JOURNAL OF SOLID STATE CHEMISTRY 13, 360–364 (1975)

Electronic Conductivity in Nonstoichiometric Cerium Dioxide*

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Received November 30, 1973; revised July 16, 1974

The electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} was measured as a function of temperature (750–1500°C) and oxygen pressure (1–10^{-22} atm). The isothermal compositional dependence of the electrical conductivity of CeO_{2-x} was determined by combining recently obtained thermodynamic data, $x = x(P_{O_2}, T)$, with the conductivity data. The compositional and temperature dependence of the electrical conductivity may be represented by the expression

$$\sigma = 410[x]e^{-(0.158+x)/kT}\ (\text{ohm cm})^{-1}$$

over the temperature range 750–1500°C and from $x = 0.001$ to $x = 0.1$.

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

$$n_{Ce'_{Ce}} = 8x/a_o^3$$

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

$$\mu = 5.2(10^{-2})e^{-(0.158+x)/kT}\ (\text{cm}^2/\text{V sec}).$$

Introduction

In a recent study (*1*) the electrical conductivity of sintered specimens of nonstoichiometric CeO_{2-x} was measured as a function of temperature from 1000 to 300°C and composition from $0.00424 \leqslant x \leqslant 0.178$. 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 $\sigma = \sigma_o e^{-Q/kT}$.

The temperature of the intersection between the high- and low-temperature regions for each composition agrees closely with the composition–temperature dependence of the miscibility gap reported by Brauer and Gingerich (*2*). The compositional and temperature dependence of the conductivity in the high-temperature region which corresponds to a single phase region was represented by the following expression $\sigma \propto xe^{-Q/kT}$ 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 $\mu = \mu_o e^{-Q/kT}$, where μ_o is independent of x. For log x between −3.0 and −1.8, Q is constant at 0.22 eV, but increases to 0.37 eV at log $x = -0.7$. In the low temperature region the activation energy, 0.61 ± 0.03 eV was found to be independent of x.

In the above study a nonequilibrium technique was employed to maintain a fixed value of x while the conductivity was measured as a function of temperature (i.e., $T \leqslant 1000$°C). The isothermal dependence of the conductivity on x was determined at 1000°C by combining two sets of equilibrium type data, $\sigma = \sigma(P_{O_2}, T = 1000°C)$ and $x = x(P_{O_2}, T = 1000°C)$ The compositional dependence was limited to 1000°C because this was the only temperature where both sets of data were available over a large region of nonstoichiometry. Because of

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* Supported by the U.S. Atomic Energy Commission, Division of Research. This is AEC Report COO-1441-22.

this limitation no attempt was made to quantitatively determine the expression

$$\sigma = A\,x\,e^{-Q/kT} \qquad (1)$$

from the above data. In addition, the expression for the electron mobility,

$$\mu = \mu_o e^{-Q/kT} \qquad (2)$$

could not be determined quantitatively because no defect model had been proposed which would allow one to determine the exact relation between $[\mathrm{Ce}'_{\mathrm{Ce}}]$ and x.

In a more recent study (*3*) in our laboratory the nonstoichiometric behavior of CeO_{2-x} (i.e., $x = x(T,P_{O_2})$) was determined in the temperature region 750–1500°C and composition region $0.001 < x < 0.178$. As discussed in this paper the predominate nonstoichiometric defect were shown to be doubly ionized oxygen vacancies, $V_O^{\cdot\cdot}$, and electrons localized on normal cerium sites, $\mathrm{Ce}'_{\mathrm{Ce}}$.

The objective of this study was to:

(1) Measure the electrical conductivity of CeO_{2-x} (i.e., $\sigma = \sigma(T,P_{O_2})$) in the same temperature and P_{O_2} region that the above thermodynamic data is available.

(2) Make a combined analysis of the equilibrium conductivity and thermodynamic data to obtain a quantitative fit of the expression

$$\sigma = A[x]e^{-Q/kT}$$

in the composition region $0.001 < x < 0.178$ and the temperature region 750–1500°C.

