THE ELECTRICAL PROPERTIES OF SOLID OXIDE ELECTROLYTES

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Contents

I. Introduction

During the past 12 years, the potentialities of oxygen-ion conducting solid electrolytes have been realized. They have been used in the construction of galvanic cells for measuring the thermodynamic and kinetic properties of oxygen-bearing systems with high accuracies, in the development of oxygen meters for both gas mixtures and liquid metals, and in the investigation of high-temperature fuel cells.

The most successful oxide electrolytes have been those based on one of the group IVB oxides ZrO_2, HfO_2, CeO_2, or ThO_2 having additions of either an alkaline earth oxide, Sc_2O_3, Y_2O_3, or a rare earth oxide. When solid solutions are formed in these systems, the presence of the di- or trivalent cations on the cation sublattice causes the formation of anion vacancies to preserve electrical neutrality. The resulting increase in the oxygen ion conductivity can lead to exclusively ionic conduction within certain ranges of temperature and oxygen pressure.

Although the suitability of an oxide system as a solid electrolyte is determined, in part, by properties such as permeability, thermal shock resistance, and resistance to chemical attack by electrode materials, ionic conductivities and transport numbers are the most important criteria. Consequently, this review deals mainly with the electrical properties of these solid solutions and indicates where further research is required. Regions of solid solubility as well as applications are presented. In addition, solid solutions based on Sc_2O_3, Y_2O_3, or a rare earth oxide are considered. Finally, ionic transport numbers of pure refractory oxides are briefly discussed.

All compositions will be given in terms of mole % and all temperatures in °C.

A. PHASE STUDIES

For an oxide system to be a potential electrolyte, some solid solubility must be exhibited. In this regard, both electronegativity and cation field strength are important parameters. The latter is defined as Z/a^2, where Z is the valence of the cation and a is the separation distance between the cation and the anion. However, the presence or absence of significant solid solubility can usually be predicted from the similarity of the cation radii.

Table I

Ionic Radii, Å

	O^{2-}	Zr^{4+}	Hf^{4+}	Ce^{4+}	Th^{4+}	Sc^{3+}	Y^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}
Moebius[1]	1.27	0.92		1.07	1.15	0.91	1.07	1.21	1.18	1.16	1.15	1.13	1.11
Ahrens[2]	1.40	0.79	0.78	0.94	1.02	0.81	0.92	1.14	1.07	1.06	1.04	1.00	0.98
	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Moebius[1]	1.10	1.09	1.08	1.07	1.06	1.05	1.04	1.03		0.80	1.10	1.24	
Ahrens[2]	0.97	0.93	0.92	0.91	0.89	0.87	0.86	0.85	0.35	0.66	0.99	1.12	1.34

Stabilized ZrO_2, stabilized HfO_2, CeO_2, and ThO_2 have the cubic fluorite structure in which the cations have eightfold coordination. Moebius[1] has deduced a set of radii for the fluorite lattice based on a radius of 1.27 Å for the O^{2-} ion, determined from separation distances between them and the geometry of the fluorite structure. These are shown in Table I along with the radii given by Ahrens[2] for sixfold coordination. The latter should be more applicable for the rare earth oxide structures in which the cations are coordinated to either six or seven anions.

B. ELECTRICAL CONDUCTIVITY MEASUREMENTS

Unfortunately, conductivity measurements on ceramic oxide systems are beset with many difficulties. Because of their high melting points (>2500°), samples are usually prepared by pressing and sintering powders. Homogeneous specimens having the equilibrium phase or phases at the sintering temperature are often difficult to achieve. Even if equilibrium is attained, the phases may be metastable at the measuring temperatures since phase boundaries are often strongly dependent on temperature. Also, the polycrystalline samples will possess regions of varying conductivity such as grain boundaries, internal surfaces due to porosity, and particle-to-particle contacts. These low-conductivity regions may often be effectively "shorted-out" to yield the bulk conductivity by the use of high measuring frequencies.

Another difficulty, arising in the case of ionic conductors, is polarization at the electrodes. If O^{2-} ions arrive at an electrode and are unable to discharge because of the presence of concentration or activation polarization, their concentration will build up and impede the approach of additional carriers. This effect produces an additional resistance which is dependent on frequency, temperature, oxygen pressure, and the electrode material.[3-5] At sufficiently high frequencies (>1500 cps), only the bulk resistance and a double layer capacity will normally be measured.

Other factors to be considered include contact resistance, electrical pickup from furnace windings, thermoelectric effects, surface conduction, and thermionic emission from the sample, lead wires, or furnace walls. Surface conduction, often aided by the presence of adsorbed gases, and thermionic emission can be eliminated by the use of three-probe measurements whereby a guard ring is placed around one of the electrodes and maintained at the same potential as the guarded electrode. Contact resistance can be avoided with four-probe measurements whereby a current is passed through the ends of the sample and the potential drop across a fixed length is recorded. Two-probe measurements are useful because of their simplicity and can yield quite accurate data at relatively low temperatures (<1400°) provided that the problem of contact resistance can be overcome.

Of course, impurities can, and often do, influence electrical conductivities markedly. Nevertheless, their effect is minimal in oxide electrolytes possessing large defect concentrations.

C. TRANSPORT NUMBER DETERMINATIONS

Several techniques have been used to separate the ionic and electronic contributions to the conductivity. A sample can be electrolyzed between reversible metal or oxygen electrodes, and the quantity of matter transferred is measured and compared to the current passed. Alternately, electrolysis can be carried out with two or more oxide pellets in series and weight losses or gains are recorded. The latter method permits the cation and anion contributions to be separated.

The usual technique is the emf method. When two different oxygen potentials are imposed on the faces of a mixed conductor, then

$$\bar{t}_i = E_{meas}/E_{thermo} \qquad (1)$$

where $\bar{t}_i$ is the average ionic transport number between the oxygen potentials defined at the electrodes, E_{meas} is the measured emf, and E_{thermo} is the thermodynamic emf calculated for the case where t_i is 1. In the presence of electronic conductivity, open-circuit oxygen transfer occurs from the high-potential to the low-potential side. The electrodes may become polarized and the emf will drop below the true value. Consequently, this method is often only accurate when E_{thermo} is small and $\bar{t}_i > 0.9$.

Since the ionic defect concentration is controlled by composition, ionic conductivity will be independent of oxygen pressure. However, the number of electronic defects will be markedly influenced by small deviations from stoichiometry and, consequently, will be dependent on oxygen pressure. Therefore, transport numbers can be determined by analyzing curves of conductivity *vs.* oxygen pressure.

Partial conductivities can sometimes be measured *via* polarization techniques. One reversible electrode and one electrode blocking to either ions or electrons are used. A small dc voltage is applied which fixes the oxygen potential at the irreversible electrode, and the conductivity is measured as a function of time. If an ionic block is used, interference from gas-electrode reactions is hard to avoid, and the method becomes inaccurate for low electronic transport numbers.

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For fairly large ionic transport numbers, oxygen permeability measurements can be used providing that sufficiently dense material is available so that transport through pores does not interfere. The individual ionic contributions can be separated by measuring diffusion coefficients and calculating partial conductivities from the Nernst–Einstein relation. Also, if one cation is mobile relative to another, electrolysis at a high oxygen pressure will produce some compositional changes at the electrode–electrolyte interfaces.

II. ZrO_2–CaO Electrolytes

A. STABILIZATION OF ZrO_2

Both ZrO_2 and solid solutions based on ZrO_2 have been studied extensively, for ZrO_2 is an extremely important refractory. Below 1000°, it has a monoclinic structure and, above 1200°, a tetragonal structure. In addition, a cubic modification exists above 2300°, although considerable disagreement has arisen over this phase.[6,7] Nevertheless, ZrO_2 can be readily stabilized in the cubic form by the addition of many different metal oxides.

In 1929, Ruff and Ebert[8] postulated that an oxide could stabilize ZrO_2 if its cation radius was similar to that of Zr^{4+} and it had a cubic structure. Dietzel and Tober[9] included the requirement that the metal–oxygen bonds of the oxide must be more ionic than those of ZrO_2. More recently, Stöcker[10] considered the various oxides capable of stabilizing cubic ZrO_2 and reached the following conclusions: (a) the oxides have the general form MO_n ($n < 2$) and cause the formation of vacancies in the anion sublattice; (b) the solid solutions have a eutectoid temperature and the lower this temperature, the more stable they will be; (c) the cubic phase will be very stable if the cation of stabilizing oxide is strongly electropositive. For the fluorite structure to be stable, the ratio of the cation to the anion radius must be greater than 0.732. For ZrO_2, this ratio is 0.724 based on the radii recommended by Moebius.[1] Evidently, cations larger than Zr^{4+} must be used. However, this is not essential since the presence of anion vacancies tends to stabilize the fluorite phase. The required close-packed structure for the cations will be favored since the repulsion energy between the anions will be reduced.

B. ELECTROLYTE PREPARATION

A highly important, but often underestimated, part of investigations involving oxide electrolytes concerns the preparation of the solid solutions. A considerable amount of erroneous data has been reported concerning the phase diagrams and electrical properties of these refractory systems because of a failure to achieve equilibrium during the preparation of the samples. During solid-state reactions, equilibrium is often attained only with great difficulty. For instance, direct mixing of the oxides necessitates the use of very high sintering temperatures. Melting may introduce errors due to reactions with crucible materials or vaporization losses. The sintering temperature can be greatly reduced if the oxide powders are finely divided, intimately mixed, and very reactive. This situation can often be realized by evaporating a nitrate mixture to dryness or coprecipitating the required metal cations as hydroxides or oxalates.

Many solid solutions and compounds based on ZrO_2 have been formed at only 500–800° *via* hydroxide coprecipitation.[11,12] The amorphous precipitates were very reactive, and phases stable at high temperatures could be produced metastably. Solid solutions are formed during coprecipitation rather than during crystallization.[13,14] Submicron, reactive oxide powders have been prepared by the thermal decomposition of metal alkoxides.[15,16] Cubic ZrO_2 could be obtained at room temperature,[15] while fully stabilized solid solutions were formed at only 850°.[16] To avoid contamination, dense homogenous samples of stabilized ZrO_2 have been produced by induction melting without a crucible.[17,18] Finally, ZrO_2–CaO single crystals have been obtained by cooling slowly from a melt.[19]

C. PHASE BOUNDARIES OF THE SOLID SOLUTIONS

Since the pioneering work of Ruff, Ebert, and Stephan,[20] considerable disagreement has arisen concerning the phase

Table II

Phase Boundaries of Cubic ZrO_2–CaO Solid Solutions

Temp, °C	*Boundaries, % CaO*	*Ref*
1200	10 and 20	21
2000	16 and 29	22
1000	16 and 27	22
1800	7 and 24	9
1400	14 and 20	9
>2000	13 and 35	23
1500	5 and 30	24
1400	16 and 27	25
1500	10 and 20	26
1500	10 and 20–30	27
1400	12–13 and 20–21	28
1900	12 and 22	29
1800	12–13 and 20–21	30
1800	3 and 25	31
1000	13 and 18	31
1500	10 and 20	32
1000	13 and 20	32
1500	10 and 21	33
1400	10 and 19	34
1500	14 and 20	35
1400	11–12 and 19–20	36

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boundaries of the single-phase fluorite region. This is indicated in Table II where the relevant data are chronologically presented. Boundaries of 12 and 20% CaO seem to best represent the results. Dixon, *et al.*,[37] placed the lower limit at 12% CaO at 1700°, while monoclinic ZrO_2 and $CaZrO_3$ were obtserved in samples containing 9.4 and 20.5% CaO, respectively, which were sintered at 2050°.[34] Only 7 or 8% CaO is needed to stabilize cubic ZrO_2 near the melting point,[12,33] but the tetragonal solid solution precipitates readily at lower temperatures. The relatively good agreement for the upper limit at 20% CaO suggests the possibility of the compound $CaZr_4O_9$. Although the existence of this compound has been considered,[35,38] it has never been identified. The monoclinic $CaHf_4O_9$ compound exists below 1450°, but the existence of $CaZr_4O_9$ could not be affirmed.[39] Replacement of Hf^{4+} ions with Zr^{4+} ions in $CaHf_4O_9$ lowers the upper temperature limit at which the compound can exist. In the case of $CaZr_4O_9$, this temperature may be too low to permit its formation.[39]

D. STABILITY OF THE SOLID SOLUTIONS

During the reaction of ZrO_2 and CaO, the compound $CaZrO_3$ first forms and then reacts with excess ZrO_2.[40] Although the compound may begin to form around 800°, temperatures of 1400–1500° may be required to form the solid solution. If the compound is not completely removed during the firing operation, only partly stabilized ZrO_2 will result. The monoclinic-tetragonal transformation of ZrO_2 will then force CaO out of the cubic solid solution and the latter appears unstable.[41] The presence of impurities also significantly aids the decomposition process.[42–44] Undoubtedly, these factors have contributed to erroneous information concerning the instability of ZrO_2–CaO solid solutions.[42,45,46] Even partly stabilized ZrO_2 containing only 0.2% total impurities destabilized very little during thermal cycling.[47]

The question of stability can best be answered by considering the eutectoid temperature for this system below which the cubic phase is unstable. Eutectoid temperatures and compositions have been given as 850°,[12] 800° and 15% CaO,[31] and 1230° and 20% CaO.[35] Garvie[35] has suggested that the disagreement evident in Table II can, in part, be accounted for by the metastable existence of the cubic phase. Therefore, phase boundaries which are too wide will result from sintering at a high temperature and then annealing at lower temperatures. Consequently, he heated reactive oxides directly to 1300–1700° and then quenched them to room temperature. However, equilibrium may not be established at the lower temperatures for he has shown boundaries of only 16–17 and 20% CaO at 1300°. The eutectoid temperature of 1230° was obtained by an extrapolation which does not appear justified.[35] Roy, Miyabe, and Diness[31] catalyzed the reactions with high-temperature, high-pressure water to produce their phase diagram. They may have achieved the true equilibrium situation which could not be realized without a catalyst. There is additional evidence to support their low eutectoid temperature. Theoretical considerations indicate that CaO should be the most effective stabilizing oxide for ZrO_2.[12] Heating for 520 hr at 1200°,[22] 350 hr at 1200°,[32] 100 hr at 1180°,[48] 800 hr at 1100°,[22] 2000 hr at 815°,[22] and 3000 hr at 700° [32] did not destroy fully stabilized ZrO_2. If the eutectoid temperature were around 1200°, some decomposition might be expected upon annealing at 1000–1150°. Therefore, ZrO_2–CaO solid solutions are thermodynamically stable above about 900° and kinetically stable below this temperature. Even the very unstable ZrO_2–MgO solid solutions could not be decomposed at 815°.[22]

E. LATTICE PARAMETERS

Reported lattice parameters, taken either directly from tables or interpolated from graphs, are shown in Table III. To facilitate comparison, values for the 15% CaO composition are given whenever possible. A lattice parameter of 5.131 Å for this composition agrees with most of the results. The lattice parameter increases linearly with CaO content across the cubic phase field. The obviously low values[21,22,24,26,54] may partly be accounted for by incomplete solution of CaO into the fluorite phase.

F. IONIC CONDUCTIVITIES

Electrical conductivity data for ZrO_2–CaO electrolytes are chronologically presented in Table IV. The values were interpolated from graphs or calculated from equations of the form

$$\sigma = Ae^{-\Delta H/RT} \tag{2}$$

where A is approximately independent of temperature ($\text{ohm}^{-1}\ \text{cm}^{-1}$) and ΔH is the activation enthalpy (kcal/mol). The max-

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Table III

Lattice Parameters (Å) for ZrO_2–CaO Solid Solutions

Composition, % CaO				
10	*12*	*15*	*20*	*Ref*
		5.120	5.128	22
5.114		5.120	5.126	21
5.122		5.129	5.136	9
5.115		5.120	5.124	24
		5.129		49
5.091		5.106	5.121	26
		5.131		50, 51
5.126		5.131	5.136	27
	5.129	5.133	5.142	28, 30
		5.130		52
	5.127			29
		5.132[a]		53
		5.120		54
	5.124	5.130	5.138	33
5.125	5.128	5.133		34
	5.126	5.131	5.140	35
5.127	5.128	5.132	5.140	36
5.126		5.131		55

[a] 16% CaO.

imum ionic conductivities determined in the investigations where conductivity was studied as a function of composition are italicized. Again, to facilitate comparison, results for the 15% CaO composition are tabulated whenever possible.

Considering the difficulties associated with conductivity measurements which were discussed in section I.B, the agreement, especially among the more recent studies, is quite satisfactory. Relatively low sintering temperatures of only about 1500° may explain some of the low values,[21,27] while no explanation can be offered for the inconsistently high value.[58] Examination of Table IV reveals a conductivity maximum of about 5.5 × 10^{-2} ohm^{-1} cm^{-1} at 1000° and 12–13% CaO, which coincides with the minimum amount of CaO necessary to stabilize ZrO_2.[28,30,37,54,59,62–65] Several authors have found a maximum within the fluorite field.[27,34,57] The ionic conductivity for the 15% CaO composition is about 2.4 × 10^{-2} ohm^{-1} cm^{-1} at 1000°. Activation energies for the 12–13 and 15% CaO compositions are 25.2 and 29.0 kcal/mol, respectively.

In agreement with eq 2, Arrhenius plots have been linear from 200 to 2000°, indicating that oxygen-ion vacancy migration is controlling the conductivity over this entire temperature range. Slope changes at 550 and 850°[57] may have resulted from

Table IV

Ionic Conductivities (ohm^{-1} cm^{-1} × 10^2) of ZrO_2–CaO Electrolytes at 1000°[a]

Composition, % CaO						
10	*12*	*13*	*14*	*15*	*16*	*Ref*
				0.19 (27.9)		21
	0.40	*0.40*				23
	2.6 (14.1)					56
				1.6 (29.1)		50
				0.28 (25.7)		27
				1.0 (23.1)		57
				13.2 (29.3)[b]		58
		6.0 (25.6)		3.4 (27.0)	2.5 (29.1)	28
	6.7 (24.5)	4.6 (27.4)	4.2 (29.0)	2.1 (30.0)		37
				2.0		51, 52
	3.7 (22.1)[c]		2.7 (25.1)	2.0 (27.2)	1.7 (28.6)	59
4.1 (24.7)	2.1 (26.7)			1.0 (29.5)	0.72 (30.6)	29
0.71 (15.7)		*4.7 (25.1)*		1.9 (29.0)	1.4 (30.9)	30
					2.7	53
				0.5 (26.1)		60
				4.1 (29.5)		61
	5.9[c]			2.8		54
	2.8[c]					62
	4.2 (27.1)			2.1 (29.7)		63
	4.8 (24.9)	5.3 (26.5)[d]	*6.2 (28.0)*[d]	4.4 (29.5)	3.1 (31.0)	34
3.8 (25.3)				2.2 (28.9)		55

[a] Activation energies (kcal/mol) are in parentheses. When several compositions were studied, the maximum conductivity is italicized. [b] 14.3% CaO. [c] 12.5% CaO. [d] Single crystals.

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impurities or incompletely stabilized ZrO_2 since the oxides were directly mixed and fired at only 1550°. In samples containing 18 and 24% CaO, higher slopes were found above 1000°.[37] In the 24% CaO sample, precipitation of $CaZrO_3$ would deplete the solid solution of CaO and shift the conductivities to higher values. However, this should not occur for the 18% CaO composition. Other authors have observed slope changes at higher temperatures.[29,58] The reason for this is not readily apparent.

1. *Effect of Composition*

The anion vacancy model for these solid solutions has been confirmed *via* density[21,50] and X-ray intensity[28,66] measurements. Both the cations and the anion vacancies are randomly distributed over the available sites.[66] In addition, Diness and Roy[67] found the major defect to be cation interstitials in samples quenched from 1800° at 1000°/sec.

Across the cubic phase region, the conductivity decreases despite the increasing number of anion vacancies. Both log A[59] and ΔH[29,34,59] in eq 2 have been shown to increase linearly with the CaO content. Obviously, the oxygen ion mobility is decreasing markedly. Ionic mobility may be expressed as

$$\mu = \frac{\nu a^2 e G}{RT} e^{-\Delta H/RT} \tag{3}$$

where ν is the vibration frequency of the anions, a is the jump distance, and G includes the activation entropy and a geometric factor dependent on the lattice structure. An increase in ΔH would reduce the mobility. This increase could result from lattice distortion due to differences in the radii of the cations,[28,54,68] the presence of Ca^{2+} ion–anion vacancy complexes,[69,70] or vacancy clustering.[34] Also, defect interactions or clustering will tend to reduce the number of available current carriers below the expected level. Vacancy ordering[27,28,34,65,71,72] will reduce the anion mobility by decreasing G in eq 3.

Recently, Carter and Roth[34] found the maximum conductivity at 14% CaO which resulted from the opposing effects of A and ΔH in eq 2. These authors introduced a "cluster" model and a "zone" model to represent the variation of conductivity with composition. In the former, the defects were assumed to interact and form clusters, and A varied as x^n where x is the mole fraction of CaO and n is a constant related to the activation entropy of the complex. The best agreement with the data resulted from a value of 7 for n, suggesting that ion transport involves a network or other multiplicative process. Their "zone" model had A varying as $e^{-m(x'-x)^2}$ where m and x' are constants. Because of the similarity of this term to a Poisson distribution, they suggested an interpretation based on composition fluctuations in the disordered phase. Since x' equalled 0.226, conduction may take place preferentially along paths with an average composition near this value. This model was supported by dielectric loss data, since loss peaks moved to lower frequencies after annealing the samples.

2. *Effect of Grain Boundaries*

Tien[58] has demonstrated that specimens containing 16% CaO have higher conductivities and lower activation energies below 1000° after they are sintered at 1600° compared to 2000°. Nevertheless, errors introduced by the presence of grain boundaries are insignificant relative to the lack of reproducibility indicated in Table IV. Grain boundaries only occupy a small volume fraction and, indeed, Carter and Roth[34] obtained identical results for single and polycrystalline specimens after correcting for a 3–6% porosity in the latter. Of course, their high sintering temperature of 2000° would result in large grain sizes and diminish the influence of grain boundaries. Grain growth[73] as well as sintering[68,74] appear to be controlled by cation diffusion in these solid solutions.

G. ORDER–DISORDER TRANSFORMATION

A superstructure develops when ZrO_2–CaO solid solutions are annealed for long times at temperatures around 1000°.[19,28,34,54,65,75–77] The cations and anion vacancies become ordered and the lattice parameter increases to four times its original size.[28] Ordering occurs more readily in single crystals[31,76,78] and at high CaO concentrations.[28,34,65,69,71,77] It has a maximum rate at 1000°[34,78] and will not occur above 1250°[34,71,78] or below 650°.[34]

Both dielectric[34] and mechanical[69] relaxation measurements have been used to study the ordering process. Dielectric loss peaks increased and moved to lower frequencies during annealing. Carter and Roth[34] suggested that the solid solutions contain zones of ordered oxygen polyhedra at all temperatures which grow by cation migration around 1000°. These zones are atomically coherent with no discontinuities or phase boundaries between them and may grow to 600 Å in size. Wachtman and Corwin[69] observed that internal friction peaks decreased during annealing and postulated that the oxygen vacancies exist in several states of binding. The more complex defect clusters would grow at the expense of the simpler ones during ordering. In both studies, the losses could be attributed to the migration of oxygen ions.

Ordering does not appreciably affect the activation energies for conduction,[28,34,65,75] although ionic conductivities are markedly lowered. For example, during annealing at 1000°, decreases of 33,[28] 30,[65] and 50%[71] have been noted in samples containing from 18 to 20% CaO. The resistivity has been observed to obey both a parabolic rate law[34,78] and first-order kinetics;[65,72] *i.e.*, it is proportional to $t^{1/2}$ and e^{-t}, where t is time, respectively. As already mentioned, ordering tends to reduce G in eq 3. Defect clusters through which oxygen ions may be extremely mobile will be removed.

