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"MIXED CONDUCTION IN SOLID OXIDE ELECTROLYTES"

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ABSTRACT

At temperatures between 800 and 1100°C, electrical conductivity and galvanic cell measurements involving ThO_2 , Dy_2O_3 , and Gd_2O_3 indicate significant ionic conductivity contributions, in addition to electronic conduction. These measurements may be rationalized either on a basis of high intrinsic ionic defect concentrations, or else ionic defects introduced by trace impurities. For ThO_2 , the latter explanation seems probable.

The P_{O_2} -dependence of ac conductivity measurements in ThO_2 - Y_2O_3 solid solutions shows a wide P_{O_2} -range of predominant ionic conductivity (σ_{ion}), with significant positive hole contributions ($\sigma_{\oplus}$) at higher oxygen activities. A dilute solution model has been used to interpret the dependences of $\sigma_{\oplus}$ on P_{O_2} and Y_2O_3 content. The behavior of $\sigma_{\oplus}$ is consistent with the existence of doubly ionized (unassociated) oxygen vacancies in electrical compensation of trivalent dopant ions. As previously reported, the ionic conductivity contribution reaches a maximum with increasing Y_2O_3 dopant content. No significant excess electron conductivity contribution ($\sigma_{\ominus}$) was indicated for any ThO_2 - Y_2O_3 composition at oxygen activities as low as those for Cr - Cr_2O_3 equilibrium coexistence.

A dc polarization technique was used for the direct measurement of $\sigma_{\oplus}$ and $\sigma_{\ominus}$ in $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ and $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ electrolytes. An improved method for the analysis of the data and experimental difficulties of this technique are discussed. A lower limit in P_{O_2} for predominant ionic conduction is reported for each electrolyte.

Galvanic cells involving the use of the $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ electrolyte were used to determine the solubility and diffusivity of oxygen in solid copper. Difficulties in the method and the reliability of the results are discussed.

MIXED CONDUCTION IN SOLID OXIDE ELECTROLYTES

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INTRODUCTION

Wagner [1] has shown theoretically that the electromotive force E of a galvanic cell involving a solid compound electrolyte with mixed ionic and electronic conduction may be expressed as

$$E = - \frac{1}{F} \int_{\mu'_x}^{\mu''_x} (t_{ion}) \frac{d\mu_x}{|Z_x|} \quad (1)$$

where t_{ion} is the sum of the ionic transference numbers, μ'_x and μ''_x are the chemical potentials of the non-metal component at the electrode-electrolyte interfaces with $\mu'_x < \mu''_x$, F is Faraday's constant, and Z_x is the valence of the X ion in the electrolyte. A number of crystalline ionic compounds, including AgI , CaF_2 , PbCl_2 , CuBr , the alkali halides, and several mixed oxide solutions, have been shown to exhibit sufficiently high ionic disorder and ionic mobility to account for an essentially exclusive ionic conductivity. Thus, such crystals have been used as solid electrolytes in galvanic cells for the determination of free energy data according to Eq. (1) with $t_{ion} \approx 1$. Further, the application of Faraday's Law to solid electrolyte galvanic cells of various ingenious experimental designs has extended the use of this technique to the study and control of the kinetics of chemical reactions, dissolution reactions, and phase changes. However, for all so-called solid electrolytes, predominant ionic conductivity ($t_{ion} > 0.99$) is limited to a definite range of chemical potentials of the metal or non-metal components. Because the equilibrium metal to non-metal ratio in an ionic compound is determined by the interaction of the compound with the metal or non-metal at fixed activities in its surroundings, the degree of non-stoichiometry may be so adjusted that significant electronic conductivity from excess electrons in the conduction band or positive holes in the valence band are introduced into the crystal. In a cell application, the use of a crystalline

electrolyte under conditions of mixed ionic and electronic conduction is unfavorable and is avoided when possible, because an exact knowledge of t_{ion} (as a function of the non-metal chemical potential) is necessary to relate E to the chemical free energy change or to relate the mass transported to the current passed in kinetic studies.

Since the introduction of ZrO_2 -base and ThO_2 -base solid electrolytes for thermodynamic measurements by Kiukkola and Wagner [2] and by Peters, et.al. [3,4], numerous scientific and engineering applications have followed. A number of such investigations have been described in previous years at this symposium.[5-9]. The particular solid electrolyte composition chosen for a given study may depend upon the details of the intended application. For example, for use in a high-temperature fuel cell [10], or for thermodynamic measurements at relatively low temperatures [11], or for use as a high-temperature furnace tube with either resistance heating [12] or radio-frequency induction heating [13, 14], the highest possible ionic conductivity is required. Use of a solid oxide electrolyte in an oxygen partial pressure gauge [15-17], or as a blocking electrode for the measurement of the partial ionic conductivity (σ_{ion}) in another oxide [16], or as a monitor for oxygen in liquid metal baths [18-26] or for the various other thermodynamic and kinetic measurements [6], the highest possible partial ionic conductivity in combination with the lowest possible partial electronic conductivity (σ_e) is generally required. Some of these applications cover a range of relatively high oxygen potentials; others involve extremely low oxygen activities. Finally, nearly all applications require electrolytes which are extremely dense (impervious to gases), chemically unreactive to the metallic electrodes, and resistant to thermal shock. Obviously, no single electrolyte composition may be expected to be best for all applications.

