Advanced Materials for Solid Oxide Fuel Cells: Hafnium- Praseodymium-Indium Oxide System

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June 1988

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SUMMARY

The HfO_2 - $\text{PrO}_{1.83}$ - In_2O_3 system has been studied at the Pacific Northwest Laboratory to develop alternative, highly electrically conducting oxides as electrode and interconnection materials for solid oxide fuel cells. A coprecipitation process was developed for synthesizing single-phase, mixed oxide powders necessary to fabricate powders and dense oxides. A ternary phase diagram was developed, and the phases and structures were related to electrical transport properties. Two new phases, an orthorhombic PrInO_3 and a rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ phase, were identified. The highest electronic conductivity is related to the presence of a bcc, In_2O_3 solid solution (ss) containing HfO_2 and $\text{PrO}_{1.83}$. Compositions containing more than 35 mol% of the In_2O_3 ss have electrical conductivities greater than $10^{-1} (\text{ohm-cm})^{-1}$, and the two or three phase structures that contain this phase appear to exhibit mixed electronic-ionic conduction. The high electrical conductivities and structures similar to the Y_2O_3 -stabilized $\text{ZrO}_2(\text{HfO}_2)$ electrolyte give these oxides potential for use as cathodes in solid oxide fuel cells.

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1.0 INTRODUCTION

Use of fuel cells is a clean and efficient means for the direct chemical conversion of fossil fuels to electrical energy. A fuel cell consists of an electrolyte sandwiched between two electrodes which converts the chemical energy of a fuel to electrical energy without combustion. The fuel, such as hydrogen, and the oxidant, such as air, are exposed to the cell's anode and cathode, respectively. The fuel is oxidized catalytically at the fuel electrode with oxygen that has been transported through the ionically conducting electrolyte. Electrons liberated at the anode are conducted through an external circuit to the air electrode where more oxygen ions are produced.

The solid oxide fuel cell (SOFC) is receiving increased consideration as a high-temperature fuel cell (see Dollard and Brown 1986; Feduska and Isenberg 1983; Fee et al. 1983, 1986; Isenberg 1985; Penner 1985). The SOFC operates near 1273 K and the high temperatures allow the direct reforming of natural gas or methane to hydrogen. The state-of-the-art SOFC uses a thin, dense, solid electrolyte of Y_2O_3 -stabilized ZrO_2 with porous electrodes (Isenberg 1985 and Fee et al. 1986). The air electrode or cathode is strontium-doped lanthanum manganite with a nickel- Y_2O_3 -stabilized ZrO_2 composite as the fuel electrode or anode. The current interconnection is Sr- or Mg-doped lanthanum chromite. These four materials exhibit considerably different thermal properties, unless modified, and generally require different multiple-step fabrication processes. The material properties critical to this multi-component system are 1) thermal compatibility among electrodes, electrolyte, and interconnection; 2) electrochemical and chemical interactions during fabrication and/or operation; 3) bonding at interfaces between materials for good electrical and thermal contacts; 4) high ionic conduction of the electrolyte; 5) high electronic (with some oxygen-ion) conduction of the porous electrodes; and 6) high electronic conduction of the interconnection in both oxidizing and reducing conditions.

A basic issue is the fabrication processes for these different material components. Present state-of-the-art methods are complex and/or require a different process for each material component (Isenberg 1985). The multiple-step operations result in limitations on processing temperatures,

processing methods, and material compositions and structures. For example, the application and fabrication of each component must be performed sequentially at a lower temperature than the preceding process. In addition, materials with better properties may be available, but cannot be used because of process limitations (Fee et al. 1986). Thus, electrode and interconnection materials with suitable properties are required that can be fabricated using fewer and more simple methods but with the required thermal, electrochemical, mechanical, and electrical properties. Ideally, the electrodes and electrolyte and possibly the interconnection could be fabricated into the final cell geometry simultaneously using the same fabrication method.

The purpose of this study, which was conducted at Pacific Northwest Laboratory (PNL), was to investigate materials based on rare-earth-stabilized HfO_2 as advanced SOFC electrode and interconnection materials. The approach was to investigate highly electrically conducting oxides with structural, thermal, and fabrication characteristics similar to the Y_2O_3 -stabilized ZrO_2 electrolyte, which can be fabricated simultaneously with, and using the same process as, the electrolyte. The new materials may provide 1) improved thermal expansion match with the electrolyte; 2) reduced or non-degrading interactions during fabrication or fuel cell operation among the electrodes, electrolyte, and interconnection; 3) mixed ionic and electronic conduction of the electrodes to enhance the electrode/electrolyte reactions and electrical charge transfer characteristics; and 4) simultaneous fabrication of electrode/electrolyte components. HfO_2 was used in this study because of its high thermal stability, isomorphic with electrical, phase, and structural properties to ZrO_2 . These rare-earth-containing hafnates were studied initially as potential electrode materials for magnetohydrodynamics direct energy conversion (Bates and Marchant 1978, 1986; Marchant and Bates 1980a,b). These studies were subsequently expanded and directed toward application for use as electronically conducting oxides for solid oxide fuel cells (Bates and Griffin 1986). The current study has recently been extended to the ZrO_2 - $\text{PrO}_{1.83}$ - In_2O_3 system, which will be the subject of a future report.

This report describes the research and development of advanced SOFC electrode and interconnection materials based on the $\text{HfO}_2\text{-PrO}_{1.83}(\text{RE}_x\text{O}_y)\text{-In}_2\text{O}_3$ system. The synthesis and fabrication processes, electrical transport, and phase equilibria of this system are described.

2.0 SAMPLE PREPARATION

The samples were formed from oxides that were coprecipitated to form powders which were dried and calcined. These powders were pressed to form green bars which were sintered at 1850 to 1875 K.

2.1 POWDER SYNTHESIS

The mixed oxides were synthesized using a coprecipitation process similar to that reported by Dole (1978). This was critical to the preparation of powders used in fabricating high-density and homogeneous samples with reproducible physical and structural properties. The basic coprecipitation process consists of dissolving the nitrates of praseodymium and indium with the hydrated oxychloride of hafnium in water. The oxychloride forms acids on dissolution. Some of the oxides were formed using solutions of hafnium sulfate instead of the hafnium oxychloride. This produced powders that required little or no ball milling and the elimination of gelatinous precipitates attributed to the presence of chlorides. The gelatinous particles were considered a source of the hard agglomerates that produced inhomogeneous structures.

The solutions were filtered through a 0.2- μm millipore filter before mixing to remove undissolved solids and impurities, such as silicates, which result in nucleation sites for particles during coprecipitation and encourage the formation of hard agglomerates. The water used in the dissolution was treated by being passed through a reverse osmosis cycle and then distilled.

The mixed acid solutions were added to an ammonium hydroxide solution using a pressure spray through a small orifice which produced acid droplets to less than 100 μm . The ammonium hydroxide solution was stirred during the introduction of the acid solution. The final pH of the liquid was 8.5. The precipitates were separated from the liquid by vacuum filtering and sequentially washed with water, acetone, toluene, and then acetone. All organic solvents and wash were of the highest reagent grade. This washing was necessary to remove oily residues that can react with the ball mill materials, thereby inhibiting sintering.