Ordering can influence conductivity measurements as evidenced by slope changes in Arrhenius plots between 1000 and 1200° for specimens containing between 16 and 20%

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CaO.[28,30,77] However, Carter and Roth[34] observed that some polycrystalline samples did not undergo any conductivity change or develop any additional diffraction peaks for annealing times of up to 3 months. Since cation diffusion, which controls the ordering transformation,[31,75] is quite slow (section II.H), slope changes would generally not be observed. Lastly, it should be noted that the long-term anneals used to study this transformation have not revealed the presence of either ZrO_2 or $CaZrO_3$, which offers further proof of the stability of the solid solutions discussed in section II.D.

H. TRANSPORT NUMBERS FOR CATIONS

Since Wagner[79] gave the correct explanation for the transport mechanism in stabilized ZrO_2, many attempts have been made to determine how close the anion transport number $t_{O^{2-}}$ is to 1.00. The radioactive tracers ^{95}Zr and ^{45}Ca and the stable isotope ^{18}O have been used to determine diffusion coefficients in ZrO_2–CaO solid solutions. The results of these investigations are summarized in Table V. The cation diffusion coefficients were extrapolated from higher temperatures for the purpose of comparison only. Such an extrapolation can distort the real situation at 1000° since diffusion along grain boundaries, free surfaces, and dislocations will have a greater influence at low temperatures.

Table V

Diffusion Coefficients in ZrO_2–CaO Solid Solutions

Composition, % CaO	*Ion*	*Diffusion coefficient at 1000°, cm²/sec*	*Activation energy, kcal/mol*	*Ref*
15	O^{2-}	3.7×10^{-8} [a]	30.4[a]	50
14.2	O^{2-}	7.9×10^{-8}	31.2	80
12, 16	Zr^{4+}	4.6×10^{-13} [b]	92.5	74
16	Ca^{2+}	2.8×10^{-13} [b]	100.2	74
15	Zr^{4+}	1.2×10^{-13} [c]	61.8	81
15	Ca^{2+}	4.4×10^{-14} [c]	98.8	81

[a] Taken from a graph; the equation gives values of 1.5×10^{-7} cm²/sec and 28.1 kcal/mol. [b] Extrapolated from 1700°. [c] Extrapolated from 1550°.

Anion diffusion coefficients are at least five to six orders of magnitude greater than cation diffusion coefficients at 1000°. The entire electrical conductivity can be accounted for by using anion diffusion coefficients in the Nernst–Einstein equation.[50,80] At higher temperatures, cation transport numbers will increase because of the high activation energies associated with cation migration. For instance, $t_{O^{2-}} = 0.99861$, $t_{Zr^{4+}} = 0.00024$, and $t_{Ca^{2+}} = 0.00115$ at 1800°.[81] Volchenkova and Pal'guev[27] measured cation transport numbers by a gravimetric method using three oxide plates in series and obtained values ranging from 0.01 to 0.001 at 1000° for samples containing 10–40% CaO. Finally, electrolysis at 1100° for 1875 hr at a current density of 21 mA/cm² revealed no measurable resistance change or apparent deterioration of the electrodes of a $ZrO_2 + 15\%$ CaO electrolyte.[82]

I. TRANSPORT NUMBERS FOR ELECTRONS

The high ionic transport number of ZrO_2–CaO solid solutions is readily apparent upon electrolysis in argon.[83, 84] The cathode becomes black and the electrolyte resistance decreases with time. Depending on the current density and temperature, either oxygen-deficient ZrO_2 or zirconium forms at the cathode. Also, electrical conductivities have been shown to be independent of oxygen pressure from 1 to 10^{-22} atm at 870°,[85] from 1 to 10^{-10} atm at 1427 and 1627°,[50] and from 1 to 10^{-12} atm at 1472°.[86] However, as a means of detecting small electronic contributions, this method is quite insensitive. For example, Baker and West[87] defined the onset of n-type conduction with emf measurements, but could not detect it from conductivity measurements at similar oxygen pressures.

Permeabilities of ZrO_2–CaO electrolytes to oxygen have been determined by several researchers.[88–90] At high oxygen pressures, the permeability varied as $P_{O_2}{}^{1/4}$ and, from its time dependence, a diffusion coefficient for oxygen of 2.4×10^{-8} cm²/sec at 1000° was calculated.[89] This value is lower than those shown in Table V since the permeation rate will be controlled by the species having the lower conductivity, in this instance electron holes. The oxygen pressure dependence is the expected one for the variation of the electron hole concentration.[85] These data[89] along with some conductivity data[37] have been analyzed by Heyne[91] who determined the transport number for electron holes as 5×10^{-4} at 1275° and 3×10^{-2} atm of oxygen.

Polarization measurements at constant currents indicated that the ionic transport number is 1 from 100 to 1100° at 10^{-9} atm of oxygen.[60] Using constant applied voltages, Patterson, Bogren, and Rapp[63] found that P_{Θ}, the oxygen pressure where $\sigma_i = \sigma_n$ or $t_i = 0.50$,[66] is $10^{-30.6}$ atm at 1000°. A value of $10^{-26.5}$ atm was determined by these authors from ac conductivity measurements using similar metal–metal oxide electrodes of Cu–Cu_2O, Ni–NiO, Cr–Cr_2O_3, Nb–NbO, and V–VO.

Most of the research dedicated to determining electronic transport numbers has involved emf measurements. For an oxygen pressure of 1 atm at the cathode and pressures of 0.2 and 10^{-17} atm at the anode, average electronic transport numbers of 0.002 and 0.006, respectively, were calculated.[82] Also, an electrolysis experiment indicated that the electronic contribution was less than 0.005 in oxygen for $ZrO_2 + 15\%$ CaO.[82] Pure ionic conduction has been demonstrated at temperatures as low as 600° with oxygen concentration cells.[34,92–94]

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Deviations from theoretical emf values below 600°[93] may have arisen owing to impurities in the electrolyte leading to extrinsic electronic conduction. Alternately, in the case of Pt electrodes, the formation of Pt oxides below 500° might interfere.[95] Deviations above 1150° of a cell having Ni–NiO and Fe–Fe_xO electrodes undoubtedly resulted from mixed potentials introduced by the argon atmosphere rather than electronic conductivity in the electrolyte.[61]

Emf measurements have also been used to establish the range of oxygen pressures where exclusively ionic conduction occurs. In 1933, Wagner[96] derived the relationship

$$E = \frac{RT}{4F} \int_{\ln P_{O_2}'}^{\ln P_{O_2}''} t_i \mathrm{d} \ln P_{O_2} \tag{4}$$

where t_i is the ionic transport number and P_{O_2}'' and P_{O_2}' are the oxygen pressures at the cathode and anode, respectively. Assuming that only ionic and n-type conductivity are present, then

$$t_i = \frac{1}{1 + (P_\Theta/P_{O_2})^{1/4}} \tag{5}$$

providing that $\sigma_n \propto P_{O_2}^{-1/4}$ [85] which implies that the mobility of the electrons is unaffected by their concentration. As mentioned previously, P_Θ is the oxygen pressure where $t_i = 0.50$. Substituting eq 5 into eq 4 and applying the condition that $P_{O_2}' \ll P_\Theta$ yield the result

$$PO = P_{O_2}''e^{-4EF/RT} \tag{6}$$

This relationship was first derived by Schmalzried.[66] Consequently, the parameter P_Θ may be determined by imposing an oxygen pressure at the anode which is at least two or three orders of magnitude lower than P_Θ. This was established by Schmalzried[66] with a Ca–CaO mixture. From eq 6, he found that $t_i = 0.50$ at an oxygen pressure of 10^{-24} atm and 1000° and, from eq 5, that $t_i = 0.98$ at 10^{-18} atm and 1000°. At 800°, t_i became 0.50 at 10^{-31} atm. A low oxygen pressure could also be achieved by coulometrically titrating oxygen out of the anode chamber. In this manner, values for P_Θ of 10^{-28} atm[97] and 10^{-23} atm[98] at 1000° have been determined. For all these studies, air was used as the reference electrode. In one case,[66] Ni–NiO was also used.

By comparing emf's for the cell NbO_2, $Nb_2O_{5-x}|ZrO_2–CaO|Fe$, Fe_xO with those measured for a similar cell with ThO_2-based electrolytes having ionic transport numbers of 1, Steele and Alcock[99] calculated a value of 10^{-23} atm for P_Θ at 1000°. Finally, Baker and West[87] established the onset of electronic conduction at 10^{-18} atm of oxygen at 1000° using H_2–H_2O electrodes. No definite transport number could be associated with this oxygen pressure.

All the aforementioned data are compared in Table VI. The discrepancies may, in part, be due to different electrolyte purities. Easily reduced impurity ions will aid the onset of n-type conductivity.[60,70] Also, emf measurements are subject to errors arising from polarization (section I.C). Both these effects produce misleadingly high electronic transport numbers. Consequently, the lower values in Table VI are to be preferred.

Table VI

Critical Oxygen Pressures for ZrO_2–CaO Electrolytes at 1000°

Log P_{O_2}		
t_i = 0.99	*t_i = 0.50*	*Ref*
−16[a]	−24	66
−15	−23	98, 99
−20	−28	97
−19[a]	−27[b]	63
−23[a]	−31[c]	63

[a] Calculated from eq 5. [b] From ac conductivity measurements. [c] From polarization measurements.

Thermodynamic investigations of stable oxide systems which have imposed low oxygen potentials on ZrO_2–CaO electrolytes have indirectly helped to establish the width of the oxygen pressure region in which the ionic transport number is approximately 1. The equilibrium oxygen pressures for some of these systems are listed in Table VII. Initially, Kiukkola and Wagner[85] demonstrated that these electrolytes could be used in contact with Fe–Fe_xO electrodes to obtain accurate thermodynamic data. Results obtained with Mo–MoO_2[101,102] and W–WO_2[102–105] electrodes were in satisfactory agreement with those from gas equilibrium measurements. In addition, successful studies with TaS_2–Ta_2O_5 (−16.4),[106] Nb_2O_4–Nb_2O_{5-x} (−16.9),[107] W–$CaWO_4$–CaO (−17.8),[108] Zn–ZnO (−17.9),[109] $UO_{2.00000}$ (−18.0),[110] and $TiO_{1.992}$ (−18.1)[111] electrodes have been reported. The numbers in parentheses are the logarithms of the equilibrium oxygen pressures at 1000°. In one case,[109] the data were extrapolated above 908°. Finally, although the cell Cr, $Cr_2O_3|ZrO_2–CaO|$air gave values for $\bar{t}_i$ (eq 1) of only

Table VII

Thermodynamic Data for Some Stable Metal Oxides at 1000°

System	*$\Delta G_f°$, kcal/mol of O_2*[100]	*Log P_{O_2}*
Fe–Fe_xO	−86.0	−14.8
Mo–MoO_2	−87.7	−15.0
W–WO_2	−91.9	−15.8
Cr–Cr_2O_3	−125.8	−21.6
Mn–MnO	−139.6	−24.0
Ta–Ta_2O_5	−143.4	−24.6
Nb–NbO	−146.4	−25.1

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0.97 at 1100° and 0.96 at 1200°,[112] excellent agreement with published values[100] for $\Delta G_f°$ of Cr_2O_3 has been obtained with galvanic cells incorporating ZrO_2–CaO electrolytes.[97,113]

Successful measurements at lower oxygen potentials have not been reported although a Mn–MnO electrode behaved adequately below 800°.[97] Electronic conductivity has been apparent when ZrO_2–CaO electrolytes contacted Mn–MnO[114] and Nb–NbO[115] electrodes, and undoubtedly influenced the results of studies involving Ta–Ta_2O_5,[116] Nb–NbO,[117] Ti–TiO,[117] and V_2O–VO[118] electrodes.

Quite recently, Vecher and Vecher[119] have indicated the importance of recognizing the difference between t_i (eq 5) and $\bar{t}_i$ (eq 1). From Tretyakov's paper,[97] they calculated that

$$\log P_{\Theta} = -\frac{60.5 \times 10^3}{T} + 19.5 \qquad (7)$$

from 900 to 1500°K. However, even if $t_i = 0.50$ at one electrode, $\bar{t}_i$ will be about 0.96 and 0.91 for reference electrodes of O_2 and Fe–Fe_xO, respectively. For emf's to be accurate within 1%, *i.e.*, $\bar{t}_i \geqslant 0.99$, it is only necessary that t_i at the anode be $\geqslant$ 0.9 for an air or oxygen reference electode. This requirement will be satisfied if

$$\log P_{O_2}' \geqslant -\frac{60.5 \times 10^3}{T} + 23.5 \qquad (8)$$

where P_{O_2}' is the oxygen pressure at the anode.[119-121] Consequently, ZrO_2–CaO electrolytes should be useful to oxygen pressures four orders of magnitude lower than those listed in column 1 of Table VI. This means that accurate thermodynamic data should be obtainable for Cr_2O_3 to 1200° and MnO to 1000–1050°[119] in close agreement with aforementioned emf studies.[97,113] The data for MnO above 800°[97] could be corrected to account for the electronic conduction.[119]

In summary, the cells $P_{O_2}' = 10^{-24}|ZrO_2\text{–CaO}|\text{air}$ and $P_{O_2}' = 10^{-20}|ZrO_2\text{–CaO}|\text{air}$ have average ionic transport numbers of 0.99 and 0.999 at 1000°, respectively. The accuracies obtainable from such cells will be solely limited by the experimental techniques.

Little has been said thus far concerning temperatures around 1600°—an important consideration since one of the most significant industrial applications of solid oxide electrolytes is their use as oxygen probes for monitoring the content of dissolved oxygen in liquid steel. Although insignificant p-type conductivity occurs at oxygen pressure of 1 atm and 1600°,[50,61] n-type conductivity has been detected below 10^{-8}–10^{-9} atm[87] and 10^{-10}–10^{-11} atm[122] at this temperature. The latter pressure is equivalent to about 200 ppm by weight of oxygen in steel. With the cell H_2, $H_2O|ZrO_2\text{–CaO}|\text{air}$, electronic conductivity could be detected at $10^{-9.5}$ atm.[123] Equations 1 and 5 were used to show that $\bar{t}_i = 0.99$ and 0.50 at oxygen pressures of 10^{-10} and 10^{-13} atm at 1600°, respectively. A similar cell having CO–CO_2 mixtures at the anode was used to demonstrate that $\bar{t}_i = 0.98$ at 10^{-8} atm.[124] Measurements like these are especially sensitive to gas leakage and porosity in the electrolytes. Other investigators have demonstrated that ZrO_2–CaO electrolytes are useful to somewhat lower oxygen pressures. Electrodes of Fe–Si–SiO_2, [114] Fe–O,[125] Fe–Ti–TiO_2,[126] and Cr–Cr_2O_3[127] have all been used to show that electronic conductivity is essentially absent at an oxygen pressure of 10^{-12} atm and 1600°, *i.e.*, about 25 ppm of oxygen in steel. Reliable results were recently claimed down to 3×10^{-13} atm, *i.e.*, about 10 ppm of oxygen in steel.[128] Still lower oxygen contents might be realized if readings could be taken within 5–10 sec.[128] The Cr–Cr_2O_3 reference electrode used in this latter investigation will reduce the driving force for the open-circuit transfer of O^{2-} ions across the electrolyte.

J. CONCLUDING REMARKS

Several ternary systems involving ZrO_2 and CaO have been studied. For example, the third components have been MgO,[129] SrO,[130] Y_2O_3,[30] La_2O_3,[25,131] Fe_xO,[49,58,132] Fe_2O_3,[49,51,58,132] NiO,[51] TiO_2,[133] and Ta.[134] Additions of both MgO[129] and Y_2O_3[30] increased the conductivity, possibly owing to reduced lattice distortion in the case of MgO because of the relatively small Mg^{2+} ions (Table I) and weaker defect interactions in the case of Y_2O_3. In a Zr^{4+} sublattice, Y^{3+} and Ca^{2+} ions will have effective charges of −1 and −2, respectively. Consequently, Y^{3+} ions would be expected to interact less strongly with anion vacancies having effective charges of +2 than Ca^{2+} ions. Indeed, ZrO_2–Y_2O_3 electrolytes have higher conductivities than those formed from the ZrO_2–CaO–Y_2O_3 ternary system.[30] For the ZrO_2–CaO–MgO system, a ZrO_2 + 9% CaO + 4% MgO sample had a conductivity of 7.4×10^{-2} ohm^{-1} cm^{-1} at 1000°.[129] Unfortunately, attempts to increase the MgO content were futile on account of the instability of ZrO_2–MgO solid solutions. Higher CaO + MgO contents permitted a greater portion of MgO to be added, but lower conductivities resulted. The addition of SrO destabilizes ZrO_2–CaO solid solutions.[130] The latter can dissolve large amounts of some transition metal oxides, for instance, 12.5% Fe_xO at 1450°.[132] Generally, the presence of transition metal ions imparts electronic conductivity to the electrolytes. The addition of 0.8 wt % V, 0.1 wt % Fe, and 0.01 wt % Cr caused 50% electronic conduction at only 10^{-16} atm of oxygen and

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1000°.[60] Kroeger[70] accounted for this result by postulating that calcium, which is an acceptor, exists in a neutral form owing to pairing or clustering of Ca^{2+} ions and anion vacancies. Thus, the donor properties of the impurity ions will be able to control the electrical behavior of the solid solutions.

The high oxygen ion mobility in ZrO_2–CaO solid solutions has rendered them very suitable solid electrolytes. Moebius[135] invoked geometric considerations of the fluorite structure to explain this mobility. The gaps between the cations through which the anions must migrate are 90% as large as the anions themselves because of the small radii of the Zr^{4+} ions. By comparison, the cations must move through gaps only 56% of their size.

Earlier reviews of the electrical behavior of ZrO_2–CaO electrolytes have been written by Subbarao[136] and Moebius.[64,76]

III. Other ZrO_2-Based Electrolytes

A. ZrO_2–Y_2O_3

As early as 1899, Nernst[137] observed ionic conductivity in ZrO_2 + 9% Y_2O_3. In 1937, Baur and Preis[138] constructed the first solid oxide–electrolyte fuel cell using this material which has recently been thoroughly discussed by Moebius.[139] Hund[140] found the fluorite phase to extend from 5 to 46% Y_2O_3 at 1300°. Density measurements verified the correctness of the oxygen vacancy model proposed by Wagner[79] for these solid solutions. Duwez, Brown, and Odell[141] fixed the limits at 7 and 55% Y_2O_3 at 2000°, and 7 and 50% Y_2O_3 at 1000°. Phase boundaries of 9 and 55% Y_2O_3 at 1500°,[142] 7 and 53% Y_2O_3 at 2000°,[143] and 9 and 45–50% Y_2O_3 at 1800°[30] have also been determined. Lower limits of 7% at 2000° [14] 8% at 1750°,[144] and 8% at 1000° [14] have also been indicated. These data convincingly place the minimum amount of Y_2O_3 needed to fully stabilize ZrO_2 at 7–8%. In addition, complete stabilization with only 6% Y_2O_3 was achieved at 850°.[16] The tetragonal-cubic transformation of ZrO_2 upon adding Y_2O_3 occurs without the appearance of a two-phase field above 1700°.[14]

Other lower limits have been suggested as 15% at 1750°,[143] >10% at 1700°,[145] >7% at 840°,[146] and 9% at 1800–2000°.[147] Again, failures to obtain equilibrium are producing these discrepancies. The similarity between the fluorite structure and the cubic, C-type rare earth oxide structure of Y_2O_3 partly accounts for the high solubility of Y_2O_3 in cubic ZrO_2.

Although the pyrochlore-type compound $Y_2Zr_2O_7$ has been identified,[143,148] its existence has recently been denied.[149,150] The similarities between the fluorite and pyrochlore structures and the scattering powers of the Zr^{4+} and Y^{3+} ions might explain this. In a binary oxide system, compounds will normally not form for cation field-strength differences less than 0.3[151] (section I.A). This difference is 0.29 in the ZrO_2–Y_2O_3 system based on Moebius' radii[1] listed in Table I.

For ZrO_2 + 10% Y_2O_3 solid solutions, lattice parameters of 5.127,[140] 5.132,[141] 5.140,[152] 5.141,[86] 5.143,[153] and 5.145 Å[14,30,147] have been given. The electrical conductivity results for this system are summarized in Table VIII in a similar manner to that for the ZrO_2–CaO system in Table IV. The agreement among the maximum conductivities obtainable from these electrolytes is remarkable.

Table VIII

Ionic Conductivities (ohm^{-1} cm^{-1} × 10^2) of ZrO_2–Y_2O_3 Electrolytes at 1000°[a]

Composition, % Y_2O_3				
8	*9*	*10*	*15*	*Ref*
13 (18.5)		7.7 (19.8)	3.6 (24.7)	37
		4.8	4.8	154
3.6			1.5	155
	10 (18.2)	*10 (20.0)*	3.1 (27.7)	30
10 (17.0)		*12 (20. 0)*		147
		5.8		156
		10		157
7.0		8.7		144
		12 (17.7)[b]	2.9 (23.7)	158
		12		153

[a] Activation energies (kcal/mol) are in parentheses. When several compositions were studied, the maximum conductivity is italicized. [b] 12% Y_2O_3.

Analogous to the ZrO_2–CaO system, the highest conductivities occur at compositions near the lower limit of the single-phase region. Although the addition of 12% CaO to ZrO_2 produces 6% anion vacancies compared to only 4.1% upon the addition of 9% Y_2O_3 to ZrO_2, the latter electrolyte is twice as conductive at 1000°. Weaker defect interactions, as mentioned in section II.J, may be the main reason for the markedly higher anion mobilities in the ZrO_2–Y_2O_3 solid solutions. The ZrO_2 + 12% CaO and ZrO_2 + 9% Y_2O_3 electrolytes have activation energies of 25 and 18 kcal/mol, respectively.

Linear Arrhenius plots (eq 2) over wide temperature ranges usually indicate the presence of only one mode of conduction, excluding the possibility that two competing modes have

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similar activation energies. For the ZrO_2–Y_2O_3 electrolytes, linear plots have been indicated between 550 and 1200°,[37] 700 and 1400°,[30] 700 and 1000°,[144] and 600 and 2100°.[156] The conductivities are not influenced by oxygen pressure.[156,157] Based on this information, it is difficult to reconcile Casselton's data.[158] For samples containing 12, 15, and 20% Y_2O_3, he found slope changes at 820 and 1200° and higher conductivities in oxygen than in argon ($P_{O_2} = 10^{-10}$ atm) above 820°. Other authors[37,154,155] have indicated that the conductivities of compositions lying near the low-yttria cubic phase boundary deviated to progressively lower values above 800° than would be expected by extrapolation of low-temperature Arrhenius plots. Precipitation of a tetragonal ZrO_2 solid solution would enrich the cubic phase in Y_2O_3, thereby lowering the conductivity (Table VIII). An increasing slope with increasing temperature for a ZrO_2 + 43% Y_2O_3 specimen[155] is consistent with the precipitation of a Y_2O_3-rich solid solution. Recently, Bauerle and Hrizo[153] reported that the resistivity divided by the absolute temperature for ZrO_2 + 10% Y_2O_3 was described by the sum of two terms having the form of the right side of eq 2. Assuming a vacancy trapping mechanism, values of the activation enthalpy for free vacancy motion and the trapping enthalpy of an oxygen vacancy by a Y^{3+} ion were 15.7 and 11.2 kcal/mol, respectively.

Heat treatments for extended times at 800–1500° [44,141,159] have not resulted in the decomposition of the solid solutions. Evidently, the eutectoid temperature is below that at which decomposition could proceed at a noticeable rate. An order-disorder transformation has been observed in samples containing 20 and 25% Y_2O_3 at about 1100° after they were annealed for 2 weeks at 900°.[30] The authors suggested that the degree of ordering would increase with the Y_2O_3 content and attain a maximum near 33% Y_2O_3, although the compound $Y_2Zr_2O_7$ was not detected.