The solid oxide electrolytes of current use exhibit the CaF_2 and CaF_2 -related structures which are known to accommodate significant concentrations of anionic defects. The CaF_2 lattice may be considered either as an FCC cation lattice containing a simple cube of anions, or as a simple cubic anion lattice with a cation at the center of alternate cubes; the latter description illustrates the loose packing in the lattice. The unusual resistance to transformation of the CaF_2 and doped- CaF_2 lattices in the presence of excessive concentrations of interstitial anions or anion vacancies (anti-Frenkel-type defects) has been ascribed by Krebs [27] to a significant homopolar (covalent) contribution to the bonding whereby the four pairs of hybrid sp^3 electrons of the anion would require tetrahedral symmetry

in the resonance bonds with neighboring cations. While evidence for an oxide like ThO₂ is not available, the x-ray determination of the electronic distribution in CaF₂ by Weiss, et. al. [28] does not indicate a significant covalent bonding contribution. Several authors [29-34] have reviewed the experimental evidence that anti-Frenkel defects predominate in fluorite-type lattices. Assuming hard-sphere ions, Mobius [30] has calculated the normalized free radius R available for the diffusion of the larger anions and the smaller cations in a CaF₂-type lattice. For the migration of an anion out of its neighboring cation tetrahedron, a free radius

$$R(\text{anion}) = \frac{r(\text{hole})}{r(\text{anion})} = 0.943 - 0.057 \left[\frac{r(\text{cation})}{r(\text{anion})} \right] \quad (2)$$

is available. For the escape of a cation from its surrounding anion cube, a free radius

$$R(\text{cation}) = \frac{r(\text{hole})}{r(\text{cation})} = 0.816 - 0.184 \left[\frac{r(\text{anion})}{r(\text{cation})} \right] \quad (3)$$

is available. Using the ionic radii $r(\text{Th}^{+4}) = 1.15\text{\AA}$ and $r(\text{O}^{2-}) = 1.27\text{\AA}$ which were recommended by Mobius [35] for the CaF₂-type lattice, Eqs. (2) and (3) may be evaluated to give $R(\text{O}^{2-}) = 0.89$ and $R(\text{Th}^{+4}) = 0.61$. Thus, both experimental observations and theoretical rationalizations substantiate predominant anion defects and anion migration in CaF₂-type lattices. Then, whether or not such phases are solid electrolytes depends upon the relative magnitudes of the anionic partial conductivity compared to the electronic partial conductivity. In this paper, the results of recent studies of mixed ionic and electronic conduction in several proven or potential solid electrolyte systems of CaF₂-type lattices are presented. In particular, ThO₂ and doped ThO₂, doped-ZrO₂ and C-type rare earth sesquioxides are considered. In addition, preliminary results from a current electrochemical determination of the solubility and diffusivity of oxygen in solid copper are presented.

MIXED CONDUCTION AND ITS DETERMINATION

If only fully ionized defects are presumed to exist at elevated temperatures in an absolutely pure polycrystal of ThO₂ (CaF₂-type lattice), then the equilibrium concentrations of ionic and electronic defects are established by the simultaneous equilibria

where the defect notation of Kröger and Vink [29,33] has been used. A fourth expression describing the intrinsic electronic equilibrium would not be independent of I-III; further, equilibria II and III are valid whether or not the band model chosen for the electronic defects is correct in detail. The neutrality condition for ThO_2 (or another oxide with such defects) would be

$$2[\text{O}_i''] + n = 2[\text{V}_\text{O}^{\bullet\bullet}] + p. \quad (2)$$

Assuming a dilute solution of defects in I-III, such that their thermodynamic activities may be equated to their concentrations [], the Kröger and Vink [29] procedure for the simplification of Eq. (2) may be used in the construction of Fig. 1. If no other defect types are in a significant concentration for a given temperature, and presuming that the oxide does not exhibit predominant intrinsic semi-conduction, Fig. 1 describes the P_{O_2} -dependence of the various defect concentrations for all conceivable experimental conditions. Then only through experiment can one establish which zone or zones of Fig. 1 is pertinent for a given P_{O_2} range of investigation. (The scale of the abscissa must be determined by experiment).

The total conductivity of a substance is given by

$$\sigma = \sum_{i=1}^s c_i q_i u_i = \sum_{i=1}^s \sigma_i \quad (3)$$

where the partial conductivity of each species σ_i , is given by the product of the concentration of the carrier c_i , its charge q_i , and its mobility u_i . Because the mobilities of electronic defects, u_0 and u_θ , generally greatly exceed those of ionic defects, predominant ionic conduction can only occur when the concentration of the ionic defects are several orders of magnitude greater than the electronic defect concentrations. Then in Fig. 1, predominant ionic conductivity might only be observed in the center of Zone II, and indeed does not occur for most oxides. Conversely, for any pure oxide with a P_{O_2} range of ionic conduction, predominant p-type and n-type electronic semi-conduction must be expected for sufficiently high P_{O_2} and low P_{O_2} , respectively.

If an aliovalent dopant ion, like trivalent yttrium, is dissolved homogeneously on a ThO_2 lattice, the term $[\text{Y}_{\text{Th}}']$ would be added to the left-hand-side of Eq. (2). Equilibria I-III are still valid except that O_i'' would only exist in extremely small concentrations. Fig. 2 is a Kröger and Vink-type diagram describing the P_{O_2} -dependences of the defect concentrations. The diagram for ThO_2 containing a divalent dopant ion like Ca^{+2} would be very similar to Fig. 2; however, for a Ta^{+5} dopant, the

predominant zone is probably $[Ta_{Th}] = n$, with predominant n-type semi-conduction [36]. Even at reasonably elevated temperatures around 1000°C native defect concentrations in absolutely pure crystals may be so low that a nominally pure crystal is better described by Fig. 2 than Fig. 1, with unintentional and even undetectible impurity species acting as the dopant ion.

