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## Doped Ceria as a Solid Oxide Electrolyte

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### ABSTRACT

Ceria ( $\text{CeO}_2$ ) doped with divalent or trivalent cations is a mixed conductor; conduction occurs predominantly by the motion of oxygen vacancies or by electrons, depending on the departure from stoichiometry. In order to establish the electrolytic domain ( $T$  vs.  $p_{\text{O}_2}$ ) at which  $(\text{CeO}_2)_{0.95}(\text{Y}_2\text{O}_3)_{0.05}$  behaves primarily as an ionic conductor with transference number  $t_i \cong 0.99$ , a careful study was made of the conductivity,  $\sigma$ , as a function of temperature and oxygen partial pressure, covering the  $p_{\text{O}_2}$  range of  $10^0$ - $10^{-22}$  atm in small steps. From these data the electrolytic domain was determined; it extends to about  $10^{-13}$  atm at  $600^\circ\text{C}$ . When compared to calcia-stabilized zirconia (CSZ), doped ceria shows a higher conductivity, lower activation energy (0.76 eV) for anion vacancy migration, and absence of polarization effects to lower temperatures. These results indicate that doped ceria may be an attractive candidate for fuel cells and other applications at temperatures below those at which CSZ is useful.

There has been much interest in oxide materials which can serve as solid oxide-ion electrolytes for applications in oxygen concentration cells and in fuel cells (1, 2). The criteria to be met include: (i) a high anionic (*i.e.*,  $\text{O}^{2-}$  ion) mobility, and (ii) negligible electronic conductivity. Item (ii) is equivalent to the statement that the ionic transference number  $t_i$  must be close to unity, although the maximum acceptable value of  $1 - t_i$  depends on the specific application. Relatively few oxides meet both of the above criteria. The two materials most often used as solid oxide electrolytes are  $\text{ZrO}_2$  and  $\text{ThO}_2$ , doped with divalent or trivalent cation impurities so as to introduce oxygen vacancies for charge compensation.

Ceria,  $\text{CeO}_2$ , has the same (fluorite) structure as thoria and (doped) zirconia, but is different in that pure  $\text{CeO}_2$  undergoes large departures from stoichiometry at elevated temperatures in a reducing atmosphere, with accompanying electronic conductivity (3). Although doped  $\text{CeO}_2$  is often mentioned as showing predominantly ionic behavior (2, 4), the exact extent of the ionic vs. electronic contributions has not been well established. Generally, the tendency has been to regard it as unsuitable as an electrolyte material because of its electronic component. Nevertheless, Takahashi *et al.* (5, 2) have made  $t_i$  measurements of  $\text{CeO}_2$  doped with  $\text{La}_2\text{O}_3$ , using galvanic cell measurements, and have even tried this material in a fuel cell. The values for  $t_i$  that they obtain, however, generally fall in the range from 0.6 to 0.9, indicating a substantial electronic contribution.

In the present paper, it is intended to investigate the ionic transference number and electrolytic domain of doped  $\text{CeO}_2$ . The term "electrolytic domain" refers here to the range of  $p_{\text{O}_2}$  and temperature at which  $t_i$  is greater than 0.99. The information will be obtained not through direct galvanic cell (emf) measurements, since these are deemed to be insufficiently

precise to obtain  $t_i$  values close to 1.0, but rather through measurement of conductivity,  $\sigma$ , as a function of  $p_{\text{O}_2}$ . Although such measurements have been performed earlier by Blumenthal *et al.* (6), one cannot obtain the type of quantitative information desired for present purposes from those measurements, primarily because of the existence of large gaps in the  $p_{\text{O}_2}$  range covered.

In the present work, with special care, it was possible to cover the entire range from  $p_{\text{O}_2} = 1$ - $10^{-22}$  atm in sufficiently close steps to obtain the electrolytic domain with reasonable precision for the case of  $(\text{CeO}_2)_{0.95}(\text{Y}_2\text{O}_3)_{0.05}$ . In addition, some of the parameters which characterize ionic migration in  $\text{CeO}_2$  are obtained. Finally, some experiments on polarization effects are reported.