2.2 POWDER PROCESSING

The powders were dried and calcined at 1073 to 1273 K in air for 4 hours. The calcined powders were ball-milled for up to 960 minutes in a neoprene-lined mill using Y_2O_3 -stabilized ZrO_2 balls in a Freon® TF milling fluid. The final surface areas of the powders, as determined by BET, varied between 12 and 17 m^2/g . The ball milling improved sintering densities to greater than 95% theoretical density.

2.3 COMPACTION

The powders were slugged at 69 MPa (10,000 psi) before passing through a -145 Tyler mesh screen. The slugged and granular powder was pressed uniaxially in steel dies at 152 MPa (22,000 psi) into a right cylinder and discs. Humidity in water-saturated air provided an adequate binder. For final compaction, the green bars were isostatically pressed in double-encapsulated plastic evacuated containers in a water-soluble oil at 228 MPa (33,000 psi).

2.4 SINTERING

The bars and discs were set on yttria-stabilized ZrO_2 furnace hardware and surrounded with a high-temperature calcined powder of a composition near that of the sample. The oxides were sintered between 1850 and 1875 K in air for 8 to 20 hours at temperature with 5-hour heatup and cooldown cycles. Sintering times and temperatures were selected according to the desired final density, powder characteristics, and oxide composition. Generally, the samples containing indium oxide were sintered at the lower temperature.

Each bar was sectioned and samples were cut from the center of the bar or disc. Each sample was characterized using x-ray diffraction (XRD) and immersion density. In addition, the compositions of selected samples were analyzed using quantitative energy dispersive x-ray spectroscopy (EDX) coupled with scanning electron microscopy (SEM).

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3.0 PHASE EQUILIBRIA

The ternary phase diagram for $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ was determined at 1823 K in air using optical microscopy, SEM coupled with EDX, XRD, and limited transmission electron microscopy (TEM) with electron diffraction. 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 $\text{HfO}_2\text{-PrO}_{1.83}$ phase relationships had been reported previously (Kravchinskaya et al. 1973) and only selected compositions were used to confirm the binary diagram. The structures and compositions of samples inside the ternary were coupled with these binary-phase diagram data to generate a ternary diagram.

The ternary-phase diagram was developed using the general phase rules associated with ternary-phase diagrams, the compositions of phases determined using quantitative EDX and x-ray diffraction crystallographic data, and the reported $\text{HfO}_2\text{-Pr}_6\text{O}_{11}$ binary diagram. These data are summarized in Table 3.1, 3.2, and 3.3. Quantitative SEM-EDX is a relatively new technique employed to study phase equilibria. In multiple-phase fields, the overall composition is determined quantitatively from large areas containing all phases. The composition of each separate phase is determined by focusing the electron beam on single-phase crystallites of sufficient size so that the beam does not penetrate or scatter beyond the volume of the single-phase region. The smallest volume examined must exceed the $1\text{-}\mu\text{m}$ -diameter and $1\text{-}\mu\text{m}$ -deep volume probed by the penetration and scatter of the 10-kV electron beam. Lower beam voltages result in instabilities; higher voltages increase the volume affected by the beam and reduced the resolution. These determined compositions represent the vortex compositions of a three-phase region and points on opposite boundary lines of a two-phase system.

The EDX is calibrated using single-crystal HfO_2 , sintered In_2O_3 , and sintered, single-phase, binary compositions of $\text{In}_2\text{O}_3\text{-PrO}_{1.83}$ and $\text{HfO}_2\text{-In}_2\text{O}_3$. These binary compositions were verified by wet chemistry. The accuracy of the quantitative SEM-EDX was determined to be within ± 1 mol%. This is achieved by reducing the electron beam voltage to 10 kV and maintaining that voltage for each spot determination. The data are recorded and the spectra

TABLE 3.1. Phases and Lattice Parameters of $\text{HfO}_2\text{-In}_2\text{O}_3$ and $\text{PrO}_{1.83}\text{-In}_2\text{O}_3$

Composition, mol%			Phases and Lattice Parameters, nm x 10 ⁻¹								
HfO ₂	PrO _{1.83}	In ₂ O ₃	Monoclinic	fcc Fluorite	Rhom- bohedral	fcc Pyrochlore	bcc	Orthorhombic			fcc
								a	b	c	
98		2		5.095							
94		6	(a)	5.102							
93		7	(a)	5.110							
93		7	(a)	5.096							
91		9	(a)	5.090							
85		15		5.09	5.15						
84		16		5.095	(b)						
83		17		5.098							
83		17	(a)	5.098							
74		26		5.108							
71		29		5.085	(b)						
71		29				10.714					
69		31		5.084	(b)						
65.5		34.5		5.08	(b)						
63		37		5.08	5.11						
60		40		(b)	(b)						
50		50		(b)			(c)				
20		80			5.17		10.12				
20		80			(b)		10.255				
3		97					10.188				

TABLE 3.1. (contd)

Composition, mol%			Phases and Lattice Parameters, nm x 10 ⁻¹								
HfO ₂	PrO _{1.83}	In ₂ O ₃	Monoclinic	fcc Fluorite	Rhom- bohedral	fcc Pyrochlore	bcc	Orthorhombic			fcc
								a	b	c	
	98	2									5.46 ^(b)
	91	9						5.67	5.92	8.18	5.46
	84	14						5.67	5.92	8.16	5.46
	76	24						5.67	5.92	8.17	5.45
	60	40					10.13	5.67	5.90	8.16	
	18	82					10.13	(d)			
	2	98					10.18				

(a) Monoclinic phase present.

(b) fcc fluorite or rhombohedral phase present. Interference made resolution difficult.

(c) bcc sesquioxide solid solution phase present.

(d) Orthorhombic phase present.

TABLE 3.2. Phases and Lattice Parameters of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ _{1p}

Composition, mol%			Phases and Lattice Parameters, nm x 10 ⁻¹								
HfO_2	$\text{PrO}_{1.83}$	In_2O_3	Monoclinic	fcc Fluorite	Rhom- bohedral	fcc Pyrochlore	bcc	Orthorhombic			fcc
								a	b	c	
80	10	10		(a)	5.128						
70	7	23		(a)	5.131						
70	10	20		(a)	5.128						
68	20	12				10.664					
65	18	17			5.164						
60	30	10				(b)	10.125				
59	7	34			5.13		(c)				
56	20	24		5.11	(a)	10.626	10.11				
56	19	25		(a)	5.17	10.68	10.13				
56	9	35			5.14	10.64	10.12				
50	25	25			5.17	10.60	(c)				
45	45	10				10.67	(c)				
45	45	10				10.676	10.12				
45	40	21				10.674	10.12				
45	40	21				10.706	10.14				
44	32	24				10.668	(c)				
43	42	15			5.147	10.68	10.12				
41	54	5					10.64	(c)			
40	40	20			5.15	10.68	(c)				
40	35	25			5.15	10.66	10.12				
40	10	50			5.151		10.12				
39	39	22			5.14	10.68	10.12				