THORIA AND THORIA-BASE ELECTROLYTES

Recently, Lasker and Rapp [37] and Bauerle [38] measured the total (ac) conductivity of "pure" ThO_2 at elevated temperatures over a wide range of P_{O_2} . As seen in Fig. 3, in both investigations a broad range of P_{O_2} -independent conductivity was found at intermediate and low P_{O_2} , while at higher P_{O_2} , σ was proportional to $P_{O_2}^{1/4}$. Use of "pure" ThO_2 as an electrolyte in a galvanic cell was used to identify the σ plateau as predominant ionic conductivity. The P_{O_2} -dependent contribution at high P_{O_2} was ascribed to p-type semiconduction. Two self-consistent rationalizations of this behavior for "pure" ThO_2 are possible: a.) the "pure" ThO_2 specimens were sufficiently pure and the defects in the experimental range are described by the right-hand half of Zone II of Fig. 1, or b.) the "pure" ThO_2 specimens contained lower valent cation impurities which masked the native defects so that the defects in the experimental range are described by the right-hand half of zone II of Fig. 2.

Considering the spectrographic analysis of the starting material in conjunction with the magnitude of σ_{ion} , Bauerle [38] reported that the σ_{ion} measured for "pure" ThO_2 was the result of the presence of 200-400 ppm of trivalent impurities. Likewise, comparison of $\sigma_{\oplus}$ for ThO_2 -0.0084 $YO_{1.5}$ with $\sigma_{\oplus}$ for "pure" ThO_2 at each temperature from the investigation of Lasker and Rapp [37] indicates the presence of 300 ppm of trivalent impurities in the "pure" ThO_2 . An interesting but unresolved question is whether truly pure ThO_2 is an intrinsic ionic conductor. Current experiments involving "pure" specimens of differing preparation procedures and higher temperatures should provide further information.

Pure oxides are not of principal interest as solid electrolytes, because by doping an oxide with a soluble aliovalent cation, the concentration of the predominant ionic defects may be drastically increased. With doped-oxide electrolytes the principal considerations are then a.) the dependences of σ_{ion} , $\sigma_{\oplus}$, and $\sigma_{\ominus}$ on the concentration of a particular dopant, and b.) the dependences of σ_{ion} , $\sigma_{\oplus}$, and $\sigma_{\ominus}$ on the choice of dopant cation (its ionic size and valence). A dilute solution model which assumes that the individual partial conductivities are proportional to the concentrations of the defects was used by Lasker and Rapp [37] to predict the $[YO_{1.5}]$ -dependences of σ_{ion} , $\sigma_{\oplus}$, and $\sigma_{\ominus}$ in

ThO₂-YO_{1.5} solutions. A schematic illustration of the predicted behavior is shown in Fig. 4. The line for pure ThO₂ in Fig. 4 is drawn on the assumption that truly pure ThO₂ would be described by zone II of Fig. 1 and would exhibit a P_{O₂}-range of predominant ionic conduction. (A previously published plot for pure ThO₂ does not correspond to Fig. 1 and is not correct [37].) According to the dilute solution model, σ_{ion} should increase in proportion to [YO_{1.5}], σ_{θ} is predicted to increase in proportion with [YO_{1.5}]^{1/2}, while σ_{θ} is expected to decrease according to [YO_{1.5}]^{-1/2} if self-interactions or interactions with other defects do not affect the mobilities.

The total (ac) conductivities for a series of ThO₂-YO_{1.5} compositions have been reported for a wide range of P_{O₂} from 800 to 1100°C [11, 37, 38]. Within the resolution of the measurements of Lasker and Rapp [37], σ_{θ} was found to obey the dilute solution P_{O₂} and [YO_{1.5}] dependencies. (Bauerle [38] does not concur on the latter point, and further measurements are needed.) Over the investigated P_{O₂}-range σ_{θ} was too small to be observed by total (ac) conductivity measurements. The absence of observable σ_{θ} for the ThO₂-0.0084 YO_{1.5} composition at Cr-Cr₂O₃ coexistence oxygen activity (presume $\sigma_{\theta} < 0.1\sigma_{ion}$), indicates that the Th_{0.85}Y_{0.15}O_{1.925} electrolyte should exhibit predominant ionic conduction ($t_{ion} > 0.99$) down to at least P_{O₂} = 3 x 10⁻²⁵ atm at 1000°C.

The dependence of σ_{ion} on [YO_{1.5}] at 1000°C from several investigations [11, 37, 38] is shown in Fig. 5; the obvious differences in the absolute magnitude of σ_{ion} may be ascribed to differing preparation and sintering procedures. σ_{ion} is found to be reasonably proportional to [YO_{1.5}] for compositions up to about 0.10 mole percent YO_{1.5} [38]. However, a flat maximum in σ_{ion} occurs near [YO_{1.5}] equal to 15 mole percent. In this range, vacancy ordering [39], vacancy clustering [40], and dopant-vacancy interactions [33] have been suggested as the cause for decreased vacancy mobility with increasing vacancy concentration. Further definitive experiments and theoretical considerations are required for the rationalization of this behavior. Considering this maximum in σ_{ion} , the composition Th_{0.85}Y_{0.15}O_{1.925} probably exhibits about the widest P_{O₂}-range of predominant ionic conductivity in the Th-Y-O system, and this electrolyte is suitable for cell applications both at relatively high and relatively low P_{O₂}. However, the relatively low absolute magnitude of σ_{ion} and the significant σ_{θ} in air or pure O₂ would discourage the use of Th_{0.85}Y_{0.15}O_{1.925} for some applications.