### Theory

*Ionic conductivity.*—It will be assumed that the only defect giving rise to ionic conductivity in  $\text{CeO}_2$  is the doubly ionized oxygen vacancy,  $V_{\text{O}}^{\bullet\bullet}$  [in the Kröger-Vink (7) notation]. If the concentration of these vacancies is denoted by  $n_v$ , we may write, for the ionic conductivity  $\sigma_i$ , the expression

$$\sigma_i = n_v q \mu_i \quad [1]$$

where  $q = 2e$  is the (positive) charge on the vacancy and  $\mu_i$  is its mobility, given by (8)

$$\mu_i = \frac{\nu a^2 q}{4kT} \exp(-\Delta G_i/kT) \quad [2]$$

Here  $\Delta G_i$  is the free energy of activation for ionic motion, expressible in terms of an enthalpy of activation  $\Delta H_i$  and entropy of activation  $\Delta S_i$  by

$$\Delta G_i = \Delta H_i - T\Delta S_i \quad [3]$$

$\nu$  is a frequency factor and  $a$  is the lattice parameter of the cubic unit cell. ( $a/2$  is the nearest neighbor oxygen spacing and, therefore, the jump distance of a vacancy.) Thus, in the semiempirical equation

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Key words: ionic conductivity, cerium dioxide, solid electrolyte, point defects.

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$$\sigma_i = \frac{C_1}{T} \exp(-E_i/kT) \quad [4]$$

the parameters  $E_i$  and  $C_1$  are given by

$$E_i = \Delta H_1 \quad [5]$$

and

$$C_1 = (\nu a^2 e^2/k) n_v \exp(\Delta S_1/k) \quad [6]$$

assuming that  $n_v$  is not temperature dependent.

The "activation energy"  $E_i$  is obtained in the usual way from a plot of  $\log \sigma_i T$  vs.  $1/T$ . It should be noted that if instead, one plots  $\log \sigma_i$  vs.  $1/T$ , a straight line will usually be obtained within experimental error, but its slope gives an apparent activation energy  $E_a$  given by

$$E_a = -\frac{d \ln \sigma_i}{d(1/kT)} = E_i - k\bar{T} \quad [7]$$

where  $\bar{T}$  is the average temperature over the range of the measurements.

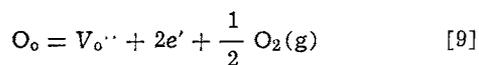
Two factors determine  $n_v$ , viz., charge compensation and nonstoichiometry. To produce vacancies by means of charge compensation we may dope with an aliovalent cation, e.g., CaO or  $Y_2O_3$ . In this way we obtain one  $V_o$  for every molecule of dopant, since the  $Ca^{2+}$  and  $Y^{3+}$  ions enter the  $CeO_2$  lattice as  $Ca''_{Ce}$  and  $Y'_{Ce}$ , respectively. Therefore

$$n_v = [Ca''_{Ce}] + \frac{1}{2} [Y'_{Ce}] \equiv n_M \quad [8]$$

that is, the quantity  $n_M$  defined here is the total effective dopant concentration. (It is defined so as to allow both Ca and Y to be present simultaneously; actually only one will be present in significant concentration at a time.) On the basis of Eq. [8] and [1], we expect that  $\sigma_i \propto n_M$  and also, from Eq. [2]-[5], that  $E_i$  is independent of both  $n_M$  and the type of aliovalent dopant. Actually, this statement is only valid at low concentrations. In fact, for ceria,  $\sigma_i$  vs.  $n_M$  is linear up to a value of  $n_M$  corresponding to less than 4% oxygen vacancies, and then it shows a broad maximum as a function of dopant concentration (2, 6). In the case of  $ThO_2:Y_2O_3$  the departure apparently takes place even earlier (9). Such results mean that defect interactions become important at high concentrations. In the case of  $ZrO_2:CaO$ , for example, it is well known that ordering effects take place (10). In the range where interactions are appreciable, the semiempirical relation [4] still holds, but the simple interpretations of  $E_i$  and  $C_1$  given by Eq. [5] and [6] no longer apply.

When vacancies are produced by departures from stoichiometry, one also obtains electronic defects which give rise to an electronic contribution to the conductivity,  $\sigma_e$ .

*Nonstoichiometry and electronic conductivity.*—The reaction which leads to nonstoichiometry is<sup>2</sup>



The electronic defect  $e'$  may be regarded as equivalent to the presence of a  $Ce^{3+}$  ion, or in defect notation,  $Ce'_{Ce}$ . The mass action equation which follows from the reaction [9] is, at low defect concentrations

$$n_v n_e^2 p_{O_2}^{1/2} = K_1(T) = K_{10} \exp(-\Delta H_1/kT) \quad [10]$$

in which  $n_e$  is the electron concentration,  $p_{O_2}$  the oxygen partial pressure, and  $\Delta H_1$  the enthalpy change of the reaction. In doped samples, we will be interested in the range where nonstoichiometry is small, specifically,  $n_e \ll n_M$ . Under these conditions  $n_v \approx n_M$  and so from Eq. [10]

$$n_e = [K_1(T)/n_M]^{1/2} p_{O_2}^{-1/4} \quad [11]$$

<sup>2</sup> For large departures from stoichiometry, singly ionized vacancies can also be produced (11), but this complication can be ignored for the purposes of this paper.