TABLE 3.2. (contd)

Composition, mol%			Phases and Lattice Parameters, nm x 10 ⁻¹								
HfO ₂	PrO _{1.83}	In ₂ O ₃	Monoclinic	fcc Fluorite	Rhom- bohedral	fcc Pyrochlore	bcc	Orthorhombic			fcc
								a	b	c	
39	39	23			(a)	10.676	(c)				
37	43	20				10.670	10.12				
36	37	27				10.672	10.12				
34	45	21				10.668					
28	55	17				10.678		5.67	5.88	8.14	
25	30	45				10.66	10.12				
25	20	55				10.64	10.1				
23	60	17				10.696		5.67	5.88	8.14	5.41
22	62	16				10.678		5.658			
21	61	18				10.680		(d)			
20	50	30				10.70	(c)	(d)			
18	65	17				10.70		(d)			
12	76	12						5.61	5.86	8.15	5.41 ^(e)
10	82	8						5.66	5.93	8.16	5.42 ^(e)
4	53	43				10.70		(d)			

(a) fcc fluorite or rhombohedral phase present. Interference made resolution difficult.

(b) fcc pyrochlore phase present.

(c) bcc sesquioxide solid solution phase present.

(d) Orthorhombic phase present.

(e) PrO_{1.83} present reported to be cubic 10.99 nm or 5.4695 nm.

TABLE 3.3. Phases and Lattice Parameters of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$

Composition, mol%				Phases and Lattice Parameters, nm x 10 ⁻¹								
HfO_2	$\text{PrO}_{1.83}$	In_2O_3	Yb_2O_3	Monoclinic	fcc Fluorite	Rhom- bohedral	fcc Pyrochlore	bcc	Orthorhombic			fcc
									a	b	c	
78	14	7	1			5.16						
50	21	15	4			5.175	10.656	10.13				
47	30	20	3			5.15	(a)	10.13				
41	17	39	3			5.88	10.670	10.160				
43	12	41	3			5.173		10.13				
25	15	57	3			5.176	10.674	10.138				

(a) fcc fluorite or rhombohedral phase present. Interference made resolution difficult.

are analyzed and compared with standard spectra using a Traco-Northern analog system. In contrast, the XRD is accurate to $\pm 5\%$ for most structures. However, some interference was observed for similar structures that differ only by size of unit cell required to accommodate all atoms.

The proposed $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary phase diagram in air at 1823 K determined by the above procedures is shown in Figure 3.1. The diagram is first discussed in terms of the binary diagrams.

3.1 $\text{HfO}_2\text{-PrO}_{1.83}$

The $\text{HfO}_2\text{-PrO}_{1.83}$ binary relationship reported by Kravchinskaya et al. (1973) was confirmed in this study. The HfO_2 is totally stabilized into a fcc fluorite structure (C) at about 24 mol% $\text{PrO}_{1.83}$. The pyrochlore $\text{Hf}_2\text{Pr}_2\text{O}_7$

FIGURE 3.1. $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ Phase Diagram at 1812 K in Air

(P) lies within the limits of 42 and 57 mol% $\text{PrO}_{1.83}$. The reported lattice parameter of the $\text{Hf}_2\text{Pr}_2\text{O}_7$ pyrochlore is 1.0662 ± 0.004 nm (Kravchinskaya et al. 1973). This compares to a lattice parameter determined in this study that varies between 1.0664 and 1.0669 ± 0.001 nm and appears relatively independent of the indium and hafnium content. The addition of In_2O_3 slightly increases the lattice parameter up to 1.070 ± 0.001 nm. However, this observed increase, although consistent, as shown in Table 3.1, is within the XRD measurement accuracy limits. The estimated solubility limits of In_2O_3 in the pyrochlore phase are from 1 to 3 mol%.

3.2 $\text{PrO}_{1.83}\text{-In}_2\text{O}_3$

An orthorhombic PrInO_3 phase (O) was found in the $\text{PrO}_{1.83}\text{-In}_2\text{O}_3$ binary with lattice parameters $a_0, b_0, c_0 = 0.567, 0.593, 0.818 \pm 0.01$ nm, respectively. The solubility limits are 30 to 36 mol% In_2O_3 . The higher indium solubility is found at the phase boundary in the two-phase region (O+B) consisting of the PrInO_3 and a bcc solid solution of $\text{PrO}_{1.83}$ in In_2O_3 . The solubility limit of HfO_2 in PrInO_3 is near 2%. The lattice parameters at maximum HfO_2 solubility in the orthorhombic PrInO_3 are $a_0 = 0.565$, $b_0 = 0.589$, and $c_0 = 0.815 \pm 0.02$ nm. The solubility limit of $\text{PrO}_{1.83}$ is about 2 to 3 mol%. The lattice parameters at maximum solubility are 1.0188 ± 0.0005 nm compared with a measured value of 1.0118 ± 0.001 nm for pure In_2O_3 .

The solubility limit 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 0.547 nm for $\text{PrO}_{1.83}$. This is in excellent agreement with crystallographic data reported by Swanson et al. (1953), which indicates a cubic lattice with unit cell of 0.54695 nm. However, Aleshin and Roy (1962) reported a cubic pyrochlore structure with a 1.099 nm (doubled) unit cell. The ionic radius of In^{+3} (0.08 nm) is smaller than that for Pr^{+4} (0.090 nm). Consequently, the lattice parameter changes may be smaller depending upon the defect formation required for charge compensation due to different valence states.

The stable cubic $\text{PrO}_{1.83}$ or Pr_6O_{11} phase appears to be converted to a fcc structure with additions of HfO_2 and/or In_2O_3 . The lattice parameter of this unit cell determined in the two-phase field containing orthorhombic and

fcc is near 0.541 nm as shown in Table 3.1b. This may be related to a transition from an oxygen deficient to a stoichiometric, oxygen fluorite phase as reported by Brauer and Willaredt (1980). Such a fcc phase was not reported by Kravchinskaya et al. (1973) for HfO_2 additions alone.

3.3 $\text{HfO}_2\text{-In}_2\text{O}_3$

The HfO_2 is also stabilized as a fcc phase (c) with 10 to 24 mol% In_2O_3 . The fcc lattice parameter of 0.511 nm decreases nearly linearly with increasing In_2O_3 content according to the expression

$$a_0 = 5.1116 - 0.09285(\text{mol\% In}_2\text{O}_3)$$

reaching a value of 0.508 nm at 35 mol% In_2O_3 . Between 24 and 35 mol% In_2O_3 , the fcc lattice appears to exist with a closely related rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ phase, which is described later. Scatter in the lattice parameter data is observed below 10 mol% In_2O_3 and appears to be related to the presence of the monoclinic HfO_2 phase, which coexists with the fcc fluorite phase at room temperature.

A rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ phase (R) was formed in the $\text{HfO}_2\text{-In}_2\text{O}_3$ binary. This phase has a lattice parameter of $a_0 = 0.517$ nm and $\alpha = 90.4$ degrees. This very small deviation in α from the 90 degrees for the In_2O_3 -stabilized HfO_2 suggests this rhombohedral phase may result from an anisotropic ordering of the fcc phase. The nominal $\text{Hf}_2\text{In}_2\text{O}_7$ composition determined by EDX was 35 mol% In_2O_3 and 65 mol% HfO_2 .

The close similarity between the fcc In_2O_3 and/or the $\text{In}_2\text{O}_3 + \text{PrO}_{1.83}$ stabilized HfO_2 and the rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ structure made it difficult to distinguish by x-ray diffraction the two phases when both were present. However, the nearly linear decrease in the lattice parameter for the fcc In_2O_3 stabilized HfO_2 to 0.508 nm at 35 mol% In_2O_3 and the larger value of the rhombohedral structure of 0.514 to 0.517 nm suggest different structures. These two phases were also observed in some instances in a two-phase field containing another phase. This, coupled with the presence of the fcc pyrochlore $\text{Hf}_2\text{In}_2\text{O}_7$ which has a lattice parameter of 1.066 to 1.070 nm, makes

a resolution of the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary diagram with high HfO_2 very complex. (A doubling of a 0.533 to 0.535-nm-unit cell is required to account for the extra atoms in the cell.) Further studies of this area are required.

Saito, Maruyama, and Kato (1983), did not report observing the rhombohedral phase; however, they fabricated samples by sintering admixtures of HfO_2 and In_2O_3 powders. Similar results were observed by Glushkova and Krzhizkanovskaya (1973). This may have inhibited the formation of the rhombohedral phase. Experiments during this study indicate that the reaction between mixed powders of In_2O_3 and HfO_2 is incomplete, with the formation of an In_2O_3 solid solution with HfO_2 surrounding the HfO_2 crystallites. This conclusion is reinforced by the electrical conductivity data, as discussed later.

The In_2O_3 forms a solid solution with HfO_2 with a rare-earth, B-type, sesquioxide structure (B). The maximum solubility of HfO_2 was not determined accurately, but appears to be near 10 mol% with a lattice parameter near 1.012 ± 0.001 nm. The bcc In_2O_3 forms a solid solution with both HfO_2 and $\text{PrO}_{1.83}$. However, the definition of combined HfO_2 plus $\text{PrO}_{1.83}$ solubility limits was very difficult because the vortices of 2 three-phase fields and 3 two-phase fields converge between 90 and 95 mol% In_2O_3 .

3.4 $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$

The major portion of the ternary phase diagram is made up of two fields containing three phases; i.e., (O + P + B) and (R + P + B). These two fields are separated by a two-phase (P + B) field. Because of the interest in high electrically conducting phases and similar thermal properties to stabilized HfO_2 (ZrO_2), the phase diagram results were concentrated in the high- HfO_2 portion of the ternary diagram, between $\text{Hf}_2\text{Pr}_2\text{O}_7$, fcc HfO_2 , and bcc In_2O_3 solid solution. Regions high in $\text{PrO}_{1.83}$ remain to be defined.

The $\text{Hf}_2\text{In}_2\text{O}_7$ rhombohedral phase appears to be stabilized with additions of $\text{PrO}_{1.83}$. However, because of the similarity in diffraction patterns to the fcc fluorite phase and the small size of this phase, the resolution and composition limits of the rhombohedral phase in the ternary were difficult to

determine quantitatively with EDX. Additions of a few mol% of Yb_2O_3 to the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ near $\text{Hf}_2\text{In}_2\text{O}_7$ also appear to stabilize the rhombohedral phase.

4.0 ELECTRICAL TRANSPORT PROPERTIES

The understanding of the electrical transport properties is critical to selecting compositions, improving properties and structures, and evaluating the performance of materials for solid oxide fuel cells. The dc electrical conductivity, Seebeck coefficients, and transference numbers were measured and related to the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ phase equilibria to determine the electrical transport characteristics of the various structures and phases.

4.1 ELECTRICAL CONDUCTIVITY

The electrical conductivity (σ) was measured to 1700 K in air using a four-point probe method. The rectangular bars, which were 3 cm long and $\sim 0.1 \text{ cm}^2$, were placed in a Pt knife-edge holder. Direct current was passed through the sample using knife edges placed near the contact area at the end of the sample bar, which was coated with Pt paste to reduce contact resistances. The electric potential along the sample was measured using knife edges set at predetermined distances on the sample side opposite the current leads. A voltmeter with an internal impedance greater than 10 megohms was used to measure the voltages and a microammeter was used to measure the current. Measurements of voltages across standard resistors in parallel with the sample current were also used to verify sample resistances. The direct current densities did not exceed 0.05 A/cm^2 . Measurements were accurate to within $\pm 10\%$. Samples temperatures were measured with calibrated Pt-Pt10Rh thermocouples referenced to the gold melting point. Temperatures were controlled to within ± 1 degree Kelvin.

One or more linear $\log \sigma$ versus $1/K$ relations were fitted to the data. The coefficients of determination were generally greater than 0.98 at high temperatures and greater than 0.95 at low temperatures.

The electrical conductivities of compositions in the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ were measured to determine the phase fields and phases that exhibited the highest electrical conductivity. Results for compositions in the $\text{HfO}_2\text{-In}_2\text{O}_3$ binary and the center of the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary were emphasized.

4.1.1 $\text{HfO}_2\text{-In}_2\text{O}_3$

The $\text{HfO}_2\text{-In}_2\text{O}_3$ system was studied initially because of the high conductivity of the bcc In_2O_3 solid solution and the similarity of the In_2O_3 -stabilized HfO_2 with the Y_2O_3 -stabilized ZrO_2 solid solution. It is essentially a binary of the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary system. The electrical conductivity results are shown in Figure 4.1 and summarized in Table 4.1 for compositions containing between 17 and 40 mol% In_2O_3 . The conductivity decreased with increasing In_2O_3 reaching a minimum value of $5 \times 10^{-1} \text{ (ohm-cm)}^{-1}$ at 1273 K near 40 mol%, which corresponds approximately to the $\text{Hf}_2\text{In}_2\text{O}_7$ rhombohedral composition. The conductivity then increased rapidly between 40 and 50 mol%; this increase is attributed to the increase in the bcc In_2O_3 solid solution phase. The conductivity should continue to increase with increasing In_2O_3 content as the bcc In_2O_3 solid solution increases in this

FIGURE 4.1. Electrical Conductivity for $\text{HfO}_2\text{-In}_2\text{O}_3$, $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ Single Crystal and $\text{HfO}_2(\text{Y}_2\text{O}_3)$

TABLE 4.1. Composition and Electrical Conductivity of $\text{HfO}_2\text{-In}_2\text{O}_3$

Sample	Composition mol%		$\text{Log}_{10} \text{ (a) } = A - BK^{-1}$		Temperature Range, K	Activation Energy, eV	Coefficient of Determination, R^2
	HfO_2	In_2O_3	A	B			
FC-13-3	0	100	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.

two-phase region, reaching values greater than those for pure In_2O_3 , greater than $10^2 \text{ (ohm-cm)}^{-1}$. It has been reported by Bates et al. (1986) that additions of oxides, such as SnO_2 , increase significantly the conductivity of pure In_2O_3 oxide, reaching a maximum at the maximum solubility of SnO_2 . The electrical 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 -stabilized HfO_2 or ZrO_2 . The extrapolation of the electrical conductivity data for 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 appeared to be effective in the fcc stabilization of HfO_2 .

