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EVALUATION OF MHD MATERIALS FOR USE IN
HIGH-TEMPERATURE FUEL CELLS

Topical Report

By
Ronald Guidotti

June 15, 1978

Work Performed Under Contract No. EC-77-C-03-1485

Montana Energy and MHD Research & Development Institute
Butte, Montana

U. S. DEPARTMENT OF ENERGY

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The Montana Energy and MHD Research and Development Institute, Inc.

Butte, Montana 59701

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Contract No. EC-77-C-03-1485

**Montana Energy and MHD Research and
Development Institute**

Submitted to

**U. S. Department of Energy
Office of Fossil Energy
Division of Power Systems**

ABSTRACT

The MHD and high-temperature fuel cell literature was surveyed for data pertaining to materials properties in order to identify materials used in MHD power generation which also might be suitable for component use in high-temperature fuel cells. Classes of MHD-electrode materials evaluated include carbides, nitrides, silicides, borides, composites, and oxides. Y_2O_3 -stabilized ZrO_2 used as a reference point to evaluate materials for use in the solid-oxide fuel cell. Physical and chemical properties such as electrical resistivity, coefficient of thermal expansion, and thermodynamic stability toward oxidation were used to screen candidate materials.

A number of the non-oxide ceramic MHD-electrode materials appear promising for use in the solid-electrolyte and molten-carbonate fuel cell as anodes or anode constituents. The MHD-insulator materials appear suitable candidates for electrolyte-support tiles in the molten-carbonate fuel cells. The merits and possible problem areas for these applications are discussed and additional needed areas of research are delineated.

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INTRODUCTION

This technology-transfer report is prepared as a part of the requirements of Contract No. EC-77-C-03-1485, "High Temperature Fuel Cell Research and Development," to identify materials developed for magnetohydrodynamic (MHD) energy conversion that may have applicability as high-temperature fuel cell components.

Generation of electrical power by MHD using a coal-fired combination creates an extremely hostile environment for the electrodes and insulation in the channel. The high temperatures and erosive and corrosive effects of the coal slag-seed mixture presents formidable materials requirements which can be met by only a limited class of compounds. The chemical and physical requirements of materials for use in the MHD generator are listed in Table 1; comparable data for the high-temperature solid-electrolyte fuel cell are presented in Table 2.

As indicated in these tables, the general materials requirements are similar for certain components. Operating conditions for the solid-electrolyte fuel cell, however, are less severe--lower current density, temperature, and pressure. The requirements for the electrical properties of the fuel cell components, on the other hand, are more stringent because of the manner of fabrication of the multi-cell stack. (See Figure 1 for a cross sectional view of Westinghouse's thin-film fuel cell stack). The electrodes, electrolyte, and interconnector used to connect individual cells together

TABLE 1.--Materials requirements for an MHD generator^{1,2}

<u>Parameter</u>	<u>Electrode</u>	<u>Interelectrode Insulator</u>
Electrical Resistivity*	$\rho < 10 \text{ ohm-cm, electronic}$	$\rho > 100 \text{ ohm-cm; dielectric breakdown} > 4\text{KV/m}$
Current density*	$> 1 \text{ A/cm}^2$	---
<u>General Requirements</u>		
Channel wall temp.		
a) Cold	$< 1200^\circ\text{C}$	
b) Intermediate	$1200^\circ \text{ to } 1700^\circ\text{C}$	
c) Hot	$> 1700^\circ\text{C}$	
Thermionic emission*	Good electron transfer between plasma & electrodes.	
Chemical stability*	Stable at $P_0 = 10^{-2} \text{ to } 10^{-3} \text{ atm}$, low vapor pressure and high melting point.	
Pressure*	Maximum of 10 atm.	
Thermal conductivity*	Able to maintain wall temperature below melting point.	
Thermal shock	Good shock resistance during start-up and cool-down; must tolerate thermal stresses due to large temperature gradients.	
Erosion resistance*	Minimum material loss under slagging conditions and when exposed to high-velocity gases and particulates.	
Corrosion resistance*	Resistant to coal slag, K_2SO_4 , K_2CO_3 , and mixtures thereof.	
Compatibility*	Must be chemically and mechanically compatible with other components; especially important for graded materials.	
Mechanical stability*	Creep resistant; no destructive phase changes from ambient to operating temperatures.	
Life*	$> 10,000 \text{ hr.}$	
Fabrication	Economical and easy to fabricate.	
Porosity	Minimum porosity (dense).	

* At temperature.

TABLE 2.--Materials requirements for a solid-electrolyte fuel cell^(3,4)

<u>Parameter</u>	<u>Interconnector</u>	<u>Cathode (Air). Electrode</u>	<u>Anode (Fuel) Electrode</u>	<u>Electrolyte</u>
Electrical Resistivity*	$\rho < 50$ ohm-cm, ~100% electronic	$\rho/\delta < 1$ ohm, electronic +	$\rho/\delta < 1$ ohm, electronic ⁺	$\rho = 25-50$ ohm-cm, ionic
Porosity	Gas-tight	Moderate; gas permeable	Moderate; gas permeable	Gas-tight
Current Density*			0.4 to 0.8 A/cm ²	
Temperature			700° to 1000°C	
Pressure*			Atmospheric	
Chemical Stability*	Stable under ox- idizing and re- ducing atmosphere; low vapor pressure	Stable in air; low vapor pressure	Stable with re- ducing atmos. ($P_{O_2} = 10^{-16}$ atm); low vapor pressure	Same as for inter- connector.
Compatibility*			Must be chemically and mechanically compatible; coefficient of thermal expansion of $10 \times 10^{-6}/^{\circ}\text{C}$.	
Mechanical Stability			Creep resistant, with no destructive phase changes from ambient to 1000°C	
Life*			> 30,000 hrs	
Fabrication			Moderate in cost and easy to fabricate	

*At temperature

+ δ = thickness, generally 20 to 50 μm

electrically are successively applied to a porous-tube substrate in the form of films 20 to 50 μm thick. The very thin layers require an electrical conductivity as high as possible to minimize power losses during operation of the fuel cell.

The MHD electrodes and interelectrode insulators are exposed to the same mildly oxidizing atmosphere ($P_{\text{O}_2} \approx 0.10$ atm, typically). The electrolyte and interconnector of the solid-electrolyte fuel cell, however, are exposed to dual atmospheres simultaneously. On the air-electrode (cathode) side, the atmosphere is quite oxidizing ($P_{\text{O}_2} \approx 0.2$ atm), while extremely reducing conditions (P_{O_2} as low as 10^{-18} atm) are found on the fuel-electrode (anode) side. Thus, while some materials may possess properties compatible under either oxidizing or reducing conditions, imposing both criteria at once severely restricts material options available.

The corrosive action of molten mixtures of coal slag, K_2SO_4 , and K_2CO_3 upon the MHD interelectrode insulator has an analogy in the molten-carbonate fuel cell. Even though the operating temperature of the fuel cell (580° to 730°C) is considerably lower than that for the typical MHD channel (1200° to 1700°C), the molten electrolyte--binary and ternary mixtures of Na_2CO_3 , K_2CO_3 , and Li_2CO_3 --is still quite corrosive. Thus, the ceramic matrix (tile) used to contain the electrolyte must be quite resistant to attack if a 40,000-hour cell life is to be realized. Candidate materials for the tile, however, do not need the extremely high melting point required of MHD interelectrode

insulators.

The general similarity of the chemical and physical properties of materials used for MHD and high-temperature fuel cells suggests the possibility, where appropriate, of transferring materials technology from one area to another. A good electricity-conducting ceramic found to be suitable for MHD electrode-use could be an appropriate candidate for the interconnector in the solid-electrolyte fuel cell. Similarly, a material which is resistant to corrosion by coal slag as an inter-electrode insulator in the MHD channel may show promise as a tile in the molten-carbonate fuel cell. As a result of the generally less stringent component requirements, materials examined for MHD use as electrodes or insulators and found to be deficient in performance may prove more than adequate for use in the solid-electrolyte or molten-carbonate fuel cells.

The purpose of this report, therefore is to examine and evaluate the published data in the MHD and fuel cell fields as related to materials properties and to identify materials used or considered for MHD power generation which also might prove suitable candidates for components in the high-temperature fuel cells.

DISCUSSION

I. SOLID-ELECTROLYTE DESIGN CONSIDERATIONS

The heart of the solid-electrolyte fuel cell is the oxide electrolyte. It is important that the oxide system chosen for use as the electrolyte have the proper electrochemical characteristics (i.e., high ionic conductivity) as well as stability from destructive phase transformations upon thermal cycling. Once an appropriate oxide has been chosen for the electrolyte, materials for the remaining cell components--air and fuel electrodes and cell interconnector--can be selected for physical and chemical compatibility with the electrolyte and each other. The physical property of prime concern is the coefficient of thermal expansion. The reason for this becomes clear after examining the current Westinghouse design for a thin-film cell shown in Figure 1.³ A substantial mismatch in thermal expansion of the electrolyte and interconnector could cause cracking of the impervious films, resulting in severe degradation or failure of the fuel cell upon thermal cycling. In order to evaluate MHD materials properly for potential use in solid-electrolyte fuel cells, it is first necessary to examine those materials which can possibly be used as oxide-conducting electrolytes. Auxiliary materials then can be screened for the remaining cell components to ensure the thermal expansion behavior is compatible with that of the chosen electrolytes.

Figure 1.--Westinghouse high-temperature fuel cell structure (from ref. 3.)

A. Ionically Conducting Oxides

The bulk of research on MHD electrodes has been oriented toward identifying materials which are good electronic conductors, because of the inherent material properties needs. The use of ionically conducting oxides for MHD electrodes has been limited due to electrolysis problems. ZrO_2 -based systems have received the most attention of the ionically conducting oxides because of the high-temperature capabilities of ZrO_2 .^{2,5,6} Oxides such as CaO or Y_2O_3 are added to the ZrO_2 to stabilize the cubic fluorite structure and prevent the occurrence of the destructive monoclinic-to-tetragonal phase change at 1100°C . Addition of CaO or Y_2O_3 imparts almost total ionic conductivity to ZrO_2 at MHD-electrode temperatures. At high enough current densities (depending upon the electrode temperature and P_{O_2}), cathodes of stabilized ZrO_2 exhibit darkening at the interface between the ceramic and metal current-leadout, as depletion of O_2 leads to electrolysis.

Problems caused by the use of ionic oxide conductors for MHD electrodes do not exist when such materials are used as solid electrolytes in fuel cells. The various oxides which have been examined for this purpose have been reviewed in detail by Etsell and Flengas.⁷ The results of their review are summarized below to justify the selection of the most promising systems as solid electrolytes for high-temperature fuel cells; evaluation of MHD materials for potential use for the remaining cell components is discussed separately.

Oxide systems based upon ZrO_2 , HfO_2 , ThO_2 , and CeO_2 have been studied extensively as solid electrolytes. Divalent (e.g., alkaline earth) and trivalent (e.g., rare earth) oxides are added to stabilize the desired cubic fluorite structure or to increase the electrical conductivity. In addition to being a good conductor, a potential solid-electrolyte should have an ionic transference number (t_i) as close to unity as possible, over the range P_{O_2} expected during fuel cell operation— ~ 0.2 atm at the cathode and $\sim 10^{-16}$ at the anode. The electrolyte also should exhibit a resistance to ordering and destabilization of the cubic solid solution after prolonged periods (10,000 hr.) at operating temperature.

1. ZrO_2 Systems

The electrical properties of typical ZrO_2 -based electrolytes are summarized in Table 3 for compositions where the conductivity is greatest. The three oxide stabilizers which best meet the desired electrical requirements are Sc_2O_3 , Y_2O_3 , and CaO . Unfortunately, the cost of Sc_2O_3 is too prohibitive to warrant serious consideration for commercial application. While Y_2O_3 is more expensive than CaO , the additional cost is justified because of the increased conductivity and greater stability of Y_2O_3 - ZrO_2 solid solutions. 7-10

2. HfO_2 Systems

The electrical transport properties of HfO_2 -based systems are, as might be expected, similar to their ZrO_2 counterparts. For ex-

TABLE 3.--Electrical properties of ZrO₂-based solid electrolytes at 1000°C and in air

Oxide Additive	Conc., m/o	ρ , Ω -cm	Transport Properties		References
			Avg. t_i	-Log P_{O_2} , atm	
Sc ₂ O ₃	8-10	4	est.>0.99	-	11,12
Y ₂ O ₃	10	10	>0.99	0 to 17	13-15
Gd ₂ O ₃	8-10	9	-	-	16
Yb ₂ O ₃	10	9	0.99	? to 10	16
CaO	12-13	17-24	>0.99	0 to 20	4,11,17-19
*MgO	20	26	-	-	10,20
Pr ₆ O ₁₁	25	37	0.95	?	21
Nd ₂ O ₃	15	59-71	0.93	0	22,23
La ₂ O ₃	5	22 ⁷	-	-	24,25
	15	330-910	0.08-0.17	0	12,22

*Cubic solid solution is unstable below 1300° to 1400°C.

ample, $\text{HfO}_2\text{-Y}_2\text{O}_3$ and $\text{HfO}_2\text{-CaO}$ solid solutions are good ionic conductors at 1000°C . The electrical conductivities, however, are only a fraction as great as the ZrO_2 solid solutions at the 10 to 12 m/o additive level, where conductivity is greatest.⁷ The use of HfO_2 solid solutions as solid electrolytes in fuel cells does not appear warranted because of lower conductivities and higher costs relative to the ZrO_2 systems.

3. ThO_2 Systems

Lower-valent oxides are added to ThO_2 solely to increase the electrical conductivity, as ThO_2 already has a cubic fluorite structure. The electrical properties of ThO_2 -based solid-electrolytes are summarized in Table 4 for a number of the more common systems. The ThO_2 -based electrolytes are characterized as being ionically conducting to a much lower P_{O_2} than the corresponding ZrO_2 systems. Unfortunately, the magnitude of the electrical conductivity is one or two orders of magnitude less for the ThO_2 solid electrolytes. More importantly, at a P_{O_2} greater than 10^{-16} atm electronic (p-type) conduction becomes significant. Thus, a fuel cell solid electrolyte based on ThO_2 is not feasible because of the incompatible electrolytic domain.

4. CeO_2 Systems

CeO_2 is similar to ThO_2 in that both have the fluorite structure. A considerable amount of research has been carried out with CeO_2 -based electrolytes because of the promise of el-

TABLE 4.--Electrical Properties of ThO₂-Based Solid Electrolytes at 1000°C
and in air

Oxide Additive	Cconc., m/o	ρ , Ω -cm	-Log P_{O_2} , atm	Transport Properties		References
				Avg. t_i	-Log $\bar{P}_{O_2}$, atm	
Y ₂ O ₃	8.1	139 to 435	> 8	>0.99	7 to 24	26,27
CaO	5	2,120	15	0.89	$1(=\bar{P}_{O_2})^*$	26
La ₂ O ₃	14	312	0.7	0.87	$1(=\bar{P}_{O_2})^*$	28,29

$$^* \bar{P}_{O_2} = \text{avg. } P_{O_2} = \frac{1}{2} [P_{O_2 \text{ cathode}} + P_{O_2 \text{ (anode)}}]$$

ectrical conductivities comparable to some of the better stabilized-ZrO₂ systems at 1000°C, but at much lower temperatures--typically 700°C. The electrical properties of a number of CeO₂-based solid-electrolytes are presented in Table 5.

Doping of CeO₂ with alkaline-earth and rare-earth oxides results in good ionic conductivities at temperatures below 1000°C and high oxygen pressures (e.g., $P_{O_2} > 10^{-5}$ atm), in many cases.⁷ However, at temperatures near 1000°C or at low oxygen pressures (e.g., $P_{O_2} < 10^{-10}$ atm), Ce⁺⁴ is reduced to Ce⁺³, which gives rise to unacceptable levels of electronic (n-type) conduction. The large increase in electrical conductivity for CaO-doped CeO₂ under strongly reducing conditions, relative to air, indicates the presence of electronic conduction. Similarly, while good ionic conductivity results when CeO₂ is doped with a number of rare-earth oxides at a P_{O_2} of 0.2-1.0 atm, the ionic transference number is strongly dependent upon P_{O_2} and drops markedly under reducing conditions. Thus, the best solid-electrolyte developed to date based upon CeO₂ would appear marginally acceptable at best. This conclusion is supported in recent work by Ross and Benjamin,³⁶ who analyzed the thermal efficiency (η_T) which could be expected for a H₂-air fuel cell utilizing various solid electrolytes.

The thermal efficiencies of cells using various CeO₂-based

TABLE 5.--Electrical properties of CeO₂-based solid electrolytes

Oxide Additive	Conc., m/o	Temp., °C	ρ , Ω -cm	-Log P _{O₂} , atm	Transport Properties		References
					Avg. t_i	-Log P _{O₂} , atm	
Y ₂ O ₃	5	700	50	0	1.0	≤ 5.5	30
		1,000	5	0	1.0	≤ 3.5	30
CaO	10	700	27	0	-	-	31
		700	4	20	-	-	31
		1,000	5	0	-	-	31
		1,000	0.5	14	-	-	31
Nd ₂ O ₃	15	727	21	0.7	1.0	0.7 to 0	32
Sm ₂ O ₃	15	727	25	0.7	0.96	0.7 to 0	32
Gd ₂ O ₃	15	727	22	0.7	1.0	0.7 to 0	32
Dy ₂ O ₃	15	727	26	0.7	1.0	0.7 to 0	32
Er ₂ O ₃	15	727	30	0.7	1.0	0.7 to 0	32
La ₂ O ₃	11	1,000	14	0.7	0.18	15	33-35

electrolytes are shown in Table 6. The Electric Power Research Institute goal for a solid-oxide fuel cell is an overall thermal efficiency of 45.5 percent. None of the CeO_2 -based systems approach the efficiency goal at 700°C , except $\text{CeO}_2\text{-La}_2\text{O}_3$; unfortunately, this combination has a power density that is too low to be of practical use in thin-film fuel cells.

5. Other Oxides

Takahashi and coworkers have conducted extensive research on development of solid-oxide electrolytes with ionic conductivities comparable to stabilized- ZrO_2 at 1000°C , but at temperatures as low as 700°C . Doped Bi_2O_3 was reported to be a good oxide conductor at a relatively high P_{O_2} at temperatures as low as 800°C .³⁷ Substituted perovskites studied included $\text{La}_{1-x}\text{Ca}_x\text{AlO}_{3-\alpha}$, $\text{La}_{1-x}\text{Ba}_x\text{AlO}_{3-\alpha}$, $\text{CaTi}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$, $\text{CaTi}_{1-x}\text{Al}_x\text{O}_{3-\alpha}$, $\text{SrTi}_{1-x}\text{Al}_x\text{O}_{3-\alpha}$, $\text{BaTh}_{0.95}\text{La}_{0.05}\text{O}_{3-\alpha}$, $\text{BaZr}_{0.9}\text{Bi}_{0.1}\text{O}_{3-\alpha}$, and $\text{BaCe}_{0.9}\text{Bi}_{0.1}\text{O}_{3-\alpha}$. The electrolyte of composition $\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{3-\alpha}$ showed the most promise.

The electrolytes listed above are not purely ionic conductors and exhibit changes in conductivity and ionic transference number as a function of P_{O_2} . This mixed conduction generally has been considered undesirable for fuel cell purposes. Takahashi⁴³ has considered the ramifications of mixed conduction in solid-oxide, high-temperature fuel cells. According to his calculations, a purely ionic electrolyte with a $t_i=1$ in a solid-electrolyte fuel

TABLE 6.--Maximum thermal efficiencies of H₂-air fuel cells with various solid electrolytes³⁶

Electrolyte	Ionic Conductivity, $10^{-2} \Omega^{-1} \text{cm}^{-1}$	P_{θ} , atm [*]	Power Density, 10^{-3} W/cm	η_t , %
ZrO ₂ -7 m/o Y ₂ C ₃	1.27	1.00×10^{-44}	1.5	50.2
CeO ₂ -18 m/o Gd ₂ O ₃	3.3	3.16×10^{-19}	4.8	40.0
CeO ₂ -5 m/o CaC	1.4	1.00×10^{-17}	2.1	35.7
CeO ₂ -5 m/o Y ₂ C ₃	1.03	5.31×10^{-18}	1.7	36.6
CeO ₂ -33 m/o La ₂ O ₃	0.14	1.34×10^{-26}	0.17	49.5

* $P_{\theta} = P_{O_2}$ where ionic σ = electronic σ (i.e., $t_i = 0.5$)

cell would be comparable in energy conversion efficiency ($\eta=0.6$) to a mixed-conductor electrolyte with $t_i=0.94$, if the conductivity were 50 percent greater.⁴³

A similar theoretical study has been published recently by Tannhauser⁴⁴ and applied to doped-CeO₂ electrolytes. The equivalent circuit used for modeling was not found to represent the system very well in practice. Still, it was felt that doped CeO₂ should be considered more suitable as a solid electrolyte in high-temperature fuel cells than believed previously.

While a number of the above substituted perovskites appear promising for use as solid electrolytes in high-temperature fuel cells, there are still areas of deficiency which must be resolved before they can be considered competitive with other, more suitable electrolyte materials.

B. Choosing a Solid-Oxide Electrolyte

As mentioned earlier, mechanical stability under thermal-cycling conditions is very important for long-term integrity of fuel cell operation. The thermal-stress problems can be approached in several ways. One involves carefully matching the coefficient of thermal expansion of the cell interconnector to that of the electrolyte. Alternatively, the interconnector can be plastic and have a low modulus of elasticity at operating temperature to minimize thermal stresses. Generally, this involves the use of a glassy matrix containing the interconnector material.⁴⁵ This approach, while possibly solving one

problem, presents additional problems of long-term chemical stability in contact with the electrolyte. In addition, incorporation of a glassy phase inherently lowers the overall conductivity of the interconnecting layers. Thus, this latter approach does not appear practical. For the purposes of this report, potential interconnector materials should have an average linear coefficient of thermal expansion (α) compatible with that of ZrO_2 -10 m/o Y_2O_3 , which is $10 \times 10^{-6} / ^\circ\text{C}$ up to 1000°C .⁴

At this time, none of the solid-oxide electrolytes for which published information is available appears to satisfy all the electrochemical requirements for efficient operation of high-temperature fuel cells at temperatures as low as 700°C . Doped- CeO systems have unacceptable electronic conduction (low t_i) resulting in low fuel cell efficiencies, while doped- ZrO_2 systems have ionic conductivities which are insufficient (at 700°C) for the desired power-density levels. In addition, little is known about the long-term behavior of the CeO_2 -based electrolytes and substituted perovskites under fuel cell conditions, although work currently is underway at the National Bureau of Standards to study long-term degradation mechanisms in CeO_2 - Gd_2O_3 and Y_2O_3 solid solutions.^{46,47}

Of all the solid-oxide electrolytes discussed above, only the ZrO_2 - CaO and ZrO_2 - Y_2O_3 solid solutions meet the requirements necessary for efficient electrochemical conversion at 1000°C of fuels such as H_2 and CO at a reasonable material cost. The ZrO_2 - Y_2O_3 system is the preferred choice for use as a solid

electrolyte in high-temperature fuel cells because of higher conductivity greater stability against long-term structural ordering. Rohr ⁴⁸ has reported a significant increase in the electrical conductivity of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solutions in which part of the Y_2O_3 has been replaced by Yb_2O_3 (e.g., $\text{ZrO}_2\text{-4 m/o Y}_2\text{O}_3\text{-4 m/o Yb}_2\text{O}_3$). Even though the conductivity may be lower for $\text{ZrO}_2\text{-10 m/o Y}_2\text{O}_3$ --the composition with the highest conductivity in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system--this composition was chosen as a reference point or basis for evaluating and screening various MHD materials for possible use as ancillary components in the solid-electrolyte fuel cell because it has been studied more extensively for this purpose. Physical and chemical properties data also are more readily available for comparison.