In spite of the fact that  $n_e \ll n_v$ , however, the electronic conductivity

$$\sigma_e = n_e e \mu_e \quad [12]$$

can become appreciable because  $\mu_e \gg \mu_i$ . Since electrons migrate by a hopping mechanism (11),  $\mu_e$  is given by

$$\mu_e = (b/T) \exp(-E_e/kT) \quad [13]$$

where  $E_e$  is a small activation energy. From Eq. [11] and [12],  $\sigma_e \propto p_{O_2}^{-1/4}$ . The total conductivity

$$\sigma \equiv \sigma_i + \sigma_e \quad [14]$$

is then clearly made up of a  $p_{O_2}$ -independent part,  $\sigma_i$ , and a part,  $\sigma_e$ , which is proportional to  $p_{O_2}^{-1/4}$ . This pressure dependence provides a convenient way to separate  $\sigma_i$  from  $\sigma_e$  and thereby to obtain the ionic transference number

$$t_i = \sigma_i/\sigma \quad [15]$$

*The electrolytic domain.*—The electrolytic domain is defined as the region, in a plot of  $\log p_{O_2}$  vs.  $1/T$  in which  $t_i$  is greater than some selected value (often 0.99) (12). Substituting [4] and [10] through [13] into Eq. [14] and [15], we obtain

$$\ln p_{O_2} = 4 \ln \left\{ \frac{t_i b e K_{10}^{1/2}}{C_1 (1 - t_i) n_M^{1/2}} \right\} - 4 \left( \frac{\Delta H_1}{2} + E_e - E_i \right) \frac{1}{kT} \quad [16]$$

which shows that a plot of  $\ln p_{O_2}$  vs.  $1/T$  for a given  $t_i$  value gives a straight line whose negative slope is  $(4/k)(\frac{1}{2}\Delta H_1 + E_e - E_i)$  and whose intercept depends on  $t_i$  and on the dopant concentration.

The straight line given by Eq. [16] separates the  $p_{O_2}$ - $1/T$  space into two regions, the region above the line being the domain for which  $t_i$  is greater than the selected value. From the intercept formula it is clear that, for  $t_i$  close to 1.0, the line shifts upward by close to 4 decades for every decade in  $(1 - t_i)$ ; for example, in going from  $t_i = 0.90$  to 0.99, the shift is 4.17 decades in  $p_{O_2}$ .

### Experimental Methods

The specimens used in this study were fabricated from nominally pure  $CeO_2$  powder (99.9% pure with respect to other rare earths). Analysis shows an aliovalent impurity content in the range 150-200 ppmw. Samples doped with  $Y_2O_3$  or CaO were prepared by mechanically mixing appropriate amounts of  $Y_2O_3$  or  $CaCO_3$  powders with the  $CeO_2$ . Cylindrical samples ( $\frac{3}{4}$  in. diam  $\times$  0.1 in. high) of the mixed powders were prepared by pressing in a steel die at 40,000 psi. The pressed specimens, covered by additional loose powder to minimize contamination and loss of dopant, were placed in high purity alumina holders and heated slowly to 1500°C in an argon atmosphere. They were held at this temperature for 12-14 hr. The densities of the samples so obtained were greater than 80% of theoretical density.

After samples were cut to size ( $12 \times 5 \times 5$  mm<sup>3</sup>) electrodes were prepared using platinum paste (Englehard No. 6082) which was fired in air at 800°C to burn off the organic binder. Such electrodes are known (13) to be porous enough to allow the sample to come to equilibrium (with respect to oxygen) with the surrounding gas phase.

Measurements were carried out inside a quartz tube suspended inside a Kanthal-wound resistance furnace. Electric feedthroughs were mounted in a stainless steel cap from which four (15 mil) platinum leads ran to the specimen through insulating alumina tubes. Fine platinum wires (5 mil) were wrapped around the sample at both ends and at 1/3 and 2/3 of the length. The sample was then suspended by spot welding the sample leads to the heavier platinum wires contained in the alumina tubes. For improved contact, the area of contact between sample and wires was also coated

with several layers of platinum paste. A standard four-probe d-c technique was used to measure the conductivity. A fixed current was passed through the sample and the potential drop across the two center leads was measured with a Keithley Model 640 vibrating capacitor electrometer (input impedance of  $10^{16}$  ohms). In addition, a-c measurements at 1592 Hz ( $10^4$  rad/sec) were made with a Wayne-Kerr Model B221A universal bridge; results obtained by the two methods were essentially identical.