Transport numbers in yttria-stabilized zirconia will now be briefly considered. Blackening of the ceramic samples, starting at the cathode and extending further toward the anode with time, has resulted from the electrolysis of ZrO_2–Y_2O_3 electrolytes.[156–158,160] Nonstoichiometric black zirconia or zirconium metal may form at the cathode owing to a depletion of oxygen or, alternately, anion vacancies may trap electrons ejected from the cathode forming color centers.[158] Using an oxygen concentration cell, Neuimin and Pal'guev[154] measured ionic transport numbers of about 0.992 at an oxygen pressure of 1 atm and 650–1100° for ZrO_2 + 15% Y_2O_3, while Bray and Merten's data[152] indicated that electronic transport numbers were no greater than 0.005 and 0.011 in oxidizing and reducing atmospheres, respectively, from 800 to 1100° for ZrO_2 + 10% Y_2O_3. The reducing atmosphere was imposed by hydrogen, saturated with water vapor at room temperature. From these results, Bray and Merten[152] estimated that $P_\Theta \leqslant 10^{-25}$ atm at 1100°. Using hydrogen at one electrode and eq 6, they calculated values for P_Θ of 10^{-27} and 10^{-31} atm at 1000°, but could not determine which was more accurate. Also, they estimated that the transport number of Y^{3+} ions, relative to Zr^{4+} ions, was no greater than 4×10^{-9}. Because of their greater charge, less interference from Y^{3+} ions compared to Ca^{2+} ions might be expected in ZrO_2-based electrolytes. From dc polarization measurements, Strickler and Carlson[30] concluded that the anion transport number in ZrO_2 + 9% Y_2O_3 is greater than 0.99. Higher conductivities observed at high dc currents were attributed to the reduction of Zr^{4+} to Zr^{3+} ions.

From the preceding discussion, it is evident that the behavior of ZrO_2–Y_2O_3 electrolytes parallels very closely that of ZrO_2–CaO electrolytes, indicating that the major component controls their properties to a great extent. Therefore, it is difficult to explain the results of Casselton[158] and Casselton and Scott[161] who found the conductivities of ZrO_2–Y_2O_3 specimens to increase with increasing oxygen pressure from 6×10^{-4} to 1 atm at 1380°, indicative of p-type conductivity arising from a dissolution of excess oxygen into the lattice according to

$$^{1}/_{2}O_2(g) + V_O^{\cdot\cdot} = O_O + 2h^{\cdot} \qquad (9)$$

where $V_O^{\cdot\cdot}$ is a doubly ionized oxygen vacancy, O_O is an oxygen ion on a normal lattice site, and $h^{\cdot}$ is an electron hole. The p-type conductivity obeyed the predicted $P_{O_2}^{1/4}$ law.[85] Since these authors passed dc currents, a depletion of O^{2-} ions in the vicinity of the cathode would drive eq 9 to the right. However, higher ac conductivities were found at 1 atm than 10^{-10} atm of oxygen above only 820°.[158] The measuring frequency of 5000 cps would appear to rule out polarization phenomena.

B. ZrO_2–La_2O_3

Early studies of this system had shown that cubic fluorite solid solutions exist between 10 and 35% La_2O_3 after melting,[162] 25 and 42% La_2O_3 at 2000°,[163] and 30 and 40% La_2O_3 at 1000°.[163] However, more recent evidence has shown that the La^{3+} ion is too large (1.21 Å) to form fluorite solid solutions.[164] Instead, solid solutions based on the compound $La_2Zr_2O_7$, which has the cubic pyrochlore structure, form in this system.[164] This structure has an ordered array of anion vacancies. Trombe and Foëx[162] did find maximum order at 33% La_2O_3. The work of Perez y Jorba, Collongues, and Lefevre[165–168] has verified the existence of this compound. It melts congruently at 2180°[165] and has a range of homogeneity extending from 33.3 to 39% La_2O_3 below 1500° and from 25 to 40% La_2O_3 near its melting point.[166–168] Strickler and Carlson[147] detected only typical pyrochlore structures in samples containing between 6 and 24% La_2O_3 fired at 1800–2000°. The cubic fluorite phase is stable only above 1800°[168] and extends from 6 to 16% La_2O_3 near liquidus temperatures.[166–168] It could be prepared metastably at only 800° *via* coprecipitation in the amorphous state, but, above 1450°, decomposed rapidly to a tetragonal ZrO_2 solid solution and $La_2Zr_2O_7$.[166] Fluorite-type solid solutions have also been observed at about 14% La_2O_3 in another phase study of this system.[169] Recently, the eutectoid was placed at 1850° and 5% La_2O_3.[170] The fluorite phase

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was stable from 4 to 8% and 2 to 18% La_2O_3 at 2000 and 2200°, respectively.[170]

Samples containing 10 and 15% La_2O_3 have lattice parameters of 5.236 and 5.275 Å, respectively.[166] These values were obtained by quenching from the molten state. For $La_2Zr_2O_7$, lattice parameters of 10.780,[162] 10.792,[171] 10.793,[164] and 10.797 Å[166] have been determined. As these parameters are about twice those given by Trombe and Foëx[162] for compositions containing between 15 and 30% La_2O_3, these authors were undoubtedly studying solid solutions based on $La_2Zr_2O_7$, not fluorite solid solutions.

At 1000°, conductivities of 4.4×10^{-3}[172] (5% La_2O_3), 2.5×10^{-3}[162] and 1.1×10^{-3}[147] (10% La_2O_3), and 2.5×10^{-3},[172] 1.1×10^{-4},[154] and 3.0×10^{-3}[147] ohm^{-1} cm^{-1} (15% La_2O_3) have been given. They are much lower than those in Tables IV and VIII, an expected result since the anion vacancies are ordered in the pyrochlore structure. Alternately, a tetragonal ZrO_2 solid solution may control the electrical properties of these mixtures.

Anthony and her coworkers[172–174] have studied the transport properties of this system. Activation energies for a ZrO_2 + 13% La_2O_3 specimen were 15.9, 34.6, and 54.9 kcal/mol at 1200–1400, 1400–1525, and 1525–1650°, respectively.[173] The conductivity was essentially independent of oxygen pressure from 1 to 10^{-6} atm at 1300° and was attributed to cation migration through the pyrochlore structure. However, an electrolysis experiment indicated that the mixture was an electronic conductor at 1300°. The presence of nonstoichiometric $La_2Zr_2O_7$ above 1400° led to a region of n-type semiconduction proportional to $P_{O_2}^{-1/4}$, while thermionic emission influenced the results above 1525°. The onset of n-type conductivity moved progressively to lower temperatures as the La_2O_3 content increased.[172] This was attributed to a decrease in the cationic conductivity resulting from the presence of fewer lattice defects as the composition approached that of $La_2Zr_2O_7$. This explanation is inconsistent with the phase diagram[168] which indicates that, from 5 to 33% La_2O_3 and below 1500°, a tetragonal ZrO_2 solid solution and stoichiometric $La_2Zr_2O_7$ should coexist. Again, the possibility that the electrical behavior of these mixtures is being controlled by the tetragonal ZrO_2 phase should not be overlooked.

Both $La_2Zr_2O_7$[171,175] and nonstoichiometric $La_2Zr_2O_7$ containing excess La_2O_3[175] are mixed p-type and ionic conductors at high oxygen pressures. The conductivity reaches a maximum at 40% La_2O_3[175] corresponding to the upper phase boundary for the pyrochlore phase. Ionic transport numbers of only 0.08–0.17 at 900–1100° and an oxygen pressure of about 1 atm were reported for ZrO_2 + 15% La_2O_3.[154]

Factors such as purity, thermal history, grain size, method of preparation, and oxygen pressure will markedly affect the conductivity of these mixtures.[174] The reactivity of the oxides, the sintering conditions, and the cooling rate after sintering will influence the phases present during electrical measurements. Although further studies of the electrical properties of ZrO_2–La_2O_3 mixtures are definitely warranted, they are not to be regarded as potential solid electrolytes.

C. ZrO_2–RARE EARTH OXIDES AND ZrO_2–Sc_2O_3

Since Y_2O_3 stabilizes ZrO_2 extremely well, the rare earth oxides might be expected to behave similarly. This should be especially true for the heavier rare earths (Gd_2O_3–Lu_2O_3) which have the same structure as Y_2O_3 and cations which are comparable in size or smaller than Y^{3+}.

French researchers have studied ZrO_2–rare earth oxide systems in considerable detail.[12–14,165,167,168,176–184] The samples were usually prepared by melting or coprecipitating the required cations as hydroxides. Crystallization of the amorphous coprecipitates occurred between 400 and 700°; the required temperature increased as either the quantity of the rare earth oxide or the radius of the rare earth cation increased.[13,14] A summary of their results and those of several other studies is given in Table IX. The oxides Ce_2O_3, Pr_2O_3, and Tb_2O_3 have been purposely omitted although cubic solid solutions can be formed between ZrO_2 and these oxides.[182,187] The cations can be easily oxidized to the +4 valence state which renders them unsuitable as solid electrolyte constituents.

Table IX

Phase Boundaries of Cubic ZrO_2–Rare Earth Oxide Solid Solutions

Oxide	*Temp, °C*	*Boundaries, % M_2O_3*	*Ref*
Nd_2O_3	2000	10 and 44	163
	1000	16 and 42	163
	2000	9–10 and 57	168, 178, 179, 181
	1000	12–13 and 40	168, 178, 179, 181
	1300	15–16 and 40	185
Sm_2O_3	2000	7 and 64	178, 179
	1000	10 and 50	178, 179
Eu_2O_3	1300	10 and 55	185
Gd_2O_3	2000	7 and 77	178, 179
	1000	9 and 50	178, 179
Dy_2O_3	1600	5 and 41	186
	2000	7 and 100	178, 179
	1000	9 and 53	178, 179
Ho_2O_3	1300	4 and 56	185
Yb_2O_3	2000	7 and 100	178, 179
	1000	7–8 and 46	178, 179

Several comments must be made about Table IX. Above certain minimum temperatures, the tetragonal and cubic ZrO_2 solid solutions are not separated by a two-phase re-

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gion.[14,168,176] Instead, the transition occurs continuously with a gradual decrease in the *c*/*a* ratio until it becomes 1 at about 7% of the rare earth oxide. The minimum temperatures are >2000, 2000, 1800, and 1500° for Nd_2O_3, Sm_2O_3, Gd_2O_3, and Yb_2O_3, respectively. In addition to the lower boundaries shown in Table IX, 6% Sm_2O_3 at 2000°,[141] 6% Gd_2O_3 at 2000°,[141] 8% Gd_2O_3 at 2000°,[188] and 7% Eu_2O_3 at 1500° [189] were necessary to achieve a single-phase cubic structure.

Pyrochlore-type compounds will form in the systems where $r_{M^{3+}}/r_{Zr^{4+}} > 1.2$ (Ce^{3+}–Gd^{3+}).[180,181] In the ZrO_2–Nd_2O_3 system, the cubic phase was postulated to be nonstoichiometric $Nd_2Zr_2O_7$ rather than disordered fluorite solid solutions.[164] Actually, the fluorite phase exists until 18% Nd_2O_3 and then transforms continuously into the pyrochlore structure.[167,178,179] However, solid solutions containing less than 20% Nd_2O_3 are unstable below 1600°.[190] At 2000°, the pyrochlore phase reverts back to the fluorite phase at 48% Nd_2O_3.[178,179] Also, the pyrochlore phase extends from 23 to 43% Sm_2O_3[178,179] and 29 to 39% Gd_2O_3[165,168,178,179] at 1000°. Order–disorder transitions, discussed by Collongues,[191] occur for $Sm_2Zr_2O_7$ and $Gd_2Zr_2O_7$ at 2400 and 1550°, respectively. Above these temperatures, the pyrochlore phase no longer exists. Consequently, some of the boundaries in Table IX encompass more than one structure, although they all define single-phase regions. The extent of nonstoichiometry of the pyrochlore compounds has been related to the radii of the cations.[180] Solubility limits of 56% Sm_2O_3 and 55% Gd_2O_3 at 2000° have also been reported.[183]

Continuous transitions between the fluorite phase and the cubic C-type rare earth oxide phase have also been observed. At 2000°, X-ray reflections of the latter first became evident at 58% Gd_2O_3,[178,188] 55% Dy_2O_3,[178] and 48% Yb_2O_3.[178] They did not appear until 65% Er_2O_3 and 63% Yb_2O_3 at 2000° in Rouanet's study.[184] The single-phase region extends to pure Dy_2O_3 and Yb_2O_3 at 2000° as shown in Table IX. However, in the ZrO_2–Dy_2O_3 system, a two-phase region in which both cubic phases coexist appears below 1650°. In the ZrO_2–Yb_2O_3 system, the rhombohedral compound $Yb_4Zr_3O_{12}$ appears below 1620°.[178,181] At 1000°, the fluorite phase transforms into this nonstoichiometric compound at 30% Yb_2O_3. Past 46% Yb_2O_3, a two-phase region begins.

The ZrO_2–Sc_2O_3 system is an interesting one because of the similar radii of the Zr^{4+} and Sc^{3+} ions (Table I). Only 6% Sc_2O_3 has been necessary to fully stabilize ZrO_2 at 2000,[141] 1800–2000,[147] and 1750°.[192] The fluorite phase was reported to extend to 32% Sc_2O_3 at 1750°.[192] Several investigators have shown that this system is quite complex.[14,193–195] At 1000°, the fluorite phase extended from 8 to 17% Sc_2O_3, while distorted fluorite structures were found between 17 and 21–22% and between 31–32 and 39% Sc_2O_3.[14,193] Strickler and Carlson[194] found only one phase in this region which appeared between 16 and 33% Sc_2O_3. They indicated that it became cubic at 800° for 16% Sc_2O_3 and 1250° for 33% Sc_2O_3, whereas Lefevre[14,193] maintained that the distorted phases were still stable at 2000°. At low temperatures, another distorted fluorite phase appeared between 12 and 13% Sc_2O_3. This phase became cubic above 580[14,193] and 610°.[194]

The Sc^{3+} ion is too small to prevent the appearance of distorted fluorite phases. More work is required to fully define the range and stability of the cubic phase. Unfortunately, this range may be extremely narrow or nonexistent. Distortion has been apparent in samples containing 10 and 15% Sc_2O_3,[37] and it has been suggested that the fluorite range narrows to only 6 to 8% Sc_2O_3 at room temperature.[147]

Lattice parameters for several ZrO_2 + 10% M_2O_3 solid solutions are listed in Table X. The oxides Pr_2O_3 and Tb_2O_3 have been included for purposes of comparison.

Table X

Lattice Parameters for ZrO_2–M_2O_3 Solid Solutions

Composition	*Lattice parameter*, Å	*Ref*
10% Pr_2O_3	5.190	182
10% Nd_2O_3	5.169	163
	5.197	37
	5.183	196
10% Sm_2O_3	5.172	147
10% Gd_2O_3	5.162	14, 196
10% Tb_2O_3	5.150	182
10% Dy_2O_3	5.142	186
10% Yb_2O_3	5.127	14
	5.130	147, 197
	5.129	196
10% Sc_2O_3	5.09	37
	5.085	147
	5.092	192

Ionic conductivities for these systems are presented in Table XI. The lower values may be indicative of two-phase systems and may, in fact, contain an electronic contribution. Once again, the maximum conductivities occur at compositions corresponding closely to the lower fluorite phase boundary and have been observed at 14–15% Nd_2O_3,[196,198] 10% Sm_2O_3,[147] 8–10% Gd_2O_3,[196] 8% Yb_2O_3,[147,196] and 8–12% Sc_2O_3.[147] Higher rare earth oxide contents result in higher activation energies and lower conductivities. In the fluorite structure, the free radius R_f between the cations through which the oxygen ions must move is given by

$$R_f = \frac{a}{\sqrt{6}} - \bar{r}_c \tag{10}$$

where a is the lattice parameter and $\bar{r}_c$ is the average cation radius.[135] Since the rare earth oxide cations are larger than the Zr^{4+} ion, the free radius will decrease and, therefore, the activation energy will increase as the rare earth oxide content

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Table XI

Ionic Conductivities (ohm^{-1} cm^{-1} × 10^2) of ZrO_2–M_2O_3 Electrolytes at 1000°[a]

	Composition, % M_2O_3				
M_2O_3	8	9	10	15	Ref
Nd_2O_3			0.60		37
				1.7	154
				3.8[c]	196[b]
				1.4 (24.9)	198
Sm_2O_3			5.8 (22.0)	2.3 (26.1)[d]	147
Gd_2O_3	11		11	3.1[d]	196[b]
Yb_2O_3		15		3.2	37
	8.8 (17.3)		11 (19.6)	3.9 (26.1)[d]	147
				4.9[d]	196[b]
Lu_2O_3	1.5			1.2	199
Sc_2O_3			24	13	37
	25 (15.2)		25 (14.9)	15 (15.8)[d]	147
	1.1			0.84	199

[a] Activation energies (kcal/mol) are in parentheses. [b] Conductivities were extrapolated from 850°. [c] 14% Nd_2O_3. [d] 16% M_2O_3.

increases. This explanation was used by Peters and Radeke[200] for the ZrO_2–Gd_2O_3 system. However, these authors gave a conductivity of only 7 × 10^{-6} ohm^{-1} cm^{-1} at 1000° for ZrO_2 + 12% Gd_2O_3. The corresponding activation energy was 20 kcal/mol. The above argument should fail for the ZrO_2–Sc_2O_3 system. Strickler and Carlson[147] have indicated that the activation energy changes very little from 6 to 16% Sc_2O_3. The presence of a second phase or a distorted structure above 12% Sc_2O_3 might partially account for the conductivity behavior in this case.

A tendency toward vacancy ordering will be present at the higher defect concentrations, especially in the systems having large trivalent metal ions. This tendency is still apparent in the ZrO_2–Gd_2O_3 system and might be observed in the ZrO_2–Dy_2O_3 system if samples were annealed for long periods of time around 1200°. Heating a ZrO_2 + 10% Yb_2O_3 specimen at 1000° for 2 weeks did not influence its conductivity,[196] but, of course, the vacancy concentration is relatively low. Both $Sm_2Zr_2O_7$ and $Sm_{2.28}Zr_{1.72}O_{6.86}$ containing 2% anion vacancies have ionic conductivities about two orders of magnitude lower than the ZrO_2–Sm_2O_3 fluorite solutions shown in Table XI.[201] These pyrochlore phases are mixed p-type and ionic conductors at high oxygen pressures. Higher defect concentrations may lead to higher ionic conductivities and ionic transport numbers. However, the pyrochlore phase can only accommodate about 3% anion vacancies.[178,179]

For a given composition, the ionic conductivity increases as the radius of the trivalent metal cation decreases. The ZrO_2–Sc_2O_3 electrolytes are twice as conductive as ZrO_2–Y_2O_3 or ZrO_2–Yb_2O_3 electrolytes at 1000°, although the stability of solid solutions in the former system must be more thoroughly investigated. Because of decreasing lattice distortion, it might be expected that the maximum conductivity in a given system would shift to higher defect concentrations as the radius of the trivalent metal cation decreased. However, such a trend is complicated by the necessity to stabilize the fluorite phase. If ZrO_2 itself had the fluorite structure, higher conductivities than those in Tables IV, VIII, and XI might have been observed at lower defect concentrations.

Nonlinear Arrhenius plots have been found in these systems[37,154,196,198,199] and have been attributed to decomposition of the solid solutions[37] and the formation of superstructures.[199] Usually, lower activation energies appear at the higher temperatures. An electrolyte composed of ZrO_2 + 8% Yb_2O_3 had a conductivity of 6 × 10^{-2} ohm^{-1} cm^{-1} at only 800°.[196] Unfortunately, the conductivity began to level off above this temperature. Extrapolation of the low-temperature Arrhenius relationship results in a conductivity of 42 × 10^{-2} ohm^{-1} cm^{-1} at 1000°. More research is required to determine the maximum obtainable stable conductivity of these solid electrolytes. In particular, a detailed investigation of the ZrO_2–Lu_2O_3 system might prove fruitful. Likewise, additions of Y_2O_3, Yb_2O_3, or Lu_2O_3 to ZrO_2–Sc_2O_3 solid solutions might stabilize them without adversely affecting their conductivities. Equilibria between ZrO_2 and mixed rare earth oxides occur more readily than between ZrO_2 and individual rare earth oxides.[202]

The transport properties of these systems should be similar to those exhibited by ZrO_2–CaO and ZrO_2–Y_2O_3 electrolytes. Oxygen concentration cell measurements have been used to show that ZrO_2 + 15% Nd_2O_3[154] and ZrO_2 + 10% Yb_2O_3[196] have ionic transport numbers of 0.93 at 750–1100° and about 1 atm of oxygen and >0.99 at 750–1000° and about 10^{-10} atm of oxygen, respectively. Gas leakage between the oxygen and air electrodes may have resulted in the ionic transport number of only 0.8 reported for ZrO_2 + 19% Nd_2O_3 at 800–1600°.[198] A ZrO_2 + 25% Pr_6O_{11} sample had a conductivity, which was 95% ionic, of 2.7 × 10^{-2} ohm^{-1} cm^{-1} at 1000° in air.[203] Guillou[198] found a similar sample exhibited 72% ionic conductivity. p-Type conductivity would be expected at high oxygen pressures on account of the stability of the Pr^{4+} ion.

Finally, it is interesting to note that ZrO_2 + 7% Nd_2O_3[154] and ZrO_2 + 5% Nd_2O_3[198] mixtures were practically pure ionic conductors at 750–1100 and 1400–1600°, respectively. These results indicate that tetragonal ZrO_2 solid solutions may be ionic conductors. About 2% of the rare earth oxides or Sc_2O_3 should dissolve in tetragonal ZrO_2.[14,168,179,190,194] These solutions are effectively stabilized since the monoclinic-tetragonal transformation temperatures are lowered below 400°.[167,197] Even monoclinic ZrO_2 will dissolve appreciable amounts of various di- and trivalent metal oxides ($\geqslant$ 1%).[22,33,141,163] Investigations of the electrical properties of these solid solutions would prove interesting.

D. ZrO_2–MgO

Several phase diagrams have been published for this system.[9,12,22,204–207] Cubic solid solutions are stable only at high temperatures and decompose to a tetragonal ZrO_2 solid solution and MgO at lower temperatures. The results of these phase studies are summarized in Table XII. Phase boundaries of 7 and 20% MgO at 2000° have also been reported.[208]

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Studies indicating cubic solid solutions at 1000°[209] and boundaries of 18 and 28% MgO at only 1400°[25] must be discounted. The cubic region extends to pure ZrO_2 above 2370°.[206,207] The solubility of MgO in tetragonal ZrO_2 may be less than 1% at 1300°.[207,210]

Table XII

Phase Relations in the ZrO_2–MgO System

Phase boundaries at 2000°, % MgO	*Eutectoid temp, °C*	*Eutectoid compn, % MgO*	*Ref*
4 and 30			204
16 and 29	1300	27	22
	1400	14	9
	1400	17	205
8 and 31	1300	26	12
8 and 27	1400	25	206
6 and 21	1400	13	207

Although there is considerable disagreement regarding the eutectoid composition, it is evident that cubic ZrO_2–MgO solid solutions are metastable below 1300–1400°. Heat treatments at 980–1375,[22] 1000–1390,[48] 1200,[42,45] and 1000–1375°[211] have resulted in the partial or complete destruction of the cubic phase. Cubic solid solutions having from 3 to 30% MgO can be metastably prepared at only 750° by crystallizing amorphous oxides which had been coprecipitated as hydroxides.[11,12,212,213] The solid solutions are formed during coprecipitation.[214] However, they decomposed above 850° and could only be regenerated by heating above 1350°. Recently, the tetragonal phase was observed to form within the cubic phase above 500°.[215] The decomposition rate reaches a maximum at 1200°[9,211] and increases when the degree of ordering or clustering of defects and impurities increases.[211] Extra X-ray diffraction lines were apparent in samples containing from 15 to 25% MgO which were heated between 1400 and 1550°, and decomposition proceeded more rapidly as the sintering time at 1520° was increased.[211] Also, the rate increases as the number of anion vacancies increases,[211] perhaps because of a greater degree of supersaturation and enhanced diffusion.

