A STUDY OF THE DEFECT STRUCTURE
OF NONSTOICHIOMETRIC CeO_2

Progress Report

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January 1, 1973 - December 31, 1973

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NO. AT(11-1)-1441

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ABSTRACT

Based on a combined analysis of electrical conductivity and thermodynamic data the conductivity, in the temperature range 700° - 1000°C, may be represented by $\sigma \propto x e^{-Q/kT}$ where Q is a function of x . This expression was rationalized in terms of the following simple relations for the electron carrier concentration $[Ce'_{Ce}] \propto x$ and the electron mobility $\mu = \mu_0 e^{-Q/kT}$ where μ_0 is independent of x , Q is independent of x from $-3.0 < \log x < -1.8$, and Q increases with x from $-1.8 < \log x < 0.7$.

The electrical conductivity data on CaO-doped CeO_2 (0.1 - 16 mole %) which involves both ionic and electronic transport has been interpreted in terms of an oxygen vacancy model.

Preliminary conductivity measurements on SrO-doped CeO_2 indicate that the P_{O_2} dependence of σ was approximately the same for both CaO and SrO₂ doped specimens. However, the mobility of oxygen vacancies appears to be larger in SrO-doped CeO_2 .

The results of the ionic transference measurements on CeO_2 doped with 2, 5 and 14 mole % CaO in the temperature and oxygen pressure ranges 700° - 1000°C and 1 to 10^{-22} atm were discussed.

The results of a thermodynamic study on CeO_{2-x} , where x was measured in the composition region $0.0003 \leq x \leq 0.3$ as a function of T and P_{O_2} , was also discussed. The thermodynamic quantities $\Delta \bar{H}_{O_2}$ and $\Delta \bar{S}_{O_2}$ were calculated from this data. On the basis of the observed dependence of $\Delta \bar{S}_{O_2}$ on x , the nonstoichiometric behavior of CeO_{2-x} was rationalized in terms of the defect reaction

in the composition region $10^{-3} < x < 10^{-2}$.

INTRODUCTION

The purpose of this research program is to determine the defect structure (i.e. the type and concentration of atomic and electronic defects and the equilibrium relationships between these defects and the external variables such as temperature and oxygen pressure) and transport properties of defects in nonstoichiometric oxides from their electrical and thermodynamic behavior. Similar studies will also be made on doped-nonstoichiometric oxides to determine the effect of the defects produced by doping on the nonstoichiometric defect structure and the transport properties of these defects. The analysis of the data should permit the calculation of the energies of formation of the various defect reactions which contribute to the defect structure. In addition, it should be possible to determine whether the law of mass action is applicable or if a more complex statistical thermodynamic treatment is necessary to explain the equilibrium relations between defects in the nonstoichiometric oxides investigated. Studies of this kind also provide information about the magnitude, temperature, and compositional dependence of the mobility of both electronic and ionic charge carriers in "pure" and doped nonstoichiometric oxides, such data has been rather sparse in the literature.

The thermodynamic and electrical property study initiated on "pure" and doped nonstoichiometric cerium dioxide has been continued. The literature on the x-ray, thermodynamic and electrical property studies on nonstoichiometric CeO_2 and CaO-doped CeO_2 has been reviewed previously.¹⁻⁵ The following is a brief summary of some of the results of previous studies in this laboratory on the electrical behavior of "pure" and CaO-doped nonstoichiometric cerium dioxide.

In a recent paper by Blumenthal, Lee and Panlener³ the results of an electrical conductivity study on sintered specimens of nonstoichiometric cerium dioxide as a function of temperature (i.e. 800° - 1500°C) and oxygen partial pressures (i.e. $1 - 10^{-21}$ atm) were described. These data were analyzed using a mass action approach. Over a range of oxygen pressures, in the composition region near stoichiometry, the isothermal dependence of the conductivity on P_{O_2} fit the following simple relation

$$\sigma \propto P_{O_2}^{1/5} \quad (1)$$

This behavior was rationalized in terms of the following defect reaction

At slightly lower oxygen pressures, σ increased more rapidly with decreasing P_{O_2} (i.e. $\sigma \propto P_{O_2}^{-1/n}$, where n varied from 5 to approximately 4 with decreasing P_{O_2}). These results were rationalized in terms of a defect model involving electrons localized on cerium atoms and triply and quadruply ionized cerium interstitials. For example, according to Le Chatelier's principle the defect reaction

should shift to the right with increasing concentration of cerium interstitials produced by larger departures from stoichiometry. Equations for the electrical conductivity were derived using the above defect reactions and the law of mass action. The above defect model was postulated based on the observed curve fit of the conductivity data with these equations.

The electron mobility in nonstoichiometric cerium dioxide was also calculated² by combining electrical conductivity³ and thermogravimetric

data⁶ for the temperature and oxygen region where the atomic defect predominates in one state of ionization. The data for the calculation in the temperature range 800° - 1200°C was selected from the oxygen pressure region where according to the analysis of the conductivity data the predominant defects are electrons localized on normal cerium ions and quadruply ionized cerium interstitials. In this composition region (i.e. near stoichiometry) the calculated electron mobility of nonstoichiometric cerium dioxide increases exponentially

$$\mu = \mu_0 e^{-0.14/kT} \quad (4)$$

with increasing temperature between 800° and 1200°C. The conduction mechanism was assumed to be a "hopping" type process with an activation energy of 0.14 eV (i.e. under the influence of an electric field the electrons localized at normal cerium ion sites move to adjacent cerium ions). The magnitude of the mobility was of the order 10^{-2} cm²/v-sec.

