydroxide was added to increase the pH, resulting in the coprecipitation of the powders. The powders were washed with water, acetone, and toluene and then dried and calcined in an air atmosphere at 1073K for 4 h. The resulting coprecipitated powder was preslugged, uniaxially pressed, and isopressed at the same pressures as the sample previously described. The pressed compact was surrounded by an In_2O_3 + HfO_2 powder and placed in an alumina crucible. Sintering in an air atmosphere at 1873K for 10 h resulted in a density of 8.49 g/cm³. The overall composition (based on SEM/EDX) was 39 mol% In_2O_3 and 61 mol% HfO_2 , which is identical to the analysis expected from mixing the original components prior to coprecipitation. Examination of a polished section of this material showed three phases. The matrix

was a single phase with a composition of 37 mol% In_2O_3 + 63 mol% HfO_2 . Inclusions with diameters of $\sim 5 \mu\text{m}$ and an overall composition of 78 mol% In_2O_3 and 22 mol% HfO_2 were found in the second area. The inclusions consisted of two phases: 1) a small granular phase $\sim 0.5 \mu\text{m}$ in diameter with an unknown composition (the phase was too small for SEM/EDX analysis) and 2) a phase with a composition of 91 mol% In_2O_3 + 9 mol% HfO_2 that completely surrounded the granular phase. The small granular phase probably precipitated during cooling, and the inclusions may have been homogeneous at higher temperatures.

A sample of the composition was corrosion tested in Montana Rosebud coal slag at 1723K for 24 h. The corrosion was uniform and both phases dissolved. The corrosion rate was $8.1 \times 10^{-3} \text{ g/cm}^2\text{h}$. The matrix grains at the interface contained small quantities of magnesium, aluminum, and silicon from the slag. A granular-shaped reaction product with a composition of 19 mol% In_2O_3 + 81 mol% HfO_2 was also found at the interface. At a distance of 116 μm from the corrosion interface, the reaction product composition was 18 mol% In_2O_3 + 82 mol% HfO_2 . At a distance of 256 μm from the reaction interface (at a location next to the bulk slag), the composition was 12 mol% In_2O_3 + 88 mol% HfO_2 . The reaction product grains surrounded by coal slag contained silicon, magnesium, aluminum, calcium, and iron, with a silicon concentration about six times the molar concentration of the other components.

A second sample containing In_2O_3 was prepared by pressing and sintering coprecipitated powder using the techniques described for the previous sample. The composition (determined by SEM/EDX) was 29 mol% In_2O_3 + 71 mol% HfO_2 , which compared favorably with that expected by the initial mixing of the liquids prior to coprecipitation (31 mol% In_2O_3 + 69 mol% HfO_2). The microstructure consisted of two intermixed granular phases: 1) 35 mol% In_2O_3 + 65 mol% HfO_2 and 2) 24 mol% In_2O_3 + 76 mol% HfO_2 . The latter phase was mottled and may actually have been two phases caused by phase separation after cooldown. The sample was corrosion tested in Montana Rosebud coal slag at 1723K for 24 h. The corrosion rate was $2.1 \times 10^{-2} \text{ g/cm}^2\text{h}$ and was uniform with a distinct corrosion interface and a reaction product buildup on the surface. A granular reaction product surrounded by coal slag found at the reaction interface had a composition of 25 mol% In_2O_3 + 75 mol% HfO_2 . At a distance of 29 μm from the

interface, the composition was 17 mol% In_2O_3 + 83 mol% HfO_2 . At 63 μm (the location of the interface between the reaction product and the bulk slag), the composition was 13 mol% In_2O_3 + 87 mol% HfO_2 . All reaction products contained slag components of aluminum, silica, calcium, and iron. The silicon had a molar concentration about three times greater than each of the other components. Flakes of HfO_2 containing silicon were located at the immediate interface between the reaction product and the bulk slag. The nominal composition was 22 mol% SiO_2 + 78 mol% HfO_2 . Phase equilibria data (Levin and McMurdie 1975) show that the equilibrium phase for this composition is a mixture of monoclinic HfO_2 and the compound HfSiO_4 . The grains found in this test did not appear to be two-phase but could be on a finer scale than can be seen with the SEM/EDX.

In both indium oxide-hafnium oxide tests, the reaction product continued to react with the slag. The resultant loss of the indium oxide-hafnium oxide compositions was much greater than rates for the tin oxide-hafnium oxide compositions, even though the tin oxide-hafnium oxide sample had a much lower density with considerable open-connected porosity and, consequently, a higher surface area for corrosion. These tests suggest that the addition of SnO_2 to HfO_2 may result in compositions that are more corrosion resistant, at least to coal slag, than compositions based on In_2O_3 additions to hafnium. Further testing is planned to verify these preliminary conclusions and to develop SnO_2 - HfO_2 compositions that will sinter to a greater density and have adequate electrical conductivity.