Experimentally measured conductivities [37] for ThO₂-YO_{1.5} solutions were converted to ionic transference numbers and a compilation of these data for 1000°C are given in Fig. 6. As predicted, the limit of predominant ionic conductivity was displaced to higher P_{O₂} with increasing [YO_{1.5}], except at the highest

dopant level. The validity or limitations of using Eq. (1) for galvanic cell measurements in a region of mixed conduction may be determined from a plot such as Fig. 6, because the emf for a cell with electrodes of known P_{O_2} may be predicted from a graphical integration. Lasker and Rapp [37] measured E for cells involving Cu/Cu₂O, Ni/NiO, and Co/CoO electrodes at 800, 900, and 1000°C for "pure" ThO₂, ThO₂ + 0.06 Y_{0.5}, and ThO₂ + 0.25 Y_{0.5} electrolytes. For the latter two electrolytes, for which t_{ion} equaled essentially unity, the measured cell potentials correspond to the thermodynamic E . However, for cells with the "pure" ThO₂ electrolyte and involving the Cu/Cu₂O electrode (in the mixed conduction range), the measured E was significantly lower than that derived from the graphical integration. There is no doubt that Eq. (1) is correct and would be verified for a mixed conduction range for a cell involving unpolarizable electrodes. However, electronic conduction in an electrolyte represents an internal shunt which allows a continuous equivalent transport of the electronic species and of oxygen ions from the electrode of high μ_{O_2} to the electrode of low μ_{O_2} [41]. For Me/MeO-type electrodes, this mass transport should effect a superficial layer of metal at the electrode/electrolyte interface of high μ_{O_2} and a layer of oxide at the electrode/electrolyte interface of low μ_{O_2} . A resulting lack of equilibrium within one or both electrodes would result in a lowered cell potential. Cell measurements near a P_{O_2} -range of significant electronic conduction are not recommended when polarizable electrodes are involved.

In addition to total (ac) conductivity ($\sigma = \sigma_{ion} + \sigma_{\oplus} + \sigma_{\ominus}$) measurements, direct measurements of only the electronic contributions ($\sigma_e = \sigma_{\oplus} + \sigma_{\ominus}$) may be made by the polarization technique described by Wagner [41, 42]. Briefly, a dc emf is applied to the cell (A)

with the electrode at the left ($x = 0$) at positive potential so that oxygen anions in the specimen are initially attracted to the reversible electrode, where they are consumed. The non-reversible (Au,Pt) electrode cannot supply oxygen ions, so that after an initial transient the ionic current vanishes and a steady-state electronic current, $I_{\infty} = I_{\oplus} + I_{\ominus}$, is measured. Assuming local equilibrium for a doped-oxide electrolyte, with $\sigma_{\oplus} \propto P_{O_2}^{1/4}$ and $\sigma_{\ominus} \propto P_{O_2}^{-1/4}$, I_{∞} through the specimen may be calculated by integrating the P_{O_2} -dependent $I_{\oplus}$ and $I_{\ominus}$ contributions over the P_{O_2} -range imposed upon the specimen by the applied potential. The resulting expression is

$$I_{\infty} = RT/FL \{ \sigma_{\oplus}^{\circ} [1 - \exp(-u)] + \sigma_{\ominus}^{\circ} [\exp(u) - 1] \} \quad (4)$$

where $\sigma_{\oplus}^{\circ}$ and $\sigma_{\ominus}^{\circ}$ are the partial positive hole and the partial excess electron conductivities, respectively, for the oxide electrolyte at the P_{O_2} of the reversible electrode, and $u = EF/RT$. This method has been previously applied at relatively low temperatures to measure electronic conductivities of halides [43-46].

Recently, Patterson, Bogren, and Rapp [47] used the Wagner polarization technique in an attempt to measure both $\sigma_{\oplus}$ and $\sigma_{\ominus}$ in $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ and $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ (discussed later) at 800-1000°C. Experimentally, the coexistence reference electrodes $\text{Cu}_2\text{O}-\text{CuO}$, $\text{Cu}-\text{Cu}_2\text{O}$, $\text{Co}-\text{CoO}$, $\text{Fe}-\text{FeO}$, and $\text{Nb}-\text{NbO}$ were used. Eq. (4) of Wagner was revised by dividing both sides by $[1 - \exp(-u)]$ to give

$$I_{\infty}/[1 - \exp(-u)] = \frac{RT}{FL} [\sigma_{\oplus}^{\circ} + \sigma_{\ominus}^{\circ} \exp(u)] \quad (5)$$