The results of an electrical conductivity study of sintered specimens of nonstoichiometric cerium dioxide as a function of temperature from 1000° - 300°C as well as a function of composition over the range $0.00214 \leq y \leq 0.0977$ were described in AEC Report C00-1441-13. These results were described in terms of a high temperature and low temperature region. In both temperature regions the conductivity of specimens with fixed departures from stoichiometry exhibit an exponential dependence on temperature

$$\sigma = \sigma_0 e^{-Q/kT} \quad (5)$$

In the high temperature region the activation energy increased with increasing values of y (i.e. 0.22 eV at $y = 0.00214$ to 0.37 eV at $y = 0.098$). The activation energy, 0.61 ± 0.03 eV, in the low temperature was independent

of y . The temperature of the intersection between the high and low temperature regions for each composition was compared with the composition-temperature dependence of the miscibility gap reported by Brauer and Gingerich.⁷

The data in the high temperature region was rationalized in terms of the following model. The electron mobility over the entire region of nonstoichiometry was assumed to be represented by Eq. (4) which was determined for near-stoichiometric conditions. The variation of Q with composition was attributed to a change in state of ionization of the cerium interstitial. An approximate value of the standard enthalpy of formation for the defect reaction

was calculated from the temperature dependence of the conductivity of specimens with fixed ratios of O/Ce and from the temperature dependence of the electron mobility given above.

As discussed in the last progress report⁸ a combined study on the electrical conductivity and ionic transference number of sintered specimens of CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO content was initiated to 1) obtain information on the diffusion coefficient for oxygen vacancies in CeO_2 and 2) to determine the effect of oxygen vacancies produced by CaO-doping on the behavior of the electronic conductivity. The results of the study on the electrical conductivity of CaO-doped cerium dioxide were described in AEC Report C00-1441-14. These results may be summarized as follows.

The electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 7.0 mole %) was measured over the temperature range 700° - 1500°C

and from 1 to 10^{-22} atm of oxygen. All specimens of CaO-doped CeO_2 exhibited mixed conduction. Predominantly ionic conductivity was observed at low temperatures and high oxygen partial pressures. Conversely, high temperatures and lower oxygen partial pressures were dominated by electronic conductivity. The electrical conductivity was rationalized in terms of a defect model involving nonstoichiometric defects (i.e. ionized cerium interstitials and localized electrons) and impurity generated defects (i.e. doubly ionized oxygen vacancies). This model is based on the agreement between the theoretically derived relation using the law of mass action

$$\sigma = \sigma_{oe} (1 - \bar{\xi}a) + A(\% \text{CaO}) \exp(-E_i/kT) \quad (7)$$

and the above electrical conductivity data. Where the electronic conductivity of nonstoichiometric "pure" CeO_2 is σ_{oe} and $(1 - \bar{\xi}a)$ is a correction for CaO-doping. The quantity, $\bar{\xi}$, is related to a geometrical blocking factor associated with the site fraction of Ca^{+2} ions on normal Ce^{+4} ion sites, a. The second term in the above expression for σ represents the ionic conductivity which is proportional to the oxygen vacancy concentration and mole % CaO.

An approximate expression for the diffusion coefficient of oxygen vacancies, D_{V_o} , in CaO-doped CeO_2 was also determined in this study. The equation

$$D_{V_o} = 1.4 \times 10^{-1} (kT) \exp(-.61/kT) \quad (8)$$

was calculated by using the above defect model for ionic conductivity, the conductivity data in the region where ionic conductivity was assumed to predominate, and the Nernst-Einstein relation.

In the above studies of the electrical behavior of "pure" and CaO-doped cerium dioxide the nonstoichiometric behavior has been rationalized in terms of a defect model involving electrons localized on cerium atoms and cerium interstitials with multiple states of ionization. This defect model is based primarily on the analysis of the oxygen pressure dependence of the electrical conductivity using the law of mass action. However, recently reported^{9a} results of O_{18} diffusion studies on "pure" and yttria-doped cerium dioxide suggest that the nonstoichiometric defects are oxygen vacancies. In addition, recent x-ray intensity and thermodynamic studies on nonstoichiometric cerium dioxide conducted in this laboratory and neutron diffraction studies at Argonne National Laboratory provide positive proof of the existence of oxygen vacancies. The results of these investigations will be discussed later in this progress report. Because of this new information, the interpretation of the results of the studies on the temperature dependence of the conductivity under constant composition conditions (AEC Report C00-1441-13) and the Electrical Conductivity of CaO-doped Nonstoichiometric Cerium Dioxide (AEC Report C00-1441-14) have been reanalyzed. The new interpretation of the results of these studies which also include more recently obtained data are presented in separate progress reports C00-1441-16 and C00-1441-17. The analysis of these results are also briefly summarized in the section on electrical properties studies in this report.