Regarding decomposition, the reproducibility among various laboratories is quite reasonable. Equilibrium may be achieved rather easily because of the small size of the Mg^{2+} ion. It begins entering into solution with ZrO_2 at a much lower temperature (480°) than the Ca^{2+}, Y^{3+}, or Ce^{4+} ions.[216]

The ZrO_2 + 15% MgO solid solution has a lattice parameter of 5.072 Å.[207] At 1000°, conductivities of 2.0×10^{-2},[57] 4.0×10^{-2},[129] and 3.4×10^{-2}[217] (15% MgO) and 3.8×10^{-2}[57] $\text{ohm}^{-1}\ \text{cm}^{-1}$ (20% MgO) have been shown, while activation energies of 19.6,[57] 33.7,[217] and 24.7[198] kcal/mol for ZrO_2 + 15% MgO have been reported. In all cases, the sintering temperature was 1550–1600°. The reactivity of the oxides, the cooling rate, and the measuring temperatures will markedly affect the conductivities. Only the cubic phase was claimed to be present in samples containing between 15 and 30% MgO which were cooled from 1550° at 100°/hr.[217] This seems unlikely from the phase diagram. Slope changes in Arrhenius plots at 450 and 750°[57] may be associated with the presence of a two-phase mixture.

The solid solutions are ionic conductors. Electrolysis in argon or vacuum results in oxygen-deficient ZrO_2 at the cathode, and the conductivity is essentially independent of oxygen pressure.[198,217] Theoretical emf's for galvanic cells having ZrO_2–MgO electrolytes have been measured.[87,93,218] p-Type conductivity is absent at 1500[87] and 1600°,[218] but n-type conductivity readily occurs under reducing conditions.[87,218] In the cell H_2, $H_2O|ZrO_2$ + 12% MgO|air, n-type conductivity was evident when the anode imposed oxygen pressures of 10^{-20} and 10^{-11} atm at 1000 and 1600°, respectively.[218]

Emf measurements must, in general, be restricted to temperatures below 850°, where the cubic phase may be kinetically stable, and above 1400° with ZrO_2–MgO electrolytes. Nevertheless, MgO could be added to ZrO_2–CaO or ZrO_2–Y_2O_3 electrolytes to lower the average cation radius (eq 10). The behavior of ZrO_2–MgO electrolytes has previously been discussed by Moebius.[64]

Any significant solid solubility of SrO in ZrO_2 has been denied.[57,130,219] Obviously, the Be^{2+} ion is too small and the Ba^{2+} ion is too large to stabilize ZrO_2.

E. ZrO_2-TRANSITION METAL OXIDES

Coprecipitation in the amorphous state permitted ZrO_2 to form cubic solid solutions with MnO, CoO, NiO, CuO, Cr_2O_3, Mn_2O_3, and Fe_2O_3 among others.[11,12,212,213] The solutions decomposed readily at 1000° and could only be regenerated by heating to very high temperatures. For example, a temperature of 2200° was necessary in the case of NiO, CoO, and Cr_2O_3.[213] An exception to this rule was MnO, for ZrO_2–MnO solid solutions reappeared at only 1250°.[212] For this system, a eutectoid point was fixed at 1180° and about 20% MnO.[12] A continuous transition from tetragonal to cubic ZrO_2 could be effected by heating coprecipitated samples at 750° under hydrogen.[12,220] The single-phase region continued to about 22% MnO.[12] This exceptional behavior is undoubtedly related to the similarity of the radii of the Zr^{4+} and Mn^{2+} cations. The trivalent cation of indium, a nontransition metal, also has a similar radius as Zr^{4+}. Cubic phase boundaries of 9 and 22% In_2O_3 at 1350–1550° have been determined for the ZrO_2–In_2O_3 system.[142]

Recently, Steele, Powell, and Moody[201] investigated fluorite phases consisting of (Zr, Ti) O_2 + Y_2O_3. The addition of TiO_2 to the ZrO_2–Y_2O_3 electrolytes produced both a marked decrease in ionic conductivity and the appearance of n-type conductivity at much higher oxygen pressures. Likewise, a lower conductivity resulted from the addition of Ta_2O_5 to these

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Table XIII

Thermodynamic Property Measurements Using ZrO_2-Based Solid Electrolytes

	References
Oxides	
Cu_2O	85, 99, 112, 113, 116, 223–229
Cu_2O^a	223, 226, 227
CuO	116, 226, 228, 230
NiO	85, 99, 102, 113, 225, 228, 231
Fe_xO^b	113, 116, 228, 231, 232
Fe_xO^c–Fe_3O_4	228, 232–234
Fe_3O_4	102, 116
Fe_3O_4–Fe_2O_3	228, 235
PbO	99, 116, 228, 236
PbO^a	116, 228
SnO^d	116
$SnO^{a,d}$	237
In_2O_3	238
MnO–Mn_3O_4	228, 235, 239
Mn_3O_4–Mn_2O_3	228
CoO	85, 113, 231
MoO_2	101, 102
WO_2	102–104
$WO_{2.72}$	103, 104
$WO_{2.90}$	104
WO_3	104
Nb_2O_4–Nb_2O_{5-x}	107
ZnO	109
Cr_2O_3	97, 113
SiO_2^e	114
Oxide Solid Solutions	
(Mg, Ni)O	240
(Mg, Fe)O	241, 242
(Fe, Ni)O	243
(Mn, Fe)O	241
$(Mn, Fe)_3O_4$	244
(Mn,Fe)O–$(Mn,Fe)_3O_4$	239, 245, 246
$Ni_yFe_{3-y}O_4$	247, 248
$Co_yFe_{3-y}O_4$	86, 248
$Mg_yFe_{3-y}O_4$	248, 249
Ternary Compounds	
$MnFe_2O_4$	239, 244, 250
$MgMoO_4$	251
$CaWO_4$	108
$SrWO_4$	252
$CuCr_2O_4$	113
$NiCr_2O_4$	113, 253
$FeCr_2O_4$	113, 254
$CoCr_2O_4$	113
$MgCr_2O_4$	113
$Cu_2Al_2O_4$	253
$NiAl_2O_4$	113, 253
$CoAl_2O_4$	113, 253
$NiTiO_3$	231
$FeTiO_3$	231
Fe_2TiO_4	231
$CoTiO_3$	231
Co_2TiO_4	231, 253
Ternary Compounds	
$PbSiO_3$	255
Pb_2SiO_4	255
Pb_4SiO_6	255
Ni_2SiO_4	231
Fe_2SiO_4	231
Liquid Silicates	
PbO–SiO_2	116, 256
SnO–SiO_2	237
NiO–SiO_2	257, 258
CoO–SiO_2	258
Sulfides	
PtS, Rh_xS, ZnS, MnS, MoS_2, NbS_2, TaS_2	106^f
Solid Alloys	
Pd–Cu	259
Pd–Ni	260, 261
Pd–Co	261
Pd–Sn	259
Pd–Fe	262
Pt–Cu	263
Pt–Ni	261
Pt–Fe	264
Au–Ni	265
Cu–Ni	266, 267
Ni–Ga^g	268
Liquid Alloys	
Pb–Ni	269
Pb–Sn	116
Cu–Zn	270
Ni–Cr	127
Fe–Cr	254
Nonstoichiometric Compounds	
UO_{2+x}	110, 271–273
$U_yTh_{1-y}O_{2+x}$	274
$U_yZr_{1-y}O_{2+x}$	275
$Ni_{1-x}O$	276–278
$Co_{1-x}O$	277
$Fe_{1-x}O$	232, 277, 279–282
Fe_2O_{3-x}	283
Nb_2O_{5-x}	107
TiO_{2-x}	111
$LiFe_5O_{8-x}$	278
$Co_yFe_{3-y}O_{4-x}$	277
$MnFe_2O_{4\pm x}$	250, 284
$Mn_yFe_{3-y}O_{4+x}$	285
$MgFe_2O_{4-x}$	286
$Mg_yFe_{3-y}O_{4-x}$	248
$MgFe_{2-y}Cr_yO_{4\pm x}$	287
Gas Mixtures	
CO–CO_2	288, 289
H_2–H_2O	123, 290

[a] Liquid. [b] Wustite in equilibrium with Fe. [c] Wustite in equilibrium with Fe_3O_4. [d] Probably SnO_2 in equilibrium with Sn. [e] Equilibrated with Fe–Si alloys dilute in Si. [f] MS was equilibrated with either MO and SO_2, MO and S_2, or M and SO_2. [g] The intermetallic compound NiGa was considered.

electrolytes.[221] In this instance, the Ta^{5+} cations will function as vacancy suppressors.

The electrical properties of ZrO_2-based solid electrolytes have recently been discussed by Paidassi and Caillat.[222]

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F. APPLICATIONS OF ZrO_2-BASED SOLID ELECTROLYTES

Zirconia-based electrolytes, especially ZrO_2–CaO, have been used in many different and interesting ways during recent years. These applications will be listed and discussed briefly in this section.

1. Thermodynamic Property Measurements

Galvanic cells incorporating solid oxide electrolytes will often yield very accurate thermodynamic data. However, there are several sources of error which must be avoided. These include chemical reaction between lead wires and electrodes or electrodes and the electrolyte, permeability or electronic conduction in the electrolyte, vaporization of the electrodes, electrical pickup from the furnace windings, thermal emf's, and thermionic emission which could result in asymmetry potentials or short-circuiting by the gaseous environment. Mixed potentials can arise from chemical reactions or interference from the cell atmosphere. The electrodes must be operating reversibly, a requirement that is often not considered. Reversibility, and often absence of mixed potentials, can be checked by either passing small currents through the cell in both directions or adding small amounts of an oxygen-bearing gas, and observing whether or not the emf returns to its original value. The emf should be unaffected by time, temperature cycling, and gas flow rate and be reproducible from run to run.

The systems which have been studied with ZrO_2-based electrolytes are listed in Table XIII. When only one binary oxide is shown, it was equilibrated with the corresponding metal (except for CuO, Fe_3O_4, $WO_{2.72}$, $WO_{2.90}$, WO_3, and SiO_2) and, consequently, free energy data were obtained for the metal-saturated oxide phase. When two binary oxides are shown, their equilibrium oxygen potentials were measured. Additional emf data are available for the cells Ni, NiO|ZrO_2–CaO|Cu, Cu_2O,[110,115,236,265,266,291] Fe, Fe_xO|ZrO_2–CaO|Ni, NiO,[101,102,117,243] Fe, Fe_xO|ZrO_2–CaO|Fe_xO, Fe_3O_4,[85,86,117,243,249,251,280,282] Fe, Fe_xO|ZrO_2–CaO|Fe_3O_4,

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Fe_2O_3,[249] Fe_xO, $Fe_3O_4|ZrO_2–CaO|Ni$, NiO,[102,243] and Co, $CoO|ZrO_2–CaO|Fe$, Fe_xO.[249,261]

Measurements on the simple binary oxides are extremely important since the data for these are needed to calculate the thermodynamic properties of the remaining systems in Table XIII (excluding alloys, nonstoichiometric compounds, and gas mixtures). In addition, a metal and its lowest oxide are almost invariably used as the reference electrode, although oxygen or air are sometimes used if the electrode chambers can be adequately separated. Accuracies exceeding ±1 mV have been achieved,[101,106,228,230,256] leading to free energy data accurate to better than ±100 cal/$^1/_2O_2$.[228] Measurements have been extended down to 400[115,233] and 350°.[110]

To study binary alloys, the alloy is equilibrated with the lowest oxide of the less noble metal, shown on the right in Table XIII. The activity of this metal can be measured directly. Polarization of the alloy electrode, discussed by Rapp and Maak,[266] can occur easily and must be avoided. Investigations of nonstoichiometric compounds lead to information about defect structures. In many instances, the composition has been varied *via* coulometric titration,[110,232,248,272,273,277,278,281,282] a technique which has been discussed by several authors.[277,292,293] Gaseous reference electrodes may be undesirable since higher emf's will usually be measured resulting in a larger error in the presence of a small electronic conductivity in the electrolyte. With regard to solid reference electrodes, Fe–Fe_xO is far superior to Ni–NiO on account of higher cation diffusion rates in the former.[293] Both Ni–NiO[294] and Co–CoO[234] electrodes polarize rather easily. The Fe_xO–Fe_3O_4 electrode behaved extremely well after an Fe–Fe_xO mixture interacted with the electrolyte.[234]

A study of the W–O system[295] has not been included in Table XIII under nonstoichiometric compounds since this system is comprised of several oxides, each having only a small range of nonstoichiometry.[104]

2. Oxygen Dissolved in Metals

Oxygen-ion conducting solid electrolytes based on ZrO_2 have been used to determine the activity of oxygen in Pb,[236,296] Sn,[296] Ni,[297,298] Co,[297,298] Ag,[296,299,300] Cu,[112,224,227,294,297,300–304] Fe[114,116,122–126,128,297,298,305–310] Cu–Sn,[229] Cu–Ag,[229] Fe–Cr,[254] and Fe–Si[114] melts. Recently, the solubility of oxygen in solid[234] and liquid[227,301] copper was measured using, in part, the method of coulometric titration. In addition, the effect of S in Co and Ni melts,[298] and the effect of S,[122,298] P,[122] C,[122] and Co, Ni, Cr, and V[306] in Fe melts on the oxygen activity has been observed. Fischer[311] has recently published a summary of many of his results. Sievert's and Henry's laws are usually obeyed, although slight deviations near the solubility limit of oxygen in liquid copper have been noted.[294,301]

Several problems are inherent in these measurements. Satisfactory conducting leads must be found that will withstand the highly corrosive liquid metals. Cermets consisting of 72% Cr and 28% Al_2O_3 in the case of Cu[229,294] and 80% Mo and 20% Al_2O_3 in the case of Fe[128] function quite well. Also, Mo, Ta, and Cr_2O_3 in Cu and Mo in Fe are often satisfactory. In the case of liquid steel, thermal shock resistance of the electrolyte must be fairly high. Instead of using a ceramic tube, an electrolyte disk is fused into the end of a quartz tube.[124,128,254,307] Alternately, an oxide powder can be rammed into the quartz tube.[124] The usual reference electrodes (air, Ni–NiO, Fe–Fe_xO) are adequate, while CO_2 (as $CaCO_3$)[307] and Cr–Cr_2O_3[128] have been suggested. Fortunately, only short immersion times in the steel are required to effect a stable reading. Times of 20–25[310] and 3–6[128] sec have been considered necessary. Lastly, electronic conduction in the electrolyte may interfere in strongly deoxidized steel. Readings have been successfully obtained down to 200,[122,123,297,310] 100,[114] and 10[128] ppm by weight of oxygen. By comparison, 3 ppm of oxygen in copper could be determined.[224] Several investigators have discussed the electrochemical determination of oxygen in liquid steel.[312–314]

An interesting extension of this technique is the electrochemical measurement of oxygen diffusion coefficients in solid and liquid metals. Successful results have been reported for solid silver,[302,315,316] liquid silver,[317,318] solid copper,[234,319] and liquid copper.[318,320] Potentiostatic or galvanostatic methods are used. In the former, a potential is applied to the cell to reduce the oxygen content in the metal at the metal–electrolyte interface to virtually zero, and the current is measured as a function of time. An appropriate solution of Fick's second law can then be applied.

3. Oxygen in High-Temperature Gases

Oxygen pressures can be monitored in O_2 (P < 1

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atm),[304,321–323] Ar–O_2,[116,323–327] CO–CO_2,[66,116,218,288,289,304] H_2–H_2O,[123,218,290,303,327,328] and CO–CO_2–H_2–H_2O[52,324,329,330] gases. In pure oxygen at reduced pressures, the Nernst equation has been verified to 10^{-5} atm at 600–750°[321] and 10^{-6} atm at 700°.[304] Deviations have been experienced below 10^{-3} atm in Ar–O_2 mixtures.[323,325] The emf became dependent on flow rate, an effect which was more severe as the oxygen pressure decreased. Under suitable flow conditions, Nernst behavior could be extended to 10^{-4} atm of oxygen.[326] In CO–CO_2 and H_2–H_2O mixtures, close agreement between measured and calculated emf's (<1%) has been observed.[52,290,328] Pressures down to those where carbon deposition occurs are readily measured in CO–CO_2 mixtures, while Nernst behavior has been observed down to 10^{-18} [218] and 10^{-19} [123] atm of oxygen at 1000° in H_2–H_2O mixtures. Measurements at temperatures as low as 400°[303,327,330] and as high as 1600[218] and 1750° [123] have been reported. The theoretical electrode potentials for these gas mixtures have been extensively discussed by Moebius,[331] while the use of an oxygen probe for controlling furnace atmospheres has been considered by Fairbank.[332]

Several interesting extensions of gas equilibria measurements are possible. The oxygen content of purified argon gas can be determined.[115,236,333] Oxygen pressures of about 10^{-15} atm at 800–1000° have been measured after the argon was dried and passed over titanium granules at 900–950°. The oxygen permeability of refractory materials can be evaluated by measuring the amount of oxygen leakage through them with solid electrolyte cells.[90,334] Lastly, the deoxidation of inert gases can be monitored.[335]

4. Fuel Cells

High-temperature solid-electrolyte fuel cells are noncorrosive, simple to construct, easy to miniaturize, require no catalysts, and offer chemical, thermal, and mechanical stability. Since the electrolyte transports O^{2-} ions to the anode, many different fuels can be used. However, the electrolytes have quite low conductivities, necessitating the use of high temperatures (>900°). With this restriction, problems of heating the cell and providing invariant, inexpensive electrode materials must be overcome. During the past 10 years, many investigations on the properties of these cells have been reported,[52,78,328,329,336–353] with special emphasis on electrolytes,[336,343,351] anode materials,[78,350] cathode materials,[78,348,349,353] anode polarization,[52,329,342,345] and cathode polarization.[342,347] The fuel cell most commonly studied is Pt, H_2, $H_2O|ZrO_2 + Y_2O_3$ or $CaO|O_2$ or air, Pt. The ZrO_2–Y_2O_3 electrolytes are preferable because of their higher conductivity and lower vacancy concentration (4.1% anion vacancies are necessary to obtain the maximum conductivity). Consequently, the tendency toward vacancy ordering or clustering during extended times at 800–1200° would be decreased. Suitable alternative electrolyte systems include ZrO_2–Yb_2O_3[345,347] and ZrO_2–Y_2O_3–MgO.[351,352] Flame-sprayed electrolyte films[354,355] result in much lower resistance losses. In addition to H_2 gas, CO,[52,329,339–341,343,351] CO–H_2,[329,341] and hydrocarbons (usually mixed with CO_2 or H_2O)[52,78,328,337,340] can be used as fuels. Equations describing the anodic oxidation of hydrocarbons have been derived.[52,356]

Suitable replacements for Pt electrodes are highly desirable. Other anode materials include C,[78,343] Ni,[343,345,347] U, Ce, or Pr oxides mixed with ZrO_2,[343] TiO_{2-x},[350] ZrO_2–NiO,[350] CeO_2–ThO_2,[351] and $U(Zr,Y)O_x$.[352] Cathode materials must withstand severe oxidizing conditions. Possible alternatives to Pt include Ag (solid or liquid),[78,340,343,345,347,352] SnO_2 (+Sb),[348] In_2O_3 (+Sb or Sn),[348] 0.95ZnO–0.05ZrO_2,[349] 0.97ZnO–0.03-Al_2O_3,[349,350] and Ce or Pr oxides mixed with ZrO_2.[343,351] The properties of many cathode materials have recently been evaluated, and doped SnO_2 and $PrCoO_3$ were found the most satisfactory.[353] Silver is attractive because of its high diffusion coefficient for oxygen, but evaporates too rapidly for many applications.

During the passage of current, processes of gas diffusion, adsorption of the fuel onto the electrode or electrolyte, discharge of O^{2-} ions, surface migration to the reaction sites, reaction of adsorbed oxygen with the fuel, and desorption of the reaction product occur at the anode. If any of these steps

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are slow, concentration or activation polarization will result. With H_2 as the fuel, polarization (excluding resistance polarization) is essentially absent at 800–1100°.[52,328,329,338,340,341,346,350] This evidence seems to refute the conclusion that the reaction $H_2 + O^{2-} \rightarrow H_2O + 2e$ is irreversible at 750–1000°.[342] The polarization observed in another study[344] at 600 and 800° may have occurred because the Pt electrodes were too dense and interfered with diffusion and desorption processes. Ideal behavior usually occurs with hydrocarbon fuels, undoubtedly since the electrode reaction involves H_2. However, significant polarization is observed with CO fuel.[52,329,340,351] This can be eliminated by adding only 3–5% H_2O to the gas stream.[329]

Several Russian investigations have been reported which dealt with polarization of Pt electrodes in contact with ZrO_2-based electrolytes in both CO–CO_2[357–361] and O_2[358,361–364] atmospheres. Polarization has been observed with CO–CO_2 mixtures at 900–1100°[357–361] and accounted for by postulating that the adsorbed oxygen concentration builds up at the anode owing to its slow reaction with CO.[359] Decreasing the CO/CO_2 ratio decreases the polarization.[329,359] Polarization is negligible at the cathode,[342,347,358,362] even at current densities of 200 mA/cm² at 800°[347] and 750 mA/cm² at 1000°.[342] Nevertheless, it is readily observable if the three-phase interface area (electrode, gas, and electrolyte) is reduced too much by making the electrodes too dense.[364]

Reviews on solid-electrolyte fuel cells are available in the literature.[365–369] Electrode processes[323,331,370,371] and fuel cell efficiencies[372,373] have also been considered.

5. Kinetics

The measurement of oxygen activities in liquid metals and gas mixtures can readily be extended to observation of the rates of various chemical reactions. The absorption and evolution of oxygen by Ag,[299,317,374] Cu,[294] PbO,[374] and PbO–SiO_2[374] after changing the oxygen pressure above the melts have been followed. In studies of this nature where the liquid and gas phases are not in equilibrium, mixed potentials, discussed by Masson and Whiteway,[317] must be avoided. This does not appear to have been the case in one investigation.[374] Also, the deoxidation of copper with magnesium[301–303,375] and iron or steel with silicon, manganese, aluminum, or titanium[126,128,305,375] can be monitored.

By continuously measuring the oxygen pressure in a gas phase, the rates of oxidation of Fe[116,376] and Fe_xO,[116] reduction of CuO,[105] Fe_2O_3,[105] Fe_3O_4,[116] Fe_xO,[116] and WO_3,[105] and decarburization of Fe,[377,378] Ni,[378] and Co[378] have been determined. The oxidation of graphite by CO_2 has been studied by measuring oxygen pressure profiles in the vicinity of the reaction surface.[378] Intermediate compounds which form during a chemical reaction are indicated by a temporary independence of the emf with time.[105] Once again, the major experimental difficulty with this technique is the elimination of mixed potentials.[376] Schmalzried[379] has discussed electrochemical methods to determine kinetic quantities with oxide electrolytes.

6. Other

By electrolyzing either CO_2 or H_2O with an oxide electrolyte, O_2 can be generated at the anode[380–382] or, alternately, the electrolysis of H_2O can be used for the purpose of preparing H_2 at the cathode.[383] Similarly, inert gases can be purified with respect to O_2,[98,384] the oxygen pressure in stationary or flowing gas mixtures can be markedly reduced,[98] and oxidizable gases can be coulometrically titrated with O_2.[384,385] For a given experiment, the permissible applied voltage across the electrolyte will be limited by the gas composition, gas flow rate, temperature, and cell geometry. Voltages which lower the oxygen pressure at the cathode too much will result in the appearance of electronic conductivity in the electrolyte.

The electrode Pt, $O_2|$stabilized ZrO_2 behaves as a reversible and noncorrosive reference electrode in silicate melts at temperatures up to 1250°.[326,386–388] Marincek[389] used a ZrO_2–CaO solid solution as a nonconsumable anode during the electrolysis of aluminum from a cryolite melt. Vacancy interaction energies have been determined in Fe_xO,[117] NbO,[117] TiO,[117] and VO,[118] but electronic conductivity in the electrolyte

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probably interfered with the results for the last three. Also, the high electrical conductivity of stabilized-ZrO_2 ceramics enables them to be used as furnace elements.[17, 390–392] They are stable in oxidizing atmospheres at temperatures in excess of 2500°.

