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A STUDY OF THE DEFECT STRUCTURE OF
"PURE" AND DOPED NONSTOICHIOMETRIC CeO_2

Progress Report

Robert N. Blumenthal

College of Engineering
Marquette University
Milwaukee, Wisconsin

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ABSTRACT

The temperature and compositional dependence of the electrical conductivity of CeO_{2-x} (i.e. $\sigma = \sigma(T, x)$), was determined by combining conductivity ($\sigma = \sigma(P_{\text{O}_2}, T)$) and thermodynamic ($x = x(P_{\text{O}_2}, T)$) data. In the temperature range 750° to 1500°C , $\sigma = 415 \times e^{-Q/kT}$ where Q is a function of x . This expression was rationalized in terms of the following simple relations for the electron concentration $n_{\text{Ce}} = \frac{8x}{3}$ and the electron mobility $\mu = 5.3 \times 10^{-2} e^{-Q/kT}$ where μ_0 is independent of x , Q is independent of x from $10^{-3} < x < 10^{-2}$, and Q increases with x from $10^{-2} < x < 0.2$.

Conductivity measurements on SrO-doped CeO_2 , between .1 and 7 mole % SrO, show that the isothermal dependence of σ on P_{O_2} is similar to previously reported behavior of CaO-doped CeO_2 . The mobility of oxygen vacancies appears to be larger for SrO-doped CeO_2 .

An electrochemical cell technique was used to measure the ionic transference number, t_i , of CeO_{2-x} as a function of temperature ($590^\circ - 1000^\circ\text{C}$) and oxygen partial p to 10^{-22} atm. The ionic transference number is controlled by impurities in the high oxygen pressure region. At low oxygen pressures t_i is small. The electrical conduction in this region is controlled by the nonstoichiometric defects and is predominantly electronic. Using the value of $t_i \approx 0.05$ an estimate of the diffusion coefficient for doubly ionized oxygen vacancies, $D_{\text{V}_\text{O}} \approx 3.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 1000°C was calculated by combining recently obtained thermodynamic and conductivity data with the Nernst-Einstein relation.

Thermogravimetric measurements were performed on CaO-doped CeO_{2-x} (i.e. $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$). $x = x(T, P_{\text{O}_2})$ was determined for values of $y = 0.01, 0.07$ and 0.14 . The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated

from this data. Near stoichiometry the variation of $\Delta\bar{S}_{O_2}$ with x is consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites. $\Delta\bar{H}_{O_2}$ is essentially a constant in this region, but increases with increasing CaO content.

INTRODUCTION

Although there has been a great deal of interest in "pure" nonstoichiometric oxides and in doping essentially stoichiometric oxides, there have been very few studies of the combined effect of doping and nonstoichiometry on their thermodynamic and electrical behavior.

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. In this investigation the thermodynamic and electrical properties of "pure" and doped nonstoichiometric oxides will be measured as a function of oxygen nonstoichiometry, dopant concentration and temperature. 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.¹⁻⁷ The following is a brief summary of some of the results of previous studies in this laboratory on the electrical and thermodynamic behavior of "pure" and CaO-doped nonstoichiometric cerium dioxide.

In a recent study⁵ the electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} was measured as a function of temperature from 1000° - 300°C and composition from $0.00424 \leq x \leq 0.178$. These results were described in terms of a high temperature and low temperature region. In both temperature regions the conductivity for fixed values of x exhibits an exponential dependence on temperature $\sigma = \sigma_0 e^{-Q/kT}$. 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 $[\text{Ce}'_{\text{Ce}}] \propto x$ 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 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. $-3.0 < \log x < -0.7$). It should be noted that although the above analysis circumvents the problem of consideration of the type of the nonstoichiometric defect and its distribution in the fluorite lattice, it does provide a very important characteristic of the nonstoichiometric defect (i.e. $[\text{Ce}'_{\text{Ce}}] \propto x$) which

must be taken into account in any detailed analysis of the defect structure of CeO_{2-x} .