Saito et al. (1983) reported electrical conductivity values for 20 to 30 mol% In_2O_3 in HfO_2 , 5 to 50 times higher than those of the present study, and a decrease in conductivity with increasing mol% In_2O_3 . The activation energy was reported to be a nearly constant value of 1.7 eV over this composition range; in this study, the activation energies vary from 1.2 to 2.3 eV, as shown in Figure 4.2. These differences are attributed to the differences in the fabrication methods. Saito, Maruyama, and Kato (1983) sintered admixtures of HfO_2 and In_2O_3 powders which could have resulted in inhomogeneous structures and the presence of the bcc In_2O_3 solid solution phase at lower In_2O_3 content. It could also have inhibited the formation of rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$ phase during sintering. The formation of the bcc phase could result in higher electrical conductivities.

Plotkin, Plyushcev, and Rozdin (1976) also measured the electrical conductivity of $\text{HfO}_2\text{-In}_2\text{O}_3$ at 90 and 293 K. The conductivities increased with increasing In_2O_3 and, at 293 K, the values ranged from 0.4 to 5 (ohm-cm)^{-1} . These values were lower than those reported here. Like the oxides described in Saito, Maruyama, and Kato (1983), the oxides were fabricated from admixed powders. The powders were calcined at 1200 K for 48 hours followed by sintering at 1450 to 1500 K for 4 hours. Thus, the conducting phase appears to be the In_2O_3 solid solution surface coating between grains.

FIGURE 4.2. Activation Energy and Electrical Conductivity at 1000 K of $\text{HfO}_2\text{-In}_2\text{O}_3$ as a Function of mol% In_2O_3

4.1.2 HfO₂-PrO_{1.83}-In₂O₃

The electrical conductivities of compositions in the center of the HfO₂-PrO₂-In₂O₃ ternary were measured to determine the phase fields, structures, and phases which exhibit the highest electrical conductivity. The compositions, structures, and electrical conductivity results are summarized in Tables 4.2 and 4.3 and in Figure 4.3. These results also include samples with similar compositions containing small amounts of Yb₂O₃. (Those compositions containing some Yb₂O₃ are shown as solid data points on the phase diagram for the HfO₂-PrO₂-In₂O₃ system in Figure 3.1. The Yb₂O₃ was considered to be similar to the PrO_{1.83} and, for consistency, was added to the PrO_{1.83} content.)

The electrical conductivity of the major phases in the HfO₂-PrO_{1.83}-In₂O₃ system was determined as a base for further study of the two- and three-phase structures in this system. The results for Hf₂In₂O₇ were discussed previously. The electrical conductivity of the orthorhombic PrInO₃ and the pyrochlore Hf₂Pr₂O₇ are low, with values between 10⁻³ and 10⁻⁴ (ohm-cm)⁻¹ at 1273 K with a high temperature dependence. The electrical conductivity of the monoclinic HfO₂ is even lower, 10⁻⁴ to 10⁻⁵ (ohm-cm)⁻¹, at 1273 K.

The electrical conductivities increase with increasing In₂O₃ content and approach maximum conductivities at all temperatures above 40 mol% In₂O₃. Figure 4.4 shows the conductivities at 923, 1273, and 1667 K. This general composition dependence is found in both the two- and three-phase fields containing Hf₂In₂O₇ and/or Hf₂In₂O₇ but with the cubic In₂O₃ solid solution. Thus, it is concluded that the major conducting phase is the In₂O₃ solid solution.

Using XRD data coupled with the ternary phase diagram in Figure 3.1, the concentrations of the In₂O₃ bcc In₂O₃ solid solution were determined for each of the HfO₂-PrO_{1.83}-In₂O₃ compositions. The logarithms of the electrical conductivity at 1273 K were compared as a function of bcc In₂O₃ solid solution and of total content. These results show a nearly linear increase up to 30 mol%, Figures 4.5a and 4.5b. At higher concentrations, the data exhibit more scatter but appear to reach a near constant value for each

TABLE 4.2. Composition and Electrical Conductivity of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$

Sample	Composition, mol%				Structure, mol% ^(a,b)			Electrical Conductivity ($\text{ohm-cm}^{-1} \log_{10} = A-B(K^{-1})$)							
								High Temperature				Low Temperature			
	HfO_2	In_2O_3	$\text{PrO}_{1.83}$	Yb_2O_3	B	P	R	A	$B(10^3)$	eV	K	A	$B(10^2)$	eV	K
AP	78	7	14	1	10	90	--	2.507	5.400	1.07	1087-1679				
								3.679	6.907	1.37	978-1651				(c)
AQ	63	2	34	4	--	50	50	2.076	6.317	1.25	1157-1706				(c)
AC	54	26	16	4	10	40	50	2.241	4.895	0.97	1212-1716				(c)
AF	57	15	24	4	10	25	60	4.378	9.695	1.93	1324-1503	-0.5501	3596	0.71	791-1242
AG					15	25	60								
LLL	47	30	20	3	30	15	65	3.273	2.840	0.56	997-1508	1.516	9953	0.198	646-997 ^(d)
KKK	41	39	17	3	30	20	50	4.496	3.120	0.620	950-1491	2.045	7773	0.15	612-950 ^(d)
FC-1	37	25	38	--	25	75	0	2.740	1.996	0.40	287-1073 ^(d)	1.01			
								4.049	4.162	0.83	1100-1782 ^(e)	1.408	1156	0.23	421-1050
FC-2	37	25	38	--	25	75	0	4.718	5.382	1.07	1100-164 ^(d)	1.175	1395	8.28	420-1075
								2.341	1.502	0.30	838-1644 ^(e)				
AO	28	54	15	3	50	20	30	1.878	2.783	0.55	987-1647	1.138	2.544	0.05	335-930
AS	35	40	21	4	50	40	10	2.178	1.328	0.26	1135-1688	0.989	0.248	0.05	710-1046
AG	50	25	21	4	15	25	60	0.956	3.178	0.63	930-1725	0.440	8.118	0.16	643-930
B4	25	55	20	--	E ^(f)	E ^(f)	--	3.160	1.904	0.30	895-1651 ^(d)	2.188	1051	0.20	697-895 ^(d)
												0.8052	8240	0.16	398-697 ^(e)
B5								3.206	1.927	0.38	898-1649 ^(d)				(c)
BB	25	45	30	--	45	55	--	3.462	1.970	0.39	800-1434	2.1278	8811	0.18	562-763
												1.005	2498	0.05	299-562
AB	29	51	12	3	50	10	40	4.66	3.846	0.764	1116-1783	1.660	4.425	0.09	512-1141

(a) B = bcc; P = Pyrochlore; R = Rhombohedral.