so that a plot of $I_{\infty}/[1 - \exp(-u)]$ vs $\exp(u)$ would yield a straight line of slope $(RT/FL) \sigma_{\ominus}^{\circ}$ and intercept $(RT/FL) \sigma_{\oplus}^{\circ}$. The results of measurements for $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ analyzed in this manner are given in Fig. 7. Also shown are the data from total conductivity measurements [37]. At relatively high P_{O_2} , meaningful values of $\sigma_{\oplus}$ were obtained despite considerable experimental difficulties. However, for the minority conductivity, $\sigma_{\ominus}$, very low values ($10^{-6} < \sigma_{\ominus} < 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$) which were P_{O_2} -independent were obtained. By removing the oxide specimen of cell (A), it was established that these apparent values of $\sigma_{\ominus}$ were in fact a measure of extraneous shunting resistances in parallel with the oxide specimen, and probably attributable to thermionic emission. The true values of $\sigma_{\ominus}$ for $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ should then be less than this apparent $\sigma_{\ominus}$ (shunt); again one would expect $\sigma_{\ominus}(\text{true}) \propto P_{O_2}^{-1/4}$. Assuming this P_{O_2} -dependence, the upper limit on $\sigma_{\ominus}(\text{true})$ may be estimated by equating $\sigma_{\ominus}(\text{true})$ to $\sigma_{\ominus}(\text{shunt})$ at Nb-NbO coexistence. Then the estimated maximum P_{O_2} values for which $t_{\text{ion}} > 0.99$ in $\text{Th}_{0.85}\text{Y}_{0.15}\text{O}_{1.925}$ equal $10^{-34.3} \text{ atm}$ at 1000°C, $10^{-39.5} \text{ atm}$ at 900°C, and $10^{-44.7} \text{ atm}$ at 800°C. Obviously, more satisfactory measurements are still needed; further, although t_{ion} may equal unity for a very low P_{O_2} , a meaningful galvanic cell measurement in such a range would be experimentally very difficult.

For ThO_2 -base electrolytes only few conductivity measurements are available to establish the dependences of σ_{ion} , $\sigma_{\oplus}$, and $\sigma_{\ominus}$ on the ionic radii and valences of the dopant ions. Steele and Alcock [11] reported that two ThO_2 - $\text{LaO}_{1.5}$ electrolytes exhibited about 10% higher ionic conductivities than the corresponding ThO_2 - $\text{YO}_{1.5}$ compositions. ThO_2 - CaO electrolytes exhibited lower ionic conductivities for equivalent (equivacancy) compositions than those with the trivalent dopants; higher p-type semiconduction was reported for the ThO_2 - CaO solutions. The solubilities of

$\text{LaO}_{1.5}$ and $\text{SmO}_{1.5}$ in ThO_2 are high, exceeding 50 mole percent [34]. The ionic radii recommended by M8bius [35] for Y^{+3} , Sm^{+3} , and La^{+3} in the fluorite lattice are 1.068, 1.125, and 1.21 $\text{\AA}$, respectively, compared to 1.15 $\text{\AA}$ for Th^{+4} . The further investigation of mixed conduction in ThO_2 - $\text{SmO}_{1.5}$ and ThO_2 - $\text{LaO}_{1.5}$ electrolytes is presently in progress; comparison with the conductivities in ThO_2 - $\text{YO}_{1.5}$ solutions [37] will be made.

ZIRCONIA-BASE ELECTROLYTES

Contrary to ThO_2 -base solutions, the CaF_2 -type phase in ZrO_2 -base solutions does not extend to pure ZrO_2 , except possibly at extremely high temperatures. The phase diagrams of ZrO_2 -base systems have been reviewed [34, 35.] Equilibria I through III should again apply, and Fig. 2 should also describe solutions of ZrO_2 with trivalent dopants. Thus, the dilute solution model would predict the same dependencies of σ_θ , σ_θ , and σ_{ion} on dopant content and P_{O_2} . ZrO_2 -base electrolytes possess two advantages over ThO_2 -base solutions: a) the predominant ionic conductivity plateau extends to 1 atm O_2 allowing for a broader choice of reference electrodes in galvanic cells, and b). the absolute magnitude of σ_{ion} is about one order of magnitude higher for similar dopant contents.

Indirect estimates [11, 16] of σ_θ in the $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ electrolyte have been made by comparing the potentials of galvanic cells involving very low P_{O_2} electrodes with Schmalzried's integration of Eq. (1) using a P_{O_2} -dependent expression for σ_{ion} [16, 48]. However, the possibility of electrode polarization in a mixed conduction range is a disadvantage to this technique. Patterson, Bogren, and Rapp [47] have recently made 2-probe measurements of the total (ac) conductivity of $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ using identical pairs of Me-MeO coexistence electrodes of known P_{O_2} with a He surrounding atmosphere. The purpose of this study was to establish the P_{O_2} -range for the onset of significant σ_θ ; the results are shown in Fig. 8. Measurements at lower P_{O_2} using Ti-TiO electrodes were not reproducible. The data of Fig. 8 indicate that the V-VO coexistence electrode is in the mixed $\sigma_{\text{ion}} + \sigma_\theta$ range for temperatures from 800 to 1000°C. The apparent onset of significant σ_θ in Fig. 8 occurs at several orders of magnitude lower in P_{O_2} than previously estimated, but yet some contamination of the electrolyte by the V-VO electrodes may have occurred.

Patterson, et. al. [47] have used the dc polarization technique described earlier to measure directly σ_θ and σ_θ in $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ at 800, 900, and 1000°C. The results of this study are given in Fig. 9. Once again, the determination of the minority electronic conductivity by the polarization technique at these high temperatures was not reliable. Further, measurements at very low P_{O_2} using Cr-Cr $_2\text{O}_3$, Nb-NbO, and V-VO electrodes did not fit Eq. (5). However, values of σ_θ for the Cu $_2\text{O}$ -CuO and Cu-Cu $_2\text{O}$ electrodes

and values of σ_0 for the Co-CoO and Fe-FeO electrodes were obtained. Extrapolation of the σ_0 data to lower P_{O_2} with lines of $P_{O_2}^{-1/4}$ dependence result in intersections with σ_{ion} at P_{O_2} values which are about 4 orders of magnitude lower than those of Fig. 8. The values in Fig. 9 are considered to be the most reliable, and indicate that predominant ionic conduction in $Zr_{0.85}Ca_{0.15}O_{1.85}$ extends to much lower P_{O_2} than has previously been reported.