In a recent thermodynamic study,⁶ thermogravimetric measurements were performed on nonstoichiometric CeO_{2-x} in the temperature range 700° to 1500°C and from oxygen pressures of 10^{-1} to 10^{-26} atm. From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2})$ was determined. The thermodynamic quantities $\Delta \bar{H}_{\text{O}_2}$ and $\Delta \bar{S}_{\text{O}_2}$ were calculated in the region $0.001 < x < 0.01$, the variation of $\Delta \bar{S}_{\text{O}_2}$ with x was consistent with a defect model involving randomly distributed $\text{V}_{\text{O}}^{\bullet\bullet}$ and Ce_{Ce}' . $\Delta \bar{H}_{\text{O}_2}$ in this region was observed to exhibit a slight dependence on x . It was postulated that the variation in $\Delta \bar{H}_{\text{O}_2}$ results from an increase in the lattice parameter with x .

In the composition region $0.01 < x < 0.1$, $x \propto P_{\text{O}_2}^{-1/m}$ with $1 < m < 5$ and in the region $0.1 < x < 0.3$, $x \propto P_{\text{O}_2}^{-1/n}$ with n increasing rapidly with x to $n = 30$. Although this behavior was assumed to be a manifestation of increasing defect interaction with increasing departure from stoichiometry it is proposed that the nonstoichiometric defects $\text{V}_{\text{O}}^{\bullet\bullet}$ and Ce_{Ce}' predominate over the entire region of nonstoichiometry.

Although there have been several defect structure analyses based on the thermodynamic and/or electrical properties of "pure" nonstoichiometric oxides and mixed stoichiometric oxides there have been very few of these type of analyses on mixed nonstoichiometric oxide systems. In order to help provide a better understanding of defect behavior and transport properties in mixed nonstoichiometric oxide systems we have initiated a comprehensive study in our laboratory to determine the effect of ionic radii, valence and concentration of the foreign cations on the thermodynamic and electrical behavior of doped-nonstoichiometric CeO_{2-x} . Cerium dioxide was selected as the host oxide in these experiments because CeO_{2-x}

exhibits a large nonstoichiometric region, an extensive solubility for foreign cations and extensive studies have been performed on the electrical and thermodynamic behavior of "pure" CeO_{2-x} .¹⁻⁷

The doping experiments on CeO_{2-x} were initiated using CaO because the calcium ion has an ionic radii similar to cerium and the addition of CaO to CeO_2 results in the formation of oxygen vacancies.⁷ Thus the concentration of CaO in solution in nonstoichiometric cerium dioxide may be represented by the formula $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$. In a recent study^{4,7} in this laboratory the electrical conductivity (0.1 to 15 mole %) CaO doped cerium dioxide specimens has been measured as a function of P_{O_2} (i.e., 1 to 10^{-22} atm) and temperature (i.e., 700° to 1500°C). The isothermal electrical conductivity in the lower temperature and higher oxygen partial pressures (i.e., near stoichiometric state) is independent of P_{O_2} . The conductivity in this region is predominantly ionic (i.e., $\sigma_i > \sigma_e$ where σ_i and σ_e are the ionic and electronic conductivities, respectively) and is directly proportional to the CaO content up to about 8 mole % CaO. At lower oxygen partial pressures and higher temperatures (i.e., larger deviations from stoichiometry) the dependence of σ on P_{O_2} is similar to "pure" CeO_2 (i.e., $\sigma_e > \sigma_i$). Unfortunately the effect of oxygen vacancies produced by CaO doping on the nonstoichiometric produced oxygen vacancies could not be ascertained quantitatively because of the problems associated with determining (a) the relative contribution of σ_i and σ_e from the total conductivity, σ_T , and (b) the effect of CaO doping and oxygen nonstoichiometry on the mobility of oxygen vacancies and electrons.

In the current investigation, the thermodynamic and electrical property study initiated on nonstoichiometric CeO_{2-x} was continued. Additional electrical conductivity data was obtained at lower temperatures

and low oxygen pressures (i.e. large departures from stoichiometry) in the temperature range $700^{\circ} - 1500^{\circ}\text{C}$. This data was combined with the previously obtained conductivity and thermodynamic data to obtain a more quantitative analysis of the proposed nonstoichiometric defect model and a better understanding of the effect of nonstoichiometry on the mobility of electrons in CeO_{2-x} .

In addition, electrical conductivity, ionic transference, and thermodynamic measurements initiated on CaO-doped CeO_2 as a function of temperature, oxygen pressure and CaO content were continued. Similar measurements were also initiated on CeO_2 doped with other oxides (e.g. SrO , ThO_2 , etc.) which have cations with different valences and ionic radii. The results of these studies will be used to determine the effect of ionic radii, valence and concentration of the dopant cation on (1) the nonstoichiometric defect structure, (2) the thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$, and (3) the mobility of electron and oxygen vacancies in doped CeO_{2-x} .