The sample temperature was measured by means of a Pt-Pt + 10% Rh thermocouple placed close to it, while the furnace was controlled to within  $\pm 1^\circ\text{C}$  by another thermocouple placed close to the furnace windings.

Atmosphere control, ranging over 22 orders of magnitude in oxygen partial pressure,  $p_{\text{O}_2}$ , was achieved as follows. For the range  $p_{\text{O}_2} = 1\text{--}10^{-4}$  atm  $\text{O}_2\text{-Ar}$  mixtures were used, and for the range  $10^{-4}\text{--}10^{-22}$  atm  $\text{CO-CO}_2$  mixtures were used. The value of  $p_{\text{O}_2}$  of a  $\text{CO-CO}_2$  mixture with known ratio  $\text{CO/CO}_2$  can be calculated at any temperature using the well-known free energy values for the  $\text{CO-CO}_2$  reaction (14). Fixed ratios of  $\text{CO/CO}_2$  premixed and analyzed, were purchased from the Matheson Gas Company, but these mixtures were limited to  $\text{CO/CO}_2$  ratios between  $10^3$  and  $10^{-3}$ . The value for  $p_{\text{O}_2}$  for  $\text{CO/CO}_2 = 10^{-3}$  is  $\sim 10^{-12}$  atm, at  $800^\circ\text{C}$ . Thus, a gap of approximately 8 decades in  $p_{\text{O}_2}$  exists between the lowest available  $\text{O}_2/\text{Ar}$  ratio and the least reducing  $\text{CO/CO}_2$ . Since critical data fall within this gap, we have closed it by setting up a system for: (a) mixing the premixed  $\text{CO/CO}_2 = 10^{-3}$  gas with pure  $\text{CO}_2$  under controlled relative flow rates, and (b) monitoring the  $p_{\text{O}_2}$  level by means of a calcia-stabilized zirconia cell located in the hot zone close to the sample under study. The same technique was also used to span the gap between other premixed pairs of  $\text{CO-CO}_2$  mixtures. In this way, it became possible to obtain  $p_{\text{O}_2}$  values from 1 to  $10^{-22}$  atm in intervals as close as desired. Further details will be described in a later publication (11).

### Results

Data for the variation of conductivity with temperature at  $p_{\text{O}_2} = 1$  atm is shown in Fig. 1 for  $(\text{CeO}_2)_{0.95}(\text{Y}_2\text{O}_3)_{0.05}$  and  $(\text{CeO}_2)_{0.9}(\text{CaO})_{0.1}$ . Good straight lines are obtained in the  $\log \sigma T$  vs.  $1/T$  plot for the range between  $400^\circ$  and  $1000^\circ\text{C}$ . In anticipation of the fact that the conductivity is almost entirely ionic in this range, the results for  $E_1$  and  $C_1$  (of Eq. [4]) are listed in Table I. Also shown, for comparison, in Fig. 1 are data (15) for calcia-stabilized zirconia

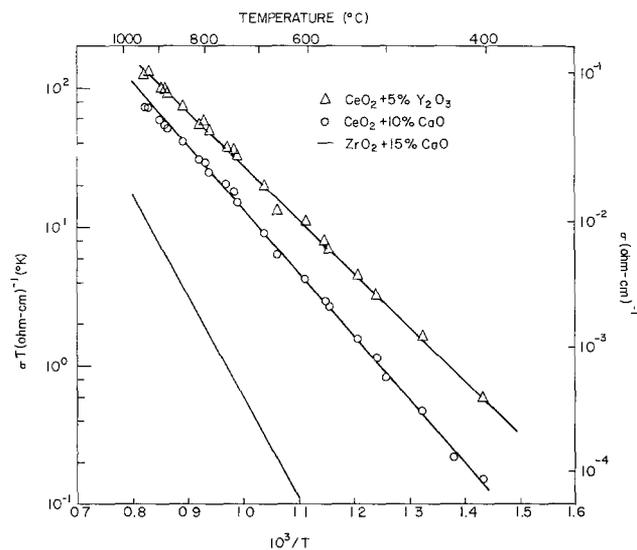


Fig. 1. Variation of conductivity with reciprocal absolute temperature for  $\text{CeO}_2$  doped with 5%  $\text{Y}_2\text{O}_3$  and with 10%  $\text{CaO}$  at 1 atm of oxygen, and comparison with data for calcia-stabilized zirconia.

Table I. Values of activation energy  $E_1$  and pre-exponential constant  $C_1$  for two compositions

$\text{CeO}_2$ doped with	$E_1$ (eV) *	$C_1$ ( $\text{ohm-cm})^{-1} \text{ } ^\circ\text{K}$
5% $\text{Y}_2\text{O}_3$	0.76	$1.95 \times 10^5$
10% $\text{CaO}$	0.91	$5.25 \times 10^5$

\* Uncertainty,  $\pm 0.015$  eV.