In the current investigation, the thermodynamic and electrical property measurements initiated on nonstoichiometric cerium dioxide were continued in order to provide additional data which would permit a more detailed interpretation of the defect structure of nonstoichiometric CeO_2 and a

better understanding of the temperature and compositional dependence of electronic transport in CeO_{2-x} . In addition, a combined study of the electrical conductivity, ionic transference and thermodynamic behavior of CaO-doped cerium dioxide was made in order to obtain information about 1) the temperature and compositional dependence of diffusion coefficients of oxygen vacancies and 2) the effect of doping on the nonstoichiometric behavior of cerium dioxide.

RESULTS AND DISCUSSION

1. Electrical Property Studies

The results of the study on the temperature dependence of the electrical conductivity of sintered specimens of nonstoichiometric cerium dioxide with fixed composition were described briefly in the last progress report⁸ and in greater detail in AEC Report C00-1441-13. In the temperature range 700° - 1000°C the temperature dependence of the conductivity of specimens with fixed O/Ce ratios was attributed to both a change in the concentration of localized electrons, $[Ce_{Ce}']$, and the mobility of these electrons with temperature. An increase in the state of ionization of the cerium interstitial, for example by a reaction of the type

was assumed to account for the increase in $[Ce_{Ce}']$ with temperature. The electron mobility was assumed to be 1) temperature dependent only over the entire region of nonstoichiometry and 2) to obey the previously reported relation

$$\mu = \mu_0 e^{-0.14/kT} \quad (4)$$

which was calculated for the region near stoichiometry. Utilizing a mass approach an approximate value of the standard enthalpy, $\Delta H \approx 1.6$ eV, for Eq. (6) was calculated from the temperature dependence of the conductivity of specimens with fixed ratios of O/Ce and from the temperature dependence of the electron mobility given above.

However, as discussed in the Introduction, this analysis based on an interstitial defect model is incorrect because a number of recent studies

provide positive proof that the nonstoichiometric atomic defects are oxygen vacancies. Because of this new information, which will be discussed later, the results of this conductivity study have been reinterpreted. The new interpretation of this data which is analyzed without the use of the law of mass action is described in AEC Report C00-1441-17 and may be summarized as follows. The results of the study on the temperature dependence of the electrical conductivity of nonstoichiometric cerium dioxide were conveniently described in terms of high temperature and low temperature regions. In both temperature regions the conductivity of specimens with fixed ratios of O/Ce exhibit an exponential dependence on temperature

$$\sigma = \sigma_0 e^{-Q/kT} \quad (9)$$

In the high temperature region Q increased with increasing departures from stoichiometry; whereas in the low temperature region Q was equal to $0.61 \pm .03$ eV over the entire nonstoichiometric region investigated. In this study the conductivity data in the high temperature region was reanalyzed.

Recently obtained thermodynamic data (i.e. $x = f(T, P_{O_2})$, where x is obtained from the formula CeO_{2-x}) (see the section on thermodynamic studies) was combined with conductivity data to obtain information about the dependence of σ on x .

The following conclusions were drawn from the combined results of these studies.

1. The compositional and temperature dependence of the electrical conductivity of nonstoichiometric CeO_{2-x} may be represented by the expression

$$\sigma \propto x e^{-Q/kT}$$

where Q is a function of x .

2. This expression was rationalized in terms of the following simple relations for the electron carrier concentration

$$[\text{Ce}'_{\text{Ce}}] \propto x \quad (10)$$

and the electron mobility

$$\mu = \mu_0 e^{-Q/kT} \quad (11)$$

where μ_0 is independent of x , Q is independent of x in the region $-3.0 < \log x < -1.8$, and Q is a function of x between $-1.8 < \log x < -0.7$.

The relation $[\text{Ce}'_{\text{Ce}}] \propto x$ implies the same nonstoichiometric atomic defect exists in predominantly one state of ionization over the entire composition region (i.e. $-3.0 < \log x < -0.7$). This result is inconsistent with an earlier interpretation of the conductivity data which involved a nonstoichiometric atomic defect with multiple states of ionization.^{3,8} As discussed later in this report (the section on thermodynamic studies), the earlier analyses are incorrect because the law of mass action is not valid in this composition region.

The major advantage of the analysis employed in this study, which combines the results of both the conductivity and thermodynamic studies, is that no assumptions have to be made regarding defect interactions. It should be noted, however, that this analysis does not provide any information about the type of nonstoichiometric defect in CeO_{2-x} . Although as discussed in the introduction the most likely defect is an oxygen vacancy.

The nature of nonstoichiometric defect and its state of ionization will be discussed later in the section on thermodynamic studies of CeO_{2-x} .

The following question also arises from this study, "Why is the activation energy, Q , a function of x ?" A current study^{9b} in this laboratory of the dependence of the lattice parameter as a function of nonstoichiometry at elevated temperatures ($800^\circ - 1000^\circ\text{C}$) shows that the lattice parameter increases with increasing x . Since the "hopping type process" for electron conduction involves an activation energy, it appears likely that the increase in the activation energy with x is associated with an increase in size of the unit cell.