Several recent investigations further indicate the wide range of applicability of ZrO_2-based electrolytes. Batteries have been constructed with anodes of Ni, Co, Fe, and Mn and a useful life of 3-5 min.[393] Stabilized ZrO_2 has been considered as a possible electrode material in magnetohydrodynamic generators which produce an emf by the movement of a plasma in a magnetic field.[198, 394–397] One electrode supplies electrons to the plasma by the oxidation of O^{2-} ions, and the other electrode removes them by the reverse process. Cells of the type $(-)\ O_2$ at $T_1|ZrO_2 + CaO$ or $Y_2O_3|O_2$ at $T_2\ (+)$ where $T_1 > T_2$ have been studied.[398–402] The thermoelectric power (Seebeck coefficient) of these cells is about $-450\ \mu V/deg$ in pure oxygen,[398, 399] decreases with decreasing oxygen pressure from 1 to 10^{-4} atm,[398, 400] and is approximately independent of temperature from 700 to 1400°.[399–401] Finally, a partial separation of the ^{16}O, ^{17}O, and ^{18}O isotopes has been effected on account of their different mobilities in a ZrO_2–Y_2O_3 electrolyte.[403]

It should be mentioned that some of the aforementioned studies were either partially or fully carried out with ZrO_2–MgO electrolytes.[218, 223, 226, 236, 259, 301, 309, 324, 326, 334, 385, 387, 388, 390] The emf's would only be expected to exhibit long-term stability below 850° and above 1400° (section III.D).

Several investigators have discussed the application of ZrO_2-based electrolytes to thermodynamic and kinetic measurements.[404–408]

IV. ThO_2-Based Electrolytes

Most of the research on the electrical properties of ThO_2-based electrolytes has dealt with ThO_2–Y_2O_3 solid solutions. Consequently, this section will be subdivided by properties, rather than by systems.

A. PHASE RELATIONS

As ThO_2 already has the cubic fluorite structure, the addition of di- and trivalent metal oxides is made solely to introduce a significant number of anion vacancies. The solubilities of the alkaline earth oxides, Sc_2O_3, Y_2O_3, and the rare earth oxides in ThO_2 are presented in Table XIV. The alkaline earth oxides are only moderately soluble and, therefore, phase studies which have indicated that 48% MgO[420] and 50% CaO[421] are soluble at 1600° must be discounted. Very slight solubility of Sc_2O_3 is indicated, although none was detected in another study.[422] Nevertheless, Y_2O_3 and the rare earth oxides are

Table XIV

Solubilities of Di- and Trivalent Metal Oxides in ThO_2

Oxide	*Temp, °C*	*Solubility, % MO or M_2O_3*	*Ref*
CaO	1700	10	409
	1800	>12	410
	1800	8	411
SrO	1800	4	411
BaO	1800	<0.5	411
Sc_2O_3	1750	~0.5	192, 195
Y_2O_3	1200	18	412
	1400	14	413
	2000	33	414
	1400	12	414
La_2O_3	1300	35	415
	1400	32	413
	1500	32	185
	1950	39	416
	1200	20	416, 417
Pr_2O_3	1400	54	418
Nd_2O_3	1400	33	413
	1500	33	185
Sm_2O_3	1400	43	413
Eu_2O_3	1800	54	418
	1500	36	418, 419
	1200	22	419
Gd_2O_3	1400	33	413
	2000	45	416
	800	19	416
Yb_2O_3	1400	5	418, 419
	1800	10	416
	1000	3	416

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quite soluble in ThO_2, although the solubility limits decrease quite drastically with decreasing temperature. The solubility is highest for the oxides from Pr_2O_3 to Gd_2O_3, which could be predicted from a consideration of the ionic radii in Table I. Brauer and Gradinger[413] and Gingerich[418] have stated that a continuous transition from the fluorite to the closely related C-type rare earth oxide structure will only be possible if their lattice parameters differ by less than 2.25% (~0.12 Å). Although this is the case for Pr_2O_3 and Nd_2O_3, these oxides have the hexagonal A-type rare earth oxide structure which invalidates the rule. The cations of the oxides which are C-type around 1400° (Tb_2O_3 to Lu_2O_3 and Y_2O_3) are too small to exhibit complete miscibility with ThO_2.

For ThO_2–Y_2O_3 solid solutions, pycnometrically measured densities of fired pellets have agreed with those calculated for the anion vacancy model.[412,414,415,423] Samples sintered in air or oxygen are brown, and the intensity of the color increases with increasing Y_2O_3 content.[414,424,425] The color is bleachable at low oxygen pressures,[424] and translucent pellets have resulted from vacuum sintering at 2000°.[99,115] The trapping of electron holes by Y^{3+} ions leading to the formation of color centers might account for the color at high oxygen pressures.[424] The anion vacancy model has also been confirmed for ThO_2–La_2O_3, ThO_2–Gd_2O_3, and ThO_2–Yb_2O_3 solutions.[416]

The following lattice parameters have been given for ThO_2 + 10% M_2O_3 solid solutions: 5.576,[412] 5.574,[413] and 5.566 Å[414] for Y_2O_3, 5.613[415] and 5.622 Å [413] for La_2O_3, 5.598 Å for Nd_2O_3,[413] 5.585 Å for Sm_2O_3,[413] and 5.584 Å for Eu_2O_3.[419]

Solid electrolytes based on ThO_2–ZrO_2 solid solutions do not seem feasible since these oxides are almost immiscible below 2000°.[426–428] Nevertheless, the presence of a di- or trivalent metal oxide may stabilize the cubic phase at lower temperatures.[429,430]

B. ELECTRICAL CONDUCTIVITIES

The available conductivity data for ThO_2–Y_2O_3 electrolytes are shown in Table XV. Since most of the compositions were given as % $YO_{1.5}$, both % Y_2O_3 and % $YO_{1.5}$ are reported. Unlike ZrO_2-based electrolytes, p-type conductivity appears at high oxygen pressures[63,99,414,423–425] and is detectable above about 10^{-6} atm.[99,424,425] Except where noted, all the measurements recorded in Table XV were taken at oxygen pressures below 10^{-8} atm and, therefore, are ionic conductivities and activation energies for ionic conduction. Excluding two studies, [412,430] all the oxides were sintered between 2000 and 2200°. Hund and Mezger[412] sintered their samples at only 1500°.

Ionic conductivity can be expressed as

$$\sigma_i = [V_{\ddot{o}}]2e\mu \qquad (11)$$

where the expression for the mobility μ is given in eq 3. For small defect concentrations, where the ionic mobility is essentially independent of the number of vacancies, the ionic conductivity will vary directly as the Y_2O_3 content since $[V_{\ddot{o}}] = {}^1/_2[YO_{1.5}]$. This proportionality was verified to 5% Y_2O_3,[424] but only to 0.5–1% Y_2O_3 in another investigation.[425] Other results indicate that it is not obeyed above about 2% Y_2O_3.[99,414] The conductivity reaches a maximum at about 8% Y_2O_3 or 3.7% anion vacancies.[99,425] Lattice distortion, defect interactions, vacancy clustering, and vacancy ordering will restrict the ionic conductivity at high defect concentrations. An increase in ΔH in eq 3 with increasing Y_2O_3 content will reduce the mobility of the anions. Interestingly enough, Steele and Alcock[99] found that ΔH decreased up to 8% Y_2O_3, while Lasker and Rapp[425] indicated that a ThO_2 + 0.4% Y_2O_3 specimen had a higher activation energy than specimens containing 0.8–14% Y_2O_3. Evidently, either a or G in eq 3 must decrease with increasing Y_2O_3 content. A better understanding of the significance of a, G, and ΔH and the nature of concentrated solutions of defects are required to adequately explain these observations.

p-Type conductivity at higher oxygen pressures results from a dissolution of oxygen into the lattice according to eq 9. The equilibrium constant for this reaction may be written as

$$K = \frac{p^2}{P_{O_2}^{1/2}[V_{\ddot{o}}]} \qquad (12)$$

if the electron hole concentration p is low so that the holes do not mutually interact. If the mobility of the holes is independent of their concentration, then the p-type conductivity will vary as $P_{O_2}^{1/4}$. Deviations from this dependence could occur if all the vacancies were not doubly ionized, all the holes were not free to conduct, or excessive association between Y^{3+} ions and anion vacancies meant that $[V_{\ddot{o}}]$ could not be considered constant in eq 12. However, ThO_2–Y_2O_3 solid solutions do follow the $P_{O_2}^{1/4}$ law.[424,425,430a] From eq 12, the p-type conductivity at constant oxygen pressure should be proportional to $[V_{\ddot{o}}]^{1/2}$. This behavior has been reasonably verified to 14% Y_2O_3,[425] although this implies that the activity coefficient for the anion vacancies is approximately independent of their concentration from 0 to 6.3% anion vacancies. However, Bauerle[424] indicated that the p-type conductivity was almost unaffected by composition from 0.5 to 5% Y_2O_3 and suggested that the electron holes may be trapped by Y^{3+} ions. This explanation appears inconsistent with the $P_{O_2}^{1/4}$ dependence that he observed. The conflicting data of these two papers necessitate further research.

Despite the fact that both ionic and p-type conductivity increase with Y_2O_3 content, ionic transport numbers increase.[425] For instance, measurable p-type conductivity appeared above oxygen pressures of 10^{-12}, 10^{-8}, and 10^{-6} atm for ThO_2 containing 0, 0.8, and 8% Y_2O_3, respectively.[425] Linear Arrhenius plots for oxygen pressures above 10^{-6} atm[99,115,414,423] indicate that the activation energies for ionic and p-type conduction are approximately equal. They are about 25 kcal/mole.[99,423] Deviations from the Arrhenius relationship were observed above 1100[414] and 1200°.[423] The high-temperature slopes were dependent on the thermal history of the sample.[423] More work is required to clarify these discrepancies.

Conductivity data for ThO_2–rare earth oxide systems are almost nonexistent. Hund[431] reported a conductivity of 3.2 ×

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Table XV

Ionic Conductivities (ohm^{-1} cm^{-1} × 10^2) of ThO_2–Y_2O_3 Electrolytes at 1000° [a]

Composition, % Y_2O_3/% $YO_{1.5}$ 2.6/5	5.3/10	7.0/13	8.1/15	14.3/25	Ref
				0.06[b,d]	412
				0.71 (24.7)[c,d]	430
0.05 (28.1)	0.20 (25.0)		0.23 (23.1)	0.10 (25.9)	99
				0.24 (24.7)[d]	115
1.3[d]					414
0.32 (27.7)			0.72 (27.7)	0.54 (27.7)	425
0.74	1.3				424
		2.9 (25.4)[e]			423

[a] Activation energies (kcal/mol) are in parentheses. [b] 12.4% Y_2O_3/22% $YO_{1.5}$. [c] 11.7% Y_2O_3/21% $YO_{1.5}$. [d] Measured in air and, therefore, values are for mixed p-type and ionic conductivity. [e] Activation energy was derived from a log σT *vs.* $1/T$ plot.

10^{-3} ohm^{-1} cm^{-1} at 1000° in air for ThO_2 + 14% La_2O_3, while Steele and Alcock[99] stated that compositions containing 5 and 8% La_2O_3 have conductivities about 10% higher than the corresponding ThO_2–Y_2O_3 solutions. The ThO_2–Nd_2O_3 system might prove an interesting one to study because of the similarity of the radii of the Th^{4+} and Nd^{3+} ions and the stability of these valence states.

The results available for ThO_2–alkaline earth oxide electrolytes are summarized in Table XVI. For each system, the maximum conductivities are shown. The conductivities of ThO_2–CaO electrolytes are one order of magnitude lower than those of ThO_2–Y_2O_3 electrolytes, although their activation energies are almost identical. Defect interactions between Ca^{2+} ions and anion vacancies will be relatively strong (section II.J). Wachtman[435] accounted for internal friction and dielectric loss peaks in ThO_2 + 1.5% CaO with a model whereby the Ca^{2+} ions are associated with anion vacancies. He suggested that the activation energy for ionic conduction may include the energy required to move a vacancy neighboring a Ca^{2+} ion, which he found to be 21.4 kcal/mol, and the energy required to separate the defect pair. In the ThO_2–CaO system, the maximum conductivity seems to occur at about 5% CaO, but remains almost constant from 5 to 15% CaO.[99,432,433] It might reasonably be expected at a lower vacancy concentration than in the ThO_2–Y_2O_3 system because of the stronger defect interactions, *i.e.*, <7–8% CaO. Above 5% CaO, the composition of the solid solution phase may not have changed since the solubility limit may have been surpassed. From Table XIV, about 10% CaO dissolves at 1800° and probably less at lower temperatures. Indeed, Ullmann[433] has shown that, above 1200°, the conductivity was independent of composition from 0 to 30% CaO, indicating that the solid solutions were decomposing. More data are needed concerning the stability of ThO_2–CaO electrolytes.

Table XVI

Total Conductivities (ohm^{-1} cm^{-1} × 10^2) of ThO_2–Alkaline Earth Oxide Electrolytes at 1000° [a]

Composition, % MO	Total conductivity[b]	Ref
5% CaO	0.075 (25.4)	432
10% CaO	0.064 (25.4)	432
5% CaO	0.047[c]	99
15% CaO	0.047[c]	99
15% CaO	0.092 (25.5)	115
5% CaO	0.049 (20.8)	433
13% BeO	0.032 (28.8)	434
13% MgO	0.10 (25.4)	434
15% SrO	0.14 (18.4)	434
15% BaO	0.44 (17.3)	434

[a] Activation energies (kcal/mol) are in parentheses. [b] Measured in air. [c] Measured at $P_{O_2} = 10^{-15}$ atm.

Unfortunately, the data for the other ThO_2–alkaline earth oxide systems[434] must be treated with much reservation. The results are entirely inconsistent with phase study work.[411] Maximum conductivities should be found at much lower alkaline earth oxide concentrations and, based on the ionic radii involved, should be lower than those found in the ThO_2–CaO system. The conductivity of ThO_2 + 15% BaO is unreasonably high. In the case of additions of BeO, MgO, and BaO, the conductivities in Table XVI must have resulted from extrinsic electronic conduction.

A comparison of Tables IV, VIII, XV, and XVI indicates that ZrO_2-based electrolytes have conductivities which are one to two orders of magnitude higher than the corresponding ThO_2-based electrolytes. In the fluorite lattice, the anions have larger gaps between the cations through which to move when the cations are small. However, since the gap sizes are 90 and 89% as large as the anions for ZrO_2 and ThO_2, respectively,[185] other factors must also be important.

C. TRANSPORT PROPERTIES

In this section, the major advantage of ThO_2-based electrolytes over ZrO_2-based ones will be discussed, this being their greater stability under highly reducing conditions. This property is particularly important at high temperatures (1200–1600°) where n-type conductivity can seriously impair the performance of ZrO_2-based electrolytes.

n-Type conductivity arises from a loss of oxygen from the lattice. Excess electrons must now be present to maintain charge neutrality. The marked stability of the Th^{4+}, Y^{3+}, La^{3+}, and Ca^{2+} ions helps the crystals resist this loss. Below 10^{-6} atm, the conductivity of ThO_2–Y_2O_3 electrolytes has been found independent of oxygen pressure down to 10^{-15},[99,424] 10^{-19},[423] and 10^{-22} [425] atm at 1000°. Markin, Bones, and Wheeler[110] mentioned that measurable electronic conduction

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(432) Z. S. Volchenkova and S. F. Pal'guev in ref 27, p 104.
(433) H. Ullmann, *Z. Chem.*, **9**, 39 (1969).
(434) Z. S. Volchenkova and S. F. Pal'guev in ref 51, p 53.
(435) J. B. Wachtman, Jr., *Phys. Rev.*, **131**, 517 (1963).

did not even result from placing thorium pellets on both sides of the electrolyte and flushing with dry hydrogen. Patterson, Bogren, and Rapp[63] estimated that $t_i > 0.99$ to at least 10^{-34} atm of oxygen at 1000° from the results of dc polarization experiments.

p-Type conductivity, proportional to $P_{O_2}{}^{1/4}$ for both ThO_2–Y_2O_3[424,425,430a] and ThO_2–CaO[5] solutions, occurs in conjunction with ionic conductivity at high oxygen pressures. About a 50% variation in conductivity between 1 and 10^{-22} atm at 870° was noted for ThO_2–La_2O_3 electrolytes.[85] Recently, Ullmann[90] determined the oxygen permeability of $ThO_2 + 11\%\ Y_2O_3$ in air. Transport proceeds *via* the unidirectional migration of O^{2-} ions and electron holes and is controlled by the mobility of the O^{2-} ions. The activation energy for permeability of 25.4 kcal/mole is in excellent agreement with the activation energies for ionic conduction in Table XV.

Transport numbers at high oxygen pressures can be determined by emf measurements. An average ionic transport number $\bar{t}_i$ can be calculated using eq 1. Providing that the oxygen pressures P_{O_2}' and P_{O_2}'' at the electrodes are not too different, $\bar{t}_i$ will be approximately equal to t_i at $\bar{P}_{O_2}$ where

$$\log \bar{P}_{O_2} = \frac{\log P_{O_2}' + \log P_{O_2}''}{2} \qquad (13)$$

They will be exactly equal if t_i varies linearly with log P_{O_2} (eq 4). Such a variation is roughly approximated for values of t_i between 0.2 and 0.8 (eq 5). From results of emf measurements with gaseous electrodes at 1000°, $\bar{t}_i = 0.89$ (15% CaO),[92] 0.87 (15% La_2O_3),[436] and 0.73 (15% Nd_2O_3)[436] at $\bar{P}_{O_2} = 10^{-1}$ atm, 0.70 (7% Y_2O_3) at $\bar{P}_{O_2} = 10^{-0.5}$ atm, [423] and 0.63 (3% Y_2O_3) at $\bar{P}_{O_2} = 10^{-0.3}$ atm.[414] Additions to ThO_2 are in parentheses. From conductivity measurements, $t_i = 0.91$ and 0.65 at oxygen pressures of 10^{-2} and 1 atm, respectively, for $ThO_2 + 7\%\ Y_2O_3$.[423] Considering the experimental difficulties associated with separating the gas streams on opposite sides of the electrolyte pellets for the emf measurements, the agreement is quite reasonable. Wimmer, Bidwell, and Tallan[423] found that the transport numbers are approximately independent of temperature from 900 to 1500° in agreement with the similarity of the activation energies for ionic and p-type conduction. Ionic transport numbers have been shown to increase somewhat with temperature from 650 to 1000°,[92] 1000 to 1400°,[414] and 400 to 1000°.[430a] Concentration polarization, resulting from open-circuit oxygen transfer through the electrolyte, might lower the emf. This polarization will be more detrimental at low temperatures. Finally, ionic transport numbers increase with Y_2O_3 content from 0 to 3,[414] 0 to 5,[424] and 0 to 8% Y_2O_3.[425]

Transport numbers at intermediate oxygen pressures can be calculated from the results of emf measurements with metal-metal oxide electrodes. Galvanic cells incorporating ThO_2-based electrolytes and electrodes of Ni-NiO and Cu-Cu_2O,[99,115,291,423,425] Fe–Fe_xO and Cu–Cu_2O,[92] and Fe-Fe_xO and Ni-NiO[99,423] have been constructed. At 1000°, these cells impose average oxygen pressures (eq 13) of $10^{-8.3}$, $10^{-10.5}$, and $10^{-12.6}$ atm, respectively.[228] For the Ni-NiO, Cu–Cu_2O cell, readings were 3-5% too low with electrolytes containing either 0.5% Y_2O_3, 14% Y_2O_3, or 5% CaO.[99] The deviations were greater if the electrolyte had been previously heated to 1450° in air or oxygen.[115] For this cell, deviations were also observed at 800–1100°[425] and $\bar{t}_i \geqslant 0.995$ at 900°.[423] For the Fe–Fe_xO, Cu–Cu_2O cell, $\bar{t}_i = 0.995$ at 1000°.[92] Lastly, for the Fe–Fe_xO, Ni–NiO cell, theoretical emf's were obtained at 1000°,[99] although small deviations and unsteady readings over a period of several days have been reported.[423] In general, these measurements do not yield accurate transference numbers when $t_i \sim 1$. An electronic contribution of 0.5% only amounts to a difference of 1 mV in 200 and, in most experiments, the emf's are only reproducible to ±1 mV. For example, the deviations tabulated by Lasker and Rapp[425] seem comparable between cells imposing average oxygen pressures of $10^{-8.3}$ and $10^{-11.2}$ atm.

Nevertheless, the above results do illustrate a very important point. Although conductivity measurements are too insensitive to detect p-type conductivity below about 10^{-6} atm of oxygen, accurate emf measurements require one or both electrodes to be at much lower oxygen potentials. For $t_i = 0.65$ at $P_{O_2} = 1$ atm,[423] $t_i > 0.999$ only when $P_{O_2} < 10^{-11}$ atm, assuming that the p-type conductivity obeys the $P_{O_2}{}^{1/4}$ law. Consequently, the electrodes should impose an average oxygen pressure on the electrolyte no greater than 10^{-11} atm. Ullmann[430a] found that, for the cell H_2, $H_2O|ThO_2 + 11\%\ Y_2O_3|Ar,O_2$ which imposed oxygen pressures of 10^{-18} and 10^{-3} atm at 1000° at the anode and cathode, respectively, $\bar{t}_i > 0{,}999$.

Successful emf studies at low oxygen potentials have indirectly confirmed the ionic behavior of ThO_2-based electrolytes. The systems which have been investigated are listed in Table XVII. The oxygen potentials were either taken directly from the respective papers or calculated.[100] In several investigations,[110,114,423,439–441] the thermodynamic data derived from the emf measurements agreed to within ±500 cal/$^1/_2O_2$ of gas equilibrium or calorimetric data. Excluding one paper,[443] there is a scatter of about 15 mV at 1000° among the results for the Nb–NbO, Fe–Fe_xO cell. Although the free energy data for NbO given by Worrell[439] differed by 2 kcal from thermal data, his results for Ta_2O_5 using a Nb–NbO reference electrode supported their accuracy. Also, Yuill and Cater[291] obtained consistent results using Worrell's data for their Ta–Ta_2O_5 and Nb–NbO reference electrodes. The cells shown in Table XVII conclusively indicate that the level of electronic conductivity in ThO_2-based electrolytes is extremely low at an oxygen pressure of 10^{-25} atm at 1000°. Usually, the emf's were steady and reproducible and the electrodes were often shown to be reversible.[99,291,439,440] Most of the scatter for the Nb-NbO, Fe-Fe_xO cell and also for the Nb-NbO, NbO-NbO_2 cell[99,439] can be attributed to interference from the cell atmosphere. Either vacuum degassing, carefully purified inert gases, or reactive metals to remove oxygen are essential for successful operation of galvanic cells at low oxygen potentials.[99,110,115,291,439]

Electronic conductivity has been observed when ThO_2-based electrolytes contacted Mn–MnO,[440] Ta–Ta_2O_5,[442] and

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(436) A. D. Neuimin and S. F. Pal'guev, *Silikaty Okisly Khim. Vys. Temp., Akad. Nauk SSSR, Inst. Khim. Silikatov, Vses. Khim. Obshch. im D.I. Mendeleeva*, 253 (1963); *Chem. Abstr.*, **62**, 15536 (1965).

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Table XVII

Emf Studies at Low Oxygen Potentials Using ThO_2-Based Electrolytes

System	*Oxygen potential at 1000°, log P_{O_2}*	*Additive to ThO_2*	*Ref electrode*	*Temp range, °C*	*Ref*
TiO_{2-x}	−18[a]	5% Y_2O_3	Fe–Fe_xO	700–1050	437
NbO_{2-x}	−20[a]	5% Y_2O_3	Fe–Fe_xO	850–1050	437
CeO_{2-x}	−21[a]	La_2O_3	Fe–Fe_xO	700–1000	438
		8% Y_2O_3		750–1100	110
US–UOS–UO_2	−22	7% Y_2O_3	Ta–Ta_2O_5 Nb–NbO	780–1085	291
NbO–NbO_2	−22	Y_2O_3[b]	NbO_2–Nb_2O_{5-x} Fe–Fe_xO	800–1050[c]	99
		7% Y_2O_3 7% CaO	NbO_2–Nb_2O_{5-x} Fe–Fe_xO	755-1025	439
Mn–MnO	−24	7% Y_2O_3	Cr–Cr_2O_3	700–1000[c]	423
		5% Y_2O_3	Ni–NiO Fe–Fe_xO	650–1000	440
		8% Y_2O_3	CO–CO_2 H_2–CO_2	1260–1550	114
Ta–Ta_2O_5	−25	7% Y_2O_3	Nb–NbO	755–1025	439
		5% CaO	Fe–Fe_xO	800–1100	441
		8% Y_2O_3	Fe–Fe_xO	700–1000	442
Nb–NbO	−25	Y_2O_3, CaO, or La_2O_3	Fe–Fe_xO	800–1100	99, 110, 115, 441, 443–445
		0.5% Y_2O_3	Ni–NiO NbO–NbO_2	800–1050[c]	99
		7% Y_2O_3	NbO–NbO_2	755-1025	439
PuO_{2-x}	−26[a]	8% Y_2O_3	Ni–NiO Fe–Fe_xO	700–1140	446
Al–Al_2O_3	−35	8% La_2O_3	Fe–Fe_xO	560–755	447
Zr–ZrO_2	−35	7% Y_2O_3	Nb–NbO	1012	448

[a] Oxygen potential for the largest value of x which was studied. [b] Several electrolyte compositions were used. [c] Assuming the same temperature range was covered as that shown for other cells in the respective papers.