(CSZ), the conductivity of which is at least a decade lower than for the two doped ceria samples in the range  $T < 900^\circ\text{C}$ , and which has an activation energy  $E_1 = 1.3$  eV.

Figure 2 shows isothermal measurements on a 5%  $\text{Y}_2\text{O}_3$  sample as a function of  $p_{\text{O}_2}$  in the range from  $635^\circ$  to  $1150^\circ\text{C}$ . For each isotherm the  $p_{\text{O}_2}$  range was covered in close enough intervals to obtain the range in which  $\sigma$  was independent of  $p_{\text{O}_2}$  as well as to observe the manner in which it increases with decreasing  $p_{\text{O}_2}$ . The constant  $\sigma$  region shrinks with increasing temperature and has practically disappeared by  $1150^\circ\text{C}$ . In accordance with Eq. [11], the increase of  $\sigma$  with decreasing  $p_{\text{O}_2}$  indicates the appearance of nonstoichiometric carriers. The nonstoichiometric component, i.e., the difference between the total  $\sigma$  and the  $p_{\text{O}_2}$ -independent value, is shown as dashed lines in Fig. 2. Although there is some scatter, the slope of  $1/4$ , predicted by Eq. [11], fits the data in all cases. A similar  $1/4$  power law has been found by Neumin *et al.* (16) for  $\text{CeO}_2\text{:La}_2\text{O}_3$  and is also obtainable from the data given by Blumenthal *et al.* (6) for  $\text{CeO}_2\text{:CaO}$ , so that the relation may be regarded as well established. It is therefore reasonable to regard the  $p_{\text{O}_2}$ -independent conductivity as  $\sigma_i$  and the  $p_{\text{O}_2}$ -dependent part as  $\sigma_e$ .

On this basis, one may obtain  $t_i$  as a function of  $\log p_{\text{O}_2}$  directly from the data of Fig. 2 as the ratio  $\sigma_i/\sigma$  where  $\sigma_i$  is the  $p_{\text{O}_2}$ -independent value. Such a plot is given in Fig. 3. The figure shows that  $t_i$  remains close to unity over a larger range of  $p_{\text{O}_2}$ , the lower the temperature.

In order to establish the electrolytic domain, we must be able to determine the  $p_{\text{O}_2}$  and  $T$  values at which a given  $t_i$  is obtained. For good precision it is convenient to select  $t_i = 1/2$ . For each temperature, the value of  $p_{\text{O}_2}$  at which  $t_i = 1/2$ , i.e.,  $\sigma_e = \sigma_i$ , was ob-

<sup>3</sup> This is not quite true when the  $p_{\text{O}_2}$ -dependent part is much greater than the  $p_{\text{O}_2}$ -independent part, since nonstoichiometry introduces vacancies as well as electrons (Eq. [9]). Since  $\mu_e/\mu_i \sim 20$  (11) in the temperature and composition range of interest,  $t_i$  will be  $\sim 0.05$  even when all of the conductivity is due to nonstoichiometry.

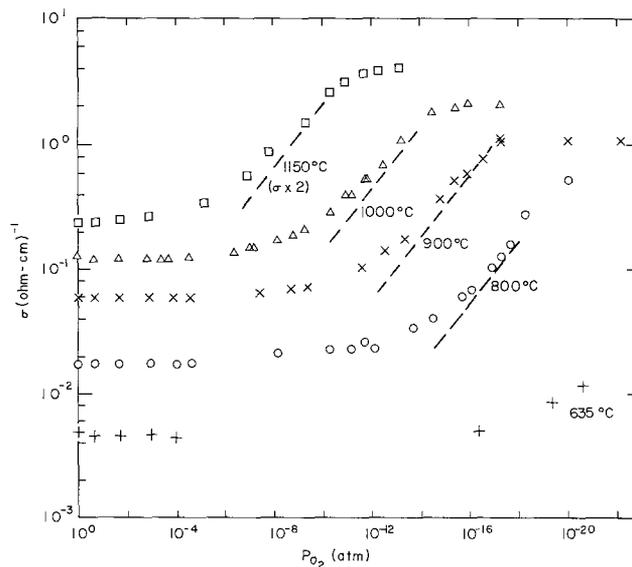


Fig. 2. Electrical conductivity as a function of  $p_{\text{O}_2}$  for a sample of  $(\text{CeO}_2)_{0.95}(\text{Y}_2\text{O}_3)_{0.05}$  at five different temperatures. The dashed lines indicate the electronic component of the conductivity,  $\sigma_e$ .