As described in the previous progress reports most of the experimental difficulties with the AC Hall mobility technique have been associated with noise problems.^{8,10} A very low noise level (e.g. $\sim 10^{-8}$ volts) is required because the electron mobility² of CeO_2 is very small (i.e. $\mu \sim 10^{-2} \text{ cm}^2/\text{v-sec}$). As discussed in the last report⁸ the major source of noise is caused by rotating of the specimen in a magnetic field. The proposed solution to this problem was to replace the magnet used currently with a low inductance type magnet. The magnetic field could then be varied by driving the magnet with an oscillating current which would eliminate the need for rotating the specimen. Prof. Seitz of the Electrical Engineering Department designed and built this double AC Hall mobility measuring system. Unfortunately to date he has been unable to obtain the necessary financial support to purchase the new magnet which will cost several thousand dollars. Because of the current situation, no Hall mobility measurements on CeO_2 have been attempted. If he is successful in obtaining the new magnet in the near future, the proposed Hall mobility study⁸ on cerium dioxide will be resumed.

While the analysis of the thermodynamic and electrical conductivity data on "pure" $\text{Ce}_{1+y}\text{O}_2$ provides information about the nonstoichiometric defect structure and electron mobility, information about the mobility of atomic defects (e.g. oxygen vacancies or cerium interstitials) in $\text{Ce}_{1+y}\text{O}_2$ are virtually nonexistent.

As described in the previous progress report⁸ a combined study of the electrical conductivity σ and the ionic transference, t_i , as a function of temperature, oxygen pressure and CaO content was initiated to obtain information on the mobility of oxygen vacancies in CeO_2 and to characterize the electronic conductivity of Ca-doped CeO_2 . The electrical conductivity study of sintered specimens of CaO-doped CeO_2 (0.1 - 7.0 mole %) was measured over the temperature range $700^\circ - 1500^\circ\text{C}$ and from 1 to 10^{-22} atm of oxygen. The results of this study were described in AEC Report C00-1441-14. These results may be summarized as follows. All specimens of CaO-doped CeO_2 exhibited mixed ionic and electronic conduction. Predominantly ionic conductivity, σ_i , was observed at low temperatures and high oxygen partial pressures. Conversely, high temperatures and lower oxygen partial pressures were dominated by electronic conductivity. The electrical conductivity was rationalized in terms of a defect model involving nonstoichiometric defects (ionized cerium interstitials and localized electrons) and impurity generated defects (doubly ionized oxygen vacancies).

As discussed in the introduction, the previous analysis of this data using a cerium interstitial nonstoichiometric defect model is incorrect because a number of recent studies provide positive proof that the nonstoichiometric defects are oxygen vacancies. Because of this new information, which will be discussed later, the interpretation of this conductivity study has been revised and is described in AEC Report C00-1441-16.

The electrical conductivity data for specimens with CaO contents between 7 - 16 mole % which was obtained in the current study is also included in this report. From these data a maximum in the ionic conductivity is observed at about 12 mole % CaO. This behavior also appears to be relatively independent of temperature and oxygen partial pressure. Also in the vicinity of the σ maximum only a very small variation in the magnitude of the conductivity with CaO content is observed. Although the reported solubility is 16 mole % CaO in air at 1600°C the dependence of temperature and oxygen pressure on the solubility of CaO-doped CeO₂ is not known. Thus the question of whether the conductivity maximum occurs because the concentration of CaO in this region exceeds the solubility of CaO in CeO₂ cannot be easily ascertained. Because of these considerations no attempt has been made to analyze the maximum in the conductivity of CeO₂ doped with CaO.

This report also contains the results of the pycnometric density and lattice parameter measurements on CaO-doped CeO₂ which were obtained in this laboratory. A comparison of the pycnometric density with the calculated values of the density based on lattice parameter data proves that doping CeO₂ with CaO produces oxygen vacancies. On the basis of this result a thermodynamic argument has been presented for the formation of oxygen vacancies as the nonstoichiometric defect in both "pure" and CaO-doped CeO₂. Thus in the above revised report the ionic conductivity is still interpreted in terms of an oxygen vacancy model. However, the nonstoichiometric defects responsible for the electronic conductivity have been qualitatively reinterpreted in terms of an oxygen vacancy model.

A study to determine the effect of valance and ionic radii of the dopant cation on the behavior of the electrical conductivity was also initiated in this investigation. There are a number of metal oxides of the type MO , M_2O_3 or MO_2 which exhibit extensive solubilities in CeO_2 . As discussed above a comprehensive study has been made on the electrical conductivity of CaO -doped CeO_2 . It should be noted that the calcium ion in the +2 valance state has approximately the same ionic value as the cerium ion in the +4 valance state. The dependence of the lattice parameter on CaO content has been reported to be $0.0004 \text{ \AA/mole \% } CaO$.¹¹ Thus the lattice parameter of CeO_2 is increased only slightly with the addition of CaO . In the preliminary study SrO was selected as a dopant because 1) the ionic radii of stronium ions ($1.14\text{\AA}$) are larger than the ionic radii of calcium ions ($1.01\text{\AA}$) and 2) the valance of Ca and Sr ions are the same, +2. The reported dependence of the lattice parameter of SrO content has been reported to be $0.004 \text{ \AA/mole \% } SrO$.¹¹