(b) Weight percent determined by X-ray diffraction - $\pm 5\%$.

(c) Data irregular at low temperatures; e.g., high scatter at room temperature.

(d) Difference on heating and cooling.

(e) Decreasing temperature.

(f) Phase present.

TABLE 4.3. Compositions of $(1-x)(0.277\text{HfO}_2 \cdot 0.63\text{PrO}_{1.83} \cdot 0.10\text{Yb}_2\text{O}_3) \cdot x\text{In}_2\text{O}_3$

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 4.3. Electrical Conductivity of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$, Including Some with a Small Percentage of Yb_2O_3

temperature, up to 60 mol% bcc solid solution. There is significantly less scatter in data when the In_2O_3 solid-solution content rather than the total content In_2O_3 is plotted against the electrical conductivities. The activation energies for these compositions also exhibit significant scatter.

FIGURE 4.4. Electrical Conductivities of $\text{HfO}_2\text{-PrO}_{1.38}\text{-In}_2\text{O}_3$ at 923, 1273, and 1667 K as a Function of In_2O_3 Content

However, there is a general decrease in both the high- and low-temperature activation energies with increases in both the In_2O_3 and the In_2O_3 (ss) concentrations. These data support the conclusion that the major conducting phase in the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ ternary is the bcc In_2O_3 (ss) and that the maximum conductivity value would be near 100 mol% In_2O_3 , measured to be near $100 \text{ (ohm-cm)}^{-1}$. The electrical conductivity of the In_2O_3 is expected to increase as the HfO_2 and $\text{PrO}_{1.83}$ are added as a solid solution, reaching a maximum at the maximum solubility as reported for other solid solutions of In_2O_3 (Bates et al. 1986).

(a)

(b)

FIGURE 4.5. Electrical Conductivity at 1273 K of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ Containing Small Amounts of Yb_2O_3 as a Function of (a) In_2O_3 Content and (b) In_2O_3 Solid Solution

Many of the compositions summarized in Figures 4.3 through 4.5 and Tables 4.2 and 4.3 contain small concentrations of up to 6 mol% of Yb_2O_3 , in addition to $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$. The conductivities, especially for LLL and KKK shown in Figure 4.3, suggest that those samples containing Yb_2O_3 exhibit higher electrical conductivities than those without Yb_2O_3 but with similar amounts of In_2O_3 . These compositions, as determined by XRD and SEM-EDX, are either two- or three-phase with one phase being bcc In_2O_3 (ss). In addition, the $\text{Hf}_2\text{In}_2\text{O}_7$ phase contains some $\text{PrO}_{1.83}$. These samples also show less hysteresis on heating and cooling than those without Yb_2O_3 . The x-ray diffraction data indicate that Yb_2O_3 tends to stabilize the $\text{Hf}_2\text{In}_2\text{O}_7$ rhombohedral phase. These results suggest that other rare-earth oxides besides $\text{PrO}_{1.83}$ may 1) form new conducting phases, 2) increase the In_2O_3 (ss), and/or 3) stabilize high-temperature phases and structures which revert on cooling either from the In_2O_3 (ss) or from another electrically conducting phase to the lower conducting pyrochlore phase.

In addition, the data also show the conductivity of a two-phase sample (AO) to be lower than that for the other oxides with observed high B phase and containing Yb_2O_3 . This composition is in a three-phase $\text{Hf}_2\text{Pr}_2\text{O}_7$, $\text{Hf}_2\text{In}_2\text{O}_7$ and In_2O_3 (ss) phase field. The lower conductivity is not consistent with the electrical conductivities of the other $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ compositions. Although not as pronounced, sample AC and AG also exhibit lower electrical conduction than the other compositions with equal In_2O_3 and In_2O_3 solid solutions. These three samples contain lower amounts of $\text{PrO}_{1.83}$. This suggests that $\text{PrO}_{1.83}$ may be requisite for higher electrical conductivities in addition to the In_2O_3 bcc phase.

It has been observed in this study that samples with composition in or near the two-phase $\text{Hf}_2\text{In}_2\text{O}_7$ region may exhibit a hysteresis on heating and cooling during the electrical conductivity measurements. (See B-1 and MMM in Table 4.3). Although the oxides were sintered at 1823 K in air and measurements were made in air, some conductivity changes did occur on thermal cycling during the conductivity measurements. The magnitude of these changes varies between 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. However, the addition of Yb_2O_3 appeared to reduce this hysteresis and may be attributed to the possible stabilization of the $Hf_2In_2O_7$ rhombohedral phase at high temperatures. This could reduce phase changes occurring during the measurement that alter conductivity values. It is possible that some vapor loss of the more volatile In_2O_3 may have resulted in a composition change. However, XRD and SEM-EDX did not detect any change, especially near the sample surface.

4.1.3 HfO_2 - $PrO_{1.83}$ - In_2O_3 Containing Yb_2O_3

To determine the effects of small additions of In_2O_3 to the HfO_2 - $PrO_{1.83}$ - In_2O_3 system on the electrical conductivity and phase structure, the electrical conductivity was measured on a nominal $0.63HfO_2 \cdot 0.27PrO_{1.83} \cdot 0.10YbO_{1.5}$ base composition containing varied amounts of In_2O_3 as shown in Table 4.3. These structures contain both the rhombohedral and pyrochlore phases in addition to the bcc In_2O_3 (ss). The electrical conductivities of the compositions listed in Table 4.4 are shown in Figure 4.4. The electrical conductivities are shown in Table 4.3. The results suggest a sharp increase in electrical conductivity near 25 mol% In_2O_3 , with a smaller increase above 30 mol%.

To determine the effect of In_2O_3 and the bcc In_2O_3 (ss) on the pyrochlore structure containing Yb_2O_3 but without the fluorite or rhombohedral phase, a series of compositions containing equal amounts of HfO_2 and $PrO_{1.83}$, 6 mol% Yb_2O_3 with varying amounts of In_2O_3 were studied in air to 1820 K (Table 4.4). The five compositions were $(0.94 x)[0.5HfO_2 \cdot 0.5PrO_{1.83}] \cdot xIn_2O_3 \cdot 0.06Yb_2O_3$ with x between 20 and 40 mol%. The weight ratio of the bcc In_2O_3 (ss) and pyrochlore HfO_2 - $PrO_{1.83}$ - In_2O_3 - Yb_2O_3 phases was determined by XRD.

The electrical conductivities are illustrated in Figure 4.6 and tabulated in Table 4.4 with a minimum conductivity between 20 and 25 mol% In_2O_3 and a sharp increase above 30 mol% In_2O_3 .