II. MHD ELECTRODE MATERIALS

Materials examined for use as MHD electrodes can be classified into three general categories: metals, non-oxide ceramics, and oxide ceramics.

A. Metals

A variety of metals has been examined for use as MHD electrodes, with the choice of materials based upon properties such as chemical inertness, electrical and thermal conductivity, and low vapor pressure at elevated temperatures. Classes of metals which have been tested include noble metals (e.g., Pt, Rh, Pd, Au, and Ag), refractory metals (e.g., W, Mo, Ta, Nb, Hf, and Zr), and base metals (e.g.,

Fe, Ni, and Cu) and their alloys. The use of noble metals in the solid-electrolyte fuel cell would be prohibitively expensive and, therefore, will not be considered further. A number of the base and refractory metals suitable for MHD electrodes at temperatures of 200° to 700°C would be limited to use as fuel electrodes in the solid-electrolyte fuel cell by P_{O_2} constraints. The equilibrium P_{O_2} s at 1000°C for a number of these metal-metal oxide systems are tabulated in Table 7.

In comparison to the P_{O_2} of 10^{-16} to 10^{-18} atm expected for the fuel, copper is stable over a wider range of P_{O_2} than any of the other base metals, i.e., CuO formation would not be expected until the P_{O_2} had reached a value of 5.75×10^{-7} atm. Unfortunately, copper has a melting point of only 1083°C, which is very close to the operating temperature of the solid-electrolyte fuel cell, thus making it unsuitable for anode use. Currently, nickel is the preferred choice for the anode in both the solid-electrolyte and molten-carbonate fuel cells. As indicated in Table 7, it has a greater stability range than either cobalt or iron, with respect to oxidation by the fuel mixture.

The present technique employed for the fabrication of the nickel anode in the solid-electrolyte fuel cell is relatively simple and straightforward. The Ni-ZrO₂ cermet electrode is prepared by first sintering (at 1600°C) a coating of NiO and CaO-stabilized ZrO₂ on a porous support tube, and reducing the mixture at 1350°C in hydrogen.⁵⁰ The result is a porous, mechanically sound structure consisting of continuous interlocking phases of ZrO₂ and nickel. The nickel anode

TABLE 7.--Equilibrium P_{O_2} for select metal-metal oxide systems at 1000°C

Metal-Metal Oxide System	-Log P_{O_2} (atm)	Reference
Cu-CuO	6.24	49
Ni-NiO	10.3	49
Co-CoO	11.9	49
Fe-Fe _{0.95} O	14.8	7
Mo-MoO ₂	15.0	7
W-WO ₂	15.8	7
Cr-Cr ₂ O ₃	21.6	7
Mn-MnO	24.0	7
Ta-Ta ₂ O ₅	24.6	7
Nb-NbO	25.1	7

produced in this manner also provides a good surface for bonding to the other cell components, such as the porous support tube, electrolyte, and interconnector films, which reduces the tendency for cracking due to thermal stresses.

There are no apparent advantages of substituting a more exotic or costlier alloy or metal for pure nickel, unless perhaps a significant resistance to sulfur poisoning was realized and the life of the fuel cell substantially increased. A number of nickel alloys, such as the Incoloy alloys and stainless steels, have increased resistance to sulfur (as H_2S), relative to pure nickel. Unfortunately, these alloys also have electrical resistivities which are an order of magnitude higher.⁵¹ With today's desulfurization technology, no serious problems are envisioned in lowering the sulfur content of the fuel to acceptable levels (<0.05 ppm) for satisfactory long-term performance of nickel anodes in fuel cells.⁵²

B. Non-Oxide Ceramics

Materials used for MHD electrodes in the non-oxide ceramic category include carbides, nitrides, silicides, and borides and their mixtures.

1. Carbides

Only a limited number of elements form carbides of potential interest for MHD electrodes, i.e., good electronic (metallic) conductors. These are generally the transition elements of Groups IVA to VIA (Ti, V, and Cr families). Elements to the left of these groups in the Periodic Table form reactive, ionic (salt-

like) carbides which are hydrolyzed by water to the hydroxide and acetylene, methane, ethylene, or mixtures thereof, depending upon the oxidation state of the metal.⁵³ The rare-earth carbides are similarly reactive to moisture. Of the elements to the right of the transition metals in the Periodic Table, only Al, B, and Si form carbides of any thermal stability. Al_4C_3 , however, is like the alkaline-earth carbides in that it hydrolyzes readily.

Physical properties for transition-metal carbides which have been studied or considered for MHD electrodes are listed in Table 8; data for several non-transition metal carbides, B_4C and SiC , are included for comparison. The transition metal carbides are characterized by high melting points and, in general, a high metallic conductivity, so that the values reported here for room temperature would be considerably higher at the solid-electrolyte fuel cell operating temperature of 1000°C . The resistivities of ZrC , HfC , and TaC , however, are reported to decrease with temperature. Carbon-deficient (metal-rich) phases show higher resistivities than the stoichiometric phases.^{54,55}

Electrical conductivity data at elevated temperatures were not readily available for most of the carbides. Sources of additional physical properties information for transition metal carbides--including the above type resistivity data--are listed in Appendix A. These references predominantly are Russian journals to which the author did not have ready access during the

TABLE 8.--Physical properties of metal carbides

Material	Melting Point, °C	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity at 25°C, $\mu\Omega\text{-cm}$	References
B_4C	2,450	4.3 (25°-871°C)	0.3-0.8 $\Omega\text{-cm}$	56,57
B-SiC	2,700	4.4 (25°-1,400°C)	2.1 $\Omega\text{-cm}$	57,58
TiC	3,250	8.3 (0°-1,400°C)	60-250	57-59
ZrC	3,550	7.5 (25°-1,350°C)	57-75	57-60
HfC	3,890	7.2 (25°-2,030°C)	109	57,59,60
VC	2,830	6.6 (25°-1,930°C)	150	57,59,60
NbC	3,500	7.3 (25°-1,450°C)	60-150	57-60
TaC	3,880	6.5 (25°-1,000°C)	30	57,59,60
MoC	2,690	-	49	58,59
Mo_2C	2,687	7.3 (25°-1,930°C)	71-97	57-59
WC	>2,755 (dec.)	5.2 (25°-2,200°C)	25-53	58-60
W_2C	2,800	-	80	59,60
Cr_3C_2	1,915	10.3 (25°-1,100°C)	75-84	57-60

allotted time. Only infrequently did the published English abstract contain numerical data for the desired physical properties. Acquisition of copies of these journal articles also was hampered seriously by recently enacted federal copyright legislation which limits the number of articles which any one organization can obtain, through interlibrary loan, from a given journal in a particular calendar year. Under the new law, only five copies of articles from the previous five years of publication of a journal are allowed per organization per year.

While the conductivities of most of the carbides are compatible with the electrical requirements for the interconnector and fuel electrodes (Table 2), none of the carbides, except for perhaps Cr_3C_2 , possess thermal-expansion properties that would be suitable for use with the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid electrolyte. Perhaps this deficiency, however, can be mitigated by suitable materials engineering.

The requirement of stability to partial pressures of oxygen as high as 0.2 atm is prohibitively stringent and does not allow the carbides to be used as interconnector material. At 1300K, all the carbides are thermodynamically unstable in air with respect to the oxides, i.e., the free energy of oxidation is extremely negative, as indicated in Table 9. Data are included in Table 9 for oxidation at 900K, also, for evaluating carbides for possible use in the molten-carbonate fuel cell.

In spite of thermodynamic predictions, however, kinetic factors can be overriding to prevent the reactions from occurring at

TABLE 9.--Free energy of oxidation of metal carbides

Reaction	-ΔG° for Reaction, kcal/g-at C		References
	T = 1300K	T = 900K	
$B_4C + 4O_2 \rightarrow 2B_2O_3 (l) + CO_2$	542.4	583.3	61
$\alpha\text{-SiC} + 2O_2 \rightarrow SiO_2 \text{ (quartz)} + CO_2$	242.2	258.0	61
$TiC + 2O_2 \rightarrow TiO_2 \text{ (rutile)} + CO_2$	223.9	239.4	61
$ZrC + 2O_2 \rightarrow ZrO_2 + CO_2$	254.2	270.9	61
$VC + 2.25O_2 \rightarrow 0.5V_2O_5 (l) + CO_2$	191.6	206.8	62,63
$1.02 \text{ NbC}_{0.98} + 2.28O_2 \rightarrow 0.51Nb_2O_5 + CO_2$	225.4	245.3	63
$TaC + 2.25O_2 \rightarrow 0.5Ta_2O_5 + CO_2$	238.1	257.8	63
$0.5 \text{ Cr}_3C_2 + 2.12O_2 \rightarrow 0.75Cr_2O_3 + CO_2$	224.9	243.8	63
$WC + 2.5O_2 \rightarrow WO_3 + CO_2$	210.0	232.3	62,63

a significant rate. For example, a protective, impervious oxide layer can form to prevent further oxidation from taking place. (The formation of a SiO_2 layer on SiC , for example, allows its use as a heating element in air at temperatures as high as 1500°C).

Even if some of the carbides in Table 8 were to form a protective oxide layer upon heating in air at 1000°C , they still would not be practical for interconnector use in the solid-electrolyte fuel cell for a number of reasons. Loss of the initially impervious interconnector film would very likely occur as the side in contact with air began oxidizing. While the transition metals in Table 8 form a continuous series of solid solutions with many of the interstitial elements, formation of a separate oxide phase would eventually occur once the oxide-solubility limit was exceeded. This would very likely result in separation at the interconnector-air electrode interface, causing rapid deterioration in cell performance and ultimately resulting in failure. Even if mechanical separation did not take place immediately, a substantial increase in the interfacial resistivity would occur during oxidation, since the oxides of the transition metals in Table 8 are poor conductors. There also is the question of the long-term chemical compatibility with the other cell components of any oxide which might form. Thus, transition metal carbides would appear suitable for high-temperature fuel cell use only under reducing conditions, i.e., as fuel electrodes.

To determine the thermodynamic stability of the carbides under typical anode conditions during fuel cell operation, values of P_{O_2} for the reactions in Table 9 were calculated for equilibrium partial pressures of CO_2 expected for fuel mixtures derived from the gasification of coal. The Lurgi Medium-Btu gasification was chosen to be representative of a process with a low conversion efficiency (37 percent) for $CO+H_2$ production, while the Combustion Engineering Medium-Btu gasification was chosen to be representative of a process with a high conversion efficiency (79 percent).

The compositions of the gas streams exiting the gasifiers are listed in Table 10, along with the equilibrium compositions at 1300K and 900K for the water-gas shift reaction:

(The higher temperature is representative of the solid-electrolyte fuel cell, while the lower temperature is applicable to the molten-carbonate fuel cell). The compositions were calculated from the relationship:

$$(2) \quad K_p = \exp(-\Delta G_{(1)}^0/RT) = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}}$$

At 1300K, $\Delta G_{(1)}^0$ is -1444 cal, which translates into a K of 1.75. The corresponding values at 900K are 1,500 cal and 0.432, respectively. The data in Table 10 indicate that the gases are very close to the equilibrium composition with regard to reaction (1) at 1300K. The equilibrium composition of the Lurgi gas, however, was substantially changed at 900K.

TABLE 10.--Gas Composition from low- and high-efficiency coal gasifiers⁶⁴

Gasification Process	Exit Gas Composition, m/o							Condition
	H ₂	CO	CH ₄	H ₂ O	CO ₂	N ₂	P _{O₂} , atm*	
Lurgi Medium-Btu	21	8	5	50	15	0.2	-	From gasifier at 1088K
	20	9	5	51	14	0.2	5.0 x 10 ⁻¹⁴	Calculated for equilibrium at 1300K.
	25	4	5	46	19	0.2	3.5 x 10 ⁻²³	Calculated for equilibrium at 900K.
Combustion Engineering	30	63	0.05	2	2	1	-	From gasifier at 1000K
	30	63	0.05	2	2	1	2.7 x 10 ⁻¹⁷	Calculated for equilibrium at 1300K.
	31	62	0.05	<1	3	-	5.3 x 10 ⁻²⁷	Calculated for equilibrium at 900K.

* For the reaction: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}(\text{g})$.

The equivalent P_{O_2} values for the two gas mixtures are determined by the equilibrium:

The equilibrium P_{CO_2}/P_{CO} values determined for the gas mixtures were used to calculate P_{O_2} from the equilibrium expression for reaction (3):

$$(4) \quad P_{O_2} = \left[\frac{P_{CO_2}}{P_{CO}} \right]^2 \left[\frac{1}{K_p^2(3)} \right]$$

The P_{O_2} values for the reactions of Table 9 are listed in Table 11 for a temperature of 1300K and in Table 12 for a temperature of 900K. At 1300K, the P_{O_2} for the high- CO_2 gas (Table 10) is higher than the P_{O_2} for oxidation of the carbides in all cases; i.e., the carbides would not be thermodynamically stable against oxidation by the fuel from the Lurgi gasifier at this temperature, according to the reactions of Table 9. The low- CO_2 gas from the Combustion Engineering gasifier, on the other hand, would be reducing enough to prevent oxidation of two carbides--WC and VC. At 900K, the difference between the P_{O_2} of the gas mixture and that for the oxidation reactions is much less than at 1300K. WC and VC are almost stable against oxidation by the high- CO_2 gas. As at 1300K, VC and WC are thermodynamically stable against formation of the higher oxides in the low- CO_2 gas from the Combustion Engineering gasifier at 900K; $NbC_{0.98}$ is almost stable under the same conditions. Thus, from the viewpoint of thermodynamic stability against oxidation, the carbides would be suited better for use in a fuel cell operating at 900K (e.g., the molten-carbonate fuel cell) on fuel from a gasifier of the Combustion Engineering type.

TABLE 11.--Calculated P_{O_2} for oxidation of metal carbides at 1300K at equilibrium P_{CO_2} of fuel gases*

Carbide/Oxide	K_p for Oxidation	P_{O_2} for Oxidation for $P_{CO_2} = 0.14 \text{ atm}^+$	P_{O_2} for Oxidation for $P_{CO_2} = 0.02 \text{ atm}^\dagger$
$B_4C/B_2O_3(l)$	$P_{CO_2}/P_{O_2}^4 = 1.56 \times 10^{91}$	9.73×10^{-24}	5.98×10^{-24}
$\alpha\text{-SiC/SiO}_2(g)$	$P_{CO_2}/P_{O_2}^2 = 5.20 \times 10^{40}$	1.64×10^{-21}	6.20×10^{-22}
$TiC/TiO_2(\text{rutile})$	$P_{CO_2}/P_{O_2}^2 = 4.37 \times 10^{37}$	5.66×10^{-20}	2.14×10^{-20}
ZrC/ZrO_2	$P_{CO_2}/P_{O_2}^2 = 5.48 \times 10^{42}$	1.60×10^{-22}	6.04×10^{-23}
$VC/V_2O_5(l)$	$P_{CO_2}/P_{O_2}^{2.25} = 1.64 \times 10^{32}$	2.01×10^{-15}	8.46×10^{-16}
$NbC_{0.98}/Nb_2O_5$	$P_{CO_2}/P_{O_2}^{2.28} = 7.76 \times 10^{37}$	1.02×10^{-17}	4.33×10^{-18}
TaC/Ta_2O_5	$P_{CO_2}/P_{O_2}^{2.25} = 1.09 \times 10^{40}$	6.70×10^{-19}	2.82×10^{-19}
Cr_3C_2/Cr_2O_3	$P_{CO_2}/P_{O_2}^{2.12} = 6.37 \times 10^{37}$	5.82×10^{-19}	2.33×10^{-19}
WC/WO_3	$P_{CO_2}/P_{O_2}^{2.5} = 2.05 \times 10^{35}$	3.42×10^{-15}	1.57×10^{-15}

*Refer to Table 9.

⁺Lurgi gasifier (Table 10); $P_{O_2} = 5.0 \times 10^{-14} \text{ atm}$.

[†]Combustion engineering gasifier (Table 10); $P_{O_2} = 2.7 \times 10^{-17} \text{ atm}$.

TABLE 12.--Calculated P_{O_2} for oxidation of metal carbides at 900K at equilibrium P_{CO_2} of fuel gases*

Carbide/Oxide	K_p for Oxidation	P_{O_2} for Oxidation at $P_{CO_2} = 0.19 \text{ atm}^+$	P_{O_2} for Oxidation at $P_{CO_2} = 0.03 \text{ atm}^+$
$B_4C/B_2O_3(l)$	4.04×10^{141}	2.61×10^{-36}	1.65×10^{-36}
$\alpha\text{-SiC/SiO}_2(q)$	4.53×10^{62}	2.05×10^{-32}	8.14×10^{-33}
* $TiC/TiO_2(\text{rutile})$	1.38×10^{58}	3.71×10^{-30}	1.47×10^{-30}
ZrC/ZrO_2	6.15×10^{65}	5.56×10^{-34}	2.21×10^{-34}
$VC/V_2O_5(l)$	1.67×10^{50}	2.28×10^{-23}	1.00×10^{-23}
$NbC_{0.98}Nb_2O_5$	3.73×10^{59}	3.59×10^{-27}	1.60×10^{-27}
TaC/Ta_2O_5	4.05×10^{62}	7.14×10^{-29}	3.14×10^{-29}
Cr_3C_2/Cr_2O_3	1.61×10^{59}	5.39×10^{-29}	2.26×10^{-29}
WC/WO_3	2.60×10^{56}	1.40×10^{-23}	6.68×10^{-24}

*Refer to Table 9.

⁺Lurgi gasifier (Table 10); $P_{O_2} = 3.5 \times 10^{-23} \text{ atm}$.

[†]Combustion engineering gasifier (Table 10); $P_{O_2} = 5.3 \times 10^{-27} \text{ atm}$.

However, thermodynamic predictions (such as above) are not realized in practice in many cases because of extremely limiting kinetic factors; i.e., the rate of oxidation may be so low that the reactions do not occur to any measurable extent. Experimental data would be needed to ascertain this, however.

In addition, the oxidation of the carbides may not proceed as written for the reactions of Table 9, and lower-oxide phases may instead be formed. The equilibrium P_{O_2} values may be more favorable from a thermodynamic-stability viewpoint under these conditions. Since solid solutions of oxygen and carbon are quite stable for many of the transition metals, formation of such solutions (i.e., oxycarbides) could be expected during the early stages of the oxidation process. Of the carbides of Table 8, MO-MC solid solutions are possible for Ti, V, and Nb, since only these elements form a crystalline metal monoxide which is stable at fuel cell temperatures. Tungsten, on the other hand, forms WO_2 as its lowest oxide.

The oxidation of TiC, VC, NbC, and WC to the lowest stable oxide was calculated at 900K and 1300K, but with CO as the preferred gaseous product. The corresponding P_{O_2} for the reaction was determined from the K_p expression and Equation (4) using, as before, values for P_{CO_2} from Table 10. These data are summarized in Table 13.

As can be seen, none of the carbides would be thermodynamically stable in the high- CO_2 fuel gas at either 900K or 1300K, while $NbC_{0.98}$ and WC would be compatible with the low- CO_2 fuel gas

TABLE 13.--Calculated P_{O_2} for oxidation of metal carbides to lower oxides at 900 and 1300K at equilibrium
 P_{CO_2} of fuel gases

Reaction*	K_p^{**} at 1300K	P_{O_2} for Oxidation for $P_{CO_2} = 0.14 \text{ atm}^{\dagger}$	P_{O_2} for Oxidation for $P_{CO_2} = 0.02 \text{ atm}^{\dagger}$
		$P_{CO_2} / K_p(3) P_{O_2}^{1.5} = 1.39 \times 10^{19}$	$P_{CO_2} / K_p(3) P_{O_2}^{1.51} = 1.07 \times 10^{16}$
$TiC + O_2 \rightarrow \beta-TiO + CO$	$P_{CO_2} / K_p(3) P_{O_2}^{1.5} = 1.39 \times 10^{19}$	1.32×10^{-18}	3.61×10^{-19}
$VC + O_2 \rightarrow VO + CO$	" $= 4.00 \times 10^{17}$	1.41×10^{-17}	3.84×10^{-18}
$1.02NbC_{0.98} + 1.01O_2 \rightarrow 1.02NbO + CO$	$P_{CO_2} / K_p(3) P_{O_2}^{1.51} = 1.07 \times 10^{16}$	2.00×10^{-16}	5.50×10^{-17}
$WC + 1.5O_2 \rightarrow WO_2 + CO$	$P_{CO_2} / K_p(3) P_{O_2}^2 = 1.46 \times 10^{22}$	1.20×10^{-15}	4.55×10^{-16}
Reaction*	K_p at 900K	P_{O_2} for Oxidation for $P_{CO_2} = 0.19 \text{ atm}^{\dagger}$	P_{O_2} for Oxidation for $P_{CO_2} = 0.03 \text{ atm}^{\dagger}$
		$P_{CO_2} / K_p(3) P_{O_2}^{0.5} = 6.64 \times 10^6$ at 1300 K and 7.31×10^{11} at 900K,	$P_{CO_2} / K_p(3) P_{O_2}^{0.5} = 6.64 \times 10^6$ at 1300 K and 7.31×10^{11} at 900K,
$TiC + O_2 \rightarrow \alpha-TiO + CO$	8.70×10^{26}	4.47×10^{-27}	1.30×10^{-27}
$VC + O_2 \rightarrow VO + CO$	1.23×10^{25}	7.63×10^{-26}	2.23×10^{-26}
$1.02NbC_{0.98} + 1.01O_2 \rightarrow 1.02NbO + CO$	1.38×10^{23}	2.19×10^{-24}	6.46×10^{-25}
$WC + 1.5O_2 \rightarrow WO_2 + CO$	5.99×10^{33}	6.59×10^{-24}	2.62×10^{-24}

* ΔG_f° for metal oxides from Reference 63.

** $K_p(3) = K_p$ for equation 3 = $P_{CO_2} / P_{CO} P_{O_2}^{0.5} = 6.64 \times 10^6$ at 1300 K and 7.31×10^{11} at 900K,

† Lurgi gasifier (Table 10).

‡ Combustion engineering gasifier (Table 10).

at 1300K. At 900K, all of the carbides except TiC--and it is borderline--would be stable against metal-monoxide formation in the low-CO₂ gas mixture. The data of Table 13 are only approximate, as they do not reflect the interaction of the MO and MC phases to form the solid solution or oxycarbide. Still, the above information points out that thermodynamic calculations are only a starting point in predicting materials compatibility, unless the exact reaction path is known with certainty. Even so, laboratory testing under the expected experimental conditions must ultimately be conducted to determine if the kinetics of a thermodynamically possible reaction are favorable or not.

The current design being used for fabrication of the anode in the thin-film solid-electrolyte fuel cell involves applying a porous Ni-ZrO₂ cermet to a ZrO₂ support tube which also is porous. The ZrO in the cermet acts as a separator to maintain the desired electrode porosity and to prevent shrinkage and excessive sintering which would result in the absence of this dispersed oxide phase. Because ZrO₂ is a poor electronic conductor, there is some problem in obtaining a Ni-ZrO₂ cermet of high enough conductivity. Westinghouse has overcome this problem to a large extent by electroplating additional nickel into the pores of the cermet.⁶⁵

Modification of the present anode-fabrication technique by substituting a powdered carbide phase for the ZrO₂ would be difficult, as carbides do not sinter except under extreme conditions (e.g., as in hot pressing or in the presence of a sintering

aid). Any overall increase in electrical conductivity could be at the expense of structural integrity. A compromise might be realized by substitution of only a portion of the oxide phase, retaining sufficient ZrO_2 to form an interlocking matrix during the initial sintering step of the fabrication process. For best results, however, the carbide should have an average linear coefficient of expansion that is within ten percent (preferably less) of that for the ZrO_2 - Y_2O_3 electrolyte of $10 \times 10^{-6}/^{\circ}C$, to minimize possible thermal stresses.