Nb–NbO[99,115] electrodes. It could be virtually eliminated by increasing the thickness[99,115,440] or changing the composition[99] of the electrolyte to increase its resistance. However, these changes produced no effect in one case.[442]

Markin and Rand[446] appear to have shown that ThO_2-based electrolytes are useful at oxygen pressures of 10^{-26} atm at 1000°. Similar data were obtained from both reference electrodes, and they agreed with an independent phase diagram study. Attempts to measure the emf of the cell Si, $SiO_2|ThO_2$–$La_2O_3|$Fe, Fe_xO (P_{O_2} for Si–SiO_2 is 10^{-28} atm at 1000°) have been unsuccessful.[449,450] However, these failures cannot definitely be attributed to electronic conductivity in the electrolyte. Worrell[448] observed a small but steady drift in the emf of a cell having a Zr–ZrO_2 electrode but, again, the reason for this could not be unequivocally determined. Two interesting low-temperature investigations should be mentioned. Barbi[447] obtained free-energy data for Al_2O_3 by first cathodically reducing the aluminum surface-oxide layer and then plotting emf *vs.* time. After equilibrium was rapidly restored at the reference electrode–electrolyte interface, the emf decayed slowly due to a decrease in the aluminum activity. This portion of the curve was extrapolated to zero time to yield the cell emf. The Al–Al_2O_3 electrode will impose an oxygen potential of 10^{-52} atm at 650° on the electrolyte. His results were in reasonable agreement with the literature.[100] Kolodney, Minushkin, and Steinmetz[451] measured the oxygen content in liquid sodium at 316° with a ThO_2 + 17% Y_2O_3 electrolyte and a Cu–Cu_2O reference electrode. An oxygen content of 10 ppm by weight represents an oxygen potential of 10^{-61} atm at this temperature. The emf's obeyed the Nernst equation but were 2–3% too low. Extrinsic electronic conduction in the electrolyte might be important at low temperatures.

Several quantitative evaluations of the range of applicability of ThO_2-based electrolytes have been attempted. Since electronic conduction was apparent in the presence of Nb–NbO but essentially absent for Mn–MnO, Steele and Alcock[99] estimated that $t_i > 0.99$ at 1000° above $10^{-24.5}$ atm of oxygen. Therefore, from eq 5, $P_\ominus \sim 10^{-33}$ atm at 1000°. This value agrees with the analysis proposed by Vecher and Vecher.[452] These authors assumed that the ratios of $P_\ominus$ to the dissociation pressure for both ZrO_2 and ThO_2 were equal. For ZrO_2, the values for $P_\ominus$ in eq 7 were used. Practically identical results were obtained by using eq 1, 4, and 5 in conjunction with the discrepancy between Barbi's results[447] and literature data[100] for Al_2O_3. This agreement must be considered fortuitous since the

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(444) V. N. Drobyshev and T. N. Rezukhina, *Zh. Fiz. Khim.*, 39, 151 (1965); *Russ. J. Phys. Chem.*, 39, 75 (1965).

(445) V. N. Drobyshev and T. N. Rezukhina, *Izv. Akad. Nauk SSSR, Metal.*, 156 (1966); *Russ. Met.*, 85 (1966).

(446) T. L. Markin and M. H. Rand in ref 116b, p 145.

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(449) A. A. Vecher, R. A. Vecher, V. A. Geiderikh, and I. A. Vasil'eva, *Zh. Fiz. Khim.*, 39, 2080 (1965); *Russ. J. Phys. Chem.*, 39, 1110 (1965).

(450) Y. I. Gerasimov in ref 116b, p 184.

(451) M. Kolodney, B. Minushkin, and H. Steinmetz, *Electrochem. Technol.*, 3, 244 (1965).

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magnitudes of this discrepancy and the error limits given for Al_2O_3[100] are comparable. From a comparison between the measured and theoretical emf's for the cell Ta, $Ta_2O_5|ThO_2–Y_2O_3|$Fe, Fe_xO, Levine and Kolodney[442] calculated that $P_\Theta = 10^{-28.6}$ atm at 1027°. This value seems inconsistently high. Similarly, the previously mentioned estimated result that $t_i > 0.99$ to at least 10^{-34} atm of oxygen at 1000°[63] appears too low. A direct determination of P_Θ was effected recently by Tretyakov and Muan.[120] Oxygen was coulometrically titrated out of the cathode chamber until the cell voltage reached a plateau. Inserting the voltage for several temperatures into eq 6 yielded the equation

$$\log P_\Theta = -\frac{56.3 \times 10^3}{T} + 13.4 \qquad (14)$$

from 1000 to 1400°K. At 1000°, $P_\Theta = 10^{-31}$ atm. For $\bar{t}_i \geqslant 0.99$

$$\log P_{O_2}' \geqslant -\frac{56.3 \times 10^3}{T} + 17.4 \qquad (15)$$

where, again, P_{O_2}' is the oxygen pressure at the anode. Equation 15 applies to an air or oxygen reference electrode which cannot be used in contact with ThO_2. For a reference electrode exerting a lower oxygen potential, the minimum permissible pressures in eq 15 will be slightly higher. However, cells of the type Mn, $MnO|ThO_2–Y_2O_3|ZrO_2–CaO|$air can be constructed to eliminate the problem of p-type conduction in the $ThO_2–Y_2O_3$ electrolyte.[120]

A comparison of eq 7, 8, 14, and 15 and estimated values of P_Θ for ThO_2-based electrolytes[99, 452] indicates that the latter are useful to oxygen pressures three to five orders of magnitude lower than ZrO_2-based electrolytes. Below 10^{-25} atm of oxygen at 1000°, this might be an academic question only. Experimental difficulties will be the determining factor.

The behavior of ThO_2-based electrolytes above 1200° has been relatively unexplored. Conductivity measurements[423] and emf measurements with the cell Mn, $MnO|ThO_2–Y_2O_3|$air[114] have indicated that transport numbers at high oxygen pressures are independent of temperature to 1500–1600°. Wimmer, Bidwell, and Tallan[423] observed n-type conductivity using blocking-electrode polarization techniques and suggested that the condition that $t_i > 0.99$ might be impossible to achieve above 1400° at any oxygen pressure. Undoubtedly, either interference from gas-electrode reactions or, alternately, easily reduced impurities in the electrolyte influenced this conclusion. The p–n transition occurs at oxygen pressures of 10^{-12} and 10^{-8} atm at temperatures of 1400 and 1600°, respectively.[423] This means that the activation energy for n-type conduction is greater than that for p-type conduction and, consequently, ionic transport numbers decrease with increasing temperature at low oxygen pressures. As yet, the critical oxygen pressures at which n-type conductivity becomes significant are unknown. Baker and West[87] stated that electronic conductivity interfered with the performance of a $ThO_2–Y_2O_3$ electrolyte in contact with $H_2–H_2O$ electrodes around 1600°. Schwerdtfeger[114] obtained accurate free energy data for MnO up to 1550°. At this temperature, the Mn–MnO electrode has an equilibrium oxygen pressure of 10^{-14} atm. Recently, it was found that $ThO_2–Y_2O_3$ electrolytes are almost solely ionic conductors in contact with the $Si–SiO_2$ electrode at 1600°, *i.e.*, at an oxygen pressure of 10^{-16} atm.[128] Satisfactory results were obtained for measurements of the oxygen contents in silicon-rich liquid iron down to less than 1 ppm oxygen by weight, *i.e.*, $<3 \times 10^{-15}$ atm.[128]

In summary, the greater stability of ThO_2-based electrolytes compared to ZrO_2-based electrolytes makes them important in applications involving low oxygen potentials. Also, their lower conductivities will reduce the open-circuit oxygen transfer between the electrodes. n-Type conductivity can be markedly increased by the presence of impurities which could introduce energy levels near the conduction band. The use of very pure materials to fabricate the electrolytes cannot be overemphasized.

D. APPLICATIONS

The thermodynamic properties of the systems listed in Table XVIII have been investigated with ThO_2-based electrolytes. Additionl emf data are available for the Ni–NiO, $Cu–Cu_2O$[291] and $Fe–Fe_xO$, $Fe_xO–Fe_3O_4$[443] cells. Several of the studies dealing with nonstoichiometric oxides used the method of coulometric titration to control composition.[437, 474, 475] Rezukhina and his coworkers have contributed all the available data on ternary compounds using $ThO_2–La_2O_3$ electrolytes and $Fe–Fe_xO$ reference electrodes, although $Mo–MoO_2$[457] and Nb–NbO[470] were also used. Measurements were occasionally extended as high as 1300°.[454, 462, 465] It is interesting to note that if the data given for $CaTiO_3$[470] are correct, and they agree reasonably well with calorimetric data,[100] then ThO_2 + 15% La_2O_3 exhibits predominantly ionic conduction at an oxygen pressure of 10^{-30} atm at 1000°. Attempts to obtain some information about $TiO_{0.5}$ by coulometric titration of titanium were unsuccessful, perhaps due to the slow diffusion of oxygen in titanium.[470]

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Table XVIII

Thermodynamic Property Measurements Using ThO_2-Based Solid Electrolytes

	References
Oxides	
Cu_2O	453
NiO	453, 454
Fe_xO	453
PbO	236
SnO_2	455
CoO	453, 456
MoO_2	457
WO_2	458, 459
Cr_2O_3	460
MnO	114, 440
Ta_2O_5	439, 441
NbO	99, 439, 441, 444
Nb_2O_{5-x}	439
NbO–NbO_2	99, 439
NbO_2–Nb_2O_{5-x}	99, 439
Al_2O_3	447
Oxide Solid Solutions	
(Mn,Ni)O	461
Ternary Compounds	
$CoMoO_3$	462
$CoMoO_4$	462
$MgMoO_3$	463
$MgMoO_4$	251, 463
$MgWO_4$	464
$CaWO_4$	108, 465
Ca_3WO_6	465
$SrWO_4$	252
$BaWO_4$	465
Ba_3WO_6	465
$NiCr_2O_4$	454
$CoCr_2O_4$	456
Ternary Compounds	
$FeCr_2O_4$	466
$NiAl_2O_4$[a]	467
$CoAl_2O_4$[a]	467
$FeAl_2O_4$	468
$CoTiO_3$	469
$CaTiO_3$	470
Silicides	
$TaSi_2$, $Ta_{4.5}Si$, Ta_5Si_3, Ta_2Si	442
Solid Alloys	
Pd–Cu	259
Pd–Sn	259
Pd–Fe	262, 471
Pt–Fe	262, 471
Au–Co	472
Au–Fe	471, 472
Co–Mo	457
Co–W[b]	458
Co–Nb	444
Fe–Nb	445
Liquid Alloy	
Fe–Mn	114
Nonstoichiometric Compounds	
$U_yPu_{1-y}O_{2\pm x}$	473
TiO_{2-x}	437, 474
NbO_{2-x}	437
$Ti_{0.5}Nb_{0.5}O_{2\pm x}$	437
Ta_2O_{5-x}[c]	475
CeO_{2-x}	110, 438
PuO_{2-x}	446
Gas Mixtures	
CO–CO_2	288, 476

[a] Contain excess Al and O in stoichiometric amounts. [b] The intermetallic compound Co_3W was considered. [c] Claimed that this phase existed until $x = 0.46$ which is rather unlikely.

Thoria-based electrolytes have been used to measure the oxygen pressure in gas mixtures,[327] the oxygen activity in liquid Pb,[236] Sn,[455] Fe,[128] and Na,[451] as a reference electrode in KCl-NaCl-Na_2O melts,[477] as elements in oxide resistor furnaces,[478–480] and in thermal cells with oxygen electrodes.[402,481] Low conductivities and the presence of p-type conductivity at high oxygen pressures preclude their use in fuel cells.

The choice of an electrolyte for a given application depends, in part, on its chemical stability toward the electrodes. For instance, ThO_2 and Al react to form $ThAl_3$,[447] and ThO_2-Y_2O_3 electrolytes interact with Fe–Fe_xO mixtures,[425,439,446] apparently resulting in the formation of $YFeO_3$.[439] The latter problem has been overcome by simply cleaning the surface of the Fe–Fe_xO electrodes between runs[446] and was not experienced by Kubik and Alcock[471] who prepared very dense electrolytes by an oxalate coprecipitation method. Electrolytes with low permeabilities are also essential when dealing with condensed phases having high vapor pressures[440] or with gas electrodes.[288,453,476] In general, ThO_2-based electrolytes are chemically quite inert. They exhibit excellent corrosion resistance in molten sodium[451] and strongly alkaline melts.[477] Despite their low conductivities, measurements can be extended to temperatures as low as 500°[115,236,327,447,455] and even 316°.[451]

Several other oxide systems provide alternative solid electrolytes to those based on ZrO_2 and ThO_2. These will now be discussed.

V. CeO_2-Based Electrolytes

A. PHASE RELATIONS

Analogous to ThO_2, CeO_2 has the cubic fluorite structure, but Ce^{4+} ions are easily reduced to the +3 valence state at low oxygen pressures. The solubilities of the alkaline earth oxides, Sc_2O_3, Y_2O_3, and the rare earth oxides in CeO_2 are presented in Table XIX. Direct reaction between CeO_2 and SrO results in the formation of $SrCeO_3$ at 1100–1200° followed by its reac-

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Table XIX

Solubilities of Di- and Trivalent Metal Oxides in CeO_2

Oxide	*Temp, °C*	*Solubility, % MO or M_2O_3*	*Ref*
MgO	1600	~2	482
CaO	1600	15	483
SrO	1600	9	483
Sc_2O_3	1750	5	192
Y_2O_3	1400	100	413, 484
	1200	100	485
	1400	32	486
La_2O_3	1275	44	487
	1600	29	488
	1600	41	489
Pr_2O_3	1400	33	490
Nd_2O_3	1400	50	490
	1400	63	413
	1600	40	488
Sm_2O_3	1400	100	413
Eu_2O_3	1400	100	491
Gd_2O_3	1400	100	413
	1600	37	488
Dy_2O_3	1400	100	413
	1600	25	186
	1600	41	488
Yb_2O_3	1400	33	413
	1400	25	488

tion with excess CeO_2 at 1500–1600° to form a cubic solid solution.[492] In another study, the compound Sr_2CeO_4 was found between 1100 and 1430°.[493] Solid solutions are not formed between CeO_2 and BaO.[483] The solubility limits of Y_2O_3 and the rare earth oxides are in considerable disagreement. Bauer and Gradinger[413] found complete miscibility in many instances, whereas miscibility gaps between the fluorite and C-type rare earth oxide structures were observed in all the systems in more recent investigations.[486,488] The attainment of equilibrium was emphasized in these latter studies. Identical results were obtained at 1600° for samples prepared by either coprecipitation or direct mixing and phase boundaries could be traced by heating and cooling between 1500 and 1700°. Therefore, these results[486,488] should be the more reliable. A degree of long-range ordering takes place at relatively low defect concentrations in these solid solutions. For instance, in the CeO_2–Y_2O_3 system, X-ray diffraction lines characteristic of the C-type rare earth oxide structure have been evident at 8,[485] 11,[486] and 18% Y_2O_3.[494] Ordering is favored by the smaller trivalent metal cations.[485,494]

The anion vacancy model for the solid solutions has been confirmed by both density[483,487] and X-ray intensity[487,490] studies. The following lattice parameters have been given for CeO_2 + 10% M_2O_3 solutions: 5.408,[485] 5.405,[413,486] and 5.404 Å[495] for Y_2O_3, 5.451 Å for La_2O_3,[487] 5.448 Å for Pr_2O_3,[490] 5.441[490] and 5.445 Å[413] for Nd_2O_3, 5.431 Å for Sm_2O_3,[413,485] 5.420[485] and 5.422 Å [413] for Gd_2O_3, 5.411[413] and 5.406 Å[186] for Dy_2O_3, and 5.392[413] and 5.393 Å[488] for Yb_2O_3. Bevan, Barker, and Martin[486] found that the lattice parameters in the CeO_2–Y_2O_3 system were proportional to $[YO_{1.5}]^2$ with the constant of proportionality changing at 5% Y_2O_3 (10% $YO_{1.5}$). They suggested that the defects (Y^{3+} ions and anion vacancies) interact strongly and that, above about 6% Y_2O_3, all the point defects are complexed and the complexes begin to interact. Complex lattice parameter dependences were also found in the case of Gd_2O_3, Dy_2O_3, Ho_2O_3, and Yb_2O_3.[488]

Ternary oxide systems involving CeO_2 might provide useful solid electrolytes. Ceria can dissolve 76% ZrO_2 at 2000°,[496] ~60% ZrO_2 at 1750°,[496,497] 50% ZrO_2 at 1550°,[496,498] and 27% ZrO_2 at 800°.[499] However, Duwez and Odell[496] have indicated that the solubility limit is only about 10% ZrO_2 at 1000°. Also, tetragonal ZrO_2 can dissolve about 20% CeO_2.[496,497,499] Ceria and ThO_2 are completely miscible.[413,495,499,500] A significant amount of CaO will dissolve in $Ce_{0.75}Zr_{0.25}O_2$ at 1350–1550°,[501,502] although the reported limit of 40% CaO appears somewhat high. The ZrO_2 + 15% CaO composition retained its fluorite structure even when 50% of the ZrO_2 was replaced with CeO_2.[382] Equimolar compositions in the CeO_2–ThO_2–CaO and CeO_2–ThO_2–$LaO_{1.5}$ systems were single-phase at 1600°.[421] It has also been stated that separation into two fluorite phases occurs at very low defect concentrations when one of the cations is present in two valence states, *e.g.*, the CeO_2–ThO_2–Ce_2O_3 system.[421,495] However, samples of $(Ce,Th)O_{2-x}$ were single phase after reduction in hydrogen until $x = 0.25$.[500]

An excellent review about ionic radii, lattice parameters, and solubility limits in ZrO_2-, ThO_2-, and CeO_2-based systems has been written by Moebius.[1]

B. ELECTRICAL CONDUCTIVITIES

The limited conductivity data available for CeO_2-based systems are summarized in Table XX. In all cases, the composition having the maximum conductivity is shown. In the CeO_2–La_2O_3 system, the conductivity increases rapidly to about 5% La_2O_3 and then increases only slightly beyond this com-

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Table XX

Total Conductivities (ohm^{-1} cm^{-1} × 10^2) of CeO_2-Based Electrolytes at 1000°[a]

Composition, % MO or M_2O_3	*Total conductivity*[b]	*Ref*
15% La_2O_3	5.1 (14.7)	503
5% La_2O_3	0.10 (20.9)[c]	504
11% La_2O_3	7.0	344, 489
15% La_2O_3	9.0 (21.0)[d]	346
15% BeO	0.65 (23.1)	505
15% MgO	2.4 (13.8)	505
15% CaO	2.5 (17.3)	505
15% SrO	6.7 (13.8)	505
10% BaO	0.49 (13.8)	505

[a] Activation energies (kcal/mol) are in parentheses. [b] Measured in air. [c] Extrapolated from 850°. [d] Extrapolated from 900°.

position.[344,489,506] A limited number of measurements have also been reported for the CeO_2–Y_2O_3 and CeO_2–Nd_2O_3 systems.[494,506,507] A CeO_2 + 7% Y_2O_3 sample had an activation energy of 19.8 kcal/mol from 360 to 800°.[494]

The results for the CeO_2–alkaline earth oxide systems are somewhat erratic. The slope changes in Arrhenius plots from 450 to 900° could have arisen from nonequilibrium conditions or impurities. Both BeO and BaO are virtually insoluble in CeO_2, and the conductivities in Table XX for these systems are only slightly greater than the conductivity of CeO_2.[505] The conductivity maximum at 15% SrO was also reported in another paper.[508] It might be reasonably expected at a lower composition since the solubility limit[483] has been surpassed and, secondly, strong interactions are present between Sr^{2+} ions and anion vacancies.[509] The interaction energy was estimated at 13.8 kcal/mol.[509] In addition, the conductivity shown for the 15% SrO composition is inconsistently high and would not be expected (Table I) to exceed that for the 15% CaO solution. From Table XX, it is evident that the conductivities of the CeO_2-based solid solutions are comparable to the ZrO_2-based systems.

Studies of the $Ce_{0.75}Zr_{0.25}O_2$–CaO system have also been made.[501,502,510] The conductivity decreased until 8% CaO and then increased to a maximum of 3 × 10^{-2} ohm^{-1} cm^{-1} at 1000° for 30–40% CaO. The corresponding activation energy was 18.4 kcal/mol.

Pal'guev and his coworkers[511] have published a summary of their electrical conductivity studies on refractory oxide systems based on ZrO_2, ThO_2, CeO_2, and $Ce_{0.75}Zr_{0.25}O_2$.