RESULTS AND DISCUSSION

A. Electrical Property Studies on "Pure" and Doped-CeO_{2-x}

The results of the study on the temperature dependence of the electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} with fixed composition (i.e. constant value of x) were described briefly in the last progress report⁸ and in greater detail in a paper accepted for publication.^{5,9} In the temperature range 700° - 1000°C the conductivity for fixed values of x exhibits an exponential dependence on temperature $\sigma = \sigma_0 e^{-Q/kT}$. A nonequilibrium technique was employed to maintain a fixed value of x while the conductivity was measured as a function of temperature. The isothermal dependence of the conductivity on x was determined at 1000°C by combining two sets of equilibrium type data, $\sigma = \sigma(P_{O_2}, t=1000^\circ\text{C})$ and $x = x(P_{O_2}, t=1000^\circ\text{C})$. The compositional and temperature dependence of the conductivity was represented by the expression $\sigma \propto x e^{-Q/kT}$ where Q is a function of x . This expression was rationalized in terms of 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 . For $\log x$ between -3.0 and -1.8, $Q = 0.22$ eV appears to be a constant but, for $\log x > -1.8$ Q increases monotonically to 0.37 eV at $\log x = -0.7$.

In the above study the compositional dependence of σ was limited to 1000°C because this was the only temperature where both $\sigma = \sigma(P_{O_2}, T)$ and $x = x(P_{O_2}, T)$ were available over a large region of nonstoichiometry. Because of the limited amount of this type of data, no attempt was made to quantitatively determine the expression $\sigma = A x e^{-Q/kT}$. In addition, the expression for the electron mobility, $\mu = \mu_0 e^{-Q/kT}$ could not be

determined quantitatively because no defect model had been proposed which would allow one to determine the exact relation between $[Ce'_{Ce}]$ and x .

In a recent study in our laboratory the nonstoichiometric behavior of CeO_{2-x} (i.e. $x = x(T, P_{O_2})$) was determined in the temperature region $700^\circ - 1500^\circ C$ and composition region $0.001 < x < 0.178$. As discussed in AEC Report C00-1441-18 and a paper recently submitted for publication, the predominate nonstoichiometric defects were shown to be doubly ionized oxygen vacancies, $V_O^{\bullet\bullet}$, and electrons localized on normal cerium sites, Ce'_{Ce} .

In order to obtain a combined analysis of the equilibrium $\sigma = \sigma(P_{O_2}, T)$ and $x = x(P_{O_2}, T)$ data over a wider range of temperature ($700^\circ - 1500^\circ C$) and composition ($10^{-3} < x < .2$), the electrical conductivity of CeO_{2-x} in the current study was measured in the same T and P_{O_2} region as the above thermodynamic study.

The results of this investigation are described in AEC Report C00-1441-22 and may be summarized as follows.

1. The compositional and temperature dependence of the electrical conductivity may be represented by the expression

$$\sigma = 415 \times e^{-Q/kT}$$

where Q is a function of x .

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

$$n_{Ce'_{Ce}} = \frac{8x}{a_o^3} \quad (2)$$

where $n_{Ce'_{Ce}}$ is the number of Ce'_{Ce} per cm^3 and a_o is the lattice parameter and (b) the electron mobility

$$\mu = 5.3 \times 10^{-2} e^{-Q/kT} \quad (3)$$

where $Q = 0.15 \pm .02$ eV between $x = 0.001$ and $x = 0.01$ and increases with x for $0.01 < x < 0.2$.

As described in the previous progress reports most of the experimental difficulties with the AC Hall mobility technique have been associated with noise problems.^{10,11} Because of these problems no Hall mobility measurements on CeO_{2-x} have been attempted during the current investigation.

As discussed in earlier progress reports^{8,10} a combined study of the electrical conductivity σ and the ionic transference number, 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 CaO-doped CeO_2 . The results of a recent study of the electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 16.0 mole %) as a function of temperature 700° - 1500°C and from 1 to 10^{-22} atm of oxygen were described in AEC Report C00-1441-16 and in a recent publication.⁷ These results may be summarized as follows.