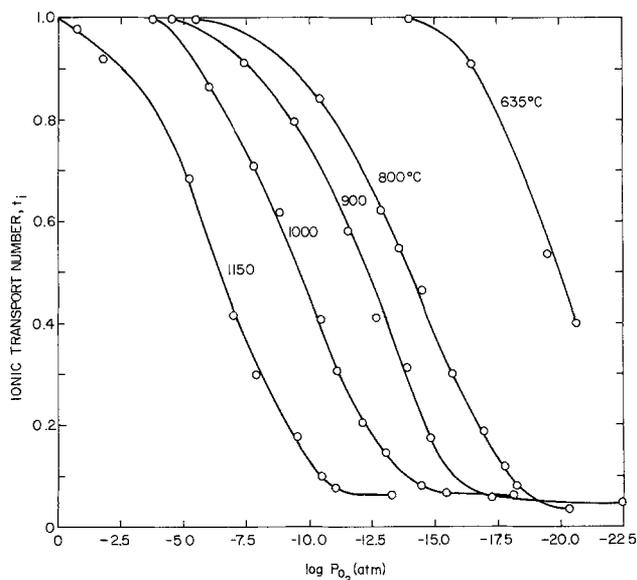


Fig. 3. The ionic transference number,  $t_i$ , as a function of  $p_{O_2}$ , as derived from Fig. 2 for various temperatures.

tained from Fig. 3. When plotted as  $\log p_{O_2}$  vs.  $1/T$  the results fall on a straight line, as shown in Fig. 4 and predicted from Eq. [16]. The same procedure was also followed for the case of  $t_i = 0.9$ . Although the data so obtained from Fig. 3 are less precise than that for the case of  $t_i = 0.5$ , the results shown in Fig. 4 strongly indicate that the domain line for  $t_i = 0.9$  is parallel to that for  $t_i = 0.5$ , as expected from Eq. [16]. Also, while Eq. [16] predicts a shift in intercept of 3.8 decades in  $p_{O_2}$  between these two  $t_i$  values, the actual shift obtained is 4.0. It thus appears that the predictions of Eq. [16] are well confirmed. It therefore seems reasonable to use this equation to extrapolate beyond the range at which  $t_i$  can be directly estimated. In particular, the predicted domain line for  $t_i = 0.99$  is shown as the uppermost line in Fig. 4. The region above this line is then the electrolytic domain for  $(CeO_2)_{0.95}(Y_2O_3)_{0.05}$ . It should be noted that, although this region is small at high temperatures, it increases rapidly with decreasing temperatures, reaching values as low as  $p_{O_2} \sim 10^{-21}$  atm at  $450^\circ C$ .

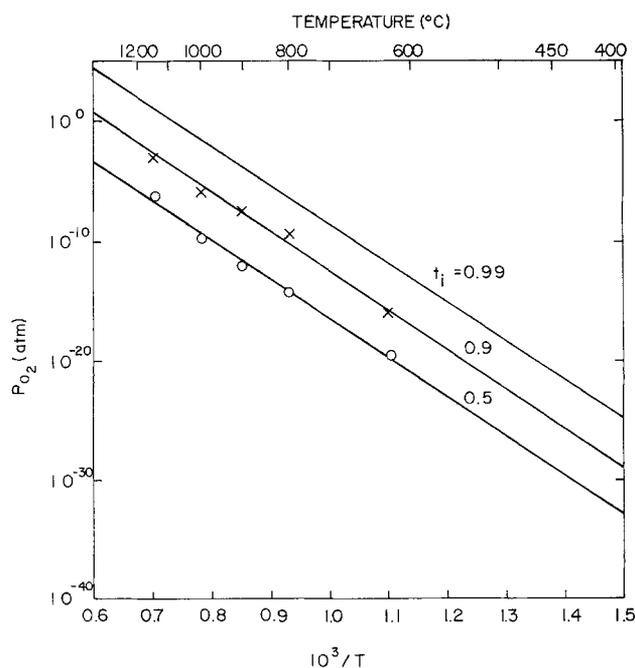


Fig. 4. Curves of  $p_{O_2}$  vs.  $T^{-1}$  at fixed values of  $t_i$  for  $(CeO_2)_{0.95}(Y_2O_3)_{0.05}$ . The upper curve, obtained by extrapolation, marks the boundary of the electrolytic domain ( $t_i \cong 0.99$ ).