Values of 9.0 to $11.7 \times 10^{-6}/^{\circ}C$ and 10.8 to $12.6 \times 10^{-6}/^{\circ}C$ have been reported for thermal expansion of TiC -Ni or -Co and Cr_3C_2 -Ni composites, for example, over a temperature range of 25 to $980^{\circ}C$. These materials also showed good oxidation resistance at elevated temperatures.⁵⁷ There is the possibility, however, of reactions between the nickel matrix and carbide phase of a composite anode taking place over a long period of time to form intermetallic compounds. A number of the nickel-transition metal intermetallics have substantial heats and free energies of formation.⁶⁶ Carbides of uranium, for example, react with nickel between 900° and $1300^{\circ}C$ to form a number of Ni-U and Ni-U-C compounds, depending on the carbide and temperature.⁶⁷ Such reactions could be detrimental to the performance of composite electrodes.

In theory, the fuel-electrode film could be solely constituted of the carbide phase, accomplished by a modified chemical vapor-deposition technique such as is currently done for the electrolyte layer of the fuel cell.⁴ This approach is not as likely to be successful, however. Even if suitable porous carbide film could be deposited with thermal-expansion properties

engineered so as to be compatible with the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ electrolyte, it appears unlikely that the conductivity can be increased sufficiently to equal that of nickel. At room temperature, for example, the electrical resistivity of nickel is only $6.87 \mu\Omega\text{-cm}$, which is about a fourth of that for the better-conducting carbides of Table 8.⁶⁸

In spite of the shortcomings of carbide materials, the possible incorporation of a carbide or carbide-based material into the anode structure of the solid-electrolyte fuel cell to increase the overall conductivity of the fuel electrode merits further attention. It may be possible to increase the coefficient of thermal expansion and maintain adequate electrical conductivity by doping the carbide phase with transition metals--many of the transition-metal carbides form a continuous series of solid solution with each other⁵⁹--or with other interstitials (e.g., Si or B). Any research effort in this area should examine critically both the short-term as well as the long-term stability of any newly developed anode material and its chemical compatibility with other cell components under typical fuel cell operating conditions.

Additionally, potential exists for using such materials as anodes in the molten-carbonate fuel cell. In this case, preparation of a thin-film (20 to $50 \mu\text{m}$) electrode would not be necessary. Typically, the electrode plaque is made by sintering or cold pressing nickel powder onto a support grid.⁶⁹ This obviates many strict requirements for thermal-expansion properties

inherent in the possible use of new materials in the solid-electrolyte fuel cell. If deemed desirable, it should not be difficult to incorporate a carbide phase into the electrode structure since nickel acts as a good binder and is used commonly to form cemented carbides for cutting bits. There may be some difficulty, however, in achieving the desired porosity, pore-size distribution, and tortuosity with such a composite electrode.

Even though the molten-carbonate fuel cell operates at a much lower temperature (an average of 660°C) than the solid-electrolyte fuel cell, the electrical conductivity of a composite electrode will, in all probability, be substantially less than that of an all nickel one. Still, if the composite anode exhibits a significantly improved resistance to sulfur relative to nickel, the net results may be beneficial enough for long-term fuel cell operation to warrant its use.

Some of the transition-metal carbides may be resistant to the molten-carbonate electrolyte. For example, Mo_2C has been electrodeposited from a high-temperature molten-salt bath containing carbonate.⁷⁰ It has also been reported, however, that TiC , ZrC , TaC , Mo_2C , and WC dissolve in molten Na_2CO_3 (and NaOH) at 900°C under vacuum to form TiO_2 , ZrO_2 , NaTaO_3 , Na_2MoO_4 , and Na_2WO_4 , respectively.⁷¹ (The fact that Mo_2C can be prepared electrolytically from a carbonate-containing bath results from the potential applied across the sample during electrolysis, which counteracts any tendency for chemical dissolution.) SiC has been reported to have

good long-term corrosion resistance to basic coal slags at maximum temperatures of 1250°C.⁷² Little is known, however, of the long-term chemical compatibility of carbides or carbide composites under actual operating conditions of the molten-carbonate fuel cell. Additional study is necessary before the suitability of such materials for fuel cell use can be evaluated properly.

In many cases, there is a large discrepancy between the electrical resistivities reported for many of the transition-metal carbides, as well as other interstitial alloys. This discrepancy is caused by a number of factors, such as differences in the method of preparation and impurity levels, inadequate analytical characterization, and the wide range of homogeneity demonstrated by a number of systems. If serious consideration is given to the possibility of using transition-metal carbides in high-temperature fuel cells, it first will be necessary to resolve these discrepancies and to obtain reliable electrical resistivity data at elevated temperatures.

2. Nitrides

The elements whose nitrides are good metallic conductors are generally the same ones that form conducting carbides: elements of the Ti, V, and Cr families. Similarly, elements that form ionic carbides also form ionic nitrides. Thus, nitrides of the alkali, alkaline-earth, and rare-earth metals hydrolyze readily:

where M is a metallic cation and x is the oxidation state of the

metal.⁷³ Like the carbides, the nitrides of B, Al, and Si also have considerable thermal stability. BN, AlN, and Si₃N₄ are electrical insulators, even at elevated temperatures. (The electrical resistivity of hexagonal BN, for example, is 1900 Ω -cm at 2000 C.)⁷⁴

Only a limited number of nitrides have been tested as MHD electrodes. The physical properties of the more stable transition-metal nitrides are listed in Table 14. Melting points are not included because of the questionable literature values in many cases. The melting point is a function of nitrogen pressure over the sample and this is not specified for most of the reported values. The melting points reported for some mononitrides (e.g., NbN), in all probability pertain to metal-nitrogen solid solutions.

In general, the transition-metal nitrides of Table 14 are much better electronic conductors and have higher coefficients of thermal expansion than the corresponding carbides. Four of the nitrides (TiN, VN, NbN, and Cr₂N) have coefficients of thermal expansion which approximate that for Y₂O₃-stabilized ZrO₂.

The nitrides are not as thermally stable as the carbides, in that they dissociate at high temperatures. The theoretical equilibrium partial pressure of nitrogen (P_{N_2}) for the dissociation of the mononitride, according to the reaction

can be calculated from the relationship

$$(7) \quad \Delta G_f^0 = -RT \ln K_p = -RT \ln P_{N_2}^{1/2}$$

Values of P_{N_2} obtained in this manner are listed in Table 15 for a

TABLE 14.--Select physical properties of transition metal nitrides⁷⁵

Material	Coefficient of Thermal Expansion(α), $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity at 25°C, $\mu\Omega\text{-cm}$
TiN _{0.98}	9.5 (20°-1100°C)	26
ZrN _{0.98}	7.24 (20°-1100°C)	28
HfN _{0.86}	6.9 (20°-1100°C)	33
VN _{0.93}	9.2 (20°-1100°C)	85
VN _{0.34}	8.1 (20°-1100°C)	123
NbN _{1.0}	10.1 (20°-1100°C)	78
NbN _{0.5}	3.26 (20°-1100°C)	142
TaN _{1.0}	3.6 (20°-700°C)	128
TaN _{0.45}	5.2 (20°-1000°C)	263
CrN _{0.93}	2.3 (20°-800°C)	640
CrN _{0.50}	9.41 (20°-1000°C)	79
MoN _{0.5}	6.2 (20°-1100°C)	20

temperature of 1300K. Data for the dissociation to a lower nitride are also included. The results indicate that the titanium-family members (Ti, Zr, Hf) form the most stable nitrides. As one moves to the right of the Periodic Table across the transition-metal series, the thermal stability of the mononitrides rapidly decreases and P_{N_2} similarly increases.

However, the calculated P_{N_2} values for MN materials are not observed in practice if lower nitride phases form during decomposition of MN, i.e., if MN does not dissociate according to reaction (6); this is the case for VN, NbN, and TaN. The P_{N_2} over NbN, for example, is an order of magnitude larger when Nb_2N , rather than Nb, is taken as the phase in equilibrium with NbN. Conversely, the P_{N_2} for the Nb_2N -Nb system is several orders of magnitude smaller than for the NbN- Nb_2N system. [By using a vacuum to drive the reaction, nitrogen can be successively removed at elevated temperatures from both NbN and TaN (e.g., by arc melting) to form lower nitrides and, eventually, pure Nb and Ta metals.⁷⁶ The nitrogen in VN, in comparison, can be taken to only the solid-solution level under comparable conditions.].

While a number of the transition-metal nitrides have a low thermal stability, all have one major shortcoming: poor resistance to oxidation. Like the carbides, the nitrides are thermodynamically unstable in air at 1300K with respect to their most stable oxides, as shown in Table 16. Oxidation to lower oxides is included for nitrides of Ti, V, Nb, and Mo, for comparison. Experimentally, the nitrides have been noted to oxidize more

TABLE 15.--Calculated equilibrium dissociation pressures of N_2 at 1300K for various transition-metal nitrides

Nitride	Dissociation P_{N_2} , atm	References
TiN	5.27×10^{-18}	61
ZrN	3.02×10^{-20}	61
HfN	2×10^{-20} (est.)	62
VN	$2.51 \times 10^{-9*}$	63
NbN	$7.01 \times 10^{-11*}$	77
TaN	$2.09 \times 10^{-12*}$	77
CrN	$3.44 \times 10^{-2*}$	63
$VN \rightarrow VN_{0.465}$	6.33×10^{-6}	63
$NbN \rightarrow Nb_2N$	6.76×10^{-10}	77
$TaN \rightarrow Ta_2N$	5.20×10^{-18}	78
$CrN \rightarrow Cr_2N$	0.413	63
$VN_{0.465}$	3.02×10^{-13}	63
Nb_2N	7.28×10^{-12}	77
Ta_2N	8.33×10^{-7}	78
Cr_2N	2.86×10^{-3}	63
Mo_2N	$3.94 \times 10^{-3**}$	62

*Calculated for hypothetical reaction: $MN \rightarrow M + 1/2 N_2$.
 **Value for 800K.

readily than the corresponding carbides.⁵⁹ Thus, their possible use in the solid-electrolyte fuel cell is limited to the fuel electrode, as in the case of the carbides.

Calculated values of P_{O_2} are listed in Table 17 for the oxidation reactions at 1300K for P_{N_2} equal to the equilibrium pressure over the nitride phases. (Oxidation of TaN and Ta₂N does not exhibit a P_{N_2} dependency in the K_p expression). Thus, at an equilibrium P_{N_2} for VN-V₂N of 2.74×10^{-6} atm (Table 15), a P_{O_2} of 4.88×10^{-16} atm is calculated for the oxidation of VN to V₂O₅ at 1300K. This is in the range of P_{O_2} expected at the fuel electrode of the solid-electrolyte fuel cell. Only the VN oxidation has a P_{O_2} that falls into the same range.

In all cases, the P_{O_2} for oxidation of nitrides to lower oxides is considerably smaller than that for the corresponding highest, stable oxide. If reaction kinetics were to favor formation of the suboxide over the highest oxide, then none of the nitrides in Table 16 would be thermodynamically stable as fuel electrodes. Even though P_{O_2} calculations indicate a number of the transition-metal nitrides would be unstable with respect to oxide formation in a fuel-gas environment, unfavorable reaction kinetics for the oxidation could permit most, if not all, of the nitrides to be used indefinitely (in this respect) under anode conditions. In other words, equilibrium may never be achieved in practical-time terms for the reactions of Table 16. To determine if kinetic factors are limiting would require actual experimental

TABLE 16.--Oxidation of transition-metal nitrides at 1300K

Reaction	$-\Delta G^\circ$ for Reaction, kcal/g-at N	References
$\text{TiN} + \text{O}_2 \rightarrow \text{TiO}_2(\text{rutile}) + 0.5\text{N}_2$	118.2	61
$\text{TiN} + 0.5\text{O}_2 \rightarrow \text{TiO} + 0.5\text{N}_2$	48.7	61
$\text{ZrN} + \text{O}_2 \rightarrow \text{ZrO}_2 + 0.5\text{N}_2$	145.4	61
$\text{HfN} + \text{O}_2 \rightarrow \text{HfO}_2 + 0.5\text{N}_2$	148 (est.)	62
$\text{VN} + 1.25\text{O}_2 \rightarrow 0.5\text{V}_2\text{O}_5(\ell) + 0.5\text{N}_2$	97.3	63
$\text{VN} + 0.5\text{O}_2 \rightarrow \text{VO} + 0.5\text{N}_2$	50.9	63
$\text{NbN} + 1.25\text{O}_2 \rightarrow 0.5\text{Nb}_2\text{O}_5 + 0.5\text{N}_2$	129.8	63,77
$\text{NbN} + 0.5\text{O}_2 \rightarrow \text{NbO} + 0.5\text{N}_2$	42.1	63,77
$\text{TaN} + 1.25\text{O}_2 \rightarrow 0.5\text{Ta}_2\text{O}_5 + 0.5\text{N}_2$	142.3	63,77
$\text{TaN} + 0.5\text{O}_2 \rightarrow \text{TaON}$	55.9 ⁺	77,79
$\text{CrN} + 0.75\text{O}_2 \rightarrow 0.5\text{Cr}_2\text{O}_3 + 0.5\text{N}_2$	90.5	63
$2.15\text{VN}_{0.465} + 2.69\text{O}_2 \rightarrow 1.08\text{V}_2\text{O}_5(\ell) + 0.5\text{N}_2$	228.1	63
$2.15\text{VN}_{0.465} + 1.08\text{O}_2 \rightarrow 2.15\text{VO} + 0.5\text{N}_2$	127.3	63
$\text{Nb}_2\text{N} + 2.5\text{O}_2 \rightarrow \text{Nb}_2\text{O}_5 + 0.5\text{N}_2$	286.9	63,77
$\text{Nb}_2\text{N} + \text{O}_2 \rightarrow 2\text{NbO} + 0.5\text{N}_2$	111.5	63
$\text{Ta}_2\text{N} + 2.5\text{O}_2 \rightarrow \text{Ta}_2\text{O}_5 + 0.5\text{N}_2$	336	63,78
$\text{Ta}_2\text{N} + 3.5\text{O}_2 \rightarrow \text{TaON} + 0.5\text{Ta}_2\text{O}_5$	255 ⁺	78,79
$\text{Cr}_2\text{N} + 1.5\text{O}_2 \rightarrow \text{Cr}_2\text{O}_3 + 0.5\text{N}_2$	182.2	63
$\text{Mo}_2\text{N} + 3\text{O}_2 \rightarrow 2\text{MoO}_3 + 0.5\text{N}_2$	263.6 [*]	61,62
$\text{Mo}_2\text{N} + 2\text{O}_2 \rightarrow 2\text{MoO}_2 + 0.5\text{N}_2$	207.5 [*]	61,62

⁺Value for 1100K.^{*}Value for 800K.

TABLE 17.--Calculated P_{O_2} for the oxidation of transition metal nitrides at 1300K for equilibrium nitride $P_{N_2}^*$

Nitride/Oxide	K_p for Oxidation	P_{O_2} at Equilibrium $P_{N_2}, \text{ atm}^+$
TiN/TiO ₂ (rutile)	$P_{N_2}^{0.5}/P_{O_2} = 7.51 \times 10^{19}$	3.07×10^{-29}
TiN/TiO	$P_{N_2}^{0.5}/P_{O_2}^{0.5} = 1.57 \times 10^8$	2.14×10^{-34}
ZrN/ZrO ₂	$P_{N_2}^{0.5}/P_{O_2}^{0.5} = 2.79 \times 10^{24}$	6.23×10^{-35}
HfN/HfO ₂	$\quad \quad \quad = 7.64 \times 10^{24}$	1.85×10^{-35}
VN/V ₂ O ₅ (ℓ)	$P_{N_2}^{0.5}/P_{O_2}^{1.25} = 2.28 \times 10^{16}$	4.88×10^{-16}
VN/VO	$P_{N_2}^{0.5}/P_{O_2}^{0.5} = 3.67 \times 10^8$	4.71×10^{-23}
NbN/Nb ₂ O ₅	$P_{N_2}^{0.5}/P_{O_2}^{1.25} = 6.66 \times 10^{21}$	7.46×10^{-22}
NbN/NbO	$P_{N_2}^{0.5}/P_{O_2}^{0.5} = 1.21 \times 10^7$	4.62×10^{-24}
TaN/Ta ₂ O ₅	$P_{N_2}^{0.5}/P_{O_2}^{1.25} = 8.41 \times 10^{23}$	8.84×10^{-27}
TaN/TaON	$P_{O_2}^{-0.5} = 1.28 \times 10^{11x}$	6.10×10^{-23x}
CrN/Cr ₂ O ₃	$P_{N_2}^{0.5}/P_{O_2}^{0.75} = 1.64 \times 10^{15}$	3.01×10^{-21}
VN _{0.465} /V ₂ O ₅ (ℓ)	$P_{N_2}^{0.5}/P_{O_2}^{2.69} = 2.24 \times 10^{38}$	2.62×10^{-17}
VN _{0.465} /VO	$P_{N_2}^{0.5}/P_{O_2}^{1.08} = 2.53 \times 10^{21}$	2.44×10^{-26}

TABLE 17.--Calculated P_{O_2} for the oxidation of transition-metal nitrides at 1300K for equilibrium nitride $P_{N_2}^*$
(Cont.)

Nitride/Oxide	K_p for Oxidation	P_{O_2} at Equilibrium $P_{N_2}^+$, atm [†]
Nb_2N/Nb_2O_5	$P_{N_2}^{0.5}/P_{O_2}^{2.5} = 1.72 \times 10^{48}$	3.01×10^{-22}
Nb_2N/NbO	$P_{N_2}^{0.5}/P_{O_2} = 5.64 \times 10^{18}$	4.78×10^{-25}
Ta_2N/Ta_2O_5	$P_{N_2}^{0.5}/P_{O_2}^{2.5} = 3.10 \times 10^{56}$	1.54×10^{-24}
$Ta_2N/(TaON + Ta_2O_5)$	$P_{O_2}^{-3.5} = 4.96 \times 10^{50^x}$	$3.28 \times 10^{-15^x}$
Cr_2N/Cr_2O_3	$P_{N_2}^{0.5}/P_{O_2}^{1.5} = 4.30 \times 10^{30}$	5.40×10^{-22}
Mo_2N/MoO_3	$P_{N_2}^{0.5}/P_{O_2}^3 = 1.04 \times 10^{72^\dagger}$	$3.87 \times 10^{-25^\dagger}$
Mo_2N/MoO_2	$P_{N_2}^{0.5}/P_{O_2}^2 = 5.00 \times 10^{56^\dagger}$	$1.12 \times 10^{-29^\dagger}$

* Refer to Table 15.

[†] P_{N_2} = equilibrium pressure of N_2 over nitride phase, or over nitride-subnitride mixture (for V, Nb, Ta, Cr, and Mo).

[†] Value for 800K.

^x Value for 1100K.

testing. Until then, nitrides should still be considered potentially usable as node material.

The data in Table 17 calculated for formation of suboxides (e.g., TiO) should be considered as only approximations, as oxynitride formation would almost certainly occur in actual practice, which could change the equilibrium P_{O_2} considerably. The effect of oxynitride formation upon P_{O_2} is evident in the oxidation of Ta_2N . At 1100K, P_{O_2} for formation of $\text{TaON} + 0.5 \text{Ta}_2\text{O}_5$ is 3.28×10^{-15} (Table 17); formation of only Ta_2O_5 results in a calculated P_{O_2} of 1.96×10^{-30} atm (at the equilibrium dissociation pressure for Ta_2N of 5.34×10^{-11} atm).

The greater thermal stability of TiN , ZrN , and HfN makes them the preferred choice of the transition-metal nitrides for consideration as possible anode material for the solid-electrolyte fuel cell. However, of these, only TiN has a coefficient of thermal expansion suitable for use with the solid electrolyte. Even though VN , NbN , and Cr_2N also have compatible thermal expansion properties, they lack the thermal stability of TiN .

Maintaining long-term stability of a nitride-based fuel electrode is important from an electrical standpoint, as the resistivity can vary substantially with nitrogen content for some materials, as shown in Figure 2 for the Ti-N and Zr-N systems.⁷⁵ (Note that the mononitrides are better conductors than the parent metals.) The compositional effect upon electrical resistivity is pronounced for both systems. Loss of one-fourth of the nitrogen

Figure 2.--Electrical Resistivity of Zr-N and Ti-N Systems at 25°C

from TiN, for example, causes a doubling of the resistivity. (TiN has a very large homogeneity range--from $\text{TiN}_{0.46}$ to $\text{TiN}_{1.16}$).⁷⁴ The data in Figure 2 thus refer to single-phase material. Titanium (as well as the other Group IVA elements) does not form lower nitrides; the only confirmed, stable phases are the mononitride (TiN) and the Ti-N (interstitial) solid solution.⁷⁴

The confirmation of the long-term stability under fuel cell operating conditions of any nitride material considered for anode use (e.g., TiN) is an item of prime concern in evaluating overall stability. The potential for compositional changes with time is inherently greater for nitrides than for the corresponding carbides because of the increased tendency for dissociation at elevated temperatures. If the equilibrium P_{N_2} is low enough at 1000°C, however, it should be possible to maintain the nitrogen pressure above this value in the fuel atmosphere and thus prevent loss of nitrogen from a nitride-based anode. Excessive dilution of the fuel mixture with nitrogen, however, would adversely effect fuel cell efficiency.

A nitride-based anode for the solid-electrolyte fuel cell could be fabricated in the form of a Ni-nitride cermet or thin nitride films, much in the same manner described earlier for a hypothetical carbide-based electrode. It would be necessary, however, to maintain a sufficiently high partial pressure of nitrogen above the nitride material to prevent dissociation during sintering and reduction. As an alternative, chemical vapor deposition of a TiN-electrode film from TiCl_4 and $\text{H}_2\text{-N}_2$ or -NH_3 gases

could be considered (facilitated by the fact that the TiCl_4 is a liquid at room temperature).

Composites of transition-metal nitrides with metals, such as nickel, are potential candidates for anodes in high-temperature fuel cells. By appropriate manipulation of composition and choice of materials, the desired thermal expansion and electrical properties can most probably be achieved. Consideration should be given to the possible formation of intermetallic compounds or solid solutions which could cause decomposition of the nitride phase over an extended period of time. This decomposition, in turn, could result in performance degradation of fuel cells using such anodes.

Like the transition-metal carbides, the nitrides, in many instances, form a continuous series of solid solution with each other (e.g., ZrN-TiN) and with other interstitials (e.g., carbon and oxygen, during carbonitride and oxynitride formation, respectively). This capability can be used to advantage for appropriate modification of the electrical and thermal expansion properties of a system to meet material requirements necessary for possible utilization in the high-temperature fuel cells.

While the thermal expansion properties of TiN (Table 14) match closely those for the ZrO_2 electrolyte, an increase in the electrical conductivity would be desirable. Addition of oxygen (as TiO) has an appreciable effect upon the electrical resistivity of TiN ,⁷⁵ as seen in Figure 3. The resistivity drops to a minimum of $11.3 \mu\Omega\text{-cm}$ at about 30 m/o TiO in TiN . Similar studies with other

Figure 3.--Electrical Resistivity of TiN-TiO solid solutions at 25°C

interstitials or transition metals could lead to further improvements in the electrical properties. All the resistivity data reported here are for room temperature; there is a need for similar data at elevated temperature for a more valid comparison with nickel for anode use (Appendix B lists other physical properties references for transition-metal nitrides).

Nitrides or nitride-based materials may be suited for use as anodes in the molten-carbonate fuel cell if significant amounts of hydroxide are not present. Thermodynamic calculations indicate that the nitrides should be compatible with molten carbonates. However, the presence of hydroxide could lead to extensive nitride corrosion, since TiN and ZrN, for example, are reportedly decomposed by molten alkali, with the evolution of NH_3 .⁷⁴

The formation of hydroxide occurs in the presence of water according to the reaction

where M is a metallic cation. The equilibrium constant for this reaction is

$$(9) \quad K_h = \frac{a_{\text{MOH}}^2 \cdot P_{\text{CO}_2}}{a_{\text{M}_2\text{CO}_3} \cdot P_{\text{H}_2\text{O}}}$$

For the ternary eutectic 43.5 m/o Li_2CO_3 -31.5 m/o Na_2CO_3 -25.0 m/o K_2CO_3 , K_h is approximately 4.06×10^{-4} at 1000K.⁶⁹ The activity (concentration, for practical purposes) of the hydroxide in the carbonate solution thus will be influenced by the $P_{\text{CO}_2}/P_{\text{H}_2\text{O}}$ ratio in the gas atmosphere over the melt. Because of the high P_{CO_2} normally present, however, the hydroxide composition is not expected to exceed several mole percent.