The electrical conductivity of sintered specimens of CaO-doped CeO_2 (0.1 - 16.0 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. Two limiting case regions were observed. At low temperatures and high oxygen pressures, the conductivity is predominantly ionic. In this region the conductivity is independent of P_{O_2} and between approximately 1 and 8 mole % CaO is proportional to mole per cent CaO. The following equation for ionic conductivity

$$\sigma_i \approx 6.0 [\text{mole \% CaO}] \exp -0.62/kT \quad (4)$$

was obtained by fitting the conductivity data in this region to an expression derived on the basis of an oxygen vacancy model. An approximate expression for the diffusion coefficient for oxygen vacancies

$$D_{V_o} \approx 3.7 \times 10^{-3} \exp -0.62/kT \quad (5)$$

was calculated from the above expression and the Nernst-Einstein relation.

At high temperatures, low oxygen partial pressures and for lower CaO contents the conductivity is predominantly electronic. In this region the magnitude and P_{O_2} dependence of σ is similar to "pure" CeO_2 . A thermodynamic argument is also presented which favors oxygen vacancies as the non-stoichiometric defect in both pure and CaO-doped CeO_2 .

In the last progress report,⁸ a study was initiated to determine the effect of valence and ionic radii of the dopant cation on the behavior of the electrical conductivity. As discussed above a comprehensive study has been made on the electrical conductivity of CaO-doped CeO_2 . CaO was selected as a dopant because the ionic radius of the calcium ion (1.01Å) is very similar to the cerium ion. The dependence of the lattice parameter on CaO content has been reported to be 0.0004Å/mole % CaO.¹² Thus the lattice parameter increased only slightly with the addition of CaO. As described in the previous report⁸ a study was initiated on SrO-doped CeO_2 to determine the effect of a large cation ($Sr^{+2} = 1.14\text{\AA}$) with the same valence as Ca^{+2} on the electrical behavior. In the current study conductivity measurements were made on SrO-doped CeO_2 (0.1, 1, 3 and 7 mole per cent) as a function of temperature (700° - 1500°C) and oxygen partial pressure ($1 - 10^{-22}$ atm).

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 for the same mole % dopant was larger for the 0.1, 1 and 3 mole % SrO doped specimens. At high oxygen pressure ($1 - 10^{-4}$ atm) and lower temperatures σ is independent of P_{O_2} . In this region σ is assumed to be predominantly ionic (i.e. $\sigma \approx \sigma_i$). For the same mole % dopant of SrO and CaO, the oxygen vacancy concentration in this region is the same. Thus the increased ionic conductivity may be explained by assuming that the mobility of oxygen vacancies is larger in the SrO-doped specimen.

As reported in a recent publication⁷ for CaO-doped CeO_2 between 1 and 8 mole %

$$\sigma_i = 6.0 [\text{mole \% CaO}] \exp -0.62/kT \quad (4)$$

A similar expression could not be obtained for the SrO- CeO_2 system because as shown in Fig. 1 insufficient data is available to determine if there is a region of composition where σ exhibits a linear dependence on mole % SrO. It is interesting to note, however, that the average value of $Q \approx 0.56 \pm .03$ eV obtained from the expression

$$\sigma = \sigma_o e^{-Q/kT} \quad (6)$$

for the 1, 3 and 7 mole % SrO specimens at $P_{O_2} = 1$ atm is smaller than the corresponding value $0.62 \pm .02$ eV obtained for the CaO doped specimens. Although this study is not completed it appears from the above data that the mobility of oxygen vacancies in SrO-doped CeO_2 is higher than in CaO-doped CeO_2 probably because the energy of motion is less. This decrease in transport energy for the vacancies appears to be related to the increase in lattice parameter as a result of the larger ionic radii of the Sr^{+2} ion as compared to Ca^{+2} ion.

Fig. 1 Isothermal plot of σ vs mole per cent SrO in CeO₂ at 1 atm O₂.

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 study on SrO-doped CeO_2 will be continued. To determine the dependence of σ_i and Q on SrO, additional samples with SrO content between 1 and 9 mole % will be used. The 9 mole % limit is imposed by the reported solubility of SrO in CeO_2 .¹²

A recent study in this laboratory has also been initiated on the electrical conductivity of ThO_2 -doped CeO_2 as a function of P_{O_2} and temperature. In this study ThO_2 was selected as a dopant because (a) the ionic radius of Th^{+4} is larger than Ce^{+4} . (b) ThO_2 has the same fluorite crystal structure as CeO_2 (a recent x-ray study¹³ has shown that ThO_2 and CeO_2 are completely soluble in one another). (c) The thorium ion has the same valence as cerium.