Preliminary conductivity measurements were made on SrO -doped cerium dioxide of a function of temperature and oxygen partial pressure. The results obtained on a sample of CeO_2 doped with 1 mole % SrO are shown in Fig. 1 where $\log \sigma$ is plotted as a function of $\log P_{O_2}$ for several different temperatures. For comparative purposes the σ of CeO_2 doped with 1 mole % CaO is represented in Fig. 1 by a dashed line. It is interesting to note that the oxygen pressure dependence of σ is approximately the same for both the CaO and SrO doped samples. However, the magnitude of the electrical conductivity is larger for the SrO doped specimen.

In the region where σ is independent of P_{O_2} , the σ is assumed to be predominantly ionic (i.e. $\sigma \approx \sigma_i$). Since the mole % dopant of SrO and CaO is the same, the oxygen vacancy concentration in this region is also

Fig. 1 A comparison of the isothermal plot of $\log \sigma$ vs $\log P_{O_2}$ for CeO_2 samples doped with 1 mole % CaO and 1 mole % SrO.

the same in both specimens. The increased ionic conductivity may then be explained by assuming that the mobility of oxygen vacancies is larger in the SrO-doped CeO_2 specimen.

At low oxygen pressure and particularly at higher temperatures the nonstoichiometric behavior controls the electrical conductivity. In this region the conductivity is predominantly electronic (i.e. $\sigma \approx \sigma_e$). The effect of the type of dopant on the oxygen nonstoichiometry is not known. Thus on the basis of the above results it cannot be ascertained whether the increase in the electronic conductivity in the SrO-doped CeO_2 specimen is caused by an increase in the concentration of electronic carriers or an increase in electronic mobility. Thermodynamic studies (i.e. the type discussed in the section on the thermodynamic investigation of CaO-doped CeO_2) should provide information on the effect of dopant on the concentration of electronic defects produced by nonstoichiometry.

The conductivity studies on SrO-doped CeO_2 will be continued. Since the reported solubility of SrO in CeO_2 is 9 mole %, measurements will be made on samples with SrO contents between 1 and 9 mole %. In addition conductivity studies will also be made on specimens of CeO_2 doped with other cations (e.g. La^{+3} , Y^{+3} , Mg^{+2} , Th^{+4} , etc.) which have different valences and ionic radii.

2. Thermodynamic Studies

As discussed in the previous progress report,⁸ a combined study of the electrical conductivity and the ionic transference as a function of temperature, oxygen pressure and CaO content was initiated to obtain information on the mobility and the diffusion coefficient of oxygen vacancies in CeO_2 . In the previous study ionic transference measurements, utilizing an oxygen concentration cell, were made on a 5 mole % CaO-doped

CeO_2 specimen over a wide range of oxygen pressure and temperature.

These results were described qualitatively in terms of a "high" and "low" oxygen pressure region.

In the high oxygen pressure region (i.e. $1 - 10^{-4}$ atm) the ionic conductivity predominated. These results also indicated the presence of some p-type conduction. In the low oxygen pressure region (i.e. obtained with CO-CO₂ gas mixtures) t_i decreased with decreasing P_{O_2} , which indicates the presence of n-type electronic conduction.

In the current study an electrochemical cell of the type

was used to measure the ionic transference number, t_i , of CeO_2 doped with 2, 5 and 14 mole % CaO in the temperature and oxygen pressure ranges 700° to 1000°C and 1 to 10^{-22} atm. The ionic transference number was combined with the total electrical conductivity⁴ to obtain both the ionic, σ_i , and electronic, σ_e , conductivities. Representative plots of $\log \sigma_i$ vs $\log P_{\text{O}_2}$ and $\log \sigma_e$ vs $\log P_{\text{O}_2}$ are shown in Figs. 2 and 3, respectively, for CeO_2 doped with 2 mole % CaO.

As shown in Fig. 2 the ionic conductivity is independent of P_{O_2} from $1 - 10^{-4}$ atm. This behavior may be explained on the basis of a fixed concentration of mobile charge-compensating oxygen vacancies arising from substitutional incorporation of calcium on cerium sites. At lower oxygen pressures, obtained with CO-CO₂ mixtures, the ionic conductivity increases with decreasing oxygen pressure. This increase may be explained by assuming that the ionic conductivity in this oxygen pressure region is controlled by nonstoichiometric defects, presumably oxygen vacancies.

Fig. 2 Isothermal plot of $\log \sigma_1$ vs $\log P_{O_2}$ for a sample of CeO_2 doped with 2 mole % CaO .

Fig. 3 Isothermal plot of $\log \sigma_e$ vs $\log P_{O_2}$ for a sample of CeO_2 doped with 2 mole-% CaO .