(3) Determine the parameters μ_o and Q in the expression for the electron mobility

$$\mu = \mu_o e^{-Q/kT}.$$

Experimental

The conductivity specimens were prepared by cold pressing and sintering CeO_2 powder obtained from the American Potash and Chemical Company (*4*, *5*). The results of a mass spectrographic analysis of a typical sintered CeO_2 specimen are given in a previous publication (*1*).

The electrical conductivity measurements of CeO_{2-x} as a function of P_{O_2} in the temperature range 750–1500°C were made in a molybdenum wound resistance furnace. A standard four-probe dc technique was employed for the electrical conductivity measurements. The experimental apparatus employed was essentially the same as that described in an earlier publication (*6*).

Oxygen partial pressures were achieved by means of two methods. For pressures from 1 to 10^{-4} atm, premixed and analyzed O_2–Ar mixtures at 1 atm total pressure were used in the study. Controlled oxygen partial pressures in the low-pressure region were obtained by introducing known mixtures of CO and CO_2 at 1 atm total pressure. The well-known free energy values for the CO/CO_2 reaction were then used to calculate the oxygen partial pressure. A linear flow rate of 0.9 cm/sec was maintained for all gas mixtures used in this investigation to avoid errors arising from thermal diffusion (*7*). Isothermal electrical conductivity measurements at 100° intervals between 1100 and 1500°C were made for both increasing and decreasing partial pressures of oxygen. In the temperature region 750–1050°C, the electrical conductivity was measured as a function of temperature in each of the O_2–Ar and CO–CO_2 gas mixtures. A constant temperature was maintained until no observable change in conductivity with time occurred, i.e., for 1/2–2 hr. The furnace temperature was then changed and a new equilibrium established. Measurements were taken for both increasing and decreasing temperatures. Since the composition of CeO_{2-x} has a unique equilibrium value for each oxygen partial pressure and temperature, the above procedure insures the measurement of equilibrium values of the conductivity, because the equilibrium state was approached from both higher and lower compositions of oxygen.

Results and Discussion

The electrical conductivity of sintered specimens of cerium dioxide was measured as a function of temperature (i.e., 750–1500°C) and oxygen pressure (1–10^{-22} atm). The measured values of the conductivity σ_{meas} for the sintered specimen have been corrected for porosity using the relation (*8*).

$$\sigma = \sigma_{\text{meas}}(\rho_{\text{theo}}/\rho_{\text{meas}}), \tag{3}$$

where ρ_{theo} is the theoretical density and ρ_{meas} is the bulk density of the sintered specimen.

The results obtained in this investigation are in excellent agreement with a previous study of the temperature and oxygen pressure dependence of the electrical conductivity of CeO_{2-x} (*5*). However, because of the additional conductivity data obtained in this study, the isothermal dependence of σ on P_{O_2} was obtained at smaller temperature increments between 750 and 1050°C and over a wider range of oxygen pressure. Thus, the $\sigma = \sigma(T, P_{O_2})$ data obtained in this study effectively overlaps the same temperature and oxygen pressure region in which the nonstoichiometric behavior of CeO_{2-x} (i.e., $x = x(T, P_{O_2})$) was recently determined (*3*).

The compositional and temperature dependence of the conductivity of CeO_{2-x}, $\sigma = \sigma(x, T)$, was determined by drawing smooth curves through isotherms of log σ vs log P_{O_2} and log x vs log P_{O_2} data and selecting values of σ and x which corresponds to the same value of P_{O_2} and T. The results of this combined analysis are shown in Figs. 1 and 2 where isotherms of log σ are plotted as a function of log x. Although the combined data are available at 25°C increments between 750 and 1050°C and 100°C increments between 1100 and 1500°C, respectively, only data at 200°C intervals are shown Figs 1 and 2 to simplify the presentation of the data. The smallest value of x for each isotherm is determined by the constraint that the error in x be less than 2% (*3*). Problems associated with carbon deposition in the conductivity study at high CO/CO_2 ratios limits the maximum value of x that could be obtained at lower temperatures.

