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TECHNICAL PROGRESS REPORT

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to

THE ATOMIC ENERGY COMMISSION

DIVISION OF RESEARCH

on

"A STUDY OF THE DEFECT STRUCTURE

OF NONSTOICHIOMETRIC CeO_2 "

MASTER

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ABSTRACT

The electrical conductivity of arc cast specimens of $\text{Ce}_{1+y}\text{O}_2$ have been measured as a function of temperature and oxygen pressure. These preliminary results indicate that although the absolute value of the conductivity for arc cast $\text{Ce}_{1+y}\text{O}_2$ specimens differs from the sintered specimens the temperature and oxygen pressure behavior is similar.

The electron mobility in $\text{Ce}_{1+y}\text{O}_2$ was calculated from the electrical conductivity and thermodynamic data and the assumption that the atomic defects exist predominantly in only one state of ionization. The data for the calculations in the temperature range $800^\circ - 1200^\circ\text{C}$ 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. The calculated electron mobilities of sintered and arc cast $\text{Ce}_{1+y}\text{O}_2$ specimens increase exponentially with increasing temperature between 800° and 1200°C . Based on the temperature dependence of the mobility, the electron conduction mechanism appears to be a hopping type process with an activation energy of 0.14eV . The magnitude of the mobility is of the order of $10^{-2} \text{ cm}^2/\text{v-sec}$.

A galvanic cell using a commercially made calcium stabilized zirconia tube was used to measure the P_{O_2} of analyzed and premixed gas mixtures of Ar-O_2 and CO-CO_2 over a wide range of oxygen pressures near 1000°C . The accuracy of the cell was evaluated by comparing these results with the reported analyses of these mixtures. A model based on thermal diffusion was used to explain the variation of the emf with flow at low flow rates. Errors due to a temperature difference across the electrolyte were also evaluated. When properly employed this cell has been shown to be a sensitive research device for the accurate measurement of the P_{O_2} over a wide range of oxygen pressures.

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. The analysis of the data should also 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 mobility of charge carriers in nonstoichiometric oxides, such data has been rather sparse in the literature.

The thermodynamic and electrical property study initiated on nonstoichiometric cerium dioxide, $\text{Ce}_{1+y}\text{O}_2$, has been continued. The literature on the x-ray, thermodynamic and electrical property studies on $\text{Ce}_{1+y}\text{O}_2$ has been reviewed previously.^{1,2} In the last Technical Report³ and in a recent paper by Blumenthal, Lee and Panlener² the results of an electrical conductivity study on sintered specimens of $\text{Ce}_{1+y}\text{O}_2$ over the temperature range 800° to 1500°C and from 1 to 10^{-21} atm of oxygen was described. Based on the agreement between the experimental conductivity data and theoretically derived relations, the nonstoichiometric defect structure of $\text{Ce}_{1+y}\text{O}_2$ was interpreted in terms of a defect structure consisting of triply and quadruply ionized cerium interstitials and localized electrons. In the region where triply ionized cerium interstitials predominate the appropriate equation is

$$\sigma^4 = (D - D_1\sigma)P_{\text{O}_2}^{-1} \quad (1)$$

In the region where quadruply ionized cerium interstitials predominate the appropriate equation is

$$\sigma^5 = (E - E_1\sigma)P_{\text{O}_2}^{-1} \quad (2)$$

The above equations were derived from mass action equations which considered the activities of the cerium ions on normal lattice sites and the vacant cerium interstitial sites to be a function of the concentration of cerium interstitials.

Based on the assumption that the electronic conduction mechanism was a "hopping type" process, the experimental activation energy for motion $0.18 \pm 0.07\text{eV}$ was calculated from the temperature dependence of the ratio E/E_i from the equation which describes a predominance of quadruply ionized cerium interstitials.

The standard enthalpies of formation for the following defect reactions in $\text{Ce}_{1+y}\text{O}_2$:

* approximate values

were determined from the temperature dependence of D and E obtained from the above expressions and the calculated temperature dependence of the electronic mobility.

In this investigation, thermodynamic and electrical property measurements initiated on $\text{Ce}_{1+y}\text{O}_2$ were continued in order to provide additional data which would permit a more detailed analysis of the proposed defect structure model for $\text{Ce}_{1+y}\text{O}_2$, and a better understanding of the electronic and ionic transport mechanisms in $\text{Ce}_{1+y}\text{O}_2$.

RESULTS AND DISCUSSION

1. Electrical Property Studies

As described in a previous report³ one of the difficulties with the current electrical conductivity studies of $\text{Ce}_{1+y}\text{O}_2$ is that only sintered specimens have been used. Recently arc cast cerium dioxide in the form of

large grained polycrystalline aggregates have become available* to this laboratory. An examination of the microstructure of the arc cast aggregate revealed a number of small microcracks which were apparently formed when the arc cast material solidified. A conductivity specimen was prepared from one of these aggregates and the conductivity was measured as a function of temperature and oxygen pressure in the same experimental set up as described previously.^{1,2} The results of this study showed essentially the same temperature and oxygen pressure behavior as observed for the sintered specimens. However, this arc cast specimen exhibited a lower conductivity than the sintered specimen with 85% of theoretical density. The most plausible explanation for the lower conductivity is that the microcracks behaved as regions of high resistivity.