Preliminary results of the temperature dependence of the conductivity in oxygen indicate that the conductivity decreases with increasing ThO_2 content. This result is consistent with the postulate that the electronic conductivity should decrease with increasing lattice parameter. The specimens used in the preliminary study were obtained by solid state.

sintering at 1900°C. The resultant densities were quite low about 50% of theoretical. The conductivity studies on ThO_2 -doped CeO_2 will be continued to determine the dependence of T , P_{O_2} and ThO_2 content on σ . The ThO_2 -doped specimens will be prepared using a different technique. They will be made by sintering a powder of ThO_2 and CeO_2 obtained by a chemical precipitation technique which will result in a more homogeneous solution of ThO_2 in CeO_2 and more dense specimens.¹³

B. Thermodynamic Studies on "pure" and CaO -doped CeO_{2-x}

As discussed in previous progress reports,^{8,14} one of the objectives of a combined study of the electrical conductivity and the ionic transference number on "pure" and CaO -doped CeO_2 was to obtain information on the mobility and the diffusion coefficient of oxygen vacancies in CeO_2 .

In the current investigation an electrochemical cell of the type

was used to measure the ionic transference number, t_i , of sintered specimens of nonstoichiometric CeO_{2-x} as a function of temperature 600° - 1000°C and oxygen partial pressure 1 to 10^{-22} atm. The results of this study are described in a paper recently submitted for publication and in AEC Progress Report C00-1441-20. The results were described in terms of a high and low oxygen pressure region. The ionic transference number was controlled by impurities in the high oxygen pressure region. In this region the electronic conductivity was p-type at lower temperatures and n-type at higher temperatures. In the low oxygen pressure region the ionic transference number is small (e.g. above 700°C, $t_i < 0.08$). The electrical conduction in this region was controlled by the nonstoichiometric defects and is predominantly electronic. Using the value of

$t_i \sim 0.05$ and estimate of the diffusion coefficient for doubly ionized oxygen vacancies, $D_{V_o} \approx 3.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 1000°C was calculated by combining recently obtained thermodynamic⁶ and conductivity data¹⁵ with the Nernst-Einstein relation. This value of D_{V_o} appears to be independent of x in the region $10^{-3} < x < 10^{-2}$. No attempt was made to determine the temperature dependence of D_{V_o} because of the uncertainty in t_i with temperature.

It is interesting to compare the above value of D_{V_o} for "pure" CeO_{2-x} with $D_{V_o} \approx 1.1 \times 10^{-5} \text{ cm}^2/\text{sec}$ calculated at 1000°C from the expression for D_{V_o} obtained from a recent electrical conductivity study on CaO-doped CeO_2 .¹⁷ Within experimental error the two calculated values of D_{V_o} are in relatively good agreement. Since the above expression for D_{V_o} was obtained for CaO contents between 1 and 8 mole %, it appears that the presence of CaO at least up to 8 mole % does not have any significant effect on the magnitude of D_{V_o} .

In the previous progress report⁸ the preliminary results of the transference measurements on CaO-doped CeO_2 were briefly described. The ionic transference number was combined with the total electrical conductivity to obtain the P_{O_2} dependence of both the ionic, σ_i , and electronic, σ_e , conductivities.

In the high oxygen pressure region ($1 - 10^{-4} \text{ atm}$) σ_i was independent of P_{O_2} . This behavior was 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 pressure, obtained with CO-CO_2 mixtures, the ionic conductivity increases with decreasing oxygen pressure. This increase was explained by assuming that σ_i in this P_{O_2} region was controlled by the nonstoichiometric

defects (i.e. oxygen vacancies). No data was obtained between the high and low oxygen regions because no gas mixtures were available that could control the P_{O_2} in this region. Since σ_i decreases between the high and the low oxygen pressure regions it appears that σ_i exhibits a minimum in the oxygen pressure region where no data can be obtained.