TABLE 4.4. Composition and Structure of $(0.94-x)[0.5\text{HfO}_2 \cdot 0.5\text{PrO}_{1.83}] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$

Sample	Composition, mol%				Phases, mol%(a,b)	
	HfO_2	$\text{PrO}_{1.83}$	In_2O_3	Yb_2O_3	Pyrochlore	bcc
FC-157	27	27	40	6	48 (50)	42 (50)
FC-153	29.5	29.5	35	6	54 (55)	36 (45)
FC-154	32	32	30	6	70 (65)	30 (35)
FC-155	34.5	34.5	25	6	75 (60)	25 (40)
FC-156	37	37	20	6	80 (67)	20 (33)

(a) Determined by EDX.

(b) Determined by XRD.

FIGURE 4.6. Electrical Conductivity of $(0.94-x) \cdot [0.5\text{HfO}_2 \cdot 0.5\text{PrO}_{1.83}] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$ in Air

4.1.4 Heat Treatment

The electrical conductivities were determined from 500 to 1600 K in air and after heat treatment in air at 1820 K for 48 hours. The electrical

TABLE 4.5. Electrical Conductivity of $(0.94-x)[0.5\text{HfO}_2 \cdot 0.5\text{PrO}_{1.83}] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$

Sample	$\text{Log } \sigma = A-B/K$		Temperature Range, K	Activation Energy, eV	Coefficient of Determination
	A	B(103)			
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	0.004
	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 1820 K for 45 h.

conductivities, as shown in Table 4.5 and Figure 4.7, 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 highest indium content--FC-156 with 20 mol%--exhibited little change at high temperatures. Below 900 K, the conductivity of the heat-treated sample was higher than the as-fabricated sample. These changes may relate to the loss of In_2O_3 or $\text{PrO}_{1.83}$ during heat treatment. All heat-treated samples experienced some small weight loss, with the greatest loss

FIGURE 4.7. Electrical Conductivity of $(0.94-x)[0.5\text{HfO}_2 \cdot 0.5\text{PrO}_{1.83}] \cdot x(\text{In}_2\text{O}_3) \cdot 0.06\text{Yb}_2\text{O}_3$ Before and After Heat Treatment in Air at 1820 K for 48 Hours (HT)

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 conductivities, similar to other samples, increased with both increasing In_2O_3 content and bcc phase content. At 1270 K, a plot of $\log \sigma$ versus mol% in the In_2O_3 was nearly linear as shown in Figure 4.8. The 25 mol% In_2O_3 composition deviated from this general pattern, exhibiting a higher bcc phase concentration, a lower electrical conductivity, and an activation energy different than expected from other trends in the data. Although there is more scatter in the data, a decrease in the electrical conductivities was also observed at 1000 K but with a large increase above 35 mol% In_2O_3 solid solution or 35 mol% In_2O_3 . This high- In_2O_3 -containing sample also exhibited the largest decrease in electrical conductivity on cooling. The reasons for these deviations are not known.

FIGURE 4.8. Electrical Conductivity at 1000 and 1273 K as a Function of In₂O₃ and In₂O₃ Solid Solution Content for HfO₂-PrO_{1.83}-In₂O₃ with 6 mol% Yb₂O₃

The electrical conductivity for these compositions is lower than conductivities for similar compositions measured earlier. The reason for these differences is not known; however, some fabrication or structural variations may be a factor. Furthermore, the small addition of Yb_2O_3 to the two-phase $\text{HfO}_2\text{-PrO}_2\text{-In}_2\text{O}_3$ phase region does not appear to stabilize the pyrochlore or a rhombohedral structure or reduce the bcc In_2O_3 solid solution.

4.1.5 Oxygen Pressure

Electrical conductivities of selected samples were measured at Marquette University, Milwaukee, Wisconsin for PNL, in conjunction with electrochemical transport measurements. Measurements were made using a four-contact ac and dc method as a function of oxygen pressure. The data for two samples, $0.38\text{HfO}_2 \cdot 0.38\text{PrO}_2 \cdot 0.206\text{In}_2\text{O}_3 \cdot 0.02\text{Yb}_2\text{O}_3$ (FC-130-1) and $0.39\text{HfO}_2 \cdot 0.391\text{PrO}_2 \cdot 0.208\text{In}_2\text{O}_3 \cdot 0.01\text{Y}_2\text{O}_3$ (FC-133-1,2), were compared with values obtained at PNL on sibling samples in air for comparison with a similar four-contact dc method.

For the Y_2O_3 -containing oxide, FC-133-1 (Figure 4.9) the initial measurements were made in 1 atm of oxygen. The conductivity was higher on heating to 1280 K than on cooling. Subsequent thermal cycling showed no hysteresis. The electrical conductivity for a similar composition measured in air at PNL using a four-contact method was lower than the Marquette results and the hysteresis was reduced. As shown in Figure 4.10, the electrical conductivity between 1090 and 1280 K increased with decreasing oxygen pressure. The experimental activation energy varied between 0.5 and 0.6 eV in oxygen partial pressure from 1 to $10^{-3.48}$ atm. The activation energies were slightly higher for the higher oxygen pressures. At very low oxygen partial pressures, that is at less than 10^{-16} atm, the electrical conductivities were relatively constant with temperature.

The increasing conductivity with decreasing oxygen partial pressure is characteristic of n-type behavior and is consistent with the transference numbers that are predominantly electronic, as described later.

In contrast, the electrical conductivity of the $0.387\text{HfO}_2 \cdot 0.387\text{PrO}_2 \cdot 0.206\text{In}_2\text{O}_3 \cdot 0.02\text{Yb}_2\text{O}_3$ showed no hysteresis after heating to 1290 K

FIGURE 4.9. Electrical Conductivity of $0.39\text{HfO}_2 \cdot 0.3\text{PrO}_{1.83} \cdot 0.208\text{In}_2\text{O}_3 \cdot 0.01\text{Yb}_2\text{O}_3$ in Oxygen and in Air

FIGURE 4.10. Electrical Conductivity of $0.39\text{HfO}_2 \cdot 0.39\text{PrO}_{1.83} \cdot 0.21\text{Yb}_2\text{O}_3$ as a Function of Oxygen Pressure

FIGURE 4.11. Electrical Conductivity of $0.31\text{HfO}_2 \cdot 0.39\text{PrO}_{1.83} \cdot 0.2\text{In}_2\text{O}_3 \cdot 0.02\text{Yb}_2\text{O}_3$ as a Function of Oxygen Pressure

(Figure 4.11). In addition, the electrical conductivity decreased with decreasing oxygen partial pressure, suggesting p-type electrical transport behavior. The activation energies between 920 and 1290 K varied between 0.6 and 0.7 eV with slightly higher energies for the lower oxygen pressures. The transference numbers detailed later also showed very high electronic transference values. For this composition, the conductivities measurements made in air at PNL were less than an order of magnitude higher than those measured at Marquette.