Assuming that oxygen vacancies, produced by CaO-doping and departure from nonstoichiometry, control the ionic conductivity over the entire oxygen pressure region investigated, there is no simple model to explain the apparent minimum in the ionic conductivity. It is possible, however, that the measured values of t_i obtained using CO-CO₂ gas mixtures are smaller than the actual values. If this occurred the calculated values of the ionic conductivity in the CO-CO₂ region would also be too small, and thus give the appearance of a minimum in the ionic conductivity. The transport of oxygen through the specimen is the most likely source of error in the measurement of t_i . The transport of oxygen occurs when the emf measurements are made under open circuit conditions because CaO-doped CeO₂ exhibits both ionic and electronic conduction. If the flux of oxygen through the specimen is sufficiently high, the emf of the cell, E_{meas} , will be reduced and thus a smaller value of t_i will be obtained because

$$t_i = \frac{E_{\text{meas}}}{E_{\text{theor}}} \quad (12)$$

where E_{Theor} is the emf of this cell when $t_i = 1$. The experimental measuring system is being modified to minimize the effect due to oxygen transport. Transference measurements using the modified system will then be made to determine if the apparent minimum in the ionic conductivity is a real effect.

The electronic conductivity exhibited a minimum in the oxygen pressure region 1 to 10^{-4} atm. In contrast to the high oxygen pressure electrical conductivity, predominant electron conduction due to increased departures from stoichiometry was observed at lower oxygen pressures. The minimum in the electronic conductivity which occurs at high oxygen pressures has been

attributed to a p to n transition. The holes most likely arise from interaction between oxygen vacancies and the oxygen in the surrounding atmosphere as follows

This type of behavior was suggested by Bauerle¹² to explain hole conduction in Y_2O_3 doped ThO_2 . Becker and Frederiske¹³ have shown that the band gap energy, E_g , of a semiconductor can be determined from electronic conductivity data which exhibits a p to n transition. E_g can be calculated from the slope of plot of $\log \sigma_{e_{\min}}$ vs $1/T$ according to the expression

$$d \log(\sigma_{e_{\min}}) / d(1/T) = - \frac{E_g}{4.606k} \quad (14)$$

where $\sigma_{e_{\min}}$ is the minimum value of σ_e . The slopes of $\log \sigma_{e_{\min}}$ vs $1/T$ plots yielded band gap energies of 2.5 and 1.3 eV for the 2 and 5 mole % CaO doped specimens, respectively. The apparent decrease in band gap energy might be considered a decrease in an effective band gap because of the increased hole concentration with increased CaO content. It should be noted that the band gap energy determined by the above technique might be in error if there is an error in the measurement of t_i .

The primary concern now is to determine whether the minimum in σ_i is a real effect or does it arise because of experimental problems associated with the measurement of t_i . After this problem is resolved, additional data will be obtained for some of the other CaO compositions used in the electrical conductivity study.⁴

An attempt will then be made to quantitatively analyze the combined data from the electrical conductivity and ionic transference study. This analysis will be employed to 1) provide information on the compositional

dependence (i.e. both CaO and oxygen content) on the mobility and diffusion coefficient of oxygen vacancies, 2) characterize the electronic conductivity of CaO-doped CeO_2 by modifying the proposed oxygen vacancy nonstoichiometric defect model for "pure" CeO_{2-x} .

As described in the last progress report⁸ several improvements were incorporated in the thermogravimetric measuring system. These modifications have significantly improved the precision and the accuracy of the weight measuring technique. Some preliminary thermodynamic data was obtained near stoichiometry employing this improved measuring technique. The departure from stoichiometry may be represented by either of the symbols y or x which are defined by the formulas $\text{Ce}_{1+y}\text{O}_2$ and CeO_{2-x} , respectively. If a cerium interstitial model is assumed the formula $\text{Ce}_{1+y}\text{O}_2$ is generally used to represent the nonstoichiometric behavior, whereas for an oxygen vacancy model the nonstoichiometric behavior is represented by formula CeO_{2-x} . The quantities y and x are simply related to one another by the following expressions

$$y = \frac{x}{2-x}; \quad x = \frac{2y}{1+y} \quad (15)$$

In the previous reports^{6,8,10} the departure from stoichiometric was represented by y since a cerium interstitial model was assumed. According to the last progress report,⁸ y was proportional to $P_{\text{O}_2}^{-1/5}$ in the region near stoichiometry. This behavior was consistent with the previously proposed defect model³ where the predominant defects were assumed to be quadruply ionized cerium interstitials. Near stoichiometry this model may be represented by the expression

$$K = y^5 P_{\text{O}_2} \quad (16)$$

where K is the mass action constant for the defect reaction

The thermodynamic quantity, $\Delta\bar{H}_{\text{O}_2}$, was calculated from the preliminary thermodynamic data obtained near stoichiometry. In the temperature range $800^\circ - 1000^\circ\text{C}$ and from $-3.5 \leq \log \gamma \leq -3.0$, an approximate value of $\Delta\bar{H}_{\text{O}_2} \approx -9.6 \text{ eV}$ was obtained. A constant value of $\Delta\bar{H}_{\text{O}_2}$ (i.e. independent of composition) is consistent with the assumption implied by the mass action approach.