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 because of polarization 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. Polarization at the electrodes resulting from oxygen transport is the most likely source of error in the measurement of t_i . To minimize polarization effects the flux of oxygen ions, J_i , through the specimen should be kept as low as possible. According to Heyne,¹⁶ J_i in a mixed conductor is given by the following expression

$$J_i = -\left(\frac{RT}{4e}\right) \sigma_T t_i \text{ grad } \ln P_{O_2} \quad (7)$$

Thus it is apparent from Eq. (7) that the best way to reduce J_i is to use as small a difference in P_{O_2} at the two electrodes as possible. In the previous study t_i was determined from the expressions

$$t_i = \frac{E_{\text{meas}}}{E_{\text{theo}}} \quad (8)$$

where

$$E_{\text{theo}} = \frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2}'} \quad (9)$$

t_i obtained from Eq. (8) is an average value corresponding to an average value of P_{O_2} and P_{O_2}' used at each electrode.

Premixed and analyzed Ar- O_2 and CO-CO₂ gas mixtures were used at each electrode to control P_{O_2} and P_{O_2}' . In general these tank mixtures were selected so that the difference between P_{O_2} and P_{O_2}' was about one order of magnitude. Since tank mixtures were used only a finite number of P_{O_2} values could be achieved at each electrode.

In the current study the experimental measuring system was modified so that a continuous variation in the partial pressure of oxygen at each electrode could be achieved. With the modified system the following procedure was used to determine t_i . Depending on the value of P_{O_2} desired, a tank mixture of either Ar- O_2 or CO-CO₂ was used to fix the value of P_{O_2} at electrode I. The P_{O_2}' at electrode II was controlled by mixing gas from another tank with the same gas mixture as used at electrode I. The oxygen partial pressure at each electrode was then measured using an oxygen gauge.¹⁷ A typical plot of data obtained using the above technique is shown in Fig. 2 where the emf is plotted versus $\log P_{O_2}$. Note that since the value of P_{O_2} at electrode I is fixed and the P_{O_2}' at electrode II can be varied continuously (i.e. $P_{O_2}' > \text{or} < P_{O_2}$) the sign of the emf, E , may be negative or positive. With this technique t_i was calculated from the slope of the line shown in Fig. 2 and the expression

Fig. 2 Isothermal plot of emf vs $\log P_{O_2}$ for an oxygen concentration cell of the
 type $P_{O_2}, Pt_1 | Ce_{1-y}Ca_yO_{2-y-x} | Pt_1, P_{O_2}$ where $y = 0.08$.

$$\left(\frac{dE}{d \ln P_{O_2}} \right)_{\text{at } P_{O_2} = P_{O_2}^{II}} = \frac{kT}{4e} (t_i)_{\text{at } P_{O_2} = P_{O_2}^{II}} \quad (10)$$

The advantages of this technique are: (1) the value of t_i may be determined uniquely for each value of P_{O_2} , (2) polarization effects can be minimized since only small differences in P_{O_2} are used at each electrode. The disadvantage of this technique is that many measurements must be made in order to obtain one value of t_i corresponding to a given value of T, P_{O_2} and CaO content. Preliminary data using this new technique on a CeO_2 specimen doped with 8 mole % CaO indicates that some of the previously reported transference data on CaO-doped CeO_2 are probably in error because of polarization at the electrodes. Because of the limited amount of new transference data available at this time, it cannot be determined whether the apparent minimum in the ionic conductivity is a real effect or not.

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.^{4,7}

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 non-stoichiometric defect model for "pure" CeO_{2-x} .^{4,6,15}

In a recent thermodynamic study on "pure" CeO_{2-x} a thermogravimetric technique was used to determine x as a function of temperature ($700^\circ - 1500^\circ\text{C}$ and P_{O_2} ($1 - 10^{-22}$ atm). The results of this study are described in a paper submitted for publication and in Progress Report C00-1441-18. These results may be summarized as follows.

The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.3$ and found to be independent of temperature. In the region $0.001 < x < 0.01$ the variation of $\Delta\bar{S}_{\text{O}_2}$ with x is consistent with a defect model involving randomly distributed doubly ionized oxygen vacancies and electrons localized on normal cerium sites. The experimental $P_{\text{O}_2}^{-1/5}$ dependence of x was rationalized on the basis of the above model and the observation that $\Delta\bar{H}_{\text{O}_2}$ (≈ 9.8 eV) exhibits a slight dependence on x . It was postulated that the variation in $\Delta\bar{H}_{\text{O}_2}$ results from an increase in the lattice parameter with x .