C. TRANSPORT PROPERTIES

At high oxygen pressures, CeO_2–rare earth oxide solutions are anionic conductors.[512] When lower valent cations are introduced into the Ce^{4+} sublattice, the formation of anion vacancies is energetically more favorable than the formation of electron holes.[513] Measurements of ionic transport numbers in the CeO_2–Y_2O_3, CeO_2–La_2O_3, and CeO_2–Nd_2O_3 systems using oxygen concentration cells[507] and electrolysis experiments[514] indicated that they are virtually unity near an oxygen pressure of 1 atm. Even for CeO_2 + 2% Y_2O_3, t_i = 0.98 at 1000°.[514] Cation transport numbers are less than 0.004 at 1000–1100°.[514] Unfortunately, n-type conductivity interferes at intermediate oxygen pressures. Emf measurements established that for CeO_2 + 11% La_2O_3, $\bar{t}_i = 0.93$ at $\bar{P}_{O_2} = 10^{-1}$ atm, but was only 0.54 at $\bar{P}_{O_2} = 10^{-8}$ atm and 1000°.[344] At $P_{O_2} = 10^{-15}$ atm and 1000°, $t_i = 0.18$.[515] Also, ionic transport numbers decrease with increasing temperature owing to the reduction of CeO_2.[344]

An important question to answer is whether or not the presence of anion vacancies helps to stabilize the Ce^{4+} ions. At low oxygen pressures

$$O^{2-} = {}^1/_2O_2(g) + V_O^{\cdot\cdot} + 2e' \qquad (16)$$

where e′ is an excess electron which can be easily accommodated by a Ce^{4+} ion. Higher vacancy concentrations will shift this reaction to the left and, of course, the concentration of Ce^{4+} ions will decrease when the La_2O_3 concentration is increased. Therefore, ionic transport numbers should increase. This conclusion contradicts a study of the reduction of CeO_2–La_2O_3 mixtures in CO–CO_2 atmospheres.[515] However, at $\bar{P}_{O_2} = 10^{-8}$ atm and 1000°, $\bar{t}_i = 0.90$ for CeO + 33% La_2O_3.[244] As expected from eq 16, n-type conductivity varies as $P_{O_2}^{-1/4}$.[515]

At high oxygen pressures, CeO_2–MgO,[92] CeO_2–CaO,[516] and CeO_2–SrO[516] solid solutions are predominantly ionic conductors from 700 to 1100°. A significant fraction of the current was carried by O^{2-} ions during the electrolysis of CeO_2 + 0.86% CaO at 450°[517] and CeO_2 + 3% CaO at 460[518] and 960°.[519] A blue-gray discoloration appeared at the cathode and became more pronounced as the CaO content increased.[517] Both current transients at low applied voltages[517] and potential distribution curves at constant currents[519] could be explained on the basis of O^{2-} ion migration. The transients were more marked at low oxygen pressures (down to 10^{-4} atm)[517] and high temperatures.[519] By measuring the conductivity of CeO_2 + 3% CaO in oxygen and argon, ranges of predominantly ionic (400–600°), mixed ionic and p-type (600–800°), and mixed ionic and n-type (>800°) conduction could be noted.[519] The results from a modified gravimetric method demonstrated that cation transport numbers are 0.00 in air at 1100° for CeO_2–alkaline earth oxide systems.[520] Again, n-type conductivity predominates at intermediate oxygen pressures. In contact with Fe–Fe_xO and Cu–Cu_2O electrodes ($\bar{P}_{O_2} = 10^{-10.5}$

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atm at 1000°), values for $\bar{t}_i$ of 0.49 and 0.05 at 700 and 1000°, respectively, were measured for a CeO_2–MgO sample.[92]

In the CeO_2–ZrO_2 system, although the conductivity was 5×10^{-2} ohm^{-1} cm^{-1} at 1000° and 25% ZrO_2,[521] the ionic contribution was shown to be less than 1% at 1000° from electrolysis experiments[521] and less than 2–3% at 600–1000° from emf measurements at high oxygen pressures.[501] Recently, a significant ionic contribution was reported for high ZrO_2 concentrations and high oxygen pressures.[522] For ZrO_2 + 25% CeO_2, $\bar{t}_i = 0.53$ and 0.30 at 1027° for $P_{O_2} = 10^{-0.5}$ and $10^{-2.5}$ atm, respectively.[522] Solid electrolytes are formed by the addition of CaO to CeO_2–ZrO_2 solid solutions.[501,502] The electronic conductivity is markedly lowered due to a stabilization of the Ce^{4+} ions and the ionic conductivity is increased. For oxygen pressures near 1 atm, $Ce_{0.75}Zr_{0.25}O_2$ + 19% CaO had ionic transport numbers between 0.96 and 1.00 from 600 to 1000°.[501] However, at $\bar{P}_{O_2} = 10^{-10.5}$ atm and 1000°, $\bar{t}_i = 0.30$ for $Zr_{0.70}Ce_{0.30}O_2$ + 15% CaO.[92] Samples of $Ce_{0.5}Zr_{0.5}O_2$ + 5 or 11% Sc_2O_3 were dominated by n-type conductivity between 1 and 10^{-15} atm of oxygen at 1000°.[201] An investigation of compositions such as $Zr_{0.95}Ce_{0.05}O_2$ + 10% Sc_2O_3 might prove interesting. Sufficient CeO_2 is added to increase the average cation radius enough to stabilize the fluorite phase. As expected, additions of ThO_2 to CeO_2–La_2O_3 solutions resulted in higher ionic transport numbers at the expense of conductivity.[523]

Takahashi[524] has briefly reviewed the conductivities and transport numbers of fluorite-type solid solutions.

D. APPLICATIONS

Solutions of CeO_2–ZrO_2[397,525] and CeO_2–ZrO_2–CaO[397] have been considered as possible magnetohydrodynamic electrodes. Recently, CeO_2–La_2O_3 electrolytes have been used in high-temperature fuel cells.[344,346,349,526] At 800 and 1000°, polarization (excluding ohmic polarization) was absent for H_2, C_2H_6, and C_3H_8 fuels, but present for CO and CH_4.[344,526] The polarization of Pt, O_2 electrodes in contact with CeO_2 + 15% CaO electrolytes at 650–1000° has been described.[527–530] Both concentration polarization,[527] resulting from the presence of dense Pt electrodes, and activation polarization[530] have been observed. The reduction of CeO_2 at the anode interferes with the fuel cell operation, although electronic contributions as high as 10% may be tolerable.[372] Takahashi, Ito, and Iwahara[344] improved the stability of CeO_2 by increasing the La_2O_3 content, but only at a sacrifice in conductivity. Low open-circuit voltages are inevitable and may only be about 65% of the theoretical value.[346] Since CeO_2–La_2O_3 electrolytes offer no improvement over ZrO_2–Y_2O_3 electrolytes with respect to ionic conductivity, their incorporation into fuel cells seems impractical.

Before applications of CeO_2-based electrolytes at high oxygen pressures can be justified, more research is required concerning their stability, the level of p-type conductivity, and the oxygen pressures at which n-type conductivity becomes significant.

VI. HfO_2-Based Electrolytes

A summary of the phase studies on HfO_2-based electrolyte systems is given in Table XXI. Hafnia forms solid solutions with MgO and CaO and 1:1 compounds ($MHfO_3$) with CaO, SrO, and BaO.[536–538] For directly mixed oxides, about 1400° was required to effect solid solution formation.[536] The phase boundaries of the fluorite phase in the HfO_2–MgO system are not well established. For the HfO_2–CaO system, an upper limit of 20–25% CaO at 1600° was also determined.[536] At 20% CaO, the stoichiometric, monoclinic compound $CaHf_4O_9$ has been identified.[39,539] This compound is stable below 1450°. The cubic solid solutions are unstable below 1450° and decompose into monoclinic HfO_2 and $CaHf_4O_9$.[39] Recently, the compound $CaHf_2Zr_2O_9$ was prepared,[540] but, as mentioned in section II.C, $CaZr_4O_9$ has not been positively identified. Lattice parameters of 5.106 and 5.112 Å have been given for the 10 and 15% CaO compositions, respectively, while 5.112 Å was given

Table XXI

Phase Boundaries of Cubic HfO_2-Based Solid Solutions

Oxide	*Temp, °C*	*Boundaries, % MO or M_2O_3*	*Ref*
CaO	1800	12 and 22	531
	2500	10 and 20	39
	2000	12 and 20	39
Sc_2O_3	1500	14 and 15	532
Y_2O_3	1800	8 and >40	533
La_2O_3	1500	30 and 41^a	534
Nd_2O_3	1500	29 and 38^b	185
Eu_2O_3	1500	11 and 56	185
Gd_2O_3	2000	10 and 50	535
	1500	15 and 56	535
Ho_2O_3	1500	8 and 55	185

^{a} Based on $La_2Hf_2O_7$. ^{b} Based on $Nd_2Hf_2O_7$.

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for the 12% CaO composition in another study.[29] They were not found to vary directly with the CaO concentration.[541]

Similar to the ZrO_2–Sc_2O_3 system, the HfO_2–Sc_2O_3 system is quite complex.[195,532] Three rhombohedral compounds appeared at 12.5, 16.7, and 40% Sc_2O_3, each exhibiting marked nonstoichiometry.[532] At 2000°, they extended from 9 to 13, 16 to 28, and 31 to 50% Sc_2O_3, respectively. The first two compounds were derived from a rhombohedral distortion of the fluorite lattice in opposite directions. Between them, an undistorted fluorite phase was detected at about 14% Sc_2O_3. The transitions from one structure to another were not continuous. They were separated by narrow two-phase regions.[532]

There are no fluorite solid solutions in the HfO_2–La_2O_3 system.[534] Cubic pyrochlore-type solutions based on $La_2Hf_2O_7$ are adjacent to large two-phase regions on both sides. The boundaries shown in Table XXI for the HfO_2–Eu_2O_3 and HfO_2–Gd_2O_3 systems contain regions where the solid solutions are ordered. For instance, the pyrochlore phase exists from 28 to 42 and 31 to 41% Gd_2O_3 at temperatures of 2000 and 1500°, respectively.[535] Continuous transitions occur between these two structures. In another investigation, only 7% Gd_2O_3 was required to stabilize the fluorite phase at 1900°, but 15% Gd_2O_3 was needed at 1500°.[542] At high temperatures, continuous transitions were observed between tetragonal and cubic HfO_2 solid solutions in the HfO_2–Sm_2O_3 system.[543]

A maximum conductivity of 2.9×10^{-2} ohm^{-1} cm^{-1} at 1000° and 8% Y_2O_3 was found in the HfO_2–Y_2O_3 system.[533] The Arrhenius relationship was obeyed between 900 and 1600° and the activation energy was 25.8 kcal/mol. The conductivity went through a slight minimum at 33% Y_2O_3 leading to speculation about the compound $Y_2Hf_2O_7$. Its existence was also considered in a recent paper about this system.[544] A sample of HfO_2 + 10% Y_2O_3 which was prepared by melting had a conductivity of 3.5×10^{-2} ohm^{-1} cm^{-1} at 1000° and an activation energy of 26.1 kcal/mol.[61] Johansen and Cleary[29] measured a conductivity of 0.40×10^{-2} ohm^{-1} cm^{-1} at 1000° for HfO_2 + 12% CaO. The activation energy was 33.0 kcal/mol from 800 to 2000°.

Emf measurements at high[537] and intermediate ($\sim 10^{-18}$ atm)[538] oxygen pressures have established that HfO_2-based solutions are pure ionic conductors around 1000°. The conductivity of samples containing more than 6% Y_2O_3 was unaffected by oxygen pressure in the range from 1 to 10^{-5} atm.[533] Electron holes, and not anion vacancies, controlled the rate of permeation of oxygen through HfO_2 + 14% CaO.[89]

Before HfO_2-based electrolytes can be properly evaluated, more investigations are needed on their stability and transport properties. However, based on the similarity of HfO_2 and ZrO_2 and the fact that lower ionic conductivities have been observed in the HfO_2-based systems, there appears to be no justifiable reason to conclude that they could offer any significant advantages over ZrO_2-based electrolytes. Hafnia could be used in ternary oxide electrolyte systems. Amounts of 100,[545,546] ~40,[420] and ~30% HfO_2[499] will dissolve in ZrO_2, ThO_2, and CeO_2, respectively.

VII. Electrolytes Based on Trivalent Metal Oxides

In this section, solid solutions based on either Sc_2O_3, Y_2O_3, or a rare earth oxide will be discussed. These oxides have either the cubic C-type, monoclinic B-type, or hexagonal A-type structure. The C-type structure, favored by small cations and low temperatures, is closely related to the fluorite structure. In the fluorite lattice, each cation is surrounded by a cube of eight anions. The C-type structure can be derived by removing one-quarter of the anions and slightly rearranging the remaining ions. For 25% of the cations, the vacancies (interstitial positions with respect to the C-type structure) lie along a body diagonal and the anions are located at the corners of slightly distorted octahedra. All six metal–oxygen distances are equal. For the remaining cations, the vacancies lie along a face diagonal resulting in distorted octahedra and three different metal–oxygen distances. In the case of the larger cations, further distortion results when a seventh anion attempts to squeeze into each octahedron. The resulting B-type or A-type structures are quite complex. In the hexagonal A-type structure, each cation has four close and three more distant oxygen neighbors, while the anions are either four- or five-coordinated.

All of the oxides have the C-type structure at low temperatures and Sc_2O_3, Y_2O_3, and the rare earth oxides from Dy_2O_3 to Lu_2O_3 retain this structure to temperatures in excess of 2000°. However, the oxides from La_2O_3 to Nd_2O_3 revert to the A-type structure at temperatures varying between 500 and 550° for La_2O_3[547–549] and 600 and 650° for Nd_2O_3.[550,551] The oxides from Sm_2O_3 to Dy_2O_3 revert to the B-type structure at temperatures of 850–950° for Sm_2O_3,[550–552] 1100° for Eu_2O_3,[550,551] 1200–1250° for Gd_2O_3,[550,551] 1850° for Tb_2O_3,[551,553] and 2150° for Dy_2O_3.[551,553] Foëx and Traverse[554] found the C–B transformation of Dy_2O_3 at only 1850° and observed A-type Sm_2O_3 and Eu_2O_3 at temperatures above 1850 and 2050°, respectively. All the transformations were concluded to be reversible by several authors,[551,552] but others have stated that the transformations occurring below 1500° are irreversible.[550,553–555]

A. ADDITIONS OF GROUP IVB OXIDES

As evident in Table XXII, considerable quantities of ZrO_2, HfO_2, CeO_2, and ThO_2 can be accommodated by the rare earth oxide structures. The solubility limits often increase markedly with temperature. For instance, at 2000°, Y_2O_3 will dissolve 24% ZrO_2[141] and 12% ThO_2,[414] while B-Gd_2O_3 will dissolve

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Table XXII

Solubilities of the Group IVB Oxides in Sc_2O_3, Y_2O_3, and the Rare Earth Oxides at 1500°

M_2O_3	*Solubility of ZrO_2 in M_2O_3*	*Ref*	*Solubility of HfO_2 in M_2O_3*	*Ref*	*Solubility of CeO_2 in M_2O_3*	*Ref*	*Solubility of ThO_2 in M_2O_3*	*Ref*
C-Sc_2O_3	10[a]	14	19	532				
C-Y_2O_3	20	141			46	486	7	414
A-La_2O_3	18	178	5	534	~10[b]	487	~1	416
A-Nd_2O_3	14	178			<10[a]	413	<10[a]	413
B-Sm_2O_3	3	178					<10[a]	413
B-Eu_2O_3							<1	419
C-Eu_2O_3							11–28	419
B-Gd_2O_3	2	178	2	535	<1	488		
C-Gd_2O_3	10–25[c]	178	5–10	535	15–44	488	18–34	416
C-Dy_2O_3	20	178			46	488	<1[d]	319
C-Yb_2O_3	18	178			13	488	2[a]	419

[a] 1400°. [b] 1300°. [c] The cubic phase has a distorted hexagonal structure in part of this region. [d] 1000°.

4% ZrO_2,[178] and 10% ThO_2.[416] The presence of a group IVB oxide stabilizes the cubic C-type structure by raising the C–A or C–B transformation temperature. Even C-La_2O_3 and C-Nd_2O_3 phases can be formed at 1500° by the addition of 47 and 39% CeO_2, respectively.[488] Of course, since higher temperatures favor the B- and A-type structures, more of the group IV oxide is required to stabilize the cubic phase as the temperature increases. For example, at 2000°, at least 24% ZrO_2,[178] 20% HfO_2[535] and 40% ThO_2[416] are required for the appearance of single-phase C-Gd_2O_3.

From a consideration of the rare earth oxide structures, it is evident that anion interstitials could be incorporated into the lattice quite readily. This defect model has been verified for Y_2O_3-ZrO_2,[556] Y_2O_3-CeO_2,[557] Y_2O_3-ThO_2,[414] and Gd_2O_3-ThO_2[416] solid solutions. Such systems are potential anion-conducting solid electrolytes. However, the anions are much less mobile in these structures than the fluorite structure[488] and the appearance of p-type conductivity at high oxygen pressures might be impossible to suppress. The cell air|Y_2O_3 + 10% ThO_2|O_2 yielded values for $\bar{t}_i$ of only 0.18 and 0.34 at 1000 and 1400°, respectively.[414] Their behavior at intermediate and low oxygen pressures has yet to be determined.

Table XXIII

Solubilities of the Alkaline Earth Oxides in Sc_2O_3, Y_2O_3, and the Rare Earth Oxides

M_2O_3	*Temp, °C*	*Solubility*	*Ref*
C-Sc_2O_3	>2000[a]	30% MgO	558
	1000	<1% MgO	559
	1700	3% CaO	560
	1000	3% CaO	560
C-Y_2O_3	2000	25% MgO	561
	1500	3% MgO	561
A-La_2O_3	>2000[a]	16% CaO	562
	1600	16% CaO	563
	>2000[a]	18% SrO	562
A-La_2O_3	2000	20% SrO	564
	>2000[a]	14% BaO	562
A-Nd_2O_3	2000	15% SrO	564
B-Sm_2O_3	>2000[a]	30% SrO	564
B-Gd_2O_3	1850	<1% CaO	565
B-Gd_2O_3	>2000[a]	22% SrO	564
B-Dy_2O_3	1800	20–30% CaO	566
B-Dy_2O_3	>2000[a]	20% SrO	564
B-Yb_2O_3	>2000[a]	33–45% CaO	566
C-Yb_3O_3	1850	<1% CaO	565

[a] Near the fusion temperature.

B. ADDITIONS OF ALKALINE EARTH OXIDES

According to Table XXIII, appreciable quantities of the alkaline earth oxides will dissove in the rare earth oxide structures at high temperatures. However, the solubilities become quite restricted at low temperatures.[559,561–563] Some solid solubility has also been indicated between MgO and B-Sm_2O_3, CaO and B-Sm_2O_3, and CaO and B-Gd_2O_3 at 1500°,[567] and between CaO and the B-type modifications of the oxides from Tb_2O_3 to Yb_2O_3 (excluding Tm_2O_3) after melting.[568] Any significant solubility has been denied between MgO and Y_2O_3 at 1650°,[569] CaO and Y_2O_3 at 1650°,[569] MgO and La_2O_3 at 2000[570] and 1400°,[25] CaO and La_2O_3 at 1850[565] and 1400°,[25] MgO and Gd_2O_3 at 1500°,[567] and SrO and C-Gd_2O_3, Dy_2O_3, and Yb_2O_3 at all temperatures.[564] The disagreement between these results and those shown in Table XXIII indicate that equilibrium is very difficult to achieve in these systems and should be approached from the high-temperature side, unless reactive

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oxide powders are prepared.[563] Consequently, the evidence against solid solubility cannot be regarded as conclusive, especially in cases where reaction was attempted at only 1100°.[571]

With respect to the different rare-earth oxide structures, divalent metal oxides have the opposite effect to tetravalent metal oxides in that they stabilize the B-type with respect to the C-type modification. Single-phase B-type Dy_2O_3 forms at 1800° upon the addition of 20% CaO.[566] However, the solutions undergo a eutectoid decomposition at 1500° into $CaDy_2O_4$ and C–Dy_2O_3. The eutectoid temperature is just below the fusion temperature in the Yb_2O_3–CaO system.[566] Compounds are formed except in the systems involving La_2O_3 or MgO,[572] although two compounds in the La_2O_3–SrO system were recently identified.[573]

Via density measurements, the anion vacancy model has been verified for La_2O_3–CaO solid solutions,[562,563] although some of the Mg^{2+} ions may reside in interstitial positions in Sc_2O_3–MgO solid solutions.[559] Only a very limited amount of conductivity data is available for these systems. In the La_2O_3–CaO system, maximum ionic conductivities of 1.9×10^{-2} [574] and 2.4×10^{-2} [563] $ohm^{-1}\ cm^{-1}$ at 1000° for the 15% CaO composition have been reported. The corresponding activation energies were 14.7 and 20.3 kcal/mol, respectively. Although solutions having this composition are unstable at 800–1200°,[562,563] very little CaO is required to produce a high level of ionic conductivity. At 5% CaO (~1% anion vacancies), the conductivity is $2.0 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$ at 1000°.[563] This value is between 80 and 230 times larger than the conductivities reported for the Sc_2O_3–CaO, Y_2O_3–CaO, and Sm_2O_3–CaO systems at a similar vacancy concentration.[201] Associated activation energies were 33.5, 33.5, and 20.5 kcal/mol, respectively. The anions are much more mobile in the hexagonal A-type structure than the cubic C-type structure. According to Pauling,[575] one-third of the anions in La_2O_3 are unusually far from their nearest neighbors (2.69 Å from the nearest La^{3+} ions and 3.21 Å from the nearest O^{2-} ions). These anions may be extremely mobile. Nevertheless, in the La_2O_3–CaO system, the conductivity increases only slightly past 3% CaO. In metastable solid solutions, there may be a marked tendency toward vacancy clustering and, also, vacancy ordering would tend to occur at relatively low defect concentrations in structures in which all the oxygen sites are not equivalent.

No further comparisons are justified until more data are available. If the monoclinic B-type structure was present in the Sm_2O_3–CaO system,[201] it appears that solid solutions having the A-type structure offer the only chance of achieving a high level of ionic conductivity.

Both conductivity measurements as a function of oxygen pressure and emf measurements have been used to show that the solid solutions are ionic conductors at intermediate oxygen pressures and mixed p-type and ionic conductors at high oxygen pressures.[201,563,574] For La_2O_3–CaO electrolytes, ionic transport numbers of 0.54 and 0.99 at 1000° and oxygen pressures of 1 and 10^{-8} atm, respectively, have been found for samples containing more than 2% CaO.[563] n-Type conductivity was not observed at 10^{-21} atm of oxygen and 1000°.[563]

Systems based on trivalent metal oxides may be useful for determining thermodynamic properties of systems which exert low oxygen potentials or for measuring the oxygen content in liquid metals or high-temperature gases. In this regard, C-type structures are desirable because of their excellent resistance to hydration.[552,569] A-Type oxides hydrate rapidly, although the presence of an alkaline earth oxide in solution greatly reduces this tendency.[562,563] More research is required on the stability and transport properties of these electrolytes before such possibilities can be fully evaluated.

An investigation of rhombohedral Bi_2O_3–SrO solid solutions has been reported.[576] An extrapolation of an Arrhenius plot to 650° indicates that the conductivity of Bi_2O_3 + 20% SrO would be $10^{-2}\ ohm^{-1}\ cm^{-1}$. However, at an oxygen pressure of about 1 atm and 600°, the ionic transport number was only 0.7 while the reduction of Bi_2O_3 interfered at intermediate oxygen pressures.

Perovskite structures based on $LaAlO_3$ containing MgO[201] or CaO[577,578] and $SrZrO_3$ containing Sc_2O_3[201] exhibit almost pure ionic conduction at intermediate oxygen pressures and are potential alternative oxide electrolytes.

VIII. Transport Properties of Refractory Oxides

Oxides which exhibit only small deviations from stoichiometry are often exclusively ionic conductors within restricted ranges of purity, temperature, and oxygen pressure. A brief discussion of their transport properties will comprise the remainder of this review.

A. BeO

The cells air|BeO|O_2 at 1000–1300[579] and 1200–1700°[580] and 66% CO + 34% CO_2|BeO|O_2 at 1000–1300°[579] have shown that BeO is essentially an ionic conductor. Investigations to determine transport numbers with a Hittorf-type experiment,[581] cation diffusion coefficients,[582–586] and anion diffusion coefficients[583,587] have indicated that BeO is a cation conductor. Excellent correlation between electrical conductivity data[579,584,588–590] and cation diffusion coefficients using the Nernst–Einstein relation can be found above 1100°. The correlation coefficient of 0.80[590] verifies the vacancy mechanism for cation migration.[582,583,585,586]

The remaining question concerns the extrinsic or intrinsic origin of the lattice vacancies. The conductivity is independent

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of oxygen pressure from 1 to 10^{-10} atm at 1300°[579] and, therefore, vacancy concentration changes arising from eq 9 and 16 are unimportant. Impurity-controlled vacancy concentrations have been suggested[584,585] and, recently, proven conclusively.[586,590] Aluminum and silicon are the major impurities which dissolve in the cation sublattice and create cation vacancies. Above 1200–1500°, depending on the impurity content, the activation energy for conduction is due solely to vacancy migration. Both cation diffusion coefficients[586] and conductivities[590] vary linearly with the vacancy concentration. At lower temperatures, the activation energy increases because of vacancy-impurity association or precipitation of impurities.[585,586,590] Cline and Newkirk[590] suggested that the latter may be more important.

Extrinsic electronic conduction may be present below about 1200° in relatively impure samples. Intrinsic ionic conduction appears to be absent even at 2135°.[586] To observe this region, higher purity BeO is required. However, it was absent at 1700° in a sample containing <25 atomic ppm total impurities and only 8 atomic ppm of Al and Si.[590] The energies of intrinsic defect formation are very high in BeO.[588]

B. MgO

In 1959, Mitoff[591] found that an Arrhenius plot for pure MgO crystals (~30 atomic ppm total impurities), when extrapolated to 1400–1600°, coincided with cation diffusion data.[592] Quite different behavior resulted for more impure specimens. Also, higher impurity levels lead to more pronounced conductivity minima at an oxygen pressure of 10^{-5} atm, indicating that impurities play a dominant role in transport processes.[591] The oxygen pressure dependences could not be rationalized without assuming the presence of a pressure-independent contribution. Since 1960, a considerable amount of emf data has become available, indicating that this contribution was ionic conductivity.