Another process which produces a molten-carbonate impurity reactive to nitrides is the decomposition of carbonate by the reaction

The equilibrium constant, K_d , for the decomposition reaction is much smaller than for the hydrolysis reaction. A K_d of 1.66×10^{-7} has been reported for the above ternary-carbonate eutectic at 1000K.⁶⁹ However, a clear understanding of the various reactions which can take place during operation of the molten-carbonate fuel cell, and the disposition of the various moieties which can form, is still lacking. Relevant oxide-carbonate phase diagrams, for example, are available only for Li_2CO_3 and $Na_2O-Na_2CO_3$.⁶⁴ Workers at Montana State University, however, currently are involved in evaluation and computation of phase diagrams pertinent to the molten-carbonate fuel cell, using a sophisticated computer program.⁸⁰

Since the operating temperature of the molten-carbonate fuel cell is significantly lower than that of the solid-electrolyte fuel cell, there will be a substantial reduction in the equilibrium dissociation pressure of nitrogen (P_{N_2}) over the nitrides. The ΔG° for the oxidation reaction will be affected similarly, which in turn will change the K_p and the P_{O_2} for oxidation. The effect of temperature upon these parameters was examined at 900 K for the oxidation of VN and $VN_{0.465}$ to V_2O_5 (l). These nitrides were chosen as they would be expected to be thermodynamically stable

with respect to V_2O_5 in the fuel-gas environment.

For the $VN-V_2O_5$ reaction, the P_{O_2} of 4.88×10^{-16} atm calculated at 1300K was reduced to 1.69×10^{-25} atm at 900K. Similarly, the P_{O_2} for the $VN_{0.465}-V_2O_5$ reaction decreased from 2.62×10^{-17} atm at 1300K to only 8.78×10^{-28} atm at the lower temperature. Thus, by lowering the temperature 400K, the vanadium nitrides are no longer thermodynamically stable in the anode environment. Similar large changes in P_{O_2} occur for the other nitrides under comparable conditions.

By strictly thermodynamic considerations, then, the nitrides would not appear, at first glance, to be as suited for use in the lower-temperature, molten-carbonate fuel cell as in the solid-electrolyte fuel cell. At the lower temperature, on the other hand, the oxidation kinetics may be less favorable, so that increased resistance to oxidation could result. This resistance will be offset, however, by an accelerating effect caused by the fluxing action of the carbonate melt. Dissolution of oxidation products in the molten carbonate as rapidly as they form will act to drive the reaction to completion. It is exceedingly difficult--impossible at times--to predict a priori which factors will be controlling. There is a definite need for experimental data in this area to resolve these questions.

3. Silicides

A third category of non-oxide ceramics which has been studied for use as MHD electrodes is the silicide. A larger number of

elements form stable silicides than carbides or nitrides. For a given element, silicon also forms a larger number of compounds than do carbon or nitrogen. In addition to the transition metals, the alkali, alkaline-earth, and rare-earth metals all form stable silicides. Aluminum does not form a silicide, although it is miscible with silicon in the liquid state.

The silicides are more closely related to the intermetallic than the typical interstitial compounds and possess many of the properties associated with metals, such as metallic luster and high electrical and thermal conductivity. Many of the silicides are metallic conductors, i.e., they have a positive temperature coefficient of resistivity. The higher silicides, however, show semiconducting behavior in many cases, much as silicon itself. The silicides also exhibit an absence of homogeneity ranges, except for VSi_2 , in marked contrast to the corresponding carbides and nitrides.⁵⁹

For high-temperature applications (up to 1500°C), the silicides of primary interest are those of Group IVA to VIA transition metals, the actinide metals, the rare-earth metals, the platinum metals, and rhenium. Since the precious-metal silicides are prohibitively expensive and the actinide silicides are radioactive, they will not be considered further in this report. While the rare-earth silicides are not as reactive to water vapor as the corresponding carbides and nitrides, they are still insufficiently inert to be considered practical for fuel cell use. As a result,

this section will concentrate on the stable silicides of the Group IVA to VIA transition metals.

The key physical properties of select transition-metal silicides are presented in Table 18. Compared to the carbides and nitrides, a larger number of the silicides have thermal expansion properties which are compatible with the Y_2O_3 -stabilized ZrO_2 for possible fuel cell use. Unfortunately, the resistivity and thermal-expansion data are either not available for many of the silicides of Table 18 or have been published in a number of foreign (mostly Russian) journals to which the author did not have ready access (these references are listed in Appendix C). Still, sufficient data are available to make reasonable value judgments regarding the possibility of utilizing such materials in high-temperature fuel cells.

The data in Table 18 show that the disilicides $TiSi_2$, $NbSi_2$, and $TaSi_2$ have the lowest resistivities as well as the most suitable thermal-expansion properties for possible use in the solid-electrolyte fuel cell. At room temperature, the reported electrical resistivity of $NbSi_2$ is actually lower than that of nickel. The temperature coefficient is probably less than that of nickel for $NbSi_2$ as well as a number of the other higher silicides, as a result of their semi-conducting nature ($TiSi_2$, however, is reported to be a metallic conductor⁸²). If this is so, the electrical conductivity of $NbSi_2$ at $1000^\circ C$ would be superior to that of nickel. The coefficient of thermal expansion for $NbSi_2$, however, exhibits a larger change over the temperature range of 20°

TABLE 18.--Select physical properties of transition-metal silicides

Silicide	Melting Point, °C	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity at 20°C, $\mu\Omega\text{-cm}$	References
Ti ₅ Si ₃	2120	11.0 (70°-1070°C)	350	57,81
TiSi	1760(p) [†]	10.4 (370°-1070°C)	36.4-39.3	81,82 *
TiSi ₂	1540	10.4 (20°-1070°C)	11.6-16.7	81,82
Zr ₂ Si	2220(dec.)	-	-	81
Zr ₅ Si ₃	2250	-	-	81
ZrSi	2150(dec.)	-	49.4	81
ZrSi ₂	1680(dec.)	-	106-161	81
Hf ₅ Si ₃	2300	-	-	57
HfSi	2100	-	-	57
HfSi ₂	1700	-	-	57
V ₃ Si	1730(p)	7.92-14.0 (20°-1070°C) *	-	57,81
V ₅ Si ₃	2150	9.54-11.2 (20°-1070°C) *	-	57,81
VSi ₂	1670	11.2-14.8 (20°-1070°C) *	9.5-13.3	57,81
Nb ₄ Si	1950(p)	-	-	81
Nb ₅ Si ₃	2480	-	-	81
NbSi ₂	1930	8.5-11.7 (20°-1070°C)	6.3	57,81
Ta _{4.5} Si	2510	-	-	81
Ta ₂ Si	2460	-	-	81
Ta ₅ Si ₃	2500	-	-	81
TaSi ₂	2200	9.54-10.8 (20°-1070°C) *	8.5-38	57,81

Table 18.--Select physical properties of transition-metal silicides
(Cont.)

Silicide	Melting Point, °C	Coefficient of Thermal Expansion (α),	Electrical Resistivity at 20°C, $\mu\Omega\text{-cm}$	References
Cr_3Si	1710	10.5 (20°-1070°C)	45.5	57,81
Cr_5Si_3	1560(dec.)	5.9-14.2 (20°-1000°C)*	114	57,81,83
CrSi	1545	11.3 (20°-770°C)	143	57,81
CrSi_2	1550	-	>250-1420	81,83
Mo_3Si	2050(dec.)	7.11 (20°-1130°C)	-	57,81
Mo_5Si_3	2100	4.3 -7.4 (20°-1070°C)*	-	57,81
MoSi_2	2030	8.10 (20°-1000°C)	21.8	57,81
W_5Si	2320	-	38.2	81
WSi_2	2165	8.28 (20°-1000°C)	33.4	57,81
Co_3Si	1210	-	-	81
Co_2Si	1332	-	-	81
CoSi	1460	12.0 (25°-1000°C)	150	81,84
CoSi_2	1326	-	64.8	81
Ni_3Si	1165(p)	-	-	81
Ni_5Si_2	1282	-	-	81
Ni_2Si	1318	-	-	81
Ni_3Si_2	845(p)	-	-	81
NiSi	992	-	-	81
NiSi_2	993(p)	-	-	81

TABLE 18.--Select physical properties of transition-metal silicides
(Cont.)

Silicide	Melting Point, °C	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity at 20°C , $\mu\Omega\text{-cm}$	References
Fe_3Si	-	-	55	81
Fe_5Si_3	-	-	170	81
FeSi	1415	-	240	81
FeSi_{2+x}	1220	-	350	81
Mn_3Si	-	-	-	81
Mn_5Si_3	-	-	-	81
MnSi	1280	-	-	81
MnSi_2	-	-	-	81

† Peritectic =(p).

* Range given for α , due to change in slope of $\Delta l/l_0$ -T plot over indicated temperature range.

to 1070°C than do TiSi_2 and TaSi_2 .

The stoichiometry of the silicide has a profound effect upon its electrical properties. The electrical resistivity data of Table 18 are plotted in Figure 4 as a function of the atomic ratio of silicon to metal. The FeSi_x , CrSi_x , and ZrSi_x systems show a rapid increase in resistivity with increase in x . CoSi_x , on the other hand, exhibits a maximum in resistivity near $x = 1$. Due to the lack of data points, it is not clear whether WSi_x shows a lack of compositional dependence in resistivity or exhibits a maximum between $x = 0.2$ and 2.

The behavior of the TiSi_x system, however, differs drastically from the other silicides in that the resistivity rapidly decreases after a very sharp maximum near $x = 0.5$ (this same behavior is evident for the nitrides of titanium, as well, as indicated in Figure 2). From $x = 1$ to 2, the resistivity of TiSi_x is lower than that of pure titanium. In addition to TiSi_2 , the disilicides of the vanadium family also have electrical resistivities of the parent metals.

Of the three types of interstitial compounds considered thus far, the silicides have the best resistance to high-temperature oxidation and increased resistance at higher silicon contents. The formation of a nonporous, adherent oxide film protects the silicide from further oxidation. Use of silicides at elevated temperatures under reducing conditions, however, can lead to destruction of the protective SiO_2 film. For MoSi_2 , for example,

Figure 4.--Electrical Resistivities of Transition-Metal Silicides at 25°C as a Function of Composition

this occurs readily above 1350°C in hydrogen:⁸⁵

MoSi₂ is perhaps the most well-known silicide employed for high-temperature applications. It has received extensive use as electrical heating elements at temperatures up to 1700°C in air. The generally recommended operating range, however, is between 1000° and 1700°C, as in this temperature interval the oxide film is dense and adherent. At temperatures between 300° and 800°C, for example, the SiO₂ which forms is porous and spalls from the element, allowing further oxidation.⁸⁵

Besides silicides of molybdenum, those of tungsten and titanium also exhibit good resistance to oxidation at high temperatures. In the case of the Ti-Si system, the protective layer is thought to be a silicate phase, rather than SiO₂.⁵⁷ The rest of the silicides in Table 18 generally form porous, nonadherent coatings which are not protective against oxidation.

The formation of a silicate or SiO₂ film under oxidizing conditions precludes the use of transition metal silicides for interconnector materials for the solid-electrolyte fuel cell, even though the thermal and electrical properties may be acceptable. The chemical-compatibility and interfacial problems discussed earlier for similar films for the carbides apply to the silicides as well. Thus, the possible use of silicides for high-temperature fuel cells should be restricted to the fuel electrode.

It would be desirable to know the P_{O_2} for the oxidation of the transition-metal silicides at 1300K in order to ascertain the

thermodynamic stability under anode conditions, as was done with the carbides and nitrides. This can be determined readily for the general reaction

once the ΔG_{Rxn}^0 is known at the desired temperature. The P_{O_2} can then be calculated from the relationship

$$(13) \quad P_{O_2} = (K_p) \exp[-2/(xz+2)] = \exp \left[\frac{\Delta G_{(12)}^0}{RT} \right] \cdot \left[\frac{2}{xz+2} \right]$$

Unfortunately, limited thermodynamic data are available in the literature for many of the silicides, especially at elevated temperatures. The bulk of the published data pertains to enthalpies of formation (ΔH_f^0) at 298 K and heat capacities; little information was readily evident for the free energies of formation for many of the silicides as a function of temperature.

Values of ΔH_f^0 at 1300 K were calculated for silicides from ΔH_f^0 at 298 K and heat capacities according to

$$(14) \quad \Delta H_{f,1300}^0(M_xSi) = \Delta H_{f,298}^0(M_xSi) + \int_{298}^{1300} \Delta C_p(M_xSi) dT$$

where ΔC_p is the difference in heat capacities of the silicide and the component elements, i.e.,

$$(15) \quad \Delta C_p(M_xSi) = C_p(M_xSi) - xC_p(M) - C_p(Si)$$

Where heat capacities were not available for the silicides, additivity of the heat capacities of the metal and silicon was assumed⁸⁶

$$(16) \quad C_p(M_xSi) = xC_p(M) + C_p(Si)$$

Combining equations 15 and 16 results in a ΔC_p of essentially zero under these conditions. Or, in other words, ΔH_f^0 is not temperature dependent. This was found to be the case for a number of

the silicides. Values of ΔH_f^0 at 298 and 1300K (calculated using reported C_p data), for example, differed by less than one percent for Nb_5Si_3 and W_5Si_3 .^{81,87,88}

Values of ΔS_f^0 were obtained from reported C_p data for the silicides as a function of temperature from the relationship

$$(17) \Delta S_{f,1300}^0(M_xSi) = \Delta S_{f,298}^0(M_xSi) + \int_{298}^{1300} \frac{\Delta C_p(M_xSi)dT}{T}$$

To calculate $\Delta S_{f,298}^0$ the value of $S_{298}^0(M_xSi)$ must first be known

$$(18) \Delta S_{f,298}^0(M_xSi) = S_{298}^0(M_xSi) - xS_{298}^0(M) - S_{298}^0(Si)$$

This is usually obtained by heat-capacity measurements down to absolute zero

$$(19) S_{f,298}^0(M_xSi) = S_0^0(M_xSi) + \int_0^{298} C_p(M_xSi)dT \approx \int_0^{298} C_p(M_xSi)dT$$

Generally, S_{298}^0 for the silicide was not reported, so that assumption of additivity of entropies was necessary. This results in a value for ΔS_{298}^0 of zero for the silicide, using equation 18. The error introduced into subsequent calculations as a result of this assumption is quite acceptable for the purposes of this report, as available data generally indicate low values of $\Delta S_{f,298}^0$ for silicides. Silicides of chromium, for example, have reported ΔS_f^0 values ranging from -0.9 to 0.3 gibbs/g-at Si at 298K.⁸⁹

The free energy of formation, ΔG_f^0 , was then calculated for the silicide at 1300K from

$$(20) \Delta G_{f,1300}^0(M_xSi) = \Delta H_{f,1300}^0(M_xSi) - T \Delta S_{f,1300}^0(M_xSi)$$

Where heat-capacity data as a function of temperature or entropy data were missing for silicides, $\Delta S_{f,1300}^0$ was set equal to zero,

so that the following resulted

$$(21) \quad \Delta H_{f,298}^0 = \Delta H_{f,1300}^0 \approx \Delta G_{f,1300}^0 \text{ (for } M_x\text{Si)}$$

The estimated thermodynamic data for a number of the silicides at 1300K (or experimental values, where obtainable) are presented in Table 19. The values of ΔG_f^0 for the silicides were used with other thermodynamic data to calculate the free energies of oxidation listed in Table 20. The corresponding K_p and equilibrium P_{O_2} values for these reactions are presented in Table 21 for formulation of the highest, stable oxide and, where applicable, the most stable suboxide. The data indicate that none of the silicides would be thermodynamically stable relative to both the highest oxide and suboxide at a fuel-gas P_{O_2} of 10^{-16} atm. At a P_{O_2} of 10^{-18} atm, only Ni_2Si and Ni_3Si would be stable against oxide formation.

At the average operating temperature of the molten-carbonate fuel cell of 900K cursory calculations indicate that none of the silicides would be thermodynamically stable with respect to oxidation. This large P_{O_2} dependency as a function of temperature was noted earlier for the nitrides and carbides.

In a number of cases, the calculated P_{O_2} data are derived from extrapolated or estimated values for ΔG_f^0 for the silicides. The true equilibrium P_{O_2} could be higher than calculated, therefore, with a resultant greater chance for silicide compatibility with the fuel gas. The formation of compound oxides or silicates in-

TABLE 19.--Thermodynamic data for transition-metal silicides

Silicide	$-\Delta H_f^\circ$, 298, kcal/g-at Si	$-\Delta H_f^\circ$, 1300, kcal/g-at Si	ΔS_f° , 1300 gibbs/g-at Si*	$-\Delta G_f^\circ$, 1300, kcal/g-at Si	References
Ti ₅ Si ₃	46.2	(46.2) [†]	(~0)	(46.2)	81
TiSi	31.0	(31.0)	(~0)	(31.0)	81
TiSi ₂	16.1	13.8	1.96	16.8	81,90
Zr ₂ Si	26.6	(26.6)	(~0)	(26.6)	91
Zr ₅ Si ₃	26.6	(26.6)	(~0)	(26.6)	91
ZrSi _{1.17}	29.4	(29.4)	(~0)	(29.4)	91
ZrSi ₂	15.0	(15.0)	(~0)	(15.0)	91
V ₂ Si	36.9	(36.9)	(~0)	(36.9)	81
NbSi _{0.55}	21	(21)	(~0)	(21)	81
Nb ₅ Si ₃	21	21.1	0.42	21.4	81,87
NbSi ₂	15	15.1	1.64	17.2	81,92
TaSi _{0.22}	32.2	-	-	37.3	81,93
Ta ₂ Si	30.7	-	-	27.2	81,93
Ta ₅ Si ₃	28.8	-	-	24.0	81,93
TaSi ₂	13.1	-	-	8.1	81,92,93
Cr ₃ Si	8.22	(8.22)	(-0.90) ^x	(7.95)	81
Cr ₅ Si ₃	8.23	(8.23)	(-0.27) ^x	(8.15)	81
CrSi	7.12	7.15 ⁺	0.28 ⁺	7.44 ⁺	81,89,94
CrSi ₂	6.36	6.20 ⁺	0.39 ⁺	6.60 ⁺	81,89,94

TABLE 19.--Thermodynamic data for transition-metal silicides (Cont.)

Silicide	$-\Delta H_f^\circ, 298,$ kcal/g-at Si	$-\Delta H_f^\circ, 1300,$ kcal/g-at Si	$\Delta S_f^\circ, 1300,$ gibbs/g-at Si*	$-\Delta G_f^\circ, 1300,$ kcal/g-at Si	References
Mo ₃ Si	21	(21)	(~0)	(21)	59
Mo ₅ Si ₃	22	(22)	(~0)	(22)	59
MoSi ₂	13.6	(13.6)	(~0)	(13.6)	59
W ₅ Si ₃	15.0	14.8	2.16	16.7	81,88,95
WSi ₂	11.2	11.4	0.37	11.9	81,88,95
Mn ₅ Si ₃	30	(30)	(~0)	(30)	59
Fe ₃ Si	9.2	(9.2)	(~0)	(9.2)	59
Fe ₅ Si ₃	4.6	(4.5)	(~0)	(4.5)	59
FeSi	9.6	(9.6)	(~0)	(9.5)	59
FeSi ₂	5.6	(5.6)	(~0)	(5.6)	59
Co ₂ Si	9.2	(9.2)	(~0)	(9.2)	59
CoSi	12.0	(12.0)	(~0)	(12.0)	59
CoSi ₂	8.2	(8.2)	(~0)	(8.2)	59
Ni ₃ Si	5.3	(5.3)	(~0)	(5.3)	59
Ni ₂ Si	10.5	(10.5)	(~0)	(10.5)	59
Ni ₃ Si ₂	10.7	(10.7)	(~0)	(10.7)	59
NiSi	10.3	(10.3)	(~0)	(10.3)	59

* $\Delta S_f^\circ, 298 \sim 0$ gibbs/g-at Si, unless noted otherwise.

†Estimated values are in parentheses.

xValues are for 298 K.

+Values are for 1023 K.