Kröger [49] has proposed a rationalization for the promotion of σ_0 by small concentrations of impurity donors in an electrolyte such as $Zr_{0.85}Ca_{0.15}O_{1.85}$. Kröger suggested that the dopant cations Ca_{Zr}'' and oxygen vacancies $V_O^{\bullet\bullet}$ are mostly associated as neutral pairs $(Ca_{Zr}''V_O^{\bullet\bullet})^x$ or clusters $(Ca_{Zr}''V_O^{\bullet\bullet})_m^x$. Significant changes in Fig. 2 and the dilute solution model are then required. Despite some preliminary success with predictions from the fully dissociated model [37], further detailed specification of the defect state must be attempted through experiment.

The ionic conductivity in ZrO_2 -base electrolytes is readily studied by total conductivity measurements in air or 1 atm O_2 , and numerous investigations have been reported. The electrical conductivities of CaO- and MgO-stabilized cubic ZrO_2 have been reviewed recently by Möblius [50]. Dixon, et. al. [51] have reported ac conductivities in air for the cubic ZrO_2 phase containing Ca^{+2} , Y^{+3} , Sc^{+3} , and Yb^{+3} ions in solution. Although the lower composition limit for stabilization of the cubic phase varies for these systems, σ_{ion} was found to increase as the size of the substituted cation decreased. The highest conductivity in each system was found at the lower composition limit of the fluorite phase, so with increasing dopant content the mobility of oxygen vacancies decreases. Strickler and Carlson [40] made systematic measurements of the ac conductivity in air for ZrO_2 - M_2O_3 systems (where M represents La, Sm, Y, Yb, or Sc). For this group of substituted cations whose ionic radii all exceed that of Zr^{+4} , σ_{ion} increased as the dopant cation radius decreased i.e., approached that of Zr^{+4} . Again in agreement with Dixon, et. al. [51], the most dilute compositions for each fluorite phase exhibited the highest σ_{ion} . Strickler and Carlson [52] also investigated quaternary compositions of the cubic ZrO_2 phase containing both Ca^{+2} and Y^{+3} ions. The composition of maximum conductivity was ZrO_2 -0.09 Y_2O_3 , indicating the higher mobility for oxygen vacancies in the presence on a trivalent dopant ion.

RARE EARTH OXIDE-BASE ELECTROLYTES

The sesquioxides of the rare earths are of particular interest as potential solid electrolytes because their structures are derived from the fluorite structure. The rare earth sesquioxides exist in one or more of three modifications: the cubic C-type, the

monoclinic B-type, and the hexagonal A-type [53]; the cation size and temperature establish the predominant structure [54, 55]. The cubic C form is built up of fluorite cubic MO_8 -group coordination polyhedra from which two anions are removed. These anion vacancies lie on a body diagonal and the cubes are aligned along that body diagonal such that the cations retain essentially the fluorite structure. Then the cubic C-type contains an ordered arrangement of anion vacancies with one-fourth of the anions removed.

Reliable measurements of the conductivities of the rare earth sesquioxides are limited. However, Schmalzried [48], and Schmalzried and Tare [57] have inferred the electrical transference behavior for several sesquioxides (rare-earth and Group III B oxides) from galvanic cell measurements. At 900°C , all of the oxides investigated (B-type Sm_2O_3 , and C-type Nd_2O_3 , Sc_2O_3 , Yb_2O_3 , Gd_2O_3 , Dy_2O_3 , and Y_2O_3) exhibited predominant ionic conductivity over an intermediate oxygen partial pressure range. In a galvanic cell involving a 1 atm O_2 electrode and a low P_{O_2} ($\text{H}_2\text{-H}_2\text{O}$ or CO-CO_2 gas mixture) electrode, Schmalzried and Tare [57] established for Sm_2O_3 , Gd_2O_3 , Dy_2O_3 , and Y_2O_3 the parameters $p_\oplus$ and $p_\ominus$ which are defined as those oxygen activities at which σ_{ion} equals $\sigma_\oplus$ and $\sigma_\ominus$, respectively [16, 48]. For each oxide, $p_\oplus$ was below 1 atm O_2 , and $p_\ominus$ was on the order of 10^{-20} atm O_2 or lower. The oxides Gd_2O_3 and Dy_2O_3 were reported to have $p_\ominus$ values lower than 10^{-20} atm, but beyond the limits of resolution by the available technique.

Tallan and Vest [58] have more recently established that Y_2O_3 of 99.99% purity is an amphoteric semiconductor over the P_{O_2} range from 10^{-1} to 10^{-17} atm at 1200 to 1600°C . The ionic contribution to the conductivity was found to be less than one percent under these conditions although at temperatures less than 900°C , mixed conduction was reported. The differences between the results of the investigations of Schmalzried and Tare [57] and Tallan and Vest [58] is rationalized by the higher purity of the materials for the latter study. The conductivity measurements of Rudolph [36] suggest an ionic plateau at intermediate oxygen pressures for A-type La_2O_3 . Based on the potential use of rare-earth oxides as solid electrolytes at very low P_{O_2} , a study of the conductivities of pure and doped Gd_2O_3 and Dy_2O_3 is currently in progress.