At larger departures from stoichiometry, $0.005 < \gamma < 0.05$, $\gamma \propto P_{\text{O}_2}^{-1/n}$ where $1 < n < 5$. On the basis of the previous analysis³ of the electrical conductivity data this behavior was rationalized on the basis of a defect model involving cerium interstitials with multiple states of ionization. The problems associated with analyzing the thermodynamic data with a defect model involving multiple states of ionization were discussed in detail in the previous progress reports.^{8,10}

In the current study additional thermodynamic data was obtained using the improved thermogravimetric technique⁸ over a wide range of temperature, $700^\circ - 1500^\circ\text{C}$, and oxygen pressures, 10^{-1} to 10^{-20} atm. This data is shown in Fig. 4 as an isothermal plot of $\log x$ versus $\log P_{\text{O}_2}$. The results of this study are described in a paper recently submitted for publication and in progress report C00-1441-18. The results and significance of this study relative to the previous and currently proposed defect structure analysis is discussed briefly below.

The thermodynamic quantities, $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$, were calculated from this data in the composition region $0.0003 \leq x \leq 0.3$, and found to be independent of temperature. To illustrate the dependence of $\Delta\bar{H}_{\text{O}_2}$ on composition a plot

Fig. 4 Isothermal plot of $\log x$ vs $\log P_{O_2}$ for "pure" CeO_{2-x} from 700° - 1500°C.

of $\Delta\bar{H}_{O_2}$ vs $\log x$ is shown in Fig. 5. $\log x$ is used since x varies over three orders of magnitude. For the purpose of convenience the thermodynamic data will be described in terms of three composition regions.

In region I, $x < 10^{-3}$, the thermogravimetric data is influenced by impurities.^{3,14} In region II, $10^{-3} < x < 10^{-2}$, $x \propto P_{O_2}^{-1/5}$ as shown in Fig. 4. In the earlier analysis,⁸ this behavior was rationalized in terms of a nonstoichiometric defect model involving a predominance of quadruply ionized cerium interstitials and localized electrons. The variation of $\Delta\bar{H}_{O_2}$ with x shown in Fig. 5 in this composition region invalidates the above analysis because the law of mass action was used. As discussed above, recent studies (e.g. diffusion coefficient of O_{18} in nonstoichiometric CeO_2 and yttria doped CeO_2 ,^{9a} x-ray and neutron diffraction of CeO_{2-x} and electrical conductivity of CaO-doped CeO_2 ⁴) confirm the presence of oxygen vacancies in nonstoichiometric cerium dioxide.

In the current thermodynamic study¹⁴ the defect structure of CeO_{2-x} was rationalized from the dependence of $\Delta\bar{S}_{O_2}$ on $\log x$ illustrated in Fig. 6. In region II, $10^{-3} < x < 10^{-2}$, the variation of $\Delta\bar{S}_{O_2}$ with $\log x$ is consistent with the following defect reaction

As shown in Fig. 5, $\Delta\bar{H}_{O_2}$ for this reaction increases from -9.8 eV at $x = 10^{-3}$ to -9.5 eV at $x = 10^{-2}$. This means the enthalpy of formation represented by Eq. (17) changes by approximately 0.3 eV over this composition region. It should be noted that the previous defect analysis of the thermodynamic data⁸ and the conductivity data³ in this composition region was based on the following isothermal dependence of x and σ on P_{O_2}

Fig. 5 $\Delta\bar{H}_{O_2}$ vs $\log x$ for CeO_{2-x} .

Fig. 6 $\Delta\bar{S}_{0_2}$ vs $\log x$ for CeO_{2-x} .

$$x \propto P_{O_2}^{-1/5} \quad (18)$$

and

$$\sigma \propto P_{O_2}^{-1/5} \quad (19)$$

These analyses were based on the law of mass action where the proportional constants for Eqs. (18) and (19) were assumed to be temperature dependent only (i.e. independent of x). Based on the law of mass action, the defect reaction given by Eq. (17) should exhibit the following dependence of x on P_{O_2}

$$x = K_I P_{O_2}^{-1/6} \quad (20)$$

where

$$K_I \propto e^{-\Delta \bar{H}_{O_2}/6kT} \quad (21)$$

The isothermal experimental observation

$$x \propto P_{O_2}^{-1/5} \quad (18)$$

was shown to be consistent with Eq. (20) when the compositional dependence of K_I was taken into account (i.e. when the variation of $\Delta \bar{H}_{O_2}$ with x from Fig. 4 was used in Eq. (21)).

As discussed above in the section on electrical conductivity the combined analysis of the conductivity and thermodynamic analysis⁵ at 1000°C shows that the electron carrier concentration, $Ce_{Ce}^{\cdot}$, is proportional to x . This relation implies that the same nonstoichiometric atomic defect exists predominantly in one state of ionization over the entire region of nonstoichiometry (i.e. $-3.0 < \log x < -0.7$). According to the

above analysis of the thermodynamic data the defect reaction given in Eq. (17) is responsible for the nonstoichiometric behavior of CeO_{2-x} in region III, $x < 10^{-2}$. Thus it appears that doubly ionized oxygen vacancy defect model, Eq. (17), is the appropriate nonstoichiometric defect reaction over the entire region of nonstoichiometry investigated (i.e. $-3 < \log x < 0.7$).