TABLE 20.--Oxidation of transition-metal silicides at 1300K

Reaction	$-\Delta G^\circ$ for Reaction, kcal/g-at Si*
$0.33\text{Ti}_5\text{Si}_3 + 2.67\text{O}_2 \rightarrow 1.67\text{TiO}_2(\text{rutile}) + \text{SiO}_2(\text{q})^\dagger$	399.2
$0.33\text{Ti}_5\text{Si}_3 + 1.83\text{O}_2 \rightarrow 1.67\text{TiO} + \text{SiO}_2(\text{q})$	283.1
$\text{TiSi} + 2\text{O}_2 \rightarrow \text{TiO}_2(\text{rutile}) + \text{SiO}_2(\text{q})$	300.7
$\text{TiSi} + 1.5\text{O}_2 \rightarrow \text{TiO} + \text{SiO}_2(\text{q})$	231.2
$0.5 \text{TiSi}_2 + 1.5\text{O}_2 \rightarrow 0.5\text{TiO}_2(\text{rutile}) + \text{SiO}_2(\text{q})$	230.1
$0.5 \text{TiSi}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{TiO} + \text{SiO}_2(\text{q})$	195.4
$\text{Zr}_2\text{Si} + 3\text{O}_2 \rightarrow 2\text{ZrO}_2 + \text{SiO}_2(\text{q})$	542.5
$0.33\text{Zr}_5\text{Si}_3 + 2.67\text{O}_2 \rightarrow 1.67\text{ZrO}_2 + \text{SiO}_2(\text{q})$	475.3
$0.85\text{ZrSi}_{1.17} + 1.85\text{O}_2 \rightarrow 0.85\text{ZrO}_2 + \text{SiO}_2(\text{q})$	306.6
$0.5\text{ZrSi}_2 + 1.5\text{O}_2 \rightarrow 0.5\text{ZrO}_2 + \text{SiO}_2(\text{q})$	248.9
$\text{V}_2\text{Si} + 3.5\text{O}_2 \rightarrow \text{V}_2\text{O}_5(\text{l}) + \text{SiO}_2(\text{q})$	370.9
$\text{V}_2\text{Si} + 2\text{O}_2 \rightarrow 2\text{VO} + \text{SiO}_2(\text{q})$	278.2
$1.82\text{NbSi}_{0.55} + 3.28\text{O}_2 \rightarrow 0.91\text{Nb}_2\text{O}_5 + \text{SiO}_2(\text{q})$	432.3
$1.82\text{NbSi}_{0.55} + 1.91\text{O}_2 \rightarrow 1.82\text{NbO} + \text{SiO}_2(\text{q})$	272.7
$0.33\text{Nb}_5\text{Si}_3 + 3.08\text{O}_2 \rightarrow 0.83\text{Nb}_2\text{O}_5 + \text{SiO}_2(\text{q})$	406.3
$0.33\text{Nb}_5\text{Si}_3 + 1.83\text{O}_2 \rightarrow 1.67\text{NbO} + \text{SiO}_2(\text{q})$	261.5
$0.5 \text{NbSi}_2 + 1.52\text{O}_2 \rightarrow 0.25\text{Nb}_2\text{O}_5 + \text{SiO}_2(\text{q})$	224.9
$0.5 \text{NbSi}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{NbO} + \text{SiO}_2(\text{q})$	181.1

TABLE 20.--Continued

Reaction	<u>-ΔG° for Reaction, kcal/g-at Si*</u>
$4.54\text{TaSi}_{0.22} + 6.68\text{O}_2 \rightarrow 2.27\text{Ta}_2\text{O}_5 + \text{SiO}_2(\text{q})$	928.6
$\text{Ta}_2\text{Si} + 3.50\text{O}_2 \rightarrow \text{Ta}_2\text{O}_5 + \text{SiO}_2(\text{q})$	489.0
$0.33\text{Ta}_5\text{Si}_3 + 3.08\text{O}_2 \rightarrow 0.83\text{Ta}_2\text{O}_5 + \text{SiO}_2(\text{q})$	432.0
$0.5\text{TaSi}_2 + 1.62\text{O}_2 \rightarrow 0.25\text{Ta}_2\text{O}_5 + \text{SiO}_2(\text{q})$	331.0
$\text{Cr}_3\text{Si} + 3.25\text{O}_2 \rightarrow 1.5\text{Cr}_2\text{O}_3 + \text{SiO}_2(\text{q})$	438.8
$0.33\text{Cr}_5\text{Si}_3 + 2.25\text{O}_2 \rightarrow 0.83\text{Cr}_2\text{O}_3 + \text{SiO}_2(\text{q})$	312.1
$\text{CrSi} + 1.75\text{O}_2 \rightarrow 0.5\text{Cr}_2\text{O}_3 + \text{SiO}_2(\text{q})$	271.1 ⁺
$0.5\text{CrSi}_2 + 1.38\text{O}_2 \rightarrow 0.25\text{Cr}_2\text{O}_3 + \text{SiO}_2(\text{q})$	223.2 ⁺
$\text{Mo}_3\text{Si} + 5.50\text{O}_2 \rightarrow 3\text{MoO}_3 + \text{SiO}_2(\text{q})$	529.8
$\text{Mo}_3\text{Si} + 4\text{O}_2 \rightarrow 3\text{MoO}_2 + \text{SiO}_2(\text{q})$	459.0
$0.33\text{Mo}_5\text{Si}_3 + 3.50\text{O}_2 \rightarrow 1.67\text{MoO}_3 + \text{SiO}_2(\text{q})$	356.5
$0.33\text{Mo}_5\text{Si}_3 + 2.67\text{O}_2 \rightarrow 1.67\text{MoO}_2 + \text{SiO}_2(\text{q})$	317.1
$0.5\text{MoSi}_2 + 1.75\text{O}_2 \rightarrow 0.5\text{MoO}_3 + \text{SiO}_2(\text{q})$	339.7
$0.5\text{MoSi}_2 + 1.50\text{O}_2 \rightarrow 0.5\text{MoO}_2 + \text{SiO}_2(\text{q})$	201.5
$0.33\text{W}_5\text{Si}_3 + 3.50\text{O}_2 \rightarrow 1.67\text{WO}_3 + \text{SiO}_2(\text{q})$	350.4
$0.33\text{W}_5\text{Si}_3 + 2.67\text{O}_2 \rightarrow 1.67\text{WO}_2 + \text{SiO}_2(\text{q})$	287.5
$0.5\text{WSi}_2 + 1.75\text{O}_2 \rightarrow 0.5\text{WO}_3 + \text{SiO}_2(\text{q})$	211.6
$0.5\text{WSi}_2 + 1.50\text{O}_2 \rightarrow 0.5\text{WO}_2 + \text{SiO}_2(\text{q})$	192.8
$0.33\text{Mn}_5\text{Si}_3 + 2.11\text{O}_2 \rightarrow 0.56\text{Mn}_3\text{O}_4 + \text{SiO}_2(\text{q})$	255.5
$0.33\text{Mn}_5\text{Si}_3 + 1.83\text{C}_2 \rightarrow 1.67\text{MnO} + \text{SiO}_2(\text{q})$	247.5

TABLE 20.--Continued

Reaction	<u>-ΔG° for Reaction, kcal/g-at Si*</u>
$\text{Fe}_3\text{Si} + 3.25\text{O}_2 \rightarrow 1.5\text{Fe}_2\text{O}_3 + \text{SiO}_2(\text{q})$	327.8
$\text{Fe}_3\text{Si} + 2.58\text{O}_2 \rightarrow 3.16\text{Fe}_{0.95}\text{O} + \text{SiO}_2(\text{q})$	245.5
$0.33\text{Fe}_5\text{Si}_3 + 2.25\text{O}_2 \rightarrow 0.83\text{Fe}_2\text{O}_3 + \text{SiO}_2(\text{q})$	254.3
$0.33\text{Fe}_5\text{Si}_3 + 1.88\text{O}_2 \rightarrow 1.75\text{Fe}_{0.95}\text{O} + \text{SiO}_2(\text{q})$	236.4
$\text{FeSi} + 1.75\text{O}_2 \rightarrow 0.5\text{Fe}_2\text{O}_3 + \text{SiO}_2(\text{q})$	210.8
$\text{FeSi} + 1.53\text{O}_2 \rightarrow 1.05\text{Fe}_{0.95}\text{O} + \text{SiO}_2(\text{q})$	199.8
$0.5\text{FeSi}_2 + 1.38\text{O}_2 \rightarrow 0.25\text{Fe}_2\text{O}_3 + \text{SiO}_2(\text{q})$	185.7
$0.5\text{FeSi}_2 + 1.26\text{O}_2 \rightarrow 0.53\text{Fe}_{0.95}\text{O} + \text{SiO}_2(\text{q})$	180.2
$\text{Co}_2\text{Si} + 2\text{O}_2 \rightarrow 2\text{CoO} + \text{SiO}_2(\text{q})$	221.0
$\text{CoSi} + 1.5\text{O}_2 \rightarrow \text{CoO} + \text{SiO}_2(\text{q})$	184.2
$0.5\text{CoSi}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{CoO} + \text{SiO}_2(\text{q})$	170.9
$\text{Ni}_3\text{Si} + 2.5\text{O}_2 \rightarrow 3\text{NiO} + \text{SiO}_2(\text{q})$	245.5
$\text{Ni}_2\text{Si} + 2\text{O}_2 \rightarrow 2\text{NiO} + \text{SiO}_2(\text{q})$	210.7
$0.5\text{Ni}_2\text{Si}_3 + 1.75\text{O}_2 \rightarrow 1.5\text{NiO} + \text{SiC}_2(\text{q})$	195.7
$\text{NiSi} + 1.5\text{O}_2 \rightarrow \text{NiO} + \text{SiO}_2(\text{q})$	181.4

* ΔG_f° for silicides from Table 18; ΔG_f° for oxides from References 61-63.

† Quartz = (q).

‡ Values are for 1000K.

Table 21:--Calculated P_{O_2} for oxidation of transition-metal silicides at 1300K *

Silicide/Oxide	K_p for Oxidation†	Equilibrium P_{O_2} , atm
Ti_5Si_3/TiO_2 (rutile)	1.29×10^{67}	7.34×10^{-26}
Ti_5Si_3/TiO	4.01×10^{47}	9.71×10^{-27}
$TiSi/TiO_2$ (rutile)	3.62×10^{50}	5.26×10^{-26}
$TiSi/TiO$	7.57×10^{38}	1.20×10^{-26}
$TiSi_2/TiO_2$ (rutile)	4.88×10^{38}	1.61×10^{-26}
$TiSi_2/TiC$	7.05×10^{32}	5.27×10^{-27}
Zr_2Si/ZrO_2	1.62×10^{91}	3.95×10^{-31}
Zr_5Si/ZrO_2	8.30×10^{79}	1.17×10^{-30}
$ZrSi_{1.17}/ZrO_2$	3.58×10^{51}	1.36×10^{-28}
$ZrSi_2/ZrO_2$	6.91×10^{41}	1.28×10^{-28}
$V_2Si/V_2C_5(s)$	2.29×10^{42}	1.52×10^{-18}
V_2Si/VO	6.04×10^{46}	4.07×10^{-24}
$NbSi_{0.55}/Nb_2O_5$	4.86×10^{72}	6.91×10^{-23}
$NbSi_{0.55}/NbO$	7.18×10^{45}	9.81×10^{-25}
Nb_5Si_3/Nb_2O_5	2.06×10^{68}	6.61×10^{-23}
Nb_5Si_3/NbO	9.22×10^{43}	9.45×10^{-25}
$NbSi_2/Nb_2O_5$	6.52×10^{37}	4.55×10^{-24}
$NbSi_2/NbO$	2.77×10^{30}	4.42×10^{-25}

Table 21:--Continued

Silicide/Oxide	K_p for Oxidation [†]	Equilibrium P_{O_2} , atm
TaSi _{0.22} /Ta ₂ O ₅	1.23×10^{156}	4.25×10^{-24}
Ta ₂ Si/Ta ₂ O ₅	1.63×10^{82}	3.24×10^{-24}
Ta ₅ Si ₃ /Ta ₂ O ₅	4.27×10^{72}	2.62×10^{-24}
TaSi ₂ /Ta ₂ O ₅	4.56×10^{55}	5.60×10^{-35}
Cr ₃ Si ₂ /Cr ₂ O ₃	6.03×10^{73}	1.99×10^{-23}
Cr ₅ Si ₃ /Cr ₂ O ₃	2.98×10^{52}	4.76×10^{-24}
CrSi/Cr ₂ O ₃	$^{+}1.77 \times 10^{59}$	$^{+}1.40 \times 10^{-34}$
CrSi ₂ /Cr ₂ O ₃	$^{+}6.19 \times 10^{48}$	$^{+}3.27 \times 10^{-36}$
Mo ₃ Si/MoO ₃	1.21×10^{89}	6.36×10^{-17}
Mo ₃ Si/MoO ₂	1.48×10^{77}	5.10×10^{-20}
Mo ₅ Si ₃ /MoO ₃	8.67×10^{59}	7.50×10^{-18}
Mo ₅ Si ₃ /MoO ₂	2.03×10^{53}	1.08×10^{-20}
MoSi ₂ /MoO ₃	7.26×10^{35}	3.22×10^{-21}
MoSi ₂ /MoO ₂	7.52×10^{33}	2.61×10^{-23}
W ₅ Si ₃ /WC ₃	8.03×10^{58}	1.48×10^{-17}
W ₅ Si ₃ /WO ₂	2.19×10^{48}	7.86×10^{-19}
WSi ₂ /WO ₃	3.72×10^{35}	4.72×10^{-21}
WSi ₂ /WO ₂	2.56×10^{32}	2.48×10^{-22}
Mn ₅ Si ₃ /Mn ₃ O ₄	9.09×10^{42}	4.37×10^{-21}
Mn ₅ Si ₃ /MnO	4.10×10^{41}	1.82×10^{-23}

Table 21.--Continued

Silicide/Oxide	K_p for Oxidation [†]	Equilibrium P_{O_2} , atm
Fe_3Si/Fe_2O_3	1.31×10^{55}	1.10×10^{-17}
$Fe_3Si/Fe_{0.95}O$	3.77×10^{49}	5.98×10^{-20}
Fe_5Si_3/Fe_2O_3	5.69×10^{42}	9.95×10^{-20}
$Fe_5Si_3/Fe_{0.95}O$	5.48×10^{39}	6.74×10^{-22}
$FeSi/Fe_2O_3$	2.78×10^{35}	5.58×10^{-21}
$FeSi/Fe_{0.95}O$	3.95×10^{33}	9.63×10^{-23}
$FeSi_2/Fe_2O_3$	1.64×10^{31}	2.40×10^{-23}
$FeSi_2/Fe_{0.95}O$	1.96×10^{30}	1.04×10^{-24}
Co_2Si/CoO	1.45×10^{37}	2.63×10^{-19}
$CoSi/CoO$	9.19×10^{30}	2.28×10^{-21}
$CoSi_2/CoO$	5.48×10^{28}	1.02×10^{-23}
Ni_3Si/NiO	1.85×10^{41}	3.11×10^{-17}
Ni_2Si/NiO	2.67×10^{35}	1.99×10^{-18}
Ni_3Si_2/NiO	8.09×10^{32}	1.57×10^{-19}
$NiSi_2/NiO$	3.10×10^{30}	4.70×10^{-21}

* Refer to Table 19.

[†] $K_p = P_{O_2}^{-n}$, where n = number of moles O_2 reacting (Table 19).

+ Values are for 1000K.

stead of simple oxide mixtures will also affect the equilibrium P_{O_2} for oxidation. Oxidation of $ZrSi_{1.17}$ to form $ZrSiO_4 + 0.17SiO_2(q)$ for example, results in a calculated P_{O_2} of 5.65×10^{-29} atm at 1300K, compared to 1.36×10^{-28} atm for formation of the mixed oxides. The use of a number of transition-metal silicides as anodes may still be possible in the face of unfavorable P_{O_2} indications, if kinetic factors (e.g., negligible oxidation rates) are more important and overriding.

Of the silicides of Table 19, V_2Si , Mo_3Si , Mo_5Si_3 , W_5Si_3 , Ni_3Si , and Ni_2Si offer the greatest potential for use as anode material in high-temperature fuel cells, based on approximate thermodynamic stabilities against oxidation. Unfortunately, no single silicide possesses this stability as well as a high electrical conductivity and thermal-expansion properties compatible with requirements of the solid-electrolyte fuel cell. Thus, some compromise will be necessary to satisfy all fuel cell needs.

The silicides are the most attractive, in terms of their overall physical properties, of the interstitial (non-oxide ceramics) compounds discussed so far for use as anode materials in high-temperature fuel cells. The stoichiometry of the silicides can be readily altered to engineer changes in the electrical as well as the thermal-expansion properties. Doping with other transition metals or interstitials is also possible to effect the desired change in physical properties.

Preparation of a thin-film silicide anode by chemical vapor deposition can be accomplished readily if this technique is seri-

ously considered for fabrication purposes and if the resultant film has the proper chemical and physical properties for use in the solid-electrolyte fuel cell.

The incorporation of silicides into the anode structure also can be accomplished, as was described earlier with the carbides and nitrides, by replacing a portion of the ZrO_2 in the ZrO_2 -Ni cermet. The silicides, though, sinter more readily and should bond better with nickel than the carbides and nitrides. The one area of concern is the possibility of the formation of nickel silicides (or silicides of other metals used for cementing) over prolonged periods of time at temperatures of 700° to $1000^{\circ}C$. Thermodynamic estimates indicate that the reaction of silicides with nickel to form Ni_2Si , Ni_3Si_2 , and Ni_3Si , for example, should not be favorable at 1300 K, except for several silicides of iron and cobalt. There is a possibility that ternary-system (M-M'-Si) compounds or solid solutions will form, as indicated by published data for the various binary-silicide systems.⁵⁹

At very high temperatures, it has been reported that the disilicides $TiSi_2$, $ZrSi_2$, $ThSi_2$, $TaSi_2$, WSi_2 , and $MoSi_2$ are soluble in liquid nickel. The lower silicides Ti_5Si_3 and $ZrSi$, on the other hand, were not attacked.⁸¹ This suggests that the lower silicides would be better suited for preparing composite electrodes using transition-metal binders, such as nickel. Kinetic data on the extent of possible interactions at temperatures of 700° to $1000^{\circ}C$ would be invaluable for such materials for engineering and evaluation purposes.

The possible use of silicides as anode material in the molten-carbonate fuel cell may be limited, as was indicated earlier for the nitrides, by the presence of hydroxide in the melt. Silicides of the Group IVA to VIA elements are reportedly soluble in molten alkali hydroxides;⁸¹ this is a function of the atmosphere used and may occur only under oxidizing conditions. Chemical compatibility data are needed under reducing conditions for silicides in contact with molten-carbonate melts containing varying amounts of impurities (e.g., hydroxides, oxides, etc.) which can be considered as representative of melt conditions during operation of the molten-carbonate fuel cell.

In addition to the lack of chemical-compatibility data for the transition-metal silicides, there is little known about the electrical and thermal-expansion properties of binary and ternary silicon-based systems. Until additional experimental data for such parameters are available--especially at the higher temperatures (700° to 1000°C)--comprehensive evaluation of the use of silicides for potential anode use in high-temperature fuel cells is not possible.

4. Borides

The last category of the non-ceramic materials to be discussed in this report is the borides. Transition-metal borides of Groups IVA to VIA have received the most attention for consideration as MHD electrodes because of their high melting points (1900° to 3000°C), low volatility and high stability at elevated temperatures, high hardness, and good electrical conductivity. The only

other class of interstitial compound with similar properties is the transition-metal carbide. The borides have the widest range of compositions for compound formation-- M_3B to MB_{12} --of all the interstitial compounds because of the chains and network configurations assumed by the boron atoms in these compounds.⁵⁹ The borides of the alkaline-earth and rare-earth metals are not reactive to water as are their corresponding carbides, nitrides, and silicides; this is indicative of the high chemical stability of borides.

The key physical properties of a number of borides are listed in Table 22. As is readily evident, data for many of the borides are missing. Data of this type, however, may be contained in a number of references listed in Appendix D which were not readily accessible during the course of this study. Thus, some of the lower borides may have thermal expansion and electrical properties which are better suited to high-temperature fuel cell needs than is indicated in Table 22.

Compared to the silicides, the transition-metal borides generally have lower electrical resistivities (the silicides of the vanadium family being the exceptions) and lower coefficients of thermal expansion. The borides are metallic conductors, i.e., they have a positive temperature-coefficient of resistivity. The resistivity of TiB_2 at $1000^{\circ}C$, for example, is two to four times as great as at room temperature (Table 22).

The electrical resistivity data of Table 22 are plotted in Figure 5 as a function of composition. The TaB_x , VB_x , and CrB_x

TABLE 22.--Select physical properties of metal borides

Boride	Melting Point, °C	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity, $\mu\Omega\text{-cm}$	Temp., °C	Reference
Ti ₂ B	2,250 (dec.)	--	--	--	57,95
TiB	2,060 (dec.)	--	40	25	57,95
TiB ₂	2,871	7.3 - 9.1 (25°-2041°C) ^x	15-28	25	57,59,95-99
"	"	--	60	1000	59
"	"	9.7 (200°-1800°C)	78	1200	100
Ti ₂ B ₅	2,093 (dec.)	--	--	--	57
ZrB	1,250 (?) (dec.)	--	9-16	25	56,59
ZrB ₂	3,040	6.7 - 8.3 (25°-1800°C) ^x	9-39	25	57,59,95,96,98,99
"	"	"	87.6	1600	95
ZrB ₁₂	2,680	--	--	--	95
HfB	2,900 (p) [†]	--	8-14	25	56,57,59
HfB ₂	3,250	6.5 - 8.2 (25°-2041°C) [*]	10-17	25	56,59,98
V ₃ B ₂	2,070	--	--	--	57
VB	2,250	--	35-40	25	57,59,95
V ₃ B ₄	2,280	--	--	--	57
VB ₂	2,430	7.56 (25°-800°C)	16	25	57,95,98
Nb ₃ B ₂	1,815	--	--	--	57
NbB	2,260	--	64.5	25	57,95
Nb ₃ B ₄	2,195	--	--	--	57
NbB ₂	3,000	6.7 - 9.1 (25°-1700°C) [*]	28-66	--	57,95,96,98

TABLE 22.--Select physical properties of metal borides (Continued)

Boride	Melting Point, °C	Coefficient of Thermal Expansion (α) $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity $\mu\Omega\text{-cm}$	Temp., °C	Reference
Ta ₂ B	1,900	--	--	--	57
Ta ₃ B ₂	2,040	--	--	--	57
TaB	2,430	--	100	25	57,95
Ta ₃ B ₄	2,650	--	--	--	57
TaB ₂	3,095	6.3 - 8.0 (25°-1700°C) ^x	68-86	25	57,95,95-98
Cr ₄ B	1,650	--	--	--	57
Cr ₂ B	1,815	--	--	--	57
Cr ₅ B ₃	1,900	--	--	--	57
CrB	2,045	--	64	25	57,95
Cr ₃ B ₄	1,930	--	--	--	57
CrB ₂	2,150	10.5, 11.1 (25°-1200°C)	22-45	25	57,95,98
Cr ₂ B ₅	2,000	--	--	--	57
Mo ₂ B	2,280 (p)	7.74 (25°-335°C)	--	--	57
α -MoB	2,180 (p)	--	45-50	25	57,95
β -MoB	2,665	--	25	25	57,95
MoB ₂	2,475 (dec.)	--	22-45	25	57,95
Mo ₂ B ₅	2,140 (p)	5.00 (25°-500°C)	25	25	57,95
W ₂ B	2,670	--	--	--	57
α -WB	2,170 (dec.)	--	--	--	57
β -WB	2,665 (dec.)	--	--	--	57
W ₂ B ₅	2,365	7.37 (10°-2210°C) ⁺	21	25	57,95

TABLE 22.--Select physical properties of metal borides (Continued)

Boride	Melting Point, °C	Coefficient of Thermal Expansion (α) $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity $\mu\Omega\text{-cm}$	Temp., °C	Reference
LaB ₆	2,150	6.30 (25°-800°C)	27	--	57,95
CeB ₆	2,190	7.20 (" ")	--	--	57
PrB ₆	--	7.56 (" ")	--	--	57
NdB ₆	2,540	7.20 (" ")	--	--	57
YB ₄	2,750 (est.)	7.68 (20°-1000°C)	--	--	57,101
YB ₆	2,300	6.12 (25 - 800°C)	--	--	57
ScB ₂	2,250	9.47 (" ")	--	--	57
GdB ₄	3,030 est.)	7.00 (20°-1000°C)	--	--	57,101
CaB ₆	2,230	6.49 (25°-800°C)	--	--	57
SrB ₆	2,230	6.67 (" ")	--	--	57
BaB ₆	2,265	6.85 (" ")	--	--	57
Ni ₃ B	1,170	--	--	--	95
Ni ₂ B	1,230	--	--	--	95
NiB	---	--	--	--	95

^x α_L calculated from X-ray data using $\alpha_L = \frac{1}{3} \alpha_c + \frac{2}{3} \alpha_a$; range of values given due to changes in slope of $\Delta L/L_0$ -T plot over indicated temperature range.

[†] Peritectic = (p).

⁺ Estimated value.

systems exhibit maxima near $x = 1$, while the CrB_x system has a maximum resistivity at $x = 2$. With the exception of the VB_x system, the resistivities of the borides are greater than that of the parent metals.

The resistivity behavior of the CrB_x system contrasts with that of CrSi_x alloys, which did not show maximum values as a function of x (Figure 4). Conversely, the borides of titanium show a general decrease in resistivity with increasing boron content, while the corresponding resistivity-composition curve for the silicides is characterized by a pronounced maxima. The resistivity-composition curves for HfB_x and ZrB_x are similar to that of the titanium borides, except with a reversed curvature (the large scatter in resistivity data for ZrB_2 makes the apparent minimum in the curve for ZrB_x inconclusive).

Four of the borides-- ZrB , ZrB_2 , HfB , and HfB_2 --have electrical resistivities of $10 \mu\Omega\text{-cm}$ or less at 25 C. However, none of them has a coefficient of thermal expansion of $\sim 10 \times 10^{-6}/^\circ\text{C}$ necessary for compatibility with the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid-electrolyte. Of the borides in Table 22, only ScB_2 , CrB_2 , and possibly TiB_2 have thermal expansion properties which would make them potentially usable in the solid-electrolyte fuel cell. The prohibitive cost of scandium compounds, however, essentially eliminate ScB_2 from further consideration.

The borides of the Group IV elements are the most resistant to oxidation. Like the silicides, they depend upon the formation of an impervious oxide film for protection against destructive oxi-

Figure 5.--Electrical Resistivities of Transition-Metal Borides at 25°C as a Function of Composition

duction. Titanium boride, for example, is reported to be stable up to 1500°C. In contrast, borides of Mo, W, V, Nb, and Ta oxidize readily at 1000°C.⁹⁵ The formation of a borate or oxide film under oxidizing conditions limits the use of metal borides in high-temperature fuel cells to the fuel electrode. Such films would result in chemical compatibility and interfacial problems with other cell components over prolonged periods of time at operating temperatures.