THE SOLUBILITY AND DIFFUSIVITY OF OXYGEN IN COPPER BY SOLID-STATE COULOMETRIC TITRATION

In 1953, C. Wagner introduced the solid-state coulometric titration technique to study the stoichiometry range of Ag_2S . This high-temperature electrochemical method may be used to fix continuously the thermodynamic activity of a component at an electrode/electrolyte interface (by setting E) while simultaneously allowing the measurement of the rate at which atoms (ions plus electrons) enter or leave the electrode (by measuring I). Alternatively, the investigator may fix the rate at which atoms leave or enter the

electrode (by setting I), and determine continuously the thermodynamic activity of the component at the electrode/electrolyte interface (by measuring E). Rickert, et. al. [60, 61] have used such a coulometric titration method to determine the diffusivity of oxygen in solid silver. Pastorek and Rapp [62] are currently using an alternative cell geometry and different experimental procedures to determine the solubility and diffusivity of oxygen in solid copper.

In the first series of experiments, the experimental cell and arrangement shown schematically in Fig. 10 (a) are used. The 3/8" diameter electrode and electrolyte tablets are pressed together at 1065°C to establish intimate Cu/Zr_{0.85}Ca_{0.15}O_{1.85} contact. A thin Al₂O₃ coating on the circumference of the Cu prevents interaction of the Cu with the surrounding He gas phase. After welding the Cu tablet to the two electrolyte tablets the cell is equilibrated at a chosen temperature (say 1000°C) with the switch in the 1 position so that the Cu electrode is equilibrated throughout to the oxygen activity corresponding to the FeO-Fe₃O₄ reference electrode. After equilibration, the switch is moved to position 2 so that a predetermined constant current passes through the cell on the left. The constant current of oxygen ions passing through the electrolyte on the left corresponds to a constant flux of oxygen atoms entering the left-hand face of the copper disk. Simultaneously, the cell voltage E is measured continuously with a vacuum-tube voltmeter (VTVM). The duration of the experiment is limited to a time which is insufficient to form Cu₂O at the Cu/electrolyte interface.

Assuming a concentration independent D_0^{Ag} , the solution to the diffusion equation for the one-dimensional diffusion of oxygen into a semi-infinite copper specimen with the boundary condition

$$\left(\frac{\partial N_0(x, t)}{\partial x} \right)_{x=0} = - \frac{I V_{Cu}}{2 F A D_0}$$

is given by

$$N_0(x, t) = N_0(t_0) + \frac{I t^{\frac{1}{2}} V_{Cu}}{F A D_0^{\frac{1}{2}} \pi^{\frac{1}{2}}} \exp \left(\frac{-x^2}{4 D_0 t} \right) - \frac{I x V_{Cu}}{2 F A D_0} \operatorname{erfc} \left(\frac{x}{2 (D_0 t)^{\frac{1}{2}}} \right) \quad (6)$$

where V_{Cu} is the molar volume of Cu, N_0 the oxygen atom fraction in Cu, and D_0 the diffusivity of oxygen in solid Cu. At $x=0$,

$$N_0(t) = N_0(t_0) + \frac{I t^{\frac{1}{2}} V_{Cu}}{F A D_0^{\frac{1}{2}} \pi^{\frac{1}{2}}}. \quad (7)$$

The voltage E indicated by VTVM is related to the instantaneous oxygen activities at the Cu/electrolyte interface by

$$E(t) - IR = \frac{1}{2F} (\mu_0' - \mu_0'') = \frac{RT}{2F} \ln \frac{a_0'(\text{Cu})}{a_0''(\text{FeO-Fe}_3\text{O}_4)} \quad (8)$$

where R is the ionic electrical resistance of the electrolyte. From Sievert's law and Henry's law for oxygen atoms in an under-saturated copper crystal

$$a_0' = f_0 N_0' \equiv P_{O_2}^{\frac{1}{2}} \quad (9)$$

whereby the standard state for oxygen atoms is defined. Rewriting Eq. (8),

$$E(t) - IR = \frac{RT}{2F} \ln f_0 N_0'(t) - \frac{RT}{4F} \ln P_{O_2}(\text{FeO-Fe}_3\text{O}_4). \quad (9)$$

The activity coefficient f_0 is tentatively evaluated from the solubility data of Phillips and Skinner [63] as

$$f_0 = \frac{P_{O_2}^{\frac{1}{2}}(\text{Cu-Cu}_2\text{O equilibrium})}{N_0^{(s)}} \quad (10)$$

where $N_0^{(s)}$ is the oxygen solubility in copper. Substituting Eq. (7) into Eq. (9),

$$E(t) - IR = \frac{RT}{2F} \left[\ln f_0 + \ln (N_0(t_0) + \frac{It^{\frac{1}{2}} V_{\text{Cu}}}{FAD_0^{\frac{1}{2}} \pi^{\frac{1}{2}}}) \right] - \frac{RT}{4F} \ln P_{O_2}'' \quad (11)$$

Expect for short times, $It^{\frac{1}{2}} V_{\text{Cu}} / FAD_0^{\frac{1}{2}} \pi^{\frac{1}{2}} \gg N_0(t_0)$, so that a plot of $[E(t) - IR]$ vs $\ln It^{\frac{1}{2}}$ should approach linear behavior with a slope $\frac{RT}{2F}$. A representative plot of data for 1000°C is shown in Fig. 11. Agreement between the predicted and the experimental slopes is satisfactory. A plot of Eq. (11) with $(P_{O_2}''/f_0) \frac{1}{2} \exp [2F(E-IR)/RT]$ vs $It^{\frac{1}{2}}$ should be linear with a slope of $V_{\text{Cu}}/FAD_0^{\frac{1}{2}} \pi^{\frac{1}{2}}$ and an intercept of $N_0(t_0)$. Fig. 12 shows such a plot of the data. The intercept of Fig. 12 equals essentially zero, as expected, and D_0 is obtained from the measured slope. In Table I are listed the diffusivity values which have been determined. These data are somewhat dependent upon the choice of f_0 from the data of Phillips and Skinner [63]. As further determinations of $N_0^{(s)}$ are made in the second part of this research, some revision of the D_0 values may be made.