More recently a cerium dioxide arc cast aggregate with an improved exterior appearance has become available. A conductivity specimen prepared from this aggregate is currently being investigated. Preliminary conductivity measurements in oxygen and in a CO-CO₂ mixture in the temperature range 800° - 1500°C indicates that the conductivity of this arc cast specimen is slightly higher than the conductivity of the 85% dense sintered specimen. The conductivity study on this specimen will be extended over the same temperature and oxygen pressure region as used for the sintered specimen.^{1,2} These results will then be analyzed using the same technique as described previously to test if the same defect structure and energies are obtained. If this study is favorable the same type of arc cast specimen will be employed for the Hall mobility measurements to be described below.

The electron mobility in Ce_{1+y}O₂ was calculated from the electrical conductivity and thermodynamic data and the assumption that the atomic defects exist predominantly in only one state of ionization. The data for the calculations in the temperature range 800° - 1200°C was selected from the oxygen pressure region where according to the analysis^{1,2} of the conductivity data the predominant defects are electrons localized on normal cerium ions and quadruply ionized cerium interstitials. The interpretation of the

*These aggregates of CeO₂ were furnished by the Materials Research Corporation.

electron conduction mechanism based on these calculations are described in a paper⁴ submitted for publication and in AEC report C00-1441-8. These results may be summarized as follows. The electron mobility of sintered and arc cast CeO_2 conductivity specimens appears to increase exponentially with increasing temperature between 800° and 1200°C. The conduction mechanism is assumed to be a hopping type process (i.e. the electrons localized at normal cerium ion sites move to adjacent cerium ions). The magnitude of the mobility is of the order $10^{-2} \text{ cm}^2/\text{v-sec}$ and the activation energy for the process is 0.14eV.

Considerable effort has been made to initiate the mobility measurements employing a high temperature AC Hall mobility technique.⁵ Most of the experimental difficulties associated with noise problem encountered with this apparatus have been eliminated. Hall mobility measurements on test materials have shown that the apparatus functions properly at room temperature. At elevated temperatures noise problems arise from temperature fluctuations in the furnace. An attempt is currently being made to reduce this problem, so that high temperature mobility measurements may be made in order to 1) check the temperature dependence of the electron mobility calculated from the thermodynamic and electrical conductivity data, and 2) test the proposed model for the compositional dependence of the mobility.

As described in the last progress report³ the preliminary data on the temperature dependence of the conductivity at constant composition appears to fit the expression

$$\sigma \sim e^{-\Delta E/KT} \quad (6)$$

where ΔE was calculated as $0.20 \pm 0.04\text{eV}$. The value of ΔE was associated with the energy of motion of "hopping type" electrons. Since the energy of motion calculated in this report from a combined analysis of the electrical conductivity and thermodynamic data is 0.14eV, it appears that the observed temperature dependence of the constant composition conductivity data may be associated with both a change in the carrier concentration and the temperature dependence of the mobility.

The experimental apparatus for the constant composition conductivity measurements has been modified so that the specimen temperature may be changed very rapidly. This technique will reduce the time the specimen is in contact

with the purified argon atmosphere and thus reduce the possibility of composition variation due to reaction with oxygen impurities. It is hoped that with this new technique the accuracy of the constant composition conductivity will be greatly improved. It should be possible then to calculate the ionization energy for the reaction

by combining this data with the observed temperature dependence of the electron mobility.⁶

2. Thermodynamic Property Studies

As described in the last Technical Report³ several problems were encountered with the ionic transference measurements on $\text{Ce}_{1+y}\text{O}_2$ using an electrochemical cell technique. In order to elucidate these problems, an investigation using a similar electrochemical cell as an oxygen gauge was initiated. A galvanic cell of the type

was employed for this study. The results of this investigation are described in a paper submitted for publication⁷ and AEC Report C00-1441-9. These results may be summarized as follows. A critical evaluation of the emf dependence on flow rate for this type of cell indicated that this effect was caused by thermal separation of gases at low flow rates and by an increase in pressure at high flow rates. The reason the emf was asymmetric, with respect to zero, when the gas mixtures at the electrodes were reversed was because of temperature gradients across the electrolyte.

These problems were either eliminated or minimized by (a) enlarging the gas inlet and exit tube in the electrode chamber to reduce pressure effects, (b) measuring the emf of the cell at high flow rates to eliminate thermal diffusion effects and (c) adjusting the location of the electrolyte in the furnace to minimize temperature gradients across the electrolyte. The accuracy of this cell was evaluated by measuring the P_{O_2} of analyzed and premixed gas mixtures of Ar-O₂ and CO-CO₂ over a wide range² of oxygen pressures at 1000°C and comparing these results with the reported analyses

of these mixtures. When properly employed this cell has been shown to be an accurate research device for the measurement of P_{O_2} over a wide range of oxygen pressures.