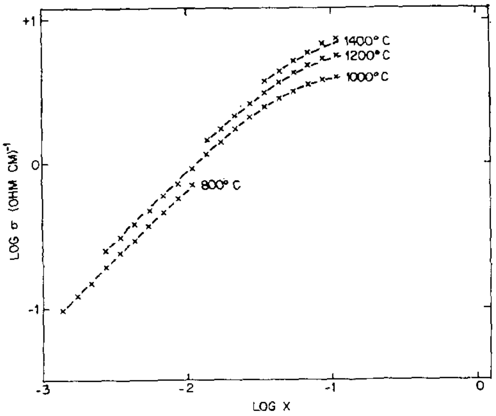

FIG. 1. Isothermal plot of log σ vs log x at 800, 1000, 1200, and 1400°C obtained by combining conductivity and thermodynamic data for CeO_{2-x}. × Experimental data; ---- plot of Eq. (5).

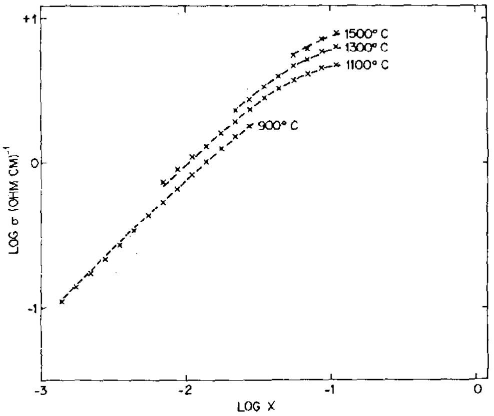

FIG. 2. Isothermal plot of log σ vs log x at 900, 1100, 1300, and 1500°C obtained by combining conductivity and thermodynamic data for CeO_{2-x}. × Experimental data; ---- plot of Eq. (5).

In a previous investigation a nonequilibrium technique was employed to maintain a fixed value of x while the conductivity was measured as a function of temperature (i.e., $T \leqslant 1000$°C). For constant values of x, the conductivity exhibited an exponential dependence on temperature

$$\sigma = \sigma_0 e^{-Q/kT}. \tag{4}$$

In this study the dependence of σ on T under conditions of constant x was determined by selecting values of σ and T for fixed values of x from a plot of the type of data shown in Figs. 1 and 2. Data selected by this method are shown in Fig. 3 where log σ is plotted as a function of $1/T$ for several different values of x. The activation energy, Q, corresponding to a given value of x was determined from Eq. (4)

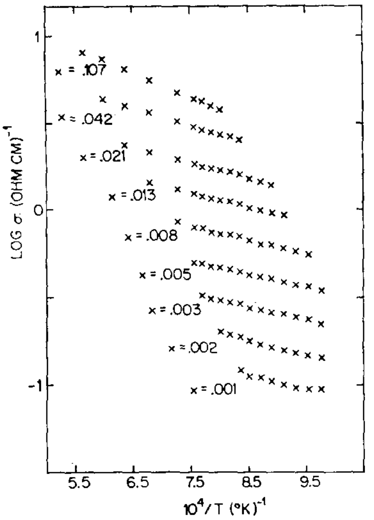

FIG. 3. Constant composition plot of log σ vs $1/T$ for several different nonstoichiometric compositions of CeO_{2-x} between $x = 0.001$ and 0.107.

and a least square curve fit of the log σ vs $1/T$ type data shown in Fig. 3.

The dependence of Q on x is shown in Fig. 4. For purposes of comparison, the values of Q determined from a previous study (*1*) are also shown in Fig. 4. Although a similar dependence of Q on x was observed, the values of Q obtained in this study are approximately 0.04–0.06 eV smaller than reported in the previous study (*1*). The dependence of Q on x obtained in this investigation is considered to be more reliable because equilibrium-type conductivity data were used, whereas in the previous study (*1*) a non-equilibrium technique was used to measure the temperature dependence of the conductivity.