4.2 SEEBECK COEFFICIENTS

The Seebeck coefficients were determined by applying a temperature gradient along the length of rectangular bars similar to those used for electrical conductivity measurements and by measuring the potential (V) and temperature (T) differences. Four Pt-Pt/10Rh thermocouples in contact with the sample bar were used to measure temperatures and potentials along the bar, providing a combination of six V/T values. The absolute Seebeck coefficient was determined from the least-squares analysis of the six data points. The 3- σ error in the A Seebeck coefficients was estimated to be $\pm 2.8\%$.

Two compositions were selected for Seebeck coefficient determination: $0.30\text{In}_2\text{O}_3 \cdot 0.033\text{Yb}_2\text{O}_3 \cdot 0.20\text{PrO}_{1.83} \cdot 0.467\text{HfO}_2$ (LLL) and $0.433\text{In}_2\text{O}_3 \cdot 0.036\text{Y}_2\text{O}_3 \cdot 0.035\text{Tb}_2\text{O}_3 \cdot 0.496\text{HfO}_2$ (MMM). The thermoelectric powers are shown in Figure 4.12. The MMM composition exhibits higher electrical conductivities and

FIGURE 4.12. Seebeck Coefficient of $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3\text{-Yb}_2\text{O}_3$ (LLL and MMM) as a Function of Temperature

lower Seebeck coefficients. However, both have moderately negative values near $100 \mu\text{V/K}$ and exhibit a maximum negative value near 900 K. Additional qualitative studies of other compositions and structures indicate the following:

- FCC In_2O_3 stabilized HfO_2 --large positive values consistent with oxygen ion vacancy conductivity
- BCC In_2O_3 (ss)--low 25 to 150 negative values consistent with an electronic conducting, degenerate semi-conductor
- $\text{Hf}_2\text{Pr}_2\text{O}_7$ --large positive values consistent with an insulator
- $\text{Hf}_2\text{In}_2\text{O}_7$ --difficult to measure, but appears to be negative.

The two- and three-phase structures appear to be combinations of these phases, which give rise to maxima and minima in the Seebeck coefficient curves as a function of temperature and to changes in the sign of the Seebeck coefficient.

4.3 TRANSFERENCE NUMBERS

In characterizing high-temperature transport properties of electrically conducting oxides for SOFC, it is important to determine the electronic and ionic contributions to the total electrical conductivity and the conductivity dependence on oxygen pressure. For applications, as SOFC electrodes and current interconnectors, the oxides must conduct electronically. To understand the transport properties and the electrochemical interactions with the solid electrolyte, the actual amount of current transported by either ions or electrons needs to be known.

Two experimental techniques were used to determine transference numbers. The electrochemical oxygen-half cell is generally the simplest, and accurate measurements can be made relatively quickly when the transference number is between 0.05 and 0.95. Details of the method have been described in many studies of transport properties.

A coulometric titration cell technique was used to measure the transference numbers with high sensitivity [$0.001 < \bar{t}_i < 0.999$ ($\bar{t}_i$ and $\bar{t}_e$ are the

average fractions transported by ionic and electronic carriers, respectively)]. The solid-state coulombic cell uses separate reference and working electrodes enclosed in an Al_2O_3 tube to measure oxygen permeability. Oxygen is pumped in and out of the interior of the cell by the application of a known electromotive force (emf) to the reference electrode, made of totally ionically conducting Y_2O_3 - or CaO -stabilized ZrO_2 .

The oxygen potentials across the working electrode are established at equilibrium and the change in emf is used to determine the transference number and mobility of the minority carrier.

Two $\text{HfO}_2\text{-RE}_x\text{O}_y\text{-In}_2\text{O}_3$ compositions were studied using the coulombic titration cell technique. The two compositions evaluated were $0.39\text{HfO}_2 \cdot 0.39\text{PrO}_2 \cdot 0.01\text{Y}_2\text{O}_3 \cdot 0.21\text{In}_2\text{O}_3$ (FC-131-3) and $0.39\text{HfO}_2 \cdot 0.39\text{PrO}_2 \cdot 0.02\text{Yb}_2\text{O}_3 \cdot 0.21\text{In}_2\text{O}_3$ (FC-130-6). For FC-131-3, the electronic transference numbers, $\bar{t}_e$, are greater than 0.99 in the 1070 to 1290 K temperature range and for oxygen partial pressures between $10^{-3.48}$ and 1 atm (Table 4.6). Lower oxygen partial pressures of 10^{-12} to 10^{-18} atm showed an even higher electronic contribution to conductivity.

For FC-130-6, the ionic transference number is even smaller than for FC-133, that is, 0.0022 at 1220 K compared to 0.010 for FC-130-1. FC-133 are n-type and appear to be degenerate semiconductors while FC-136 are p-type. These data are consistent with the electrical conductivity and Seebeck coefficient data described previously. However, the reason for the difference due specifically to Y_2O_3 and Yb_2O_3 is not understood.

TABLE 4.6. Transference Numbers for FC-133-1

Temperature, K	$\bar{t}_e$	$\bar{t}_i = 1 - \bar{t}_e$
1220	0.990	0.010
1170	0.993	0.007
1120	0.994	0.006
1070	0.995	0.005

5.0 CONCLUSIONS

The following conclusions can be made concerning solid oxide fuel cells:

- An aqueous, coprecipitation process was developed for synthesizing homogeneous, crystalline powders for fabricating high-density oxides for phase equilibria and electrical transport studies.
- A ternary phase diagram at 1824 K was developed for the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ in air. The development utilized a new, quantitative, micro-spot energy dispersive x-ray spectrographic system coupled with scanning electron microscopy, x-ray diffraction, and metallography. Two new phases were identified: an orthorhombic PrInO_3 and a rhombohedral $\text{Hf}_2\text{In}_2\text{O}_7$.
- In_2O_3 forms a bcc solid solution containing up to 10 mol% $\text{HfO}_2 + \text{PrO}_{1.83}$. The HfO_2 is as stable as the fcc, fluorite phase with from 10 to 24 mol% In_2O_3 .
- The high electronic conductivity in the $\text{HfO}_2\text{-PrO}_{1.83}\text{-In}_2\text{O}_3$ system appears related to the presence of the In_2O_3 solid solution. This phase appears to be an n-type, degenerate semiconductor.
- The $\text{Hf}_2\text{In}_2\text{O}_7$ phase is an oxide semiconductor with conductivities at 1000 K near $5 \times 10^{-1} \text{ (ohm-cm)}^{-1}$. The PrInO_3 phase is an electrical insulator.
- The two- or three-phase oxides containing more than 35 mol% In_2O_3 solid solution have electrical conductivities [$<10^1 \text{ (ohm-cm)}^{-1}$], suitable as electrodes for solid oxide fuel cells. These oxides are mixed ionic-electronic conductors with less than 0.2% ionic conduction. The structures of the oxides between 35 and 50 mol% In_2O_3 solid solution have thermal and chemical properties compatible with the Y_2O_3 -stabilized $\text{ZrO}_2(\text{HfO}_2)$ solid electrolyte.

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