In the composition region $0.01 < x < 0.1$, $x \propto P_{\text{O}_2}^{-1/n}$ with $1 < n < 5$ and in the region $0.1 < x < 0.3$, $x \propto P_{\text{O}_2}^{-1/n}$ with n increasing rapidly with x to $n = 30$. This behavior was assumed to be a manifestation of increasing defect interaction with increasing departure from stoichiometry.

Although there have been several defect structure analyses based on the thermodynamic and/or electrical properties of "pure" nonstoichiometric oxides and mixed stoichiometric oxides there have been very few of these type of analyses on mixed stoichiometric oxide systems. In order to help provide a better understanding of defect behavior and transport properties in mixed nonstoichiometric oxide systems, we have initiated a comprehensive study in our laboratory to determine the effect of valence, ionic radius, and concentration of foreign cations on the thermodynamic and electrical behavior of nonstoichiometric CeO_2 .

In the last study period a thermogravimetric investigation of the nonstoichiometric behavior of CaO-doped CeO_2 was initiated. Preliminary data was obtained for a 7 mole % CaO-doped CeO_2 on the dependence of x on P_{O_2} at 800° , 1000° and 1200°C .⁸

In the current study the thermodynamic study on CaO-doped CeO_2 was continued. The results of this study are described in detail in a paper recently submitted for publication and in AEC Technical Report C00-1441-21. These results are summarized briefly as follows.

Thermogravimetric measurements were performed on CaO-doped nonstoichiometric cerium dioxide (i.e. $\text{Ce}_{1-y}\text{Ca}_y\text{O}_{2-y-x}$) in the temperature range $750^\circ - 1500^\circ\text{C}$ and from oxygen pressures of 10^{-1} to 10^{-22} atm. From this data the deviation from stoichiometry $x = x(T, P_{\text{O}_2}, y)$ was determined for values of $y = 0.01$, 0.07 and 0.14 . The thermodynamic quantities $\Delta\bar{H}_{\text{O}_2}$ and $\Delta\bar{S}_{\text{O}_2}$ were calculated in the region $0.001 \leq x \leq 0.2$ and found to be independent of temperature.

In the composition region near stoichiometry $\Delta\bar{H}_{\text{O}_2}$ exhibits only a slight dependence on x for the 1 and 7 mole % CaO samples (i.e. less than 0.2 eV variation between $x = 10^{-3}$ and $x = 10^{-2}$). For the 14 mole % CaO sample $\Delta\bar{H}_{\text{O}_2}$ is independent of x between $x = 10^{-3}$ and $x = 3 \times 10^{-2}$. It is interesting that for "pure" CeO_{2-x} , $\Delta\bar{H}_{\text{O}_2}$ exhibits a greater dependence on x . It is postulated that the increase in $\Delta\bar{H}_{\text{O}_2}$ with CaO content is associated with the corresponding increase in the lattice parameter. The insensitivity of $\Delta\bar{H}_{\text{O}_2}$ with x may result from the dilatation of the lattice by CaO which has the effect of masking out the dependence of the lattice parameter on x .

At large deviations from stoichiometry the dependence of $\Delta\bar{H}_{\text{O}_2}$ on x appears to be independent of CaO content up to at least 7 mole %. However, $\Delta\bar{H}_{\text{O}_2}$ for the 14 mole % CaO-doped specimen exhibits a different dependence on x .

Discussion of the dependence of $\Delta\bar{S}_{O_2}$ on x and y is directed towards two different regions of x . In the near stoichiometric region (i.e. $x < 0.01$) there is good agreement between the measured and calculated dependence of $\Delta\bar{S}_{O_2}$ on x for $y = 0.01, 0.07$ and 0.14 . The calculated values of $\Delta\bar{S}_{O_2}$ were obtained from the expression¹⁵

$$\Delta S = \frac{1}{2} S_{O_2}^O + \Delta S_T^V - R \ln [x+y] - 2 R \ln x - R \ln 2 \quad (11)$$

Thus, in this composition region, it appears that the variation of $\Delta\bar{S}_{O_2}$ with x is consistent with a random distribution of doubly ionized oxygen vacancies, $V_O^{\bullet\bullet}$, and electrons localized on cerium sites, Ce'_{Ce} .