The thermodynamic stability of the metal borides under the reducing conditions at the anode in high-temperature fuel cells can be estimated from ΔG_f^0 data for the borides at elevated temperatures, using a simplified reaction for oxidation

The equilibrium P_{O_2} for oxidation then can be calculated from

$$(23) \quad P_{O_2} = (K_p) \exp[-4/(2xz+3)] = \exp \frac{\Delta G_{(22)}^0}{RT} \cdot \frac{4}{(2xz+3)}$$

ΔG_f^0 information for many of the borides is even less evident than that for the silicides--even at lower temperatures.

Thermodynamic data which was readily available are presented in Table 23. For some borides, only ΔH_f^0 at 298K was found. In these cases, ΔG_f^0 at 1300K was set equal to ΔH_f^0 at 298K, as was done with the silicides (Table 19). Examination of $\Delta H_{f,298}^0$ and $\Delta G_{f,1300}^0$ data for TiB , TiB_2 , and ZrB_2 in Table 23 show less than ten percent difference in these values. Thus, this would appear to be adequate, as a first approximation, for purposes of calculating the thermodynamic stabilities of the borides toward oxidation. The free energy changes for oxidation

TABLE 23.--Thermodynamic data for select metal borides

<u>Boride</u>	<u>$-\Delta H^\circ_f, 298$ kcal/g-at B</u>	<u>$-\Delta H^\circ_f, 3000$ kcal/g-at B</u>	<u>References</u>
TiB	38.3	37.1	61
TiB ₂	33.4	30.8	61
ZrB ₂	38.6	35.8	61
HfB ₂	39.0	(39.0)*	102
TaB ₂	23.2	(23.2)	103
Mo ₂ B	22.6	27.9	104
W ₂ B	20.8	23.5	104
WB	14.1	(14.1)	105
Co ₃ B	-	-30.9 ⁺	106
Co ₂ B	-	64.3 ⁺	106
LaB ₆	5.12	(5.12)	107

* Estimated values are in parentheses.

⁺ Values are for 1200K.

of a select number of metal borides are presented in Table 24 (additional data may be contained in a number of the references of Appendix D, which then would permit later up-dating of the information in Table 24). The corresponding values of K_p and P_{O_2} for the oxidation reactions at 1300K are listed in Table 25.

Only M_2B and W_2B are thermodynamically stable toward oxidation under P_{O_2} conditions of 10^{-16} to 10^{-18} atm expected at the fuel electrode in the solid-electrolyte fuel cell. Tungsten boride would be stable only at a P_{O_2} of 10^{-18} atm. This is true for formation of the higher as well as the lower oxides. None of the borides are thermodynamically stable with respect to their oxides at 900K, under conditions expected at the fuel electrode in the molten-carbonate fuel cell. This parallels similar behavior for the other interstitial compounds under comparable conditions. Kinetic factors, of course, could still permit the use of borides which are not predicted to be stable in the fuel gas environment. The formation of borates rather than mixed oxides, as indicated in Table 20, will influence the equilibrium P_{O_2} for oxidation, analogous to the previously noted effect of silicate formation during oxidation of silicides.

None of the borides possess the desired resistance to oxidation, high electrical conductivity, and compatible thermal expansion properties which would make it ideally suited for use in the solid-electrolyte fuel cell. Thus, some modification or compositional changes in the borides will be necessary in order to meet all the fuel cell requirements.

TABLE 24.--Oxidation of select metal borides at 1300K

Reaction	$-\Delta G^\circ$ for Reaction kcal/g-at B	References
$\text{TiB} + 1.75\text{O}_2 \rightarrow \text{TiO}_2(\text{rutile}) + 0.5\text{B}_2\text{O}_3(\ell)$	246.6	61,108
$\text{TiB} + 1.25\text{O}_2 \rightarrow \beta\text{TiO} + 0.5\text{B}_2\text{O}_3(\ell)$	177.1	61,63,108
$0.5\text{TiB}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{TiO}_2(\text{rutile}) + 0.5\text{B}_2\text{O}_3(\ell)$	168.0	61,108
$0.5\text{TiB}_2 + \text{O}_2 \rightarrow 0.5\beta\text{TiO} + 0.5\text{B}_2\text{O}_3(\ell)$	133.3	61,63,108
$0.5\text{HfB}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{HfO}_2 + 0.5\text{B}_2\text{O}_3(\ell)$	178.5	62,102,108
$0.5\text{ZrB}_2 + 1.25\text{O}_2 \rightarrow 0.5\text{ZrO}_2 + 0.5\text{B}_2\text{O}_3(\ell)$	180.0	61,108
$0.5\text{TaB}_2 + 1.33\text{O}_2 \rightarrow 0.25\text{Ta}_2\text{O}_5 + 0.5\text{B}_2\text{O}_3(\ell)$	179.4	63,103,108
$\text{Mo}_2\text{B} + 3.75\text{O}_2 \rightarrow 2\text{MoO}_3(\ell) + 0.5\text{B}_2\text{O}_3(\ell)$	293.7	61,104,108
$\text{Mo}_2\text{B} + 2.75\text{O}_2 \rightarrow 2\text{MoO}_2 + 0.5\text{B}_2\text{O}_3(\ell)$	257.6	61,104,108
$\text{W}_2\text{B} + 3.75\text{O}_2 \rightarrow 2\text{WO}_3 + 0.5\text{B}_2\text{O}_3(\ell)$	336.0	61,104
$\text{W}_2\text{B} + 2.75\text{O}_2 \rightarrow 2\text{WO}_2 + 0.5\text{B}_2\text{O}_3(\ell)$	260.7	61,104
$\text{WB} + 2.25\text{O}_2 \rightarrow \text{WO}_3 + 0.5\text{B}_2\text{O}_3(\ell)$	222.7	61,105,108
$\text{WB} + 1.75\text{O}_2 \rightarrow \text{WO}_3 + 0.5\text{B}_2\text{O}_3(\ell)$	185.0	61,105,108
$\text{Co}_3\text{B} + 2.25\text{O}_2 \rightarrow 3\text{CoO} + 0.5\text{B}_2\text{O}_3(\ell)$	254.7*	106,108
$\text{Co}_2\text{B} + 1.75\text{O}_2 \rightarrow 2\text{CoO} + 0.5\text{B}_2\text{O}_3(\ell)$	252.4*	106,108
$0.17\text{LaB}_6 + 0.89\text{O}_2 \rightarrow 0.083\text{La}_2\text{O}_3(\ell) + 0.5\text{B}_2\text{O}_3(\ell)$	138.7*	62,107,108

* Values for 1200K.

TABLE 25.--Calculated P_{O_2} for oxidation of metal borides at 1300K

Boride/Oxide	K_p for Oxidation	P_{O_2} for Oxidation atm
TiB/TiO ₂ (rutile)	$P_{O_2}^{-1.75} = 2.85 \times 10^{41}$	2.05×10^{-24}
TiB/TiO	$P_{O_2}^{-1.25} = 5.96 \times 10^{29}$	1.51×10^{-24}
TiB ₂ /TiO(rutile)	$P_{O_2}^{-1.25} = 1.80 \times 10^{28}$	2.49×10^{-23}
TiB ₂ /TiO	$P_{O_2}^{-1} = 2.60 \times 10^{22}$	3.85×10^{-23}
HfB ₂ /HfO ₂	$P_{O_2}^{-1.25} = 1.02 \times 10^{30}$	9.80×10^{-25}
ZrB ₂ /ZrO ₂	$P_{O_2}^{-1.25} = 1.84 \times 10^{30}$	6.14×10^{-25}
TaB ₂ /Ta ₂ O ₅	$P_{O_2}^{-1.38} = 1.45 \times 10^{30}$	1.16×10^{-22}
Mo ₂ B/MoO ₃ (s)	$P_{O_2}^{-3.75} = 2.36 \times 10^{49}$	6.82×10^{-14}
Mo ₂ B/MoO ₂	$P_{O_2}^{-2.75} = 2.05 \times 10^{43}$	1.78×10^{-16}
W ₂ B/WO ₃	$P_{O_2}^{-3.75} = 3.06 \times 10^{56}$	8.65×10^{-16}
W ₂ B/WO ₂	$P_{O_2}^{-2.75} = 6.81 \times 10^{43}$	1.15×10^{-16}
WB/WO ₃	$P_{O_2}^{-2.25} = 2.77 \times 10^{37}$	2.28×10^{-17}
WB/WO ₂	$P_{O_2}^{-1.75} = 1.27 \times 10^{31}$	1.68×10^{-18}
Co ₃ B/CoO	$P_{O_2}^{-2.25} = 2.46 \times 10^{46*}$	$2.41 \times 10^{-21*}$

TABLE 25.--Calculated P_{O_2} for oxidation of metal borides at 1300K (Continued)

Boride/Oxide	K_p for Oxidation	P_{O_2} for Oxidation, atm
Co_2B/CoO	$P_{O_2}^{-1.75} = 9.19 \times 10^{45*}$	$5.43 \times 10^{-27*}$
LaB_6/La_2O_3	$P_{O_2}^{-0.875} = 1.8 \times 10^{25*}$	$1.4 \times 10^{-29*}$

* Values are for 1200K.

Metal borides can be incorporated into the fuel electrode of the solid-electrolyte fuel cell by several techniques. A thin-film anode could be fabricated solely from the boride by chemical vapor exposition. Zirconium boride films have been prepared in this manner using metal halide mixtures¹⁰⁹, as well as borane mixtures.¹¹⁰ The film could be applied by plasma spraying,^{111,112} although this generally does not produce as coherent a film as does CVD. R-F sputtering also can be used for the preparation of thin films. The sputtering process is generally much slower than CVD, however. For fuel cell applications, the morphology and physical properties of the film are equally as important as the chemical composition. All of these factors will require evaluation in any of the above techniques and are considered for thin-film fabrication of the solid-electrolyte fuel cell.

An alternate anode-fabrication technique involves the use of metal binders to form a cermet. Thus, part of the ZrO_2 in the ZrO_2 -Ni cermet currently used for the solid-electrolyte fuel cell could be replaced by a metal boride or boride-based material. Unfortunately, nickel forms a number of stable borides (see Table 22). At 1000°C, the metal boride could begin to react with the nickel to form intermetallic compounds, eutectic solutions, or solid solutions after prolonged periods. The resulting change in the electrical and thermal expansion properties could be detrimental to a fuel cell utilizing such a cermet electrode.

There are indications that a number of the metal borides react with nickel at temperatures expected in the solid-electrolyte fuel

cell. The system TaB_2 -Ni, for example, forms an eutectic at 1090°C at 17 a/o TaB_2 .⁵⁹ Similar behavior has been indicated for TaB_2 -Fe and -Co systems, and between Fe, Co, or Ni and TiB_2 or ZrB_2 .⁵⁹ Tungsten boride is reported to form a liquid phase with nickel at 1300K which indicates boride dissolution occurs to form a eutectic.¹¹³ In the V-B-Ni system, a phase of composition $Ni_{20.4}V_{2.6}B_6$ has been observed at a temperature as low as 800°C.¹¹⁴ Extreme caution must be exercised, therefore, in choosing suitable boride-transition metal combinations for anode use in high-temperature fuel cells to avoid the reactivity problems outlined above. These potential compatibility problems do not occur when nickel is used to bond transition-metal nitrides and carbides under similar conditions because of the instability of carbides and nitrides of nickel and the low solubility of carbon and nitrogen in nickel at 1000°C.

The borides are reported to be soluble in molten alkali,⁹⁵ which would appear to preclude their use as anodes in the molten-carbonate fuel cell. However, without oxygen present, no feasible chemical reactions can be written to describe possible dissolution mechanisms. It appears likely, therefore, that borides would be compatible with the molten-carbonate eutectic in the absence of substantial amounts of hydroxide and water vapor and under suitable reducing conditions, as would exist at the fuel electrode. Compatibility studies should be conducted under such conditions if serious consideration is given to the use of boride materials as anodes.

5. Composite, Non-Oxide Ceramics

A number of composite, non-oxide ceramics have been examined for use as MHD electrodes. Addition of SiC to ZrB_2 was found to increase the oxidation resistance of this material by the formation of a protective SiO_2 film at high temperatures.¹¹⁵ MoSi_2 also has been used with ZrB_2 for this purpose.¹¹⁶ LaB_6 has been added to ZrB_2 to increase its thermionic emission for MHD use.¹¹⁷ The properties of such materials also makes them candidates for possible use in high-temperature fuel cells.

While many of the carbides, nitrides, silicides, and borides have certain materials properties which would make them potentially suitable for anode use in the solid-electrolyte fuel cell, invariably no one material appears to satisfy all of the fuel cell needs. Thus, modification of the chemical composition of a promising material or combining it with a second or third material would appear to be necessary to effect the desired change(s) in physical properties (e.g., thermal coefficient of expansion, electrical resistivity, melting point, etc.). Such effects are not as critical for anode use in the molten-carbonate fuel cell, although chemical compatibility with the carbonate then becomes a primary prerequisite.

The effect of various interstitials upon the properties of a given metal is typified for the case of titanium in Table 26. Addition of TiSi_2 to TiB_2 would be expected to increase the coefficient of thermal expansion and the electrical conductivity, but lower the P_{O_2} for oxidation, if the effects were additive. This

TABLE 26.--Comparison of select physical properties of interstitial compounds of titanium

Compound	Melting Point, °C	Coefficient of Thermal Expansion, $10^{-6}/^{\circ}\text{C}$	Electrical Resistivity at 25°C, $\mu\Omega\text{-cm}$	P_{O_2} for oxidation to TiO_2 (rutile) at 1300K, atm
TiC	3,250	8.3 (0°-1,400°C)	60-250	$1.39 \times 10^{-21}^*$
TiN	(func. of P_{N_2})	9.5 (20°-1,100°C)	26	$3.07 \times 10^{-29}^+$
TiSi	1,760 (dec.)	10.4 (370°-1,070°C)	39	5.26×10^{-26}
TiB	2,060 (dec.)	?	40	2.05×10^{-24}
TiO	⁶¹ 1,750	¹¹⁸ 6.6 (25°C)	⁵⁹ 300	⁵⁹ 4.37×10^{-24}
TiSi ₂	1,540	10.4 (20°-1,070°C)	11.6-16.7	1.61×10^{-26}
TiB ₂	2,871	7.3-9.1 (25°-2,040°C)	15 - 28	2.49×10^{-23}
TiO ₂ (rutile)	⁶¹ 1,838	⁵⁷ 8.82 (25-1,500°C)	$>10^{10}$	0

* For $P_{\text{CO}_2} = 0.1$ atm.

+ For $P_{\text{N}_2} =$ equilibrium dissociation pressure of 5.27×10^{-18} atm.

may not always be the case, however, as evidenced by the minimum in the electrical resistivity of TiN-TiO solid solutions as a function of composition (Figure 3).

In general, silicides have higher thermal coefficients of electrical resistivity (TCOER) than carbides and nitrides. The TCOER for mixed interstitial compounds varies, depending upon the material and composition. HfC and TaC, for example, have low TCOERs compared to TiC and ZrC. Chromium carbide (Cr_3C_2) also has a low TCOER. The TCOER increases with WC content for solid solutions with TiC, ZrC, and VC.¹¹⁹

The coefficient of thermal expansion for interstitial alloys is similarly affected by composition, as indicated in Table 27 by data for Zr and Hf. Substitution of oxygen for carbon and nitrogen raises the coefficient of thermal expansion. Similarly, for TiCO_y , α increases with increasing y at constant $(x+y)$ or x .¹²¹

Thus, by appropriate choice of materials, composites may be engineered to have the desired physical properties such as increased oxidation resistance, higher electrical conductivity, or compatible coefficient of thermal expansion for the particular use envisioned. In certain cases, it will not always be possible to determine a priori the value of a specific physical property for a composite material based on the values of the individual components. A CrB_2 - TiB_2 composite, for example, has a higher electrical resistivity at high temperatures than each of the individual component borides.⁵⁹ This may result from the formation of a compound between the borides rather than a simple solid so-

TABLE 27.--Effect of composition upon the thermal expansion properties of interstitial alloys of zirconium and hafnium ¹²⁰

<u>Composition</u>	<u>Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$</u> [*]
ZrC _{0.957}	6.86
ZrC _{0.83} ⁰ _{0.18}	7.14
ZrN _{0.76} ⁰ _{0.19}	7.60
HfC _{0.95}	6.75
HfC _{0.66} ⁰ _{0.21}	6.80
HfC _{0.57} ⁰ _{0.13}	7.30
HfN _{1.1}	7.88
HfN _{0.74} ⁰ _{0.16}	8.08

* Assumed temperature range of 25° to 1000°C.

lution. The nature of the interaction between components of a potential composite must be known before effects upon the properties of the resultant material can be predicted.

Knowledge of the intersolubilities of refractory phases is important when the preparation of composite materials is being considered. In some cases, the component compounds may be completely mutually soluble (e.g., TaC-TiC or ZrB_2 - TiB_2).¹²² In other instances, one material may be only partially soluble in a second or third material (e.g., TiB_2 in TaSi_2 , MoSi_2 , or TiC).¹²² Compound formation may result in still a third possibility (e.g., TaC or MoB_2 with TaSi_2 , Nb_5Si_3 , or MoSi_2).¹²² Solubility limitations can therefore place constraints on the range of concentrations which can be considered in composites for potential use in the high-temperature fuel cells.

Considerable research has been conducted in the development, for a variety of purposes, of composite materials based on interstitial alloys. In some cases, the goal was to develop a hard, refractory material for use in cutting tools and dies. Composites also have been examined as a means of reducing corrosion in situations where a particular material alone did not satisfy the necessary requirements. Addition of BN to TiB_2 , TiC, or ZrB_2 , for example, resulted in a container material suitable for vaporization of molten aluminum.¹²³ Because BN is an insulator, however, the electrical resistivity of the composite was considerably higher than the interstitial alloys without BN. At 25°C,

the resistivity of a 70 w/o TiB_2 -30 w/o BN composite was $180 \mu\Omega\text{-cm}$,¹²³ compared to only $15\text{-}28 \mu\Omega\text{-cm}$ for TiB_2 alone (Table 22). While the desired goal of corrosion resistance may have been attained, the considerable increase in electrical resistivity of the composite, as a result of the presence of BN, makes its use as a heater to vaporize aluminum impractical. In addition, the addition of BN resulted in reduced resistance to moisture. The moisture resistance was improved, however, when TiN was incorporated into the composite.¹²⁴

As indicated in the example for the TiB_2 -BN composite, improvement or change in one property of a material by composite formation can also result in undesired changes in other properties. In the case of the solid-electrolyte fuel cell, design of a composite to have suitable thermal-expansion properties may cause an unacceptable increase in the electrical resistivity or a reduced stability toward oxidation; it may be impractical to fabricate, by conventional techniques, a thin-film fuel cell using such a composite material. These factors all must be considered when such materials are considered for potential use in the solid-electrolyte fuel cell.

Perhaps the most promising area of use of composite and cermet refractories is for the anode in the molten-carbonate fuel cell. A number of the individual interstitial compounds of transition metals are being examined already for use as electrocatalysts in low-temperature aqueous fuel cell systems.^{46,47} Similar work with boride and silicide

composites as anodes also has been reported. Cermets of noble and transition metals with carbides, oxides, and nitrides have shown promise as cathode materials.¹²⁶

Refractory composites also have been used for electrolytic applications at high temperatures. Composites of 80 w/o TiB_2 -20 w/o TiC and 95 w/o ZrB_2 -5 w/o Mo were tested as cathodes in the electrolysis of cryolite melts for aluminum production.¹²⁷ (Electrical resistivities of TiB_2 - TiC composites ranged from 62 to $125 \mu\Omega\text{-cm}$ at 1000°C .)¹²⁸ Composite cathodes of ZrB_2 and TiB_2 also were used in aluminum-reduction cells at 990° to 1010°C .¹²⁹ The corrosive nature of the melt in the aluminum cell parallels that of the molten-carbonate cell.

There is a vast number of possible combinations of interstitial alloys with each other and with suitable transition metals to form multicomponent systems with considerable promise in high-temperature fuel cells, especially the molten-carbonate fuel cell. Published research relative to this specific application, however, has been rather limited. There is a definite need to evaluate critically the most promising candidate materials for this application, in order to determine whether additional in-depth research in this area is warranted.

It is interesting to note that work of this nature has been reported just recently by the Institute of Gas Technology. Tungsten carbide is being explored (along with other materials) as a sintering inhibitor for the porous nickel or cobalt anodes of the molten-carbonate fuel cell.¹³⁰ Initial tests indicate

that ten w/o WC added to a cobalt anode results in an increase in the measured surface area. Electrochemical tests have not yet been conducted, however.

C. Oxide Ceramics

The oxide ceramics have received the most attention for use as MHD electrodes because of their inherent stability in an oxidizing environment at high temperatures. For discussion purposes, the oxides in this section of the report will be grouped into the following general categories: perovskites and pseudoperovskites, spinels, ZrO_2 -based oxides, and other metal oxides.

1. Perovskites

The physical properties of perovskites used for MHD electrodes are listed in Table 28. Melting point data were not always available for many of the complex, multicomponent systems. However, since most of these materials were being used or tested at temperatures of $1500^{\circ}C$ or higher, their melting points are at least greater than this. The rare-earth nickelates and cobaltates are exceptions, however, in that they are not stable at MHD-electrode temperatures. ($La_{0.5}Sr_{0.5}CoO_3$, for example, begins to decompose in air at $1200^{\circ}C$.)¹⁴⁴ The bulk of the electrical (d-c) conductivity data are reported for temperatures of 1000° and $727^{\circ}C$, to be representative of operating temperatures of the solid-electrolyte and molten-carbonate fuel cells, respectively.

The chromite-type oxides have received the most attention, with the major emphasis on $LaCrO_3$ -based systems. Pure $LaCrO_3$ is not suitable for use at electrode use at MHD temperatures because

TABLE 28.--Select physical properties of perovskites and pseudo-perovskites

Oxide	Coefficient of Thermal Expansion (α), 10 ⁻⁶ /°C*	Electrical (d-c) Resistivity, Ω -cm	Temp., °C	-Log P _{O₂} (atm)	References
LaCrO ₃	8.92 (25°-1,000°C)	1.4-10; 1.1-8	727; 1,000	0	131-133
		16; 15	727; 1,000	3	132
		27; 10	727; 1,000	4	131
LaCr _{0.5} Al _{0.5} O ₃	-	4	1,000	0.7 ⁺	4
LaCr _{0.8} Co _{0.2} O ₃	11.5 (25°-1,000°C)	-	-	-	134
LaCr _{0.5} Co _{0.5} O ₃	19.0 (25°-1,000°C)	-	-	-	4
LaCr _{0.8} Ni _{0.2} O ₃	9.2 (25°-1,000°C)	-	-	-	4
SmCrO ₃	-	10	1,000	0.7	4
YCrO ₃	8.0 (25°-1,000°C)	0.36	1,000	0.7	133, 135
		0.79	727	0.7	135
		1.8	1,000	est 5 (Ar)	135
		6.7	727	est 5 (Ar)	135
NdCrO ₃	8.3 (25°-1,000°C)	4	1,000	0.7	4, 133
NdCrO ₃ -CaO	-	0.25	1,300	0.7(?)	136
La _{0.99} Sr _{0.01} CrO ₃	-	1.0	727- 1,000	0.7	132
La _{0.98} Sr _{0.02} CrO ₃	-	0.25; 0.28	727- 1,000	0	131
La _{0.97} Sr _{0.03} CrO ₃	-	0.33	727- 1,000	0.7	132, 137
La _{0.94} Sr _{0.06} CrO ₃	-	0.22	727- 1,000	0.7	132
La _{0.90} Sr _{0.10} CrO ₃	9.2 (50°-287°C)	0.32	727	2	132, 137

TABLE 28.--Select physical properties of perovskites and pseudo-perovskites (Cont.)