In Fig. 2, the points at  $p_{O_2} = 1$  atm do not agree exactly with the data as a function of temperature shown in Fig. 1. It is believed that some of the discrepancies are due to the drastic expansions and contractions of the sample which occurred during the successive cycles of reduction and oxidation which were carried out. (Other samples have even shown evidence of cracking after such repeated cycling.) It is therefore believed that the temperature dependence of  $\sigma$  at a given  $p_{O_2}$  as obtained from Fig. 2 is not nearly as reliable as are the relative values of  $\sigma$  vs.  $p_{O_2}$  at each given temperature.

Aside from the question of the magnitude of  $t_i$ , the other factor that limits the utility of a material as a solid electrolyte is the onset of polarization. This factor usually sets the low temperature limit of usefulness of a given electrolyte. In order to determine at which level of current density significant polarization sets in, the voltage across a  $(CeO_2)_{0.95}(Y_2O_3)_{0.05}$  sample was measured as a function of time when current was applied in steps. Figure 5 shows the results of some of these measurements at  $635^\circ C$ , first when the current is increased in steps of 1 mA and then in steps of 10 mA. The results show no evidence of polarization up to  $I \sim 4$  mA (current density  $\sim 20$  mA/cm<sup>2</sup>). On the other hand, at 10 mA, polarization is apparent. Such polarization behavior suggests the onset of ion blocking. Often the behavior is dependent on the type of electrodes used (17). In the present work, only the platinum paste electrodes (described in the Experimental Methods section) were used.

## Discussion

**Ionic mobility parameters.**—Values of the activation energy  $E_i$  and pre-exponential constant  $C_i$  for the two doped materials studied are given in Table I. The 10% CaO specimen clearly falls in the range where interaction effects are important, as indicated by its composition being at about the value at which a maximum occurs in the plot of  $\sigma$  vs.  $n_M$  (6). Since  $E_i$  increases in the interaction range (10) it is not surprising that  $E_i$  for  $(CeO_2)_{0.9}(CaO)_{0.1}$  is substantially higher than for

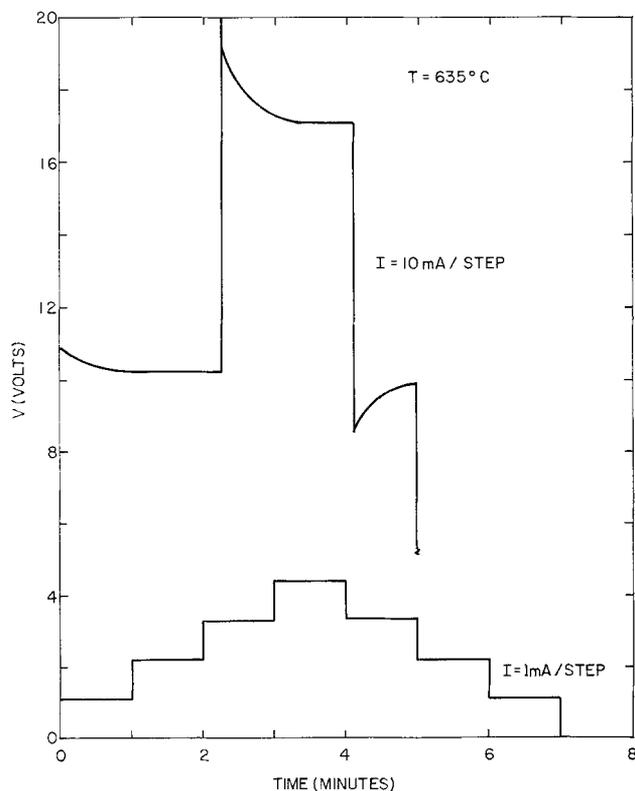


Fig. 5. The d-c potential across a sample of  $(CeO_2)_{0.95}(Y_2O_3)_{0.05}$  at  $635^\circ C$  as a function of time, when the current is applied and removed in steps of 1 or 10 mA.

(CeO<sub>2</sub>)<sub>0.95</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.05</sub>. The latter composition may still fall in the range where interaction effects are small, and it is therefore interesting to compare it to results at still lower concentrations. Data for 1 and 2% CaO are available from Blumenthal *et al.* (6), although the range of temperature covered is smaller, and therefore the precision poorer, than that in the present work. In addition, the activation energies that they reported were obtained from plots of  $\log \sigma$  vs.  $1/T$  instead of  $\log \sigma T$  vs.  $1/T$ , so that the additional correction given by Eq. [7] is required. In this way their "best value" is found to be 0.72 eV. This agrees with the present result of 0.76 eV to within experimental error.<sup>4</sup> Accordingly, we may conclude that (i) interaction effects are relatively small in the 5% Y<sub>2</sub>O<sub>3</sub> specimen,<sup>5</sup> and (ii) the activation energy for migration of V<sub>O</sub><sup>••</sup> in CeO<sub>2</sub> is close to 0.76 eV. This value is lower than the activation energy of about 0.85 eV obtained by Steele and Floyd (19) for oxygen self-diffusion in Y<sub>2</sub>O<sub>3</sub>-doped ceria, as well as the value of 0.86 eV obtained by Lay and Whitmore (20) for dielectric relaxation in CeO<sub>2</sub>:CaO. (The latter represents the activation energy for migration of a vacancy which is associated with a Ca<sup>2+</sup>ce.)