The isothermal dependence of σ on x and the dependence of Q on x determined in this investigation were used to obtain a quantitative fit of Eq. (1). The best fit of the experimental data, $\sigma = \sigma(x, T)$, using Eq. (1) was obtained from the expression

$$\sigma = 410[x]e^{-Q/kT}(\text{ohm cm})^{-1} \qquad (5a)$$

where

$$Q = 0.158 + x\ (\text{eV}). \qquad (5b)$$

Equation (5) is represented by a solid line in Fig. 4. Although Eq. (5) is not the best representation of the dependence of the calculated values of Q on x, it does lie within the experimental error in Q (i.e., $\pm$ 0.02 eV). A comparison between the calculated and the experimentally determined dependence of the conductivity on composition and temperature is shown in Figs. 1 and 2 where the dashed line represents Eqs. (5a) and (5b). Excellent agreement is observed between the values of σ calculated from Eqs. (5a) and (5b) and the experimentally determined values.

In a recent study the ionic transference number, t_i, of CeO_{2-x} was measured as a function of temperature (600–1000°C) and oxygen partial pressure (1–10^{-22} atm) (*9*). In the composition region $10^{-3} < x < 0.2$, between 700 and 1000°C, t_i was less than 0.08 with an average value of about 0.05. The electrical conduction in this region was reported to be predominantly electronic and controlled by the nonstoichiometric defects, $V_O^{\cdot\cdot}$, and $\mathrm{Ce}'_{\mathrm{Ce}}$. The concentration of oxygen vacancies is related to the deviation from stoichiometry, x, in CeO_{2-x} by the expression (*9*).

$$n_V = 4x/a_0^3 \qquad (6)$$

where a_0 is the lattice parameter (*10*) of CeO_{2-x} and $n_{V_O^{\cdot\cdot}}$ is the number of oxygen vacancies/cm^3. Since according to the electroneutrality relation

$$2n_V = n_{\mathrm{Ce}'_{\mathrm{Ce}}}, \qquad (7)$$

$$n_{\mathrm{Ce}'_{\mathrm{Ce}}} = 8x/a_0^3 \qquad (8)$$

where $n_{\mathrm{Ce}'_{\mathrm{Ce}}}$ is the number of electrons localized on normal cerium atom/cm^3.

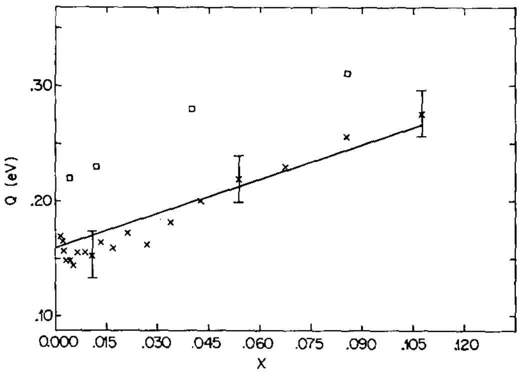

FIG. 4. The dependence of the experimental activation energy, Q, on x. × This study; □ Blumenthal and Hofmaier (*1*).

The electron mobility in CeO_{2-x} has been reported (*11*) to be a "hopping" type process which may be characterized by an expression of the type

$$\mu = \mu_0 e^{-Q/kT}. \qquad (9)$$

The following expression for the electron mobility as a function of temperature was obtained by combining Eqs. (5a), (5b), and (8) with the results of a recent lattice parameter study on CeO_{2-x} (*10*).

$$\mu = 5.2(10^{-2})e^{-(0.158+x)/kT}(\mathrm{cm^2/V\ sec}). \qquad (10)$$

An interesting observation to make from Eq. (10) is that the calculated value of μ is only slightly dependent on x between $10^{-3} < x < 10^{-2}$ but decreases more rapidly with x for $x > 10^{-2}$. It is postulated that the decrease in mobility, which is a result of the increase in Q with x, is related to the observed increase in a_0 with x (*10*).

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