Emf measurements on the cell Fe, $Fe_xO|MgO|Ni$, NiO have resulted in values for $\bar{t}_i$ of 0.96[593] and 0.82[594] at 1100° and 0.9 at 1040°.[595] For this cell, $\bar{P}_{O_2} = 10^{-11}$–10^{-12} atm. However, higher temperatures favor electronic conduction. For the cell air$|MgO|O_2$, Mitoff[596] measured values for $\bar{t}_i$ of 0.9, 0.5, and 0.15 at 1000, 1300, and 1500°, respectively. Later, using a guard ring to protect against surface conduction, he obtained values of 0.88, 0.59, and 0,33 at 1016, 1292, and 1510°, respectively, for this cell.[597] Pal'guev and Neuimin[579] reported a value of 0.87 at 1300°. Activation energies of 46.2 and 81.5 kcal/mol for ionic and electronic conduction, respectively, have been determined.[596] At 1290°, a maximum ionic transport number of 0.65 occurred at $\bar{P}_{O_2} \sim 10^{-5}$ atm,[596] although a figure of 0.95 has also been given for these conditions.[579] Low oxygen pressures also favor electronic conduction. For instance, $\bar{t}_i = 0.20$ for $\bar{P}_{O_2} = 10^{-10}$ atm at 1290°[596] and for $\bar{P}_{O_2} = 10^{-22}$ atm at 1040°.[595] From an analysis of conductivity data,[591] Schmalzried[598] calculated that $P_{\oplus}$ (P_{O_2} where $\sigma_i = \sigma_p$) = $10^{-2.2}$ atm and $P_{\ominus} = 10^{-6.5}$ atm at 1300°.

Because of high, and often unstated, impurity contents, the electrical properties of MgO and other refractory oxides are either difficult or impossible to appraise. Generally, impurities increase the electronic contribution, although they can significantly affect the ionic conductivity by altering the number of lattice defects. Based on transport number experiments[581] and diffusion coefficients for Mg^{2+} [592] and O^{2-} [599] ions, Mg^{2+} migration is responsible for the ionic current (excluding the possibility of impurity ions). Mitoff[596] observed that the addition of Li to MgO lowered the ionic transport number. The introduction of Li^+ ions on the cation sublattice will lower the cation vacancy concentration, thereby lowering the ionic conductivity. Higher conductivities due to the presence of Fe^{3+} ions[591,600] may have been partially caused by an increase in the number of cation vacancies. An investigation of the effect of ions such as Sc^{3+} and Al^{3+} would be interesting. Intrinsic cation conductivity may occur at the higher temperatures since intrinsic Mg^{2+} diffusion has been observed between 1400 and 1600°,[592] The activation energy was 79 kcal/mol. High ionic transport numbers near an oxygen pressure of 1 atm[579,596,597] may be possible because of strong interactions between electron holes and cation vacancies.

Davies[601] concluded that O^{2-} ions are the charge carriers at certain oxygen pressures from the similarity between the activation energy for electrical conductivity and extrinsic O^{2-} diffusion. However, the conductivities were about three orders of magnitude too high to be accounted for by O^{2-} migration. Despite the agreement between Lewis and Wright's results[602] at 400–750° and other conductivity data[591] extrapolated to these temperatures, extrinsic electronic conduction undoubtedly predominated in their relatively impure MgO (99.9%).

As a solid electrolyte, MgO would be valuable at steelmaking temperatures, but the preceding discussion indicates that such an application is impractical because of high electronic transport numbers. Consequently, results concerning the activity of oxygen dissolved in molten iron[603–606] must be considered qualitative only, although a significant ionic contribution in MgO at high temperatures has been indicated.[87,605–607] However, Mitoff[591] concluded from an electrolysis experiment that ionic transport was negligible at 1600°. It would be interesting to determine transport numbers of very pure MgO (>99.999%), although intrinsic electronic conduction arising from thermally created defects could interfere above 1500°.[596]

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C. CaO

Calcium oxide has been found to be an amphoteric semiconductor at 600[608] and 800–1000° [609] with the p–n transition at oxygen pressures of 10^{-5} [608] and 10^{-2} [609] atm. An analysis[610] of Rudolph's results[609] indicated that $P_{O_2}{}^{\pm 1/4}$ dependences were obeyed near the p–n transition and that a considerable fraction of ionic conductivity was present. Current passage through CaO is accompanied by oxygen evolution[611] and cells of the type Fe–O|CaO|air yielded appreciable emf values.[612] Nevertheless, there is no established pattern for the magnitude of the ionic contribution. From emf measurements, $\bar{t}_i$ = 0.5–0.6 at $\bar{P}_{O_2} \sim 1$ atm and 1100–1300°,[579] 0.6–0.9 at $\bar{P}_{O_2} = 10^{-5}$–10^{-8} atm and 900–1300°,[579] and 0.6–0.7 at $\bar{P}_{O_2} = 10^{-11}$–10^{-14} atm and 800–1000°.[92,501] However, a comparison of the electrical conductivities calculated from the Nernst–Einstein relation using Ca^{2+} diffusion data ($D \sim 10^{-14}$ cm²/sec at 1000°)[613–615] and measured directly at $P_{O_2} \sim 10^{-4}$ atm[615] indicated that the ionic contribution is less than 2% at 950–1400°.[615] Although this comparison does not account for anion transport, the portion of ionic conduction attributed to Ca^{2+} migration, determined from Ca^{2+} transport numbers, accounted for all the ionic conductivity.[613] These transport numbers, measured by a gravimetric method, were only 0.01–0.001 at 900–1400°.[613,614] It is interesting that the activation energy measured by Surplice[616] is similar to that for Ca^{2+} diffusion,[613,614] although he attributes the conductivity to either electrons or O^{2-} ions.

Since errors arising from emf measurements such as electrode polarization or gas leakage between electrode compartments lead to low ionic transport numbers, it is evident that under certain conditions the ionic transport in CaO is very significant. To define these conditions properly, the effect of impurities must be studied.

D. SrO and BaO

p-Type conductivity predominates at high oxygen pressures for these oxides[609,617,618] and only a small ionic contribution is present.[610] For SrO, $\bar{t}_i$ = 0–0.1 at $\bar{P}_{O_2} \sim 1$ atm and 1000–1200°.[579] However, ionic transport becomes significant at intermediate oxygen pressures for SrO[579,610] and $\bar{t}_i$ = 0.6–0.9 at $\bar{P}_{O_2} = 10^{-6}$–10^{-8} atm and 900–1200°.[579] Oxygen ions are probably the ionic current carriers. A defect structure has been proposed for SrO postulating the predominance of Frenkel disorder on the anion sublattice.[619] Oxygen interstitials are very mobile in this oxide.[619]

E. Sc_2O_3, Y_2O_3, AND THE RARE EARTH OXIDES

The conductivity of Y_2O_3,[507] La_2O_3,[507,609,620,621] Nd_2O_3,[507,620] Sm_2O_3,[620] and Gd_2O_3[621] increases as the oxygen pressure is increased, indicative of p-type conductivity. From electrolysis experiments *in vacuo* ($P_{O_2} \sim 10^{-8}$ atm) at 600°, Noddack and Walch[621,622] concluded that $t_i < 0.05$ and usually $t_i < 0.01$ for the rare earth oxides. Linear current–voltage curves from 0 to 5 V in air or vacuum at 600–1300° supported this conclusion,[621,622] although electrode–gas reactions could have prevented charge buildup at the electrodes. However, ionic conduction predominates in these oxides at low temperatures and intermediate oxygen pressures.[507,598,623,624] Schmalzried[598] demonstrated that Sc_2O_3, Nd_2O_3, Sm_2O_3, and Yb_2O_3 exhibit purely ionic conduction at 800–1000° in cells of the type Fe, Fe_xO|M_2O_3|Ni, NiO. Tare and Schmalzried[623] used galvanic cells with gas electrodes to define the parameters $P_\oplus$ and $P_\ominus$ for Y_2O_3, Sm_2O_3, Gd_2O_3, and Dy_2O_3 at 667–930°. For all the oxides, $P_\oplus = 10^{-2}$–10^{-4} atm and $P_\ominus < 10^{-19}$ atm except Dy_2O_3 for which $P_\oplus \sim 10^{-9}$ atm. Therefore, $t_i > 0.9$ from $P_{O_2} = 10^{-6}$–10^{-8} atm to $P_{O_2} < 10^{-15}$ atm.

Impurities play a dominant role in ionic conduction. For 99.996% Y_2O_3, t_i = 0.30 at 700° and 0.15 at 800° and an oxygen pressure of 10^{-15} atm.[625] The purity of Y_2O_3 was 99.9% in Tare and Schmalzried's investigation.[623] Higher temperatures virtually eliminate the ionic contribution. For Y_2O_3, it was less than 1% from 10^{-1} to 10^{-17} atm of oxygen and 1200–1600°.[625] No emf was produced from the cell air|Y_2O_3|O_2 at 1000–1400°.[414] Similarly, ionic transport in Sc_2O_3 is only significant at low temperatures.[626]

An analysis[610] of conductivity data for La_2O_3[609] indicated that p-type conductivity obeyed a $P_{O_2}{}^{1/4}$ dependence. This dependence has been verified for La_2O_3[563] and also found for Nd_2O_3.[154,507] Whenever only small deviations from stoichiometry occur, which must be the case if ionic transport numbers are significant,[595] this proportionality will be observed regardless of the predominant lattice defects if they are fully ionized. At P_{O_2} = 1 atm and 1000°, t_i = 0.09 for 99.99% La_2O_3.[563] Somewhat higher ionic transport numbers (0.2–0.3) have been reported for 99.9% La_2O_3 under similar conditions.[507,574,610] Again, the ionic conductivity appears to be impurity controlled. The ionic transport number increases to 0.91 at an oxygen pressure of 10^{-8} atm and would become almost 0.99 at 10^{-12} atm except that n-type conductivity appears below 10^{-11} atm at 1000°.[563] Higher temperatures favor electronic conduction. The very weak oxygen pressure dependences for B–Gd_2O_3 and Dy_2O_3 observed by Rapp[319] from 1 to 10^{-7} atm at 1000° could be indicative of a significant ionic contribution.

The ionic conductivity in La_2O_3 has been attributed to O^{2-} ion migration.[563] Diffusion coefficients for oxygen in A–Nd_2O_3 and B–Sm_2O_3 are about 10^{-9} cm²/sec at 1000°,[627] indicating that the anions are very mobile in the hexagonal A-type and monoclinic B-type rare earth oxide structures. For cubic

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C-type oxides, anion diffusion coefficients are also about 0^{-9} cm^2/sec at 1000°,[628,629] whereas cation self-diffusion coefficients in Y_2O_3 and Er_2O_3 are about 10^{-14} and 10^{-17} cm^2/sec, respectively, at 1000° (extrapolated from 1400°).[630] Anion interstitials are more mobile than anion vacancies.[629] In the C-type structure, the anion interstitial positions form nonintersecting strings in the $\langle 111 \rangle$ directions along which the anions can move rapidly.

It is evident from the preceding discussion that Sc_2O_3, Y_2O_3, and the rare earth oxides will function as solid electrolytes under certain conditions. The fuel cell $NH_3|Pr_6O_{11}|$air yielded an emf of 400–420 mV at 750°,[631] and an electrochemical cell has been described in which the solid electrolyte was essentially Y_2O_3.[632]

F. ZrO_2 and HfO_2

Considerable disagreement exists pertaining to transport numbers in both monoclinic[633–635] and tetragonal[633,636,637] ZrO_2. Ionic transport numbers will be highest at oxygen pressures near the oxygen pressure corresponding to the minimum conductivity since the ionic conductivity is virtually unaffected by oxygen pressure in this region.[638] Conductivity minima have been reported at 10^{-9} [633] and 10^{-16} [634] atm at 1000° for monoclinic ZrO_2 and at 10^{-4}, [637] 10^{-6}, [633] and 10^{-7} [636] atm at 1300° for tetragonal ZrO_2. The minima shifted to higher oxygen pressures at higher temperatures (1300–1700°),[636] although they were also shown to be essentially temperature independent from 1230 to 1330° [633] and 1200 to 1500°.[637]

A $P_{O_2}{}^{1/5}$ dependence found by Rudolph[609] at 1–10^{-4} atm and 900–1000° has been analyzed to be a combination of p-type conductivity obeying a $P_{O_2}{}^{1/4}$ law and a pressure-independent ionic contribution.[610] The cell Fe, $Fe_xO|ZrO_2|Cu$, Cu_2O indicated that $\bar{t}_i = 0.9$ from 600 to 950°.[92,501] However, $t_i < 0.01$ at an oxygen pressure of 10^{-2} atm and 1000°.[634] Nonlinear Arrhenius plots[635] cannot be taken as evidence of mixed conduction.

For tetragonal ZrO_2, a polarization technique involving dc conductivity measurements at zero and infinite time led to values for t_i of 0.9 and 0.4 at $P_{O_2} = 10^{-9}$ atm and 1300 and 1600°, respectively.[636] The ionic transport number reached 0.55 at $P_{O_2} = 10^{-4}$ atm and 1600°,[636] although intrinsic semiconduction has been observed above this temperature.[639] McClaine and Coppel[637] did not find the polarization technique applicable because of electrode-gas reactions and space charge polarization, but estimated that t_i could be 0.4–0.5 at $P_{O_2} \sim 10^{-13}$ atm and 1200° from differences between ac and dc conductivities. Therefore, little doubt exists that ZrO_2 is a mixed conductor.

Fully ionized zirconium vacancies[634] and oxygen vacancies[636] have been postulated to be the predominant defects at high and low oxygen pressures, respectively. The ionic current carriers in ZrO_2 are not known with certainty, but O^{2-} ions are probably responsible.[637] However, a suggestion that ionic conductivity arises from a coupled transport of oxygen vacancies and interstitials[633] has been discredited.[640] Moebius[76] has briefly discussed the conductivity of ZrO_2.

Also for HfO_2, results are in substantial disagreement. A complex oxygen pressure dependence and a conductivity maximum at $P_{O_2} = 10^{-3}$ atm and 900–1300° has been reported.[633] For purer HfO_2 samples, Tallan, Tripp, and Vest[641] found a minimum conductivity at 10^{-10} atm and 1500° which shifted to lower pressures at lower temperatures. They determined that the conductivity was essentially electronic from 1000 to 1500°. Yet, from galvanic cell measurements, $\bar{t}_i$ = 0.01, 0.02, 0.71, and 0.94 at 1000° and $\bar{P}_{O_2} = 10^{-1}$, 10^{-3}, 10^{-8}, and 10^{-13} atm, respectively.[642] These data were consistent with conductivity measurements at high oxygen pressures.[642] At 1000° and $\bar{P}_{O_2} = 10^{-8}$ atm, a value for $\bar{t}_i$ of 0.59 has also been given.[99] In addition, almost pure ionic conduction was indicated at 700 to 1000° from measurements on the cell $CO,CO_2|HfO_2|O_2$ where $CO/CO_2 = 200/1$.[643]

p-Type conductivity at high oxygen pressures, proportional to $P_{O_2}{}^{1/5}$, has been accounted for with a model involving fully ionized hafnium vacancies,[641,642] but the mechanism of ionic transport has not been clarified. Higher purity samples must be studied before definite statements can be made concerning the suitability of ZrO_2 of HfO_2 as solid electrolytes.

G. CeO_2

Anionic conduction appears in CeO_2 only at low temperatures and high oxygen pressures. However, even under these conditions, CeO_2 is predominantly an n-type semiconductor.[609] Emf measurements have shown that ionic transport numbers are 0.1–0.2 at $P_{O_2} \sim 1$ atm at 700–1000°.[501,507] The cation transport number was less than 0.004 at 1100°.[514] Electrolysis experiments,[622,644] the presence of ohmic behavior,[519,622] and the absence of voltage–time transients[519] have indicated that ionic conduction in CeO_2 is insignificant.

H. ThO_2

Polarization arising from the passage of dc current through ThO_2 crystals held under vacuum at 600–1300° was linked to ionic transport.[645] Although p-type conductivity, proportional to $P_{O_2}{}^{1/4}$,[89,424,425,610] prevails at high oxygen pressures,[646] con-

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duction is almost exclusively ionic at intermediate oxygen pressures. The conductivity of ThO_2 was independent of oxygen pressure below 10^{-8} atm at 1000°[424] and below 10^{-12} atm at 800–1100°.[425] n-Type conductivity appeared at 10^{-22} atm and 1000°.[425]

In the cell Co, CoO|ThO_2|Ni, NiO, $t_i > 0.9$ for ThO_2 at 800–1100°.[425] Lower values are found when ThO_2 contacts a Cu–Cu_2O electrode ($P_{O_2} = 10^{-6.2}$ atm at 1000°).[92,99,425] No more than 10% ionic conduction remains at an oxygen pressure of 1 atm.[414,425,610] Donneaud[326] set up the cell O_2|ThO_2|$Na_2Si_2O_5$|ZrO_2–MgO|O_2 which involved ThO_2 and ZrO_2–MgO tubes dipping into the silicate melt. If ThO_2 were an electronic conductor, the cell emf would be dependent on the oxygen pressure over the melt, whereas ionic conduction would be indicated by a dependence of the emf on the oxygen pressure inside the ThO_2 tube. However, an inconsistently high value for the ionic transport number of ThO_2 of 0.8 at an oxygen pressure of about 1 atm and 1250° was determined.

The fluorite lattice can accommodate large concentrations of anion vacancies and interstitials[647] and permits the anions to move much more easily than the cations.[135] Anion and cation diffusion coefficients are 10^{-11}[648] and 10^{-17}[649] cm^2/sec at 1000°, respectively. The entire electrical conductivity of ThO_2 above 1100° was accounted for by using anion diffusion data.[433] The anionic conductivity is extrinsic since the lattice defect concentration is controlled by aliovalent impurities. Bauerle[424] successfully extrapolated a $\log \sigma_i$ *vs.* $\log [YO_{1.5}]$ plot for ThO_2–Y_2O_3 solid solutions to the known impurity content of ThO_2 (400 ppm cation impurities). The major impurities were Ce^{3+} ions. Ullmann[433] claimed to have observed intrinsic ionic conduction above 1100°, but did not give an analysis for his ThO_2 specimens. Theoretical calculations made by Chebotin[513] indicated that Schottky defects are energetically much more favorable than Frenkel defects on the anion sublattice in both ThO_2 and CeO_2.

I. Al_2O_3

Generally, Al_2O_3 is an electronic conductor, although impure samples exhibit mixed conduction.[650–652] Pappis and Kingery[653] ruled out ionic conductivity at 1300–1750° because of the much greater mobilities of electronic defects compared to ionic defects. A comparison of measured and calculated conductivities using the Nernst–Einstein relation indicated that neither O^{2-} ions[654] nor Al^{3+} ions[655] were mobile enough to contribute significantly. Hittorf-type experiments at 1550–1750° showed that $t_{Al^{3+}} \lesssim 0.05$.[654] Also, no ionic contribution could be detected at $P_{O_2} \sim 1$ atm and 1250°.[326,387]

Other investigators have reported significant ionic conduction in Al_2O_3 from emf measurements at 1170[598] and 1550°.[87] Matsumura[652] found that $t_i \sim 0.8$ at $P_{O_2} \sim 1$ atm and 900°. Although both he and Schmalzried[598] demonstrated that Al_2O_3 becomes a predominantly electronic conductor above 1300°, Fischer and Ackermann[656] have recently reported anion transport numbers of 0.6–0.7 at 1600–1700° for Al_2O_3 tubes containing molten aluminum and dipping into molten iron.

Table XXIV

Electrical Properties of Solid Oxide Electrolytes

a. Electrical Conductivities

Electrolyte	*% anion vacancies*	*Ionic conductivity at 1000°, $ohm^{-1} cm^{-1} \times 10^2$*	*Activation energy, kcal/mol*	*Ref*
ZrO_2 + 12% CaO	6.0	5.5	25.2	28, 30, 37, 54, 63
ZrO_2 + 9% Y_2O_3	4.1	12	18.4	30, 37, 147
ZrO_2 + 10% Sm_2O_3	4.5	5.8	22.0	147
ZrO_2 + 8% Yb_2O_3	3.7	8.8	17.3	147
ZrO_2 + 10% Sc_2O_3	4.5	25	14.9	37, 147
ThO_2 + 8% Y_2O_3	3.7	0.48	25.4	99, 425
ThO_2 + 5% CaO	2.5	0.047	25.5	99
CeO_2 + 11% La_2O_3	5.0	8.0	21.0	344, 346, 489
CeO_2 + 15% CaO	7.5	2.5	17.3	505
HfO_2 + 8% Y_2O_3	3.7	2.9	25.8	533
HfO_2 + 12% CaO	6.0	0.40	33.0	29
La_2O_3 + 15% CaO	2.7	2.4	20.3	563

b. Transport Numbers

Electrolyte	*Temp, °C*	*Oxygen pressure range for $t_i \geqslant 0.99$*	*Ref*
ZrO_2–CaO	1000	1 to 10^{-20}	63, 97
	1600	1 to 10^{-12}	114, 127
ThO_2–Y_2O_3	1000	10^{-7} to 10^{-24}	99, 120, 423, 452
	1600	10^{-7} to 10^{-16}	114, 128, 423
La_2O_3–CaO	1000	10^{-8} to $<10^{-21}$	55, 563

Self-diffusion studies of O^{2-} ions[657] and Al^{3+} ions[658] in Al_2O_3 indicate that the cations are more mobile. However, grain boundaries markedly increase the anion mobility[657] which could become important in fine-grained Al_2O_3.[659] From thermoelectric measurements and approximate activation energy calculations, Matsumura[652] accounted for the ionic transport by the migration of triply ionized aluminum vacancies of extrinsic origin. The possibility of mobile ionic impurities should not be neglected.

As for MgO, results obtained from galvanic cells having Al_2O_3 electrolytes[605,606,660,661] can be considered qualitative only.

J. SiO_2

Fused SiO_2 is an ionic conductor from 1 to 10^{-16} atm of oxygen at 1000°[598] by virtue of the migration of impurities, usually Na^+ ions.[662,663] The diffusion coefficient for oxygen is about 10^{-14} cm^2/sec at 1000°.[663,664]

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IX. Summary and Conclusions

The important electrical properties of solid oxide electrolytes are summarized in Table XXIV. In fuel cells where perhaps 5 or 10% electronic conduction can be tolerated but high ionic conductivities and cell voltages are required, only ZrO_2-based electrolytes are suitable, although CeO_2-based systems may be acceptable in some cases. The stability of ZrO_2–Sc_2O_3 electrolytes must be thoroughly investigated before their potentialities can be fully evaluated. Small additions of either ThO_2 or Y_2O_3 may serve to fully stabilize them without seriously affecting their conductivities.

For high-temperature thermodynamic measurements, more than 1% electronic conduction will seriously affect the results. Together, the ZrO_2- and ThO_2-based electrolytes satisfactorily cover the entire oxygen pressure range normally encountered. Investigations of ionic transport numbers as a function of temperature and oxygen pressure are very helpful since correction factors can be applied to emf measurements for small electronic contributions. However, the purity of the oxide materials must be carefully controlled since the presence of easily oxidized or reduced impurities can drastically affect transport numbers and render reproducibility impossible. Several authors have discussed the emf's obtainable from galvanic cells involving solid electrolytes exhibiting mixed conduction.[66,96,404,407,598,665–674]

Solid solutions based on the A-, B-, or C-type rare earth oxide structures may, for certain applications, provide alternative electrolytes to those based on the fluorite structure. The oxides Sc_2O_3, Y_2O_3, La_2O_3, Nd_2O_3, Gd_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, and Lu_2O_3 offer the best possibilities because of the stability of the trivalent cations. Further research on such systems should be of considerable scientific, and perhaps practical, interest.

Within certain restricted ranges of temperature and oxygen pressure, BeO, MgO, ThO_2, Sc_2O_3, Y_2O_3, and the rare earth oxides are essentially pure ionic conductors. Soluble impurities are necessary to achieve a significant level of ionic conductivity. With the exception of BeO, the influence of impurities on the electrical behavior of the refractory oxides has not been adequately determined. More research is required in this direction before transport mechanisms can be properly defined.

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