A sample of a current leadout material of composition 54 mol% In_2O_3 + 15 mol% PrO_2 (labeled PrO_2 for simplicity although the actual stoichiometric composition is Pr_6O_{11}) + 3 mol% Yb_2O_3 + 28 mol% HfO_2 was prepared from coprecipitated powders using the method described earlier. The sintered sample consisted of two phases: 1) the interconnected matrix grains with compositions of 79 mol% In_2O_3 + 7 mol% PrO_2 + 2 mol% Yb_2O_3 + 12 mol% HfO_2 and 2) small granular inclusions in the matrix grains and along the edges with compositions of 9 mol% In_2O_3 + 32 mol% PrO_2 + 4 mol% Yb_2O_3 + 55 mol% HfO_2 . The sample was corrosion tested in molten potassium sulfate (K_2SO_4) for 168.5 h at 1373K. The density was only 5.37 g/cm^3 with large amounts of open porosity. During the test, the

porosity filled with K_2SO_4 , resulting in a large reaction interface between the K_2SO_4 and the sample. The corrosion rate of $3.2 \times 10^{-5} \text{ g/cm}^2\text{h}$ was close to the lower detection limit for this test. Post-test examination showed little reaction between the sample and the potassium sulfate. SEM/EDX examination showed a slightly higher concentration of In_2O_3 in the K_2SO_4 than expected. Therefore, some corrosion selectivity towards In_2O_3 appears to be occurring. Both solid phases contained potassium (up to 5 mol% K_2O) but not sulfur. Consequently, sulfur does not appear to interact with the solid but remains with the K_2SO_4 . The low corrosion rate, especially with the low porosity of the sample, suggests that this material is relatively inert to K_2SO_4 . Further testing with denser materials and for longer periods of time will be required to better determine the corrosion resistance and mechanism.

ELECTRICAL CONDUCTIVITY MEASUREMENTS

The electrical conductivities of six samples are given in this report; their compositions, densities, and phases as determined by x-ray diffraction are listed in Table 1. Electrical conductivity data are plotted in Figure 1 as a function of the reciprocal temperature. The lines are the least squares curves fit to the data. The calculated parameters for the conductivity and the temperature range where curve fits are valid are given in Table 2. Only Sample 4, which has a high indium content (54 mol% In_2O_3), had adequate conductivity over the required temperature range for a current leadout. This material was corrosion tested in molten K_2SO_4 as reported previously and was relatively inert to K_2SO_4 corrosion. The material will be corrosion tested in molten coal slag. If the corrosion resistance is adequate, further testing will be required to determine the applicability to a sandwich-type electrode with a refractory cap. Compositions are being adjusted to obtain a pyrochlore equilibrium phase that may lead to a very high electrical conductivity. This pyrochlore phase may also lead to a high corrosion resistance. As can be seen by the identified phases for each composition shown in Table 1, the pyrochlore phase was not obtained. The pyrochlore phase was expected, but not found, in Sample 4 because the praseodymium and hafnium atoms were present in nearly equal concentrations.

TABLE 1. Electrical Conductivity Compositions for Figure 1

Sample No.	Composition, mol%	Density, g/cm ³	Phase Identifications (a)
1	5 CeO ₂ + 5 PrO ₂ + 90 HfO ₂	9.0	50% M HfO ₂ 50% FCC HfO ₂ SS
2	32 PrO ₂ + 7 Yb ₂ O ₃ + 61 HfO ₂	8.8	80% FCC HfO ₂ SS 20% FCC PrO ₂ SS
3	50 SnO ₂ + 50 TiO ₂	4.6	Ordered SnO ₂ structure with extra line similar to a tetragonal cell
4	54 In ₂ O ₃ + 15 PrO ₂ + 28 HfO ₂ + 3 Yb ₂ O ₃	5.4	FCC In ₂ O ₃ SS strong FCC PrO ₂ SS medium FCC HfO ₂ SS weak
5	7 In ₂ O ₃ + 14 PrO ₂ + 1 Yb ₂ O ₃ + 77.7 HfO ₂	8.2	FCC HfO ₂ SS
6	40 In ₂ O ₃ + 60 HfO ₂	6.5	FCC HfO ₂ SS

(a) FCC = face-centered cubic
SS = solid solution
BCC = body-centered cubic
P = pyrochlore
M = monoclinic.

FIGURE 1. Electrical Conductivity as a Function of Temperature for Several Compositions Based on HfO_2

TABLE 2. Equations from Least Square Fit of Data from Table 1 and Figure 1

Sample No.	Equation Describing Least Squares Fit of Curves in Table 1, $\text{Log}_{10}\sigma =$	Temperature Range of Fit, K
1	$3.3559 - 7.3874 \times 10^3 \text{ K}^{-1}$	975 to 1669
2	$2.7164 - 5.7537 \times 10^3 \text{ K}^{-1}$	959 to 1631
3	$3.8814 - 9.2466 \times 10^3 \text{ K}^{-1}$	1042 to 1669
4	$3.8783 - 2.7834 \times 10^3 \text{ K}^{-1}$	987 to 1652
	$1.1381 - 2.5439 \times 10^2 \text{ K}^{-1}$	335 to 930
5	$3.6787 - 6.9075 \times 10^3 \text{ K}^{-1}$	979 to 1651
6	$5.4647 - 1.1535 \times 10^4 \text{ K}^{-1}$	986 to 1655

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