Oxide	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}^{\ast}$	Electrical (d-c) Resistivity, $\Omega\text{-cm}$	Temp., $^{\circ}\text{C}$	$-\text{Log } P_{\text{O}_2}$ (atm)	Reference
$\text{La}_{0.87}\text{Sr}_{0.13}\text{CrO}_3$	-	0.12	727-1,000	0.7	131,134
$\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$	10.9 (25°-1,000°C)	0.031;0.029	727;1,000	0	131,134
		0.10	727-1,000	0.7	132
$\text{La}_{0.80}\text{Sr}_{0.20}\text{CrO}_3$	-	0.06	727-1,000	0.7	132
$\text{La}_{0.84}\text{Sr}_{0.16}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$	10.0 (25°-1,000°C)	-	-	-	134
LaCrO_3 -8 m/o CaO	-	0.27	1,000	0.7	138
		0.39	727	0.7	138
LaCrO_3 -24 m/o CaO	-	0.31	1,000	0.7	138
		0.26	727	0.7	138
LaCrO_3 -32 m/o CaO	-	0.26	1,000	0.7	138
		0.30	727	0.7	138
$\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$	-	0.32	727	2	137
$\text{La}_{0.92}\text{Ba}_{0.08}\text{CrO}_3$	10.3 (25°-1,000°C)	-	-	-	134
$\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_2$	8.8 (100°-1,400°C)	0.1 -0.27	1,000	0.7-5.2	139,140,4
		0.36 -0.40	600	0.7-5.2	140
		0.16 -0.13	1,000; 727	0.7-5.2	141
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$	9.9 (25°-1,000°C)	0.3 -0.42	1,000	0.7	4,142
	9.8 (25°-1,000°C)	0.46	727	0.7	142

TABLE 28.--Select physical properties of perovskites and pseudo-perovskites (Cont.)

Oxide	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}^*$	Electrical (d-c) Resistivity, $\Omega\text{-cm}$	Temp., $^{\circ}\text{C}$	$-\log P_{\text{O}_2}$ (atm)	References
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.5}\text{Al}_{0.5}\text{O}_3$	10.8 (25°-1,000°C)	1.0	1,000	0.7	4,142
$\text{Al}_{0.5}\text{O}_3$	10.7 (25°-1,000°C)	1.5	727	0.7	142
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.25}\text{Al}_{0.75}\text{O}_3$	-	3.2	1,000	0.7	142
		5.6	727	0.7	142
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Co}_{0.25}\text{O}_3$	16.7 (25°-1,000°C)	-	-	-	143
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$	19.9 (25°-1,000°C)	-	-	-	143
$\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.25}\text{Co}_{0.75}\text{O}_3$	20.6 (25°-1,000°C)	-	-	-	143
$\text{LaCr}_{0.5}\text{Co}_{0.5}\text{O}_3$	19.0 (25°-1,000°C)	-	-	-	134
$\text{LaCr}_{0.95}\text{Mg}_{0.05}\text{O}_3$	-	0.13-0.14	1,000	0.7-5.2	140,141
		0.15-0.16	727	0.7-5.2	140
$\text{LaCr}_{0.85}\text{Mg}_{0.15}\text{O}_3$	9.3 (25°-1,000°C)	-	-	-	134
LaCoO_3	23 (25°-1,000°C)	0.001	750	0.7	143,144
$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$		0.001	1,000	0	4
		0.01	1,000	Vacuum	4
LaNiO_3	14.1 (25°-1,000°C)	-	-		4

TABLE 28.--Select physical properties of perovskites and pseudo-perovskites (Cont.)

Oxide	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}$	Electrical (d.c.) Resistivity, $\Omega\text{-cm}$	Temp., $^{\circ}\text{C}$	-Log P_{O_2} (atm) ²	References
$\text{LaNi}_{0.9}\text{Co}_{0.1}\text{O}_3$	14.9 (25°-1,000°C)	-	-	-	4
$\text{La}_{0.9}\text{Co}_{0.1}\text{NiO}_3$	14.5 (25°-1,000°C)	-	-	-	4
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	-	0.02	1,000	0.7	4
YFeO_3	11.0 (25°-1,000°C)	-	-	-	133
LaFeO_3	10.6 (25°-1,000°C)	-	-	-	133
$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$	-	0.017	727- 977	0.7	145
$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	-	0.055	727- 977	0.7	145
$\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$	-	0.0055	900	0.7	144
$\text{La}_{0.25}\text{Sr}_{0.75}\text{FeO}_3$	-	0.014	800-1,000	0.7	146
$(\text{La}_{0.75}\text{Sr}_{0.25})\text{Fe}_{0.5}\text{O}_3$	-	0.0046	1,027	0.7	146
$\text{Y}_{0.95}\text{Ca}_{0.05}\text{FeO}_{3-y}$	10.7-11.8 (25°-1,1100°C) 3 ranges)	0.074	1,000	0.7-5.2	147
		0.086	727	0.7-5.2	147
$\text{Y}_{0.90}\text{Ca}_{0.10}\text{FeO}_{3-y}$	-	0.064	1,000	0.7	147
		0.084	727	0.7	147
		0.14;0.11	727;1,000	3.0-5.2	147
$\text{Y}_{0.85}\text{Ca}_{0.15}\text{FeO}_{3-y}$	10.8-12.0 (20°-1,100°C; 3 ranges)	0.074	727-1,000	0.7-5.2	147

TABLE 28.--Select physical properties of perovskites and pseudo-perovskites (Cont.)

Oxide	Coefficient of Thermal Expansion (α) $10^{-6}/^{\circ}\text{C}^*$	Electrical (d-c) Resistivity, $\Omega\text{-cm}$	Temp., $^{\circ}\text{C}$	$-\text{Log } P_{\text{O}_2}$ (atm)	References
$\text{Y}_{0.70}\text{Ca}_{0.24}\text{Fe}_{0.90}$	-	0.26;0.20	727;1,000	0.7	147
$\text{Zr}_{0.10}\text{O}_{3-y}$		0.44;0.30	727;1,000	3	147
		0.44;0.47	727;1,000	5.2	147
$\text{Y}_{0.68}\text{Ca}_{0.32}\text{Fe}_{0.80}$	10.6-12.1 (20°-1,100°C; 3 ranges)	0.066;0.046	727;1,000	0.7	147
$\text{Zr}_{0.20}\text{O}_{3-y}$		1.3;0.09	727;1,000	3	147
		1.5;1.0	727;1,000	5.2	147

* In air.

+ Air.

of volatilization of chromium oxides [e.g., CrO_3 , CrO_2 , and $\text{CrO}_2(\text{OH})$]. While the electrical conductivity is essentially wholly electronic ($t_i > 0.995$ at 980°C),¹³² it also shows a strong P_{O_2} dependency. The increase in resistivity under reducing conditions is thought to result from the formation of triply-ionized chromium vacancies.¹³² The substitution of La^{+3} by divalent cations such as Mg^{+2} , Ca^{+2} , Sr^{+2} , and Ba^{+2} , however, leads to a substantial increase in the electrical conductivity (p-type) by the formation of Cr^{+4} for charge compensation.¹³¹ The electrical resistivities of alkaline-earth-doped LaCrO_3 show only a slight P_{O_2} and temperature dependency, as can be seen by the data in Table 28.

When a portion of the Cr^{+3} in LaCrO_3 is replaced by Al^{+3} , the desired reduction of the volatilization of chromium oxides is obtained;^{142,143} unfortunately, it also causes an increase in the electrical resistivity. However, the resistivity remains more than adequate to meet MHD-electrode requirements of less than ten $\Omega\text{-cm}$. The Al^{+3} substitution has a second effect upon the physical properties of doped- LaCrO_3 in that the coefficient of thermal expansion is increased. In addition, the destructive rhombohedral-to-orthorhombic phase transformation is eliminated⁴ in the 25° to 1000°C temperature range.

In evaluation of the oxides of Table 28 for possible use in the high-temperature solid-electrolyte fuel cell, it can be seen that virtually all the materials have electrical resistivities which are compatible with the requirement of $50 \Omega\text{-cm}$ for the

interconnector (Table 2). However, potential interconnector candidates must be primarily electronic conductors and simultaneously must be stable under both severe reducing conditions ($P_{O_2} = 10^{-16}$ to 10^{-18} atm) as well as an air environment at 1000°C . Not all of the oxides of Table 28 have been examined at such low values of P_{O_2} , nor have transference measurements been carried out for many of them. The P_{O_2} dependence of conductivity for a number of the perovskites, however, suggests the presence of an undesirable ionic contribution. In addition, the candidate oxide must have a coefficient of thermal expansion which closely matches that of the Y_2O_3 -stabilized ZrO_2 electrolyte of $10 \times 10^{-6}/^{\circ}\text{C}$.

With these needs in mind, researchers at Westinghouse evaluated many perovskites for possible interconnector use. The most promising candidate was doped, substituted- LaCrO_3 . By adjusting the Al^{+3} content, a very close thermal expansion match was obtained with adequate electrical conductivity at a composition of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$. The physical and chemical properties of this material have subsequently been studied extensively by Westinghouse. It now appears that the Mg^{+2} substitutes for Cr^{+3} rather than the La^{+3} and that only about half the Mg^{+2} added in the above composition actually goes into solid solution.¹⁴⁹ In other words, there appears to be evidence for second-phase formation, where excessive MgO exsolves.

At a low P_{O_2} , loss of O_2 from $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ become pronounced at 10^{-18} atm. Under these conditions, oxygen

vacancies are formed and the electrical resistivity increases.

There is concern that oxygen transport (leakage) then could occur as a result of ionic conduction during operation of the solid-electrolyte fuel cell, which would affect the performance adversely. This process is under study by R. Ruka at Westinghouse in relation to possible deleterious long-term effects upon the performance of their thin-film solid-electrolyte battery.¹³⁴

In their overall physical properties, the Mg^{+2} - and Sr^{+2} -doped $LaCrO_3$ s have the most promise of the perovskites of Table 28 for use as interconnector material for the high-temperature solid-electrolyte fuel cell. The rare-earth cobaltates and nickelates are not expected to be stable under the reducing conditions of the anode side of the fuel cell. The equilibrium P_{O_2} for CoO and NiO , for example, is greater than that of the fuel (Table 7), so that formation of elemental Co and Ni would probably result at $1000^\circ C$ for $LaCoO_3$ and $LaNiO_3$, according to the reaction:

where M is a metal cation. This is an approximation, of course, as the free energy of formation of $LaCoO_3$ will be more negative than the sum of the component oxides as a result of compound formation. The equilibrium P_{O_2} , under these conditions, would be less than that indicated in Table 7. Lacking ΔG_f^0 data for $LaCoO_3$ and $LaNiO_3$ at $1000^\circ C$, the P_{O_2} for reaction 24 was not calculated for fuel cell conditions.

Similar arguments apply for the case of the stability of fer-

rites in a strongly reducing environment, although the rare-earth ferrites have a much greater thermal stability than the corresponding nickelates and cobaltates.¹⁴⁵

In comparison to the non-oxide ceramics previously discussed, the electrical resistivities of the conducting perovskites are orders of magnitude greater. Their lower conductivities makes the perovskites unattractive for possible use as anode materials in the solid-electrolyte fuel cell. This is aggravated, as discussed above, by the instability problems of certain perovskites under extremely reducing conditions. Of course, these materials could be reduced deliberately to form a metal cermet, much as is now done by Westinghouse with a sintered NiO-ZrO_2 mixture to form the fuel cell anode. In the case of LaCoO_3 or LaNiO_3 , for example, a Co- or Ni- La_2O_3 cermet would form (see equation 24). This offers no advantages, however--indeed, it proffers disadvantages--and would be more costly than the technique presently used.

The potential for using the conducting perovskites as anodes or cathodes in the molten-carbonate fuel cell is more limited than in the solid-electrolyte fuel cell by the high probability for chemical reaction. As the molten carbonate is basic, basic and amphoteric metal oxides offer the best chance for compatibility. An alternate possibility is to use the oxide in the form of the final reaction-product, so that the likelihood of further reaction is reduced substantially. This is the rationale by which LiAlO_2 --the product of reaction of Al_2O_3 and the carbonate

melt--was chosen as the preferred tile matrix in the current molten-carbonate fuel cell program.

While a number of the conducting perovskites have been subjected to corrosion tests in the molten coal slag (as would be experienced by the electrodes in the MHD channel), there has been only a limited amount of compatibility testing with molten-carbonate melts. In one test, a doped chromite of composition $\text{La}_{0.84}\text{Ca}_{0.16}\text{CrO}_3$ was found to react with molten K_2CO_3 at 925°C .¹⁵⁰ The apparent reaction was between the carbonate and the chromite portion of the oxide (La_2O_3 and CaO do not form stable oxy-anion compounds)

Thus, perovskite chromites do not appear to be compatible with the molten-carbonate melt. Even if corrosion is not a problem, the higher electrical resistivity of the conducting perovskites makes them uncompetitive with the nickel and cobalt anodes (and alloys thereof) currently used.

In addition to selective doping of LaCrO_3 to improve its properties for MHD-electrode use, formation of LaCrO_3 cermets has also been explored. Addition of chromium to LaCrO_3 increases the electrical conductivity and the resulting cermet has a high resistance to oxidation. Representative electrical resistivity data for Cr-LaCrO_3 cermets are shown in Table 29. Cermets of this type would offer no advantage over the less expensive and more easily fabricated Ni-ZrO_2 cermet for anode use in the solid-

TABLE 29.--Electrical resistivities of LaCrO_3 -Cr cermets at 1027°C ¹³⁸

Cr Content of Cr-LaCrO_3 Cermet, w/o	Electrical (d-c.) Resistivity, $\Omega\text{-cm}$
0	1.0
20	1.5×10^{-2}
30	4.1×10^{-4}
40	1.3×10^{-4}
50	1.0×10^{-4}
60	2.8×10^{-5}
70	1.9×10^{-5}
80	1.6×10^{-5}

electrolyte fuel cell, or over the nickel or cobalt plaques in the molten-carbonate fuel cell.

The rare-earth nickelates and cobaltates of Table 28 which do not appear suitable for use as anodes in the solid-oxide fuel cell perform quite well as cathodes. Brown, Boveri, and Cie have reported success in using plasma-sprayed cathodes of Bi-doped LaNiO_3 in cells operating at 1000°C for over four years.⁴⁸ Plasma-sprayed Sr-doped LaMnO_3 and LaCoO_3 also are effective air electrodes. While PrCoO_3 shows a high electronic conductivity, it tends to scale from the electrolyte surface, most likely because of the incompatibility in the coefficients of thermal expansion of the two materials.

Even though the rare-earth cobaltates, nickelates, and manganates have adequate electrical conductivity for use as cathode materials, their thermal expansion characteristics are not compatible with that of the Y_2O_3 -stabilized ZrO_2 electrolyte, which has a lower α . These materials would appear promising candidates for the cathode in the molten-carbonate fuel cell (where thermal expansion properties are not as critical), provided they are not reactive with the melt. Increasing the electronic component of conductivity of these materials would make them even more attractive as cathode materials. This area of research merits further attention.

The Sr-doped, Cr-substituted YFeO_3 (Table 28) has electrical and thermal expansion properties which make it promising as a possible cathode material for the solid-oxide fuel cell using a

ZrO₂ electrolyte. No tests of this nature have been reported yet, however. One area of concern is the long-term chemical compatibility of the ZrO₂ and ferrite. The high mobility of Fe⁺³ could result in degradation of cell performance as a result of increased interfacial resistance caused by Fe⁺³ diffusion. A diffusion coefficient of iron, D_{Fe}, in Fe₃O₄ of $8.3 \times 10^{-11} \text{ cm}^2/\text{sec}$ at 1027°C has been reported at a P_{O₂} of 10⁻¹⁰ atm, increasing to $3.6 \times 10^{-9} \text{ cm}^2/\text{sec}$ at a P_{O₂} of 10⁻⁶ atm.¹⁵¹

The two oxides (non-perovskites) which have received the most attention at Westinghouse for cathodes in the solid-oxide fuel cell are Sb-doped SnO₂ and Sn-doped In₂O₃.¹⁵² The electrical and thermal expansion properties of these oxides are compared in Table 30. The severe thermal expansion mismatch of the Sb-doped SnO₂ made its use as cathode material impractical, even though it has a high electrical conductivity. Sn-doped In₂O₃ has a higher conductivity and a value of α which is more compatible with the ZrO₂ electrolyte. It has been successfully tested as a cathode in the solid-oxide fuel cells at 1000°C for 1100 hours.¹⁵²

While the Sn-doped In₂O₃ is a better conductor than the rare-earth nickelates, cobaltates, and manganates and has much better thermal expansion properties, problems can result when it is used alone as the cathode. Because it is an almost purely electronic conductor, it must be porous to allow rapid mass transfer at the three-phase interface (air, cathode, and electrolyte).^{154,155} At high current densities, oxygen diffusion through the porous film can become the rate-limiting step in the electrochemical process,

TABLE 30.--Electrical conductivity and thermal-expansion properties of Doped SnO_2 and In_2O_3 at 1000°C

<u>Oxide</u>	<u>Form</u>	<u>Coefficient of Thermal Expansion (α), $10^{-6}/^\circ\text{C}$</u>	<u>Electrical (d-c) Resistivity, $\Omega\text{-cm}$</u>	<u>References</u>
SnO_2 -3w/o Sb_2O_5^*	CVD Film	5.0	1.3×10^{-3}	4,65
In_2O_3 -2.4w/o SnO_2	Sintered bar	8.95	1.5×10^{-3}	65
$(\text{In}_2\text{O}_3$ -2.4w/o $\text{SnO}_2)$ + 2w/o kaolin ⁺	Sintered bar	9.23	-	65
In_2O_3 -2.4w/o SnO_2	CVD film	-	0.6×10^{-3}	65

* Sb_2O_4 is the actual stable SbO_x phase under firing conditions.

+ Kaolin added as a sintering aid.¹⁵³

resulting in severe electrode polarization. By incorporation of a highly-conducting perovskite (e.g., LaNiO_3 , PrCoO_3 , etc.) into the In_2O_3 cathode structure, however, the electrochemical reduction of oxygen can take place at the two-phase interface between the air and the cathode, because the mixed conductivity of the perovskite phase now permits oxide-ion mobility.

The development of a better, mixed-conducting cathode material based on perovskite-type oxides merits further research for improving the electron and mass-transfer processes during oxygen reduction, thereby reducing polarization losses.

2. Spinel

A number of the spinel oxides have been studied for use as MHD electrodes. The physical properties of these materials are presented in Table 31. In general, the spinels have considerably lower electrical resistivities and coefficients of thermal expansion than perovskites.¹³³

A number of the spinels have electrical conductivities high enough for use as interconnector material in the high-temperature solid-oxide fuel cell. The bulk of the spinels, however, are mixed conductors, which would predicate against their use for this purpose. The coefficients of thermal expansion also are less than that for the ZrO_2 electrolyte. Only CoCr_2O_4 of the spinels of Table 31 has been studied as a possible interconnector, and that was years ago before the improved perovskites were developed.¹⁵⁶ As might be expected, the results were not encouraging.

TABLE 31.--Select physical properties of spinels

Oxide	Coefficient of Thermal Expansion (α), 10 ⁻⁶ /°C*	Electrical (d-c) Resistivity, Ω-cm	Temp., °C	-Log P _{O₂} (atm)	References
CoCr ₂ O ₄ (48% T.D.) [†]	7.28 (25°-1,000°C)	22	1,000	0.7 ⁺	133,156
		0.002	1,000	14	156
CoCr ₂ O ₄ -1 m/o V(64% T.D.)	-	15	1,000	0.7	156
CoCr ₂ O ₄ -2 m/o V(70% T.D.)	-	10	1,000	0.7	156
CoCr ₂ O ₄ -2 m/o Mn	-	6	1,000	0.7	156
		50	1,000	14	156
NiAl ₂ O ₄ -15 m/o Fe ₃ O ₄ (87% T.D.)	-	17;7.7	727;1,000	0.7	157
		12;3.2	727;1,000	3-5.3	157
Fe ₃ O ₄	-	0.0054	727-1,000	?	158
		0.004	1,227	4	159
Fe ₃ O ₄ -29.5 m/o Co ₃ O ₄		2.6;0.14	727;1,000	3-5.3	160
MgCr ₂ O ₄	7.08 (25°-1,000°C)	5;0;3.0	727;1,000	0.7-5.2	133,161,162
MgCr ₂ O ₄ -20 m/o Fe ₃ O ₄	-	24 ;4.3	727;1,000	3-5.2	160
MgCr ₂ O ₄ -33 m/o Fe ₃ O ₄	-	13 ;1.0	727;1,000	3-5.2	160
MgAl ₂ O ₄ -10 m/o Fe ₃ O ₄ (82.7% T.D.)	-	555 ;143	727;1,000	0.7	163
		400 ;115	727;1,000	3	163
		263 ;103	727;1,000	5.3	163
MgAl ₂ O ₄ -15 m/o Fe ₃ O ₄ (80% T.D.)		204 ;50	727;1,000	0.7-3	163
		250 ;71	727;1,000	5.3	163
MgAl ₂ O ₄ -20 m/o Fe ₃ O ₄	-	19	1,000	3-5.2	160
MgAl ₂ O ₄ -25 m/o Fe ₃ O ₄	9.7 (100°-1400°C)	26	1,000	2-5.2	160
		5.6;1.7	600;1,000	0.7	141
		1.6	1,000	3-5.2	141

TABLE 31.--Select physical properties of spinels (Cont.)

Oxide	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}\text{C}^*$	Electrical (d-c) Resistivity, $\Omega\text{-cm}$	Temp., $^{\circ}\text{C}$	-Log P_{O_2} (atm)	References
(MgAl_2O_4 -25 m/o Fe_3O_4) + 40 w/o Cr	-	0.0032	727-1,000	0.7 (?)	164
FeAl_2O_4 -8.3 m/o MnAl_2O_4	-	19 ; 3.1	727; 1,000	0.7	163
		4.3 ; 1.4	727; 1,000	5.3	163
FeAl_2O_4 -25 m/o Fe_3O_4	9.0 (100°-1400°C)	1.0 ; 0.22	600; 1,000	0.7	141
		0.24; 0.05	600; 1,000	3-5.2	141
FeAl_2O_4 - 27 m/o Fe_3O_4	-	0.081	1,227	8	145
FeAl_2O_4 -75.5 m/o Fe_3O_4	-	0.0081	1,227	8	145

* In air.

† T.D = theoretical density.

+ Air.

The hercynite (FeAl_2O_4) spinels have the lowest electrical resistivities, but are limited in their stability under varying reducing conditions. The resistivities of these materials show a strong P_{O_2} dependency. At low values of P_{O_2} , reduction of Fe^{+3} to Fe^{+2} increases the concentration of current carriers via electron "hopping" between the two oxidation states of iron. The equilibrium P_{O_2} for the various oxides of iron are listed in Table 32 for temperatures of 1300 and 900K.

At a P_{O_2} of 10^{-16} to 10^{-18} atm at the anode of a fuel cell operating at 1300K Fe_3O_4 would not be stable toward reduction to Fe. This would rule out the use of Fe_3O_4 -containing mixtures as possible fuel electrodes in the solid-electrolyte fuel cell. In comparison at 900K Fe_3O_4 would be the thermodynamically stable phase which, in theory, would allow hercynite- Fe_3O_4 mixtures to be used as anodes in the molten-carbonate fuel cell. Even if there were no chemical compatibility problems, it does not appear likely that such materials would be considered seriously for use as fuel electrodes in such cells, as the electrical resistivities are at least two orders of magnitude greater than the nickel and cobalt anodes currently used.

While several of the Fe_3O_4 -containing oxides have low electrical resistivities under reducing conditions, their much higher values under more oxidizing conditions precludes their consideration as possible air electrodes for high-temperature fuel cells. The thermodynamically-stable oxide of iron in air at 900 and 1300K is Fe_2O_3 , which is a poor electronic conductor.