The nonlinear variation of $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ exhibited in the composition region III (i.e. $-2 < \log x < 0.7$) is probably due to defect interactions. An attempt will be made to analyze the thermodynamic data in this region using the defect reaction represented by Eq. (17) in conjunction with a statistical thermodynamic model which considers defect interactions. This model will also attempt to take into consideration the observed variation in the lattice parameter with composition at high temperatures.^{9b} It is interesting to note for example that in the composition region, $x > 10^{-1}$, $\Delta\bar{H}_{\text{O}_2}$, $\Delta\bar{S}_{\text{O}_2}$ and the lattice parameter^{9b} are very dependent on x .

In the current thermodynamic study a thermogravimetric investigation of the nonstoichiometric behavior of CaO-doped CeO_2 was initiated. The preliminary data from the thermogravimetric measurements at 800°, 1000° and 1200°C for a 7 mole % CaO-doped CeO_2 sample are shown in Fig. 7, where $\log \Delta W/W$ is plotted versus $\log P_{\text{O}_2}$. The isothermal lines for "pure" CeO_2 are shown for the sake of comparison. The departure from stoichiometry x is proportional to $\Delta W/W$ and may be easily calculated from this data.¹⁴ The addition of calcia to CeO_2 tends to change the observed P_{O_2} dependence of the thermogravimetric data from $P_{\text{O}_2}^{-1/5}$ to $P_{\text{O}_2}^{-1/4}$ over a significant oxygen pressure region at 800° and 1000°C, and to lesser extent at 1200°C. As discussed in Progress Report C00-1441-16, this behavior is consistent with a defect model in which calcium ions substitute

Fig. 7 Isothermal plot of $\log \Delta W/W$ vs $\log P_{O_2}$ for CeO_2 doped with 7 mole % CaO from 800° - 1200°C.

for cerium ions and produce charge compensating oxygen vacancies. If the concentration of oxygen vacancies produced by CaO-doping is larger than those produced by nonstoichiometric behavior, then the overall oxygen vacancy concentration is essentially fixed by the dopant concentration. Using a mass action approach it can be shown that under isothermal conditions x should exhibit a $P_{O_2}^{-1/4}$ dependence.⁴ The mass action approach, however, would require that $\Delta\bar{H}_{O_2}$ be independent of x for a given CaO. Unfortunately an accurate determination of $\Delta\bar{H}_{O_2}$ was not possible because data on the isothermal dependence of x on P_{O_2} was available for only three temperatures. Future studies will be concerned with measuring the isothermal dependence of x on P_{O_2} on CaO-doped CeO_2 samples. The dependence of x and CaO content on $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ will also be determined from this data.

RELATED RESEARCH STUDIES

The materials science research program on metal oxides at Marquette University is a broadly based program which includes the following areas of research:

1. Preparation of ceramic and single crystals of metal oxides.
2. Defect structure studies.
3. Electronic and atomic transport studies.
4. Dielectric behavior.
5. Mechanical behavior.
6. Optical behavior.

Several faculty members in the College of Engineering are involved in this program.

The work sponsored by the Atomic Energy Commission under Contract AT(11-1)-1441 with Marquette University is concerned primarily with determining the defect structure and transport properties of defects in "pure" and doped nonstoichiometric cerium dioxide. These studies are complemented by other research studies in the metal oxide program at Marquette University. Three of these studies which are directly related to the AEC sponsored work will be discussed briefly below.

1. A vapor transport technique has been developed in this laboratory for growing single crystals of CeO_2 .¹⁵ This research was originally sponsored by the Advanced Research Projects Agency, however, it is now supported by Marquette University. The availability of single crystals of CeO_2 is particularly important for measurements on the transport properties of defects in CeO_2 .

2. A high temperature x-ray technique is being used to determine the lattice parameter of nonstoichiometric CeO_{2-x} as a function of x at 800° , 900° and 1000°C . A high temperature gas pycnometer is also being used to measure the volume of a single crystal of CeO_{2-x} as a function of x at 800° , 900° and 1000°C . A combined analysis of these data will be employed to provide direct confirmation of the nature of the nonstoichiometric defects in CeO_{2-x} at elevated temperatures.⁹⁶

3. High temperature x-ray and neutron diffraction studies on CeO_{2-x} are being employed to determine the isothermal dependence of the intensity of the diffraction peak on nonstoichiometry. An analysis of these data should provide information about the nature and the location of nonstoichiometric defects in CeO_{2-x} . Preliminary results from this study confirm the presence of oxygen vacancies in CeO_{2-x} .

All of the above studies are being conducted in the Materials Science Laboratory facilities at Marquette University with the exception of the neutron diffraction study. The neutron diffraction study on CeO_{2-x} is being conducted at Argonne National Laboratory by Mr. John Faber, a Ph.D. candidate in the materials science program, and Dr. M. H. Mueller of Argonne National Laboratory. Mr. Faber's major research advisor is Prof. Martin Seitz of the Electrical Engineering Department. Dr. Mueller is also acting as a co-advisor to Mr. Faber.

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