Inserting the value of C<sub>1</sub> for (CeO<sub>2</sub>)<sub>0.95</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.05</sub> into Eq. [6], we obtain for the effective frequency factor  $\nu'$  (defined so as to include the activation entropy term)

$$\nu' = \nu \exp(\Delta S_i/k) = 1.4 \times 10^{13} \text{ sec}^{-1}$$

From this result, and the expectation that the attempt frequency  $\nu$  falls in the mid 10<sup>12</sup> range, we may conclude that the entropy of activation is positive but not very large ( $\Delta S_i/k \sim 0.7$ -1.8).

**Electrolytic domain and polarization.**—In Fig. 4, it was demonstrated that the present method of separating  $\sigma_i$  and  $\sigma_e$  through measurement of  $\sigma$  vs.  $p_{O_2}$  can be used successfully to obtain the electrolytic domain. Equation [16] shows that the slope of the lines in Fig. 4 gives the energy  $\frac{1}{2}\Delta H_1 + E_e - E_i$ . The experimental value obtained is 1.61 eV. Using the values  $E_i = 0.76$  eV from the present work, and  $E_e = 0.3$  eV from Neumin *et al.* (16),<sup>6</sup> we obtain  $\Delta H_1 = 4.2$  eV for the energy of the reaction [9] (see Eq. [10]). The value for the same reaction energy  $\Delta H_1$  obtained in pure CeO<sub>2</sub> (11) is 4.7 eV, thus indicating that  $\Delta H_1$  may have decreased slightly with doping.

As remarked earlier, the domain of primarily electrolytic conduction ( $t_i \geq 0.99$ ) for (CeO<sub>2</sub>)<sub>0.95</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.05</sub>, though small near 800°C broadens rapidly with decreasing temperature. While the widely used calcia-stabilized zirconia (CSZ) has a wider range of electrolytic behavior at elevated temperatures (12) [e.g., down to  $p_{O_2} = 10^{-15}$  atm at 1000°C, as against only  $10^{-2}$  for (CeO<sub>2</sub>)<sub>0.95</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.05</sub>], it is well known (17) that its usefulness is limited by the onset of appreciable polarization below 800°-1000°C, as well as its low conductivity at these temperatures. Such factors limit the applicability of CSZ as a solid oxide electrolyte in a fuel cell to temperatures above 1000°C, and in an oxygen cell to temperatures above 800°C. The material (CeO<sub>2</sub>)<sub>0.95</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.05</sub>, on the other hand, has a conductivity about 10 times larger than CSZ at 900°C (see Fig. 1) and, because of its smaller activation energy, this factor increases to nearly 100 at 600°C. Accordingly, the question of whether doped CeO<sub>2</sub> can be useful as a solid oxide electrolyte, by comparison to CSZ, then centers on whether polarization for CeO<sub>2</sub> is absent to lower temperatures. The results of Fig. 5 provide evidence that this is indeed the case, showing that at 635°C polarization is completely negligible to current densities of 20 mA/cm<sup>2</sup> and higher. Similar results were obtained for CeO<sub>2</sub>:La<sub>2</sub>O<sub>3</sub> by Takahashi *et al.*

<sup>4</sup> For both the 1 and 2% CaO specimens, the plot of Blumenthal *et al.* could indeed have been drawn slightly steeper.

<sup>5</sup> Further evidence in support of this statement comes from comparing  $T$  vs.  $p_{O_2}$  plots at constant  $t_i$  from the present work with data from reference 6 (18).

<sup>6</sup> A similar value for  $E_e$  was also obtained by the present authors for pure CeO<sub>2</sub> (11).

(5), who also found significant polarization for CSZ already at 800°C for current densities less than 1 mA/cm<sup>2</sup>.

Takahashi *et al.* also carried out preliminary measurements using CeO<sub>2</sub>:La<sub>2</sub>O<sub>3</sub> as an electrolyte in a fuel cell at 1000°C and obtained a maximum output of 0.17W. They concluded that the output was limited by the low value of  $t_i$  at that temperature. However, now that the electrolytic domain is established, it is clear that fuel cells utilizing doped ceria as the electrolyte are more likely to be successful at lower temperatures, when operating with fuels which generate oxygen partial pressures within the allowable domain.

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