TABLE 32.--Equilibrium P_{O_2} for iron oxide mixtures*

	Temp., K	-Log P_{O_2} (atm)
Fe-Fe _{0.95} O	1300	15.1
	900	23.9
Fe _{0.95} O-Fe ₃ O ₄	1300	13.1
	900	23.6
Fe ₃ O ₄ -Fe ₂ O ₃	1300	1.48
	900	13.3

* Thermodynamic data from Reference 61 used for calculation purposes.

In short, none of the spinels of Table 31 appear to offer any promise for possible use in the solid-electrolyte or molten-carbonate fuel cell when compared to more suitable, alternate materials.

3. ZrO_2 -Based Oxides

In addition to the perovskites, ZrO_2 -based oxides also have received considerable attention for use as MHD electrodes because of high-temperature stability of ZrO_2 . However, since it is an ionic conductor, doping with various rare-earth oxides (mainly CeO_2) is necessary to impart the desired electronic conductivity and to avoid electrolysis problems. The physical properties of ZrO_2 -based oxide systems examined for MHD electrodes are presented in Table 33.

Compared to the perovskites and spinels, the ZrO_2 -based oxides have electrical resistivities which are considerably higher. These materials also exhibit mixed conduction, which is dependent upon the P_{O_2} of the surrounding atmosphere. In many cases, the ionic transport numbers vary considerably with temperature.¹⁶² Except for Y_2O_3 -doped ZrO_2 --the preferred solid electrolyte for high-temperature fuel cell use--the oxides of Table 33 do not appear to have suitable application in either the solid-electrolyte or the molten-carbonate fuel cell. The electrical and thermal expansion properties are not compatible with the requirements of the electrode or interconnector.

III. MHD INSULATOR MATERIALS

A number of materials have been examined for use as interelectrode insulators in the MHD channel. Generally, they have been the refractory oxides or oxide composites. Because they are insula-

TABLE 33.--Select physical properties of ZrO_2 -based oxide systems

Oxide	Coefficient of Thermal Expansion (α), $10^{-6}/^{\circ}C^*$	Electrical (d-c) Resistivity, Ω -cm	Temp., $^{\circ}C$	-Log P_{O_2} (atm)	References
ZrO_2 -12 m/o Y_2O_3	10.9 (25°-1,000°C)	17	1,000	0.7 [†]	4,165
		185	727	0.7	165
		17	1,000	6	165
		161	727	6	165
ZrO_2 -42 m/o $PrO_{1.83}$	-	~ 1	1,400	0.7	166
ZrO_2 -63 m/o $PrO_{1.83}$	-	~ 1	1,400	0.7	166
ZrO_2 -18 m/o CeO_2	11.5 (100°-1,400°C)	670	1,000	0.7	165,167
		5.3×10^3	727	0.7	165,167
		330	1,000	6	165,167
		2.5×10^3	727	6	165,167
ZrO_2 -30 m/o CeO_2	-	100	1,000	0.7	166
ZrO_2 -50 m/o CeO_2	12.2 (100°-1,400°C)	143	1,000	0.7	165,167
		10^4	727	0.7	165,167
		42	1,000	6	165,167
		910	727	6	165,167
ZrO_2 -75 m/o CeO_2	13.2 (100°-1,400°C)	26	1,000	0.7	165,167
		10^3	727	0.7	165,167
		5	1,000	6	165,167
		110	727	6	165,167
ZrO_2 -78 m/o CeO_2 - 2 m/o Ta_2O_5	13.6 (100°-1,400°C)	7	1,000	0.7	165,167

TABLE 33.--Select physical properties of ZrO_2 -based oxide systems (Continued)

Oxide	Coefficient of Thermal Expansion (α), 10 ⁻⁶ /°C*	Electrical (d-c) Resistivity, Ω-cm	Temp., °C	-Log P_{O_2} (atm)	References
-	-	450	727	0.7	165,167
-	-	12	1,000	6	165,167
-	-	77	727	6	165,167
ZrO_2 -12 m/o CeO_2 -3 m/o Y_2O_3	-	23	1,000	0.7	166
-	-	250	727	0.7	166
ZrO_2 -10 m/o La_2O_3 -10 m/o CeO_2	-	320	1,027	0.7	138
ZrO_2 -20 m/o La_2O_3 -10 m/o CeO_2	-	320	1,027	0.7	138
ZrO_2 -10 m/o La_2O_3 -20 m/o CeO_2	-	100	1,027	0.7	138
ZrO_2 - 5 m/o La_2O_3 -15 m/o CeO_2	-	79	1,027	0.7	138
ZrO_2 -10 m/o Nd_2O_3 -10 m/o CeO_2	-	28	1,027	0.7	138
ZrO_2 -10 m/o Nd_2O_3 -20 m/o CeO_2	-	48	1,027	0.7	138
ZrO_2 -20 m/o Nd_2O_3 -20 m/o CeO_2	-	63	1,027	0.7	138

* In air

+ Air

tors, these materials would have no application as active components in the solid-electrolyte fuel cell. They would have potential use, however, as tile candidates in the molten-carbonate fuel cell. A listing of materials used for considered as MHD electrode insulators is presented in Table 34.

All these materials have melting points (or dissociation temperatures, for the nitrides) above 1500°C; therefore, no problems are anticipated in their potential use as tiles in the molten-carbonate fuel cell at 600° to 750°C. The electrical resistivities at 1000°C are more than adequate for tile use, also being generally greater than $10^3 \Omega\text{-cm}$. The primary area of concern regarding the suitability of the materials of Table 34 for tile use is their chemical and electrochemical compatibility with the carbonate melt.

Both BN and Si_3N_4 suffer from low resistance to moisture, which would reduce their usefulness as tiles at the fuel electrode side. Over long periods of cell operation, oxidation of Si_3N_4 could occur slowly at the cathode side of the fuel cell. This oxidation would be accelerated by the fluxing action of the basic carbonate solution. These potential problems appear to rule out the use of BN and Si_3N_4 as tiles. SiO_2 -containing materials such as SiAlON , $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and $2\text{MgO} \cdot 2\text{SiO}_2$ do not appear suitable for the use, as well, because of the reactivity of the SiO_2 portion of these ceramics with the molten carbonate to form silicate:

MgO has been used in the past in sintered form as tile material and in powdered form to form a paste for containment of the carbon-

TABLE 34.--Materials used or considered for MHD electrode insulators

<u>Material</u>	<u>Reference</u>
<u>Nitrides</u>	
BN	2,168,169
Si_3N_4	2,138
SiAlON	1,162
<u>Perovskites</u>	
SrZrO_3	170
CaZrO_3	2
$\text{Sr}_{0.97}\text{La}_{0.02}\text{ZrO}_3$	170
SrHfO_3	2
CaHfO_3	2
LaAlO_3	171
SrZrO_3 -14 m/o CeO_2	137
SrZrO_3 - 6 m/o SrTiO_3 -1.5 m/o Ta_2O_5	137
<u>Spinel</u> s	
MgAl_2O_4	172,173
<u>Other Oxides</u>	
Al_2O_3	2
MgO	2,165
ZrO_2	2
ThO_2	2
$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1
$2\text{MgO} \cdot 2\text{SiO}_2$	1
CeO_2 -82 m/o HfO_2	174

ate electrolyte.⁶⁹ The MgO was not sufficiently inert, however, for long cell lifetimes. Work at the National Bureau of Standards has shown that MgO forms a eutectic with K_2CO_3 at 2 m/o and $896^\circ C$.¹³⁷

$MgAl_2O_4$ spinel (MgO combined with Al_2O_3) has shown good resistance to molten coal slag-seed mixtures.¹⁷⁵ $MgAl_2O_4$ recently was examined by General Electric Company as a possible tile material in part of its molten-carbonate research program. Powdered $MgAl_2O_4$ appeared to react with a melt of 62 m/o Li_2CO_3 - K_2CO_3 at $640^\circ C$ in a CO_2 -enriched air atmosphere after two hours. The following reaction was presumed to occur:

This was confirmed by X-ray diffraction analysis of the sample afterward, which showed the presence of $LiAlO_2$ and the absence of $MgAl_2O_4$.

These results are somewhat surprising, as the calculated free energy of reaction for equation 27 is $+21,608$ cal/mole $MgAl_2O_4$ at $900K$.⁶¹ This corresponds to an equilibrium constant of only 5.65×10^{-6} , which approximated the P_{O_2} (in atm) for this reaction. The P_{O_2} was not specified for the test, but was certainly greater than the above value, which should have prevented reaction (26) from taking place. As no lines of MgO were reported in the diffraction pattern, perhaps the reaction which actually occurred was not the one written in equation (27); this could explain the apparent discrepancy between the observed and predicted behavior of $MgAl_2O_4$ with the carbonate melt. Other alkaline-earth spinels of Al_2O_3 may be more corrosion resistant to the carbonate melt.

Similar corrosion tests in the $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic are currently underway at MERDI, with nonstoichiometric MgAl_2O_4 spinels as well as other candidate tile materials as part of the current fuel cell contract. In the MERDI tests, however, high-density crucibles of the test materials are being used initially in an atmosphere of CO_2 at a temperature of 727°C . (Subsequent tests with powdered samples are planned also.) Preliminary tests with crucibles of pure MgO , 65 m/o $\text{MgO-Al}_2\text{O}_3$, 35 m/o $\text{MgO-Al}_2\text{O}_3$, and MgAl_2O_4 , indicate that the corrosion rate is lowest when nonstoichiometric MgAl_2O_4 spinels are employed; i.e., when either excess Al_2O_3 or MgO is present.⁸⁰ The disagreement between test results by General Electric and MERDI on the corrosion behavior of MgAl_2O_4 is probably a result of the high-density samples used in the latter case. Finely divided Al_2O_3 , for example, is quite reactive to molten carbonate while high-density Al_2O_3 is relatively inert.

ZrO_2 has been examined as a support material for the molten-carbonate fuel cell, but was found to exhibit a chemical stability which was dependent upon the P_{O_2} . This could cause problems during actual fuel cell operation.⁶⁹

While data for the chemical compatibility of ThO_2 with molten carbonates do not appear to have been published, its radioactivity would make it less than desirable for tile use.

No corrosion data on molten carbonates was found for the remaining oxides of Table 34. The hafnates and zirconates, however, would appear to be promising test candidates for electrolyte-support materials, as they would be the final products of reaction between

the parent oxides (HfO_2 and ZrO_2) and the carbonate melt. This is analogous to the present use of LiAlO_2 for tiles in the molten-carbonate cell by reaction of Al_2O_3 and Li_2CO_3 .⁶⁴ Once the LiAlO_2 has formed, further reaction does not occur. Thus, molten-carbonate corrosion studies of the alkaline-earth zirconates and hafnates appear merited.

The preferred molten-carbonate electrolyte is an eutectic mixture of 62 m/o Li_2CO_3 and 38 m/o K_2CO_3 , with a melting point of 491°C .⁶⁴ There is the possibility of metathesis reactions taking place between zirconates, for example, and the components of the molten-carbonate melt:

where M is an alkaline-earth metal. At fuel cell temperatures of 670°C , the alkaline-earth carbonate would begin to decompose

so that a mixture of alkaline-earth oxide and alkali zirconate would result. There is considerable question, however, as to the stability and solubility of alkali zirconates in the molten-carbonate environment. If stable, solid reaction products are formed, the rate of corrosion may slow or stop after a short period of time, so that even slightly reactive oxides may be suitable for electrolyte-support use.

TiO_2 , like the other dioxides of the titanium family, forms oxy-anion complexes with basic oxides. The titanates differ from the zirconates and hafnates, however, in the ease in which lower-valent titanium is formed. ZrO_2 and HfO_2 do not form stable lower oxides under normal circumstances. Formation of Ti^{+3} under reducing con-

ditions would introduce unwanted electronic conductivity into the oxide by electron exchange between Ti^{+3} and Ti^{+4} in the crystal lattice. Reduced $SrTiO_3$, for example, is semiconducting.¹⁷⁶

Thus, for good insulating properties under the P_{O_2} gradient to which the tile is exposed during normal fuel cell operation, oxides which readily assume multivalent oxidation states should be avoided. This would include oxides of Ti, V, Nb, Cr, Mo, W, Mn, and Sn--all of which form oxyanion compounds. Except for the titanates, niobates, and some stannates, these oxyanion compounds have limited thermal stability as well.

Calculation of the equilibrium P_{O_2} for the Ti_2O_3 - TiO_2 couple yields a value of 2.1×10^{-34} atm at 900K.⁶¹ Similarly, P_{O_2} for the NbO_2 - Nb_2O_5 couple is found to be 3.4×10^{-29} atm. This would indicate that the lower oxides of titanium and niobium would not be stable at the P_{O_2} of 10^{-16} atm expected at the fuel electrode. However, the probability of the formation of oxygen vacancies under reducing conditions is high, and this likewise would reduce the insulating qualities of these materials and make them less suitable as candidates for tiles in the molten carbonate fuel cell.

In comparison, tantalum does not form lower oxides, even under severely reducing conditions. Thus, alkaline-earth and possibly alkali tantalates may insulate sufficiently to merit consideration as electrolyte-containment material.

Other perovskites potentially suitable for tile use are the rare-earth aluminates. As with the zirconates and hafnates, there is the possibility of metathesis reactions occurring

Lacking thermodynamic data for LaAlO_3 , however, it is not possible to calculate if the ΔG_f^0 of reaction is favorable or not. Thus, direct experimental testing of these materials is necessary to determine compatibility with molten carbonates.

It is important to note that the rate of corrosion of ceramics by molten carbonates can be accelerated greatly in the presence of an applied d-c field. A material which may be apparently inert to the molten carbonate under emf-free conditions can experience catastrophic failure in the presence of an imposed emf.¹⁷⁷ The corrosion rate of MgO in molten K_2SO_4 , for example, is increased by two orders of magnitude in the presence of an applied d-c field.¹⁷⁸ Thus, any realistic screening program for material compatibility with the molten-carbonate electrolyte should incorporate testing in the presence of an applied emf of magnitude comparable to that expected under typical fuel cell operating conditions.

SUMMARY AND CONCLUSIONS

I. SOLID-ELECTROLYTE FUEL CELL

A. Electrolyte

A number of oxide-ion conductors were evaluated as solid electrolyte to establish a reference point for comparison of other compatible materials for ancillary components in the high-temperature solid-oxide fuel cell. It was concluded that ZrO_2 -10 m/o Y_2O_3 is the preferred electrolyte for use in the fuel cell at a temperature of 1000°C , as it has been studied the most extensively for this application and its long-term behavior under fuel cell conditions is defined more completely.

A number of other oxides, such as doped- CeO_2 and substituted perovskites (e.g., aluminates, titanates, and bismuthates) show considerable promise for use as solid electrolytes at temperatures as low as 700°C . Additional research is needed, however, before these mixed conductors can equal Y_2O_3 -stabilized ZrO_2 in electrochemical performance. At such time, the MHD literature can be re-evaluated to identify materials compatible for use with these improved oxides.

B. Interconnector

A variety of MHD-electrode materials were examined for possible use as interconnectors in the solid-electrolyte fuel cell. The carbides, nitrides, silicides, and borides are not suitable because of their poor oxidation resistance at the air side of the interconnector.

The bulk of the spinels examined are mixed conductors and exhibit a strong P_{O_2} dependence in electrical conductivity, which makes them

unsuitable for interconnector use. Only CoCr_2O_4 has been studied as an interconnector, and its performance was not entirely satisfactory. The electrical properties of ZrO_2 -based oxides also do not meet the interconnector requirements. Of the perovskites, Mg- and Sr-doped $\text{LaCr}_{1-x}\text{Al}_x\text{O}_3$ have the best overall physical properties for use as interconnectors. Westinghouse presently is using the composition $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ as the interconnector in their thin-film solid-electrolyte battery, because its coefficient of thermal expansion is compatible with that of the Y_2O_3 -stabilized ZrO_2 electrolyte and its electrical properties are not significantly temperature and P_{O_2} dependent.

C. Cathode

As was noted for the interconnector, carbides, nitrides, silicides, and borides are not suitable for use as cathodes because of the incompatible oxidizing environment. However, a number of the rare-earth nickelates, cobaltates, and manganates, have been operated successfully as air electrodes in solid-electrolyte fuel cells. These materials have adequate electrical conductivity, but their thermal expansion properties do not match those of Y_2O_3 -stabilized ZrO_2 . These perovskite mixed-conductors are best used in the solid-electrolyte fuel cell by incorporation into the air electrode to increase oxygen ion mobility and thus reduce cathode polarization.

Sr-doped, Cr-substituted YFeO_3 has electrical and thermal expansion properties which appear promising as a potential cathode material. The expected high mobility of iron, however, may pose chemical compatibility problems with the electrolyte of the fuel cell.

over long periods of operation.

None of the spinels and ZrO_2 -based oxides examined appear suitable for use as cathodes when compared to the current choice of Sn-doped In_2O_3 .

D. Anode

Metals and non-oxide ceramics appear to have the best promise for use in the solid-electrolyte fuel cell as anodes.

1. Metals

Of the metals used for MHD electrodes, nickel and cobalt and perhaps some of their alloys would be suitable for use as anodes in the solid-electrolyte fuel cell. These materials are being used already for this application in the form of ZrO_2 -metal cer-mets.

2. Non-Oxide Ceramics

Table 35 lists the best non-oxide ceramics in each category for key materials properties (electrical conductivity, thermal expansion, and thermodynamic stability toward oxidation) for consideration as anode components in the solid-electrolyte fuel cell. No single compound in each category meets all of the key materials properties requirements necessary for optimum anode use. The non-oxide ceramics have the best potential for utilization in the form of composites or mixtures with other ceramics or metals (e.g., nickel). These materials optimally would be used to replace a portion of the ZrO_2 in the Ni- ZrO_2 cermet anode currently used in order to increase the electrical conductivity. The silicides offer the most promise, as they are generally better con-

TABLE 35.--Possible non-oxide ceramics for anode use in the solid electrolyte fuel cell as related to key materials properties

Highest Electrical Conductivity	Coefficient of Thermal Expansion Compatible with ZrO_2 Electrolyte	Thermodynamically Stable Toward Formation of Highest Oxide at 1300 K	Thermodynamically Stable Toward Formation of Lowest Stable Suboxide at 1300 K
WC, TaC	Cr_3C_2	None (high- CO_2 gas) [*] VC, WC (low- CO_2 gas) ⁺	None (high- CO_2 gas) NbC, WC (low- CO_2 gas)
Mo_2N , TiN	TiN, VN, NbN, Cr_2N	VN, V_2N	None
$NbSi_2$, $TaSi_2$, VSi_2 , $TiSi_2$	Ti_5Si_3 , TiSi, $TiSi_2$, V_5Si_3 , VSi_2 , $NbSi_2$, $TaSi_2$, Cr_3Si	V_2Si , Mo_5Si , Mo_3Si , Mo_3Si , W_5Si_3 , Fe_3Si , Ni_3Si , Ni_2Si	None
ZrB, ZrB_2 , HfB, HfB_2	ScB_2 , CrB_2	Mo_2B , W_2B , WB	Mo_2B , W_2B , WB

* Lurgi gasifier (See Table 10).

+ Combustion engineering gasifier (see Table 10).

ductors and a larger number meet the other two key anode requirements.

3. Oxide Ceramics

The oxide ceramics are not considered competitive with the non-oxide ceramics for anode use because their electrical resistivities are orders of magnitude greater.

II. MOLTEN-CARBONATE FUEL CELL

A. Cathode

The air electrode in the molten-carbonate fuel cell is excessively oxidizing for the possible use of carbides, nitrides, silicides, and borides. Perovskites, such as the rare-earth nickelates, cobaltates, and manganates offer promise in this area, however. Corrosion studies of these materials in molten carbonates first are necessary to ascertain chemical compatibility. Reduction in the ionic component of electrical conductivity by modification of the chemical composition then would be merited for the more promising materials. None of the spinels or ZrO_2 -based oxides evaluated have suitable electrical properties for use as cathodes.

B. Anode

Metals and non-oxide ceramics appear to have the best promise for use in the molten-carbonate fuel cell as anodes.

1. Metals

Of the metals used for MHD electrodes, nickel and cobalt and perhaps some of their alloys would be suitable for use as anodes in the solid-electrolyte fuel cell, and are in use already for

this application.

2. Non-Oxide Ceramics

Except for the thermal-expansion data, the properties listed in Table 35 would be applicable equally for evaluating non-oxide ceramics for anode use in the molten-carbonate fuel cell, except that the temperature would be 900K instead of 1300K. The thermodynamic stability of non-oxide ceramics toward oxidation is increased at 900K, so more materials can be considered suitable for anode use. There is some question, however, as to the chemical compatibility of these materials with the molten carbonate. The carbides are supposedly soluble under vacuum and the nitrides, silicides, and borides also are said to be reactive, but perhaps only under oxidizing conditions. Corrosion information is needed under a fuel-gas environment before final conclusions can be drawn regarding the overall suitability of the non-oxide ceramics as anodes or anode constituents in molten-carbonate fuel cells.

3. Oxide Ceramics

The oxide ceramics are not considered likely candidates for anodes in the molten-carbonate fuel cell because of high electrical resistivities, relative to more suitable alternate materials (e.g., nickel), and chemical-compatibility problems with the electrolyte.

C. Electrolyte Support

The materials utilized as MHD interelectrode insulators are best suited at electrolyte-support tiles in the molten-carbonate fuel cell. Nitrides such as BN and Si_3N_4 suffer from low resistance to water

vapor, while SiO_2 -rich materials are reactive with the electrolyte. MgO has been used already as tile material but has an unacceptable solubility in the molten carbonate. Materials which appear promising for screening as tile materials include: alkaline-earth hafnates and zirconates, lithium and alkaline-earth tantalates, and rare-earth aluminates. The corresponding titanates and niobates are less promising candidates.

III. FUTURE RESEARCH

To evaluate properly the many promising MHD materials delineated in this report for utilization in high-temperature fuel cells will require an experimental research effort to verify the predicted suitability or nonsuitability.

A. Basic Information

There are major discrepancies in the published literature for resistivity data for many of the non-oxide ceramics. In a number of cases, there is little reliable information regarding electrical properties at elevated temperatures. It is felt that this is due, in large part, to poor characterization (e.g., analysis) of the samples.

Reliable data on the electrical resistivities of non-oxide ceramics at temperatures of 700° to 1000°C would be helpful in confirming the projected suitability of these materials for use in high-temperature fuel cells, based on presently available information. Factors which must be considered in such research are method of preparation (e.g., chemical synthesis, CVD, r-f sputtering), and stoichiometry, and purity of the prepared material. Such research could

serve to resolve existing discrepancies in published values of resistivity and would aid in the formulation of better candidate materials for use in high-temperature fuel cells.

B. Stability Toward Oxidation

Kinetic factors can prevent predicted oxidation reactions from occurring at significant or measurable rates. Reliable data are needed for the kinetics of oxidation and the stable products formed during oxidation under typical fuel-gas conditions of anode materials such as carbides, nitrides, silicides, borides, and their composites. A temperature range of 700° to 1000°C would be representative of both the molten-carbonate and solid-oxide high-temperature fuel cells.

C. Chemical and Electrochemical Compatibility

Any new promising material considered for incorporation into components of the high-temperature fuel cells must pass a chemical compatibility test. This is especially important for non-oxide ceramic cermets considered for anodes. At the anode, the possibility of alloy and intermetallic-compound formation should be examined as a function of composition, temperature, time, and the gas environment. The effect of such interaction upon the electrical and thermal properties of the cermet should be determined.

In the solid-oxide fuel cell, the main area of concern will be interaction of anode candidates at interfaces with other cell components. This interaction should also be studied under the influence of an applied d-c field, as electrotransport processes will be promoted under these conditions.

In the molten-carbonate fuel cell, the main area of concern will be the chemical reaction of anode and tile materials with the molten carbonate. Corrosion rate of candidate non-oxide ceramics (considered for anode use) under typical fuel cell conditions would be desirable, both in the absence and the presence of an applied emf. Similar information is needed for potential candidates based on oxy-anion compounds (e.g., zirconates).

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APPENDIX A

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