At larger deviations from stoichiometry the dependence of $\Delta\bar{S}_{O_2}$ on x is similar for "pure" CeO_{2-x} and the 1 and 7 mole % CaO specimens. In this composition region the calculated dependence of $\Delta\bar{S}_{O_2}$ on x deviates from the measured dependence. This is the same region where $\Delta\bar{H}_{O_2}$ exhibits a significant dependence on x . This behavior is interpreted as due to an increase in the defect-defect interaction and undoubtedly the onset of defect-defect interaction.

Similar thermodynamic studies will also be initiated on CeO_2 doped with other cations (e.g. Sr^{+2} , Th^{+4} , etc.) which have different valences and ionic radii. The results of these studies will be used to determine the effect of the ionic radii, valence and concentration of the dopant cation on (1) the thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$, and (2) the nonstoichiometric defect structure. As described above the results of these studies will also be combined with the corresponding results from the electrical conductivity and transference studies to obtain information about the mobility of electrons and oxygen vacancies in doped CeO_{2-x} .

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 .¹⁸ 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 . Single crystals of CeO_2 have also been furnished to Dr. Wench of MIT for a room temperature x-ray study on the crystalline phases present in the cerium-oxygen system.

2. A high temperature x-ray and neutron diffraction study on the isothermal dependence of the intensity of the diffraction peaks on nonstoichiometry in CeO_{2-x} has recently been completed. The analysis of this data confirms the presence of oxygen vacancies as the predominate nonstoichiometric defect in CeO_{2-x} .

3. A high temperature x-ray study on CeO_{2-x} is being used to determine the isothermal dependence of the lattice parameter on x at 800° , 900° and 1000°C . A high temperature gas pycnometer is also being used to measure the volume of single crystal and polycrystalline CeO_{2-x} as a function of x . A dilatometric study has also been initiated to determine the dependence of the isothermal change in length of single and polycrystalline samples as a function of x . A combined analysis of these data (i.e. $\frac{\Delta a}{a}$, $\frac{\Delta V}{V}$ and $\frac{\Delta l}{l}$ as a function of x) will be employed to provide a direct confirmation of the defect structure in CeO_{2-x} at elevated temperatures.

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} was conducted at Argonne National Laboratory by Dr. John Faber, a recent Ph.D. graduate in the materials science program, and Dr. M. H. Mueller of Argonne National Laboratory. Since Dr. Faber recently accepted a post-doctoral position at Argonne it appears likely that a neutron diffraction study on CaO-doped CeO_{2-x} may be initiated at Argonne.

REFERENCES

1. R. N. Blumenthal, Technical Report, C00-1441-6 (1968).
2. R. N. Blumenthal and R. J. Panlener, J. Phys. Chem. Solids, 31, 1190 (1970).
3. R. N. Blumenthal, P. W. Lee and R. J. Panlener, J. Electrochem. Soc., 118, 123 (1971).
4. R. N. Blumenthal, Technical Report, C00-1441-16 (1972).
5. R. N. Blumenthal, Technical Report, C00-1441-17 (1972).
6. R. N. Blumenthal, Technical Report, C00-1441-18 (1972).
7. R. N. Blumenthal, F. S. Brugner and J. E. Garnier, J. Electrochem. Soc., 120, 1230 (1973).
8. R. N. Blumenthal, Technical Report, C00-1441-19 (1972).
9. R. N. Blumenthal and R. L. Hofmaier, to be published in the J. Electrochem. Soc.
10. R. N. Blumenthal, Technical Report, C00-1441-15 (1971).
11. R. N. Blumenthal, Technical Report, C00-1441-12 (1970).
12. H. H. Mobius, Z. Chem., 4, 81 (1964).
13. H. J. Whitfield, D. Roman and A. R. Palmer, J. Inorg. Nucl. Chem., 28, 2817 (1966).
14. R. N. Blumenthal, Technical Report, C00-1441-14 (1970).
15. R. N. Blumenthal, Technical Report, C00-1441-22 (1973).
16. L. Heyne, Mass Transport in Oxides, National Bureau of Standards Special Publication 296, p. 149.
17. R. N. Blumenthal, Technical Report, C00-1441-9 (1969).
18. W. M. Hirthe, R. N. Blumenthal and M. A. Seitz, Technical Progress Report No. 3, Advanced Research Projects Agency (1970).