With the elucidation of the problems effecting the cell emf measurements, the ionic transference measurements on $Ce_{1+y}O_2$ have been resumed. The same cell assembly as used in the evaluation of the oxygen gauge has been employed except the calcia-zirconia tube has been replaced with a $Ce_{1+y}O_2$ disc sealed on the end of the alumina tube.^{7,8} The ionic transference of $Ce_{1+y}O_2$ will be measured as a function of oxygen pressure and temperature.

Thermogravimetric measurements of $Ce_{1+y}O_2$ have been extended to both higher temperatures and lower pressures of oxygen. Also the previously existing data⁹ has been rechecked after various improvements were made in both the experimental system and experimental technique.³ Initial analysis of the thermogravimetric data indicated that the proposed method of testing the defect model³ by evaluating the expression^{1,2}

$$K_I = \frac{y^5 P_{O_2}}{F(y)} \quad (8)$$

at temperatures above 1200°C was not adequate. Therefore a new method has been developed for quantitative analysis which requires less limiting assumptions than the previous method, while simultaneously yielding more information. This method is currently being tested.

The combined results of the thermogravimetric data from 800° to 1400°C for seven sintered specimens are shown in Fig. 1 where $\log y$ in $Ce_{1+y}O_2$ is plotted vs $\log P_{O_2}$. Also shown are several points on the 800°C isotherm from Bevan and Kordis¹⁰ to illustrate the excellent agreement with their work. The data from specimens 1 thru 3 has been reported previously.⁹ Data from specimens 4 thru 7 has been obtained more recently by using premixed and analyzed CO-CO₂ mixtures and extends to higher temperatures and over a wider range of P_{O_2} . In general the more recent data contains less scatter and better reproducibility. The thermogravimetric measurements are currently being extended to both higher and lower temperatures and over wider ranges of P_{O_2} .

Fig. 1 Thermogravimetric data of nonstoichiometric $Ce_{1+y}O_2$ from 800° to 1400°C where y in $Ce_{1+y}O_2$ is shown as a function of the partial pressure of oxygen.

Recently emphasis has been placed on analysis of the thermogravimetric data to test the proposed defect model.^{1,2} The defect structure analysis of the thermodynamic data should in principle be a more direct method than the corresponding analysis of the electrical conductivity data because the electronic mobility is not involved. Another advantage of the thermodynamic study is that single crystals are not required since the data is independent of the state of aggregation of the specimen.

Analysis of the thermogravimetric data above 1200°C with Eq. (8) indicated that more than one state of defect ionization predominates, contrary to the assumption of a single state of ionization used in the derivation of Eq. (8). When two states of ionization exist it is not possible to derive a simple nonlinear equation, $y = f(y, P_{O_2})$, as can be done with electrical conductivity.¹¹ In addition the proposed defect model^{1,2} contains terms to account for large departures as well as defect interaction parameters both of which further complicate the model. However, if one assumes that two states of ionization predominate and applies all the equations of the model to a particular thermodynamic state, $y(T, P_{O_2})$, the result is a system of six nonlinear simultaneous equations in seven unknowns. Five of the six equations can be written for one state of ionization.^{1,2} The sixth equation results from the equilibrium of the ionization reaction

where all quantities have been previously defined.^{1,2} If the same set of equations is again applied to another thermodynamic state at the same temperature and with the same two states of ionization predominating, the result is 12 equations in 12 unknowns since the mass action constants are functions of temperature alone and are therefore equivalent.

The new method of analysis then consists of solving the system of 12 simultaneous nonlinear equations for proper combinations of data points and averaging the results of the individual solutions. An extension of Newton's method¹² for nonlinear equations is used coupled with a nonlinear interaction technique for initial estimation of the unknown quantities. Unfortunately, the system of equations is extremely "ill-conditioned" and hence their solution is a rather delicate procedure.

The results obtained thus far for the 800°C isotherm are shown in Fig. 2. The four curves represent a defect model which includes electrons localized on normal cerium sites, cerium interstitials in four different states of ionization and limiting values for the interaction parameters α and β . The concentrations of all species present as well as the mass action constants can be calculated. Consequently all ionization energies can be determined. Hence the new method allows one to completely determine all quantities corresponding to an assumed defect model which includes more than one state of ionization. Previously this was not possible.

This analysis will be continued and applied to all available thermogravimetric data. In addition, other models such as oxygen vacancies in all possible states of ionization will be tested using the new method. And finally, statistical mechanical models will be employed to help elucidate the nature of the defects present and the salient features of the defect interactions in $\text{Ce}_{1+y}\text{O}_2$ at large departures from stoichiometry.

Fig. 2 Initial results of analysis at 800°C for the defect model described in this report.

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