In a second series of experiments, the experimental setup of Fig. 10 (b) is being used. After equilibration of the cell with the switch in the 1 position, the switch is moved to position 2 so that a small voltage (say 50 mv) is imposed on both sides of the double cell. Then for a fixed and known change in a_0' at both faces of the Cu specimen, the instantaneous rate of entry of oxygen atoms into the copper is indicated by the current passed, which is recorded. The solution to the diffusion equation for the copper specimen of finite thickness is given by

$$N_0(x,t) = N_0(E_2) - [N_0(E_2) - N_0(E_1)] \sum_{n=1,3,5,\dots}^{\infty} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{l}\right) \exp(-n^2 \pi^2 D_0 t / l^2) \quad (12)$$

where E_1 is the initial cell potential (which need not be zero), E_2 is the second cell potential, and l is the thickness of the Cu specimen. Through differentiation of Eq. (12), the instantaneous current I for the two cells is given by

$$I = \frac{16FAD_0}{l V_{Cu}} [N_0(E_2) - N_0(E_1)] \sum_{n=1,3,5,\dots}^{\infty} \exp(-n^2 \pi^2 D_0 t / l^2) \quad (13)$$

The total oxygen received by the specimen is given by

$$\int_0^{\infty} \frac{I(t) dt}{2F} = \frac{V_E}{V_{Cu}} [N_0(E_2) - N_0(E_1)] \quad (14)$$

where V_E is the volume of the Cu specimen. Because very small currents are involved for long times, the integral of Eq. (14) is not derived from a graphical integration of the measured current. Rather, because $I(t)$ should be given by Eq. (13), I data from short times may be used to evaluate Eq. (14). However, a knowledge of D_0 is required for this method. Eq. (14) may then be solved for $N_0(E_1)$, and $N_0(s)$ is given by

$$N_0(s) = N_0(E_1) \left[\frac{P_{O_2}(\text{Cu-Cu}_2\text{O})}{P'_{O_2}(E_1)} \right]^{\frac{1}{2}} \quad (15)$$

Alternatively, Eq. (13) may be rewritten

$$I = B \sum_{n=1,3,5,\dots}^{\infty} \exp(-n^2 / \tau) t \quad (16)$$

where

$$B = [N_0(E_2) - N_0(E_1)] \frac{16FAD_0}{l V_{Cu}}$$

$$\text{and } \tau = l^2 / \pi^2 D_0.$$

For $t/\tau \gg 0.5$, $I \approx B \exp(-t/\tau)$.

Then a plot of $\log I$ vs t will approach linear behavior with a slope of $-1/2.303\tau$ and an intercept of $\log B$. Thus, a value for D_0 is derived from the slope, and $N_0(s)$ is obtained from the intercept. These experiments are currently in progress.

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Table I

Diffusivity of Oxygen in Copper

<u>Electrode</u>	<u>T(°C)</u>	<u>I(μa)</u>	<u>Theor. Slope (RT/2F)</u>	<u>Expt'l Slope</u>	<u>D_O^{Cu} ($\frac{\text{cm}^2}{\text{sec}}$)</u>
FeO-Fe ₃ O ₄	1030	100	.129	.144	4.83 x 10 ⁻⁵
FeO-Fe ₃ O ₄	1030	80	.129	.130	3.33 x 10 ⁻⁵
FeO-Fe ₃ O ₄	1000	200	.126	.129	4.09 x 10 ⁻⁵
FeO-Fe ₃ O ₄	1000	100	.126	.139	4.09 x 10 ⁻⁵
FeO-Fe ₃ O ₄	1000	100	.126	.131	3.16 x 10 ⁻⁵
FeO-Fe ₃ O ₄	1000	80	.126	.134	4.09 x 10 ⁻⁵
FeO-Fe ₃ O ₄	950	50	.121	.126	1.86 x 10 ⁻⁵
FeO-Fe ₃ O ₄	950	40	.121	.121	2.24 x 10 ⁻⁵
FeO-Fe ₃ O ₄	900	20	.116	.113	3.18 x 10 ⁻⁵

Best Tentative Expression:

$$D_0^{\text{Cu}} (\text{cm}^2/\text{sec}) = 5.0 \times 10^{-3} \exp\left(-\frac{12,500}{RT}\right)$$

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Fig 1 - Defect Equilibria in Pure ThO_2 .

Fig 2 - Defect Equilibria in Y_2O_3 - Doped ThO_2 .

Fig 3 - A.C. Total Conductivity for "Pure" Thoria as a Function of Temperature and Oxygen Partial Pressure.

Fig 4 - Schematic Illustration of Effect of $YO_{1.5}$ Content on Partial Electrical Conductivities in $ThO_2-YO_{1.5}$ Electrolytes.

Fig 5 - Ionic Conductivity as a Function of Mole % $\text{YO}_{1.5}$ or % Anionic Vacancies at 1000°C.

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(a)

(b)

Fig. 10 Schematic Diagrams of Experimental Arrangement for Determination of Solubility and Diffusivity of Oxygen in Solid Copper by Solid-State Coulometric Titration Technique.

Fig. 11 Plot of Data from Coulometric Titration of Oxygen into Copper.

Fig. 12 Plot of Data from Coulometric Titration of Oxygen into Copper.