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Conductivity measurements on ceria at high oxygen pressures

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The a.c. conductivity of high purity ceria has been measured at oxygen pressures and temperatures in the ranges 0.01 to 400 atm and 700 to 1100° C respectively. Similar measurements have been made on impure ceria over the same temperature range for oxygen pressures up to 100 atm. The conductivity isotherms obtained exhibit flattish minima where the ionic contribution to the conductivity is a maximum, a region at low oxygen pressures, where n-type conduction occurs and increases with diminishing pressure, and a high pressure region where p-type conduction occurs and increases with pressure. Activation energies derived for the conductivity minima are 1.55 and 0.85 eV for the high purity and impure ceria respectively; the higher value for the high purity material implies that a significant electronic contribution is present.

1. Introduction

In common with other quadrivalent oxides of the rare earth elements, ceria shows a marked increase in electrical conductivity as the temperature is raised; both ionic and electronic conduction processes are involved, the last being dependent on oxygen pressure. The ionic conduction arises from the movement of O^{2-} ions into anion vacancies which are considered to arise principally from the presence of anion impurities of lower valency than cerium.

Kevane *et al.* [1] found that with high purity ceria at temperatures below about 700° C an isothermal pressure conductivity relation has effectively three regions: a region of oxygen pressures where the conduction is mainly ionic and has little pressure dependence; a region of low pressures where the conduction is electronic (n-type) and increases with diminishing pressure as the CeO_2 becomes increasingly oxygen-deficient; finally, a region at higher pressures near atmospheric where the conductivity increases with oxygen pressure, and is p-type. The n-type conduction has been well studied at temperatures above 1000° C, (see for example [1–6]), but no data appear to be available for the ionic and p-type conduction at the higher temperatures, presumably because of the high oxygen pressures required. Exploration of this field is the basis of the present work which involves conductivity measurements on ceria at oxygen pressures and temperatures in the ranges 0.01 to 400 atm and 700 to 1100° C respectively.

2. Experimental

2.1. Materials

For preparing pellets of high-purity ceria, Specpure CeO_2 powder from Johnson Matthey was used. This material contained less than 100 ppm of other rare earths and yttria, 8 ppm of manganese and 7 ppm of iron. The pellets were made by pressing the powder isostatically at 5×10^7 kg fm^{-2}, heating initially at 1200° C for 8 h, then sintering at ~ 2000° C in air for 8 h. Some pellets of an impure, i.e. technical grade ceria which contained about 0.5% of total impurities were made in a similar manner, but were sintered in air at 1700° C for 24 h. The principle aliovalent cations in this material in ppm were, calcium, 1700; potassium, 250; copper, 100; zinc, 60; lead, 40. The remaining impurities were other rare earths.

All the finished pellets were in the form of circular discs about 13 mm diameter and 3 to 5 mm thick. For use at the highest pressures which necessitated employment of a narrow furnace tube, quadrant-shaped samples were cut from the discs. The average density of the pellets, determined by Archimedes method, was 92 ± 3% of the theoretical density. Platinum contacts were formed on the pellets by coating with platinum paste and firing. Where gold contacts were used, a heavy deposition of the metal was made by vacuum evaporation.

2.2. Apparatus and method

For heating under pressure, an internally heated pressure-vessel was employed, the cast body and lids of which were made of silicon brass (Tungum). The use of non-ferrous metal is preferable, where heating in high pressure oxygen is required because accidental overheating can sometimes cause steel to burn away in the oxygen [7]. A sectional view of the vessel is shown in Fig. 1. Power terminals for the furnace current were of similar design to those shown for introducing the leads for conductance measurements. Thermocouple wires, (Pt–Pt + 13% Rh) were introduced by a device described previously [8]. All the entry devices were mounted radially around the vessel. For pressures below 250 atm, the bore of the Nichrome wound furnace tube was 20 mm, for higher pressures it was reduced to 11 mm to reduce gas turbulence. An earthed platinum liner, (not shown) was fitted inside the furnace tube.

To obtain pressures of oxygen greater than cylinder pressure, a single-stage intensifier, (Pressure Products Limited, type SC 1550) was used. Low partial pressures of oxygen were provided by oxygen–nitrogen mixtures. A Wayne–Kerr Universal Bridge, Type B221 operating at 1592 Hz was used for the conductance measurements.

Temperature was controlled manually within ± 1° C, the conductance at a given pressure becoming constant within the 10 min period required to stabilize the furnace temperature. With thoria and thoria–yttria [9] the time periods necessary to obtain constant conductance values were about 1 to 2 h, which appears to confirm a much slower diffusion rate of oxygen in these materials compared with ceria.

At the end of the high pressure runs the ceria pellets were often found to be cracked around the edges, so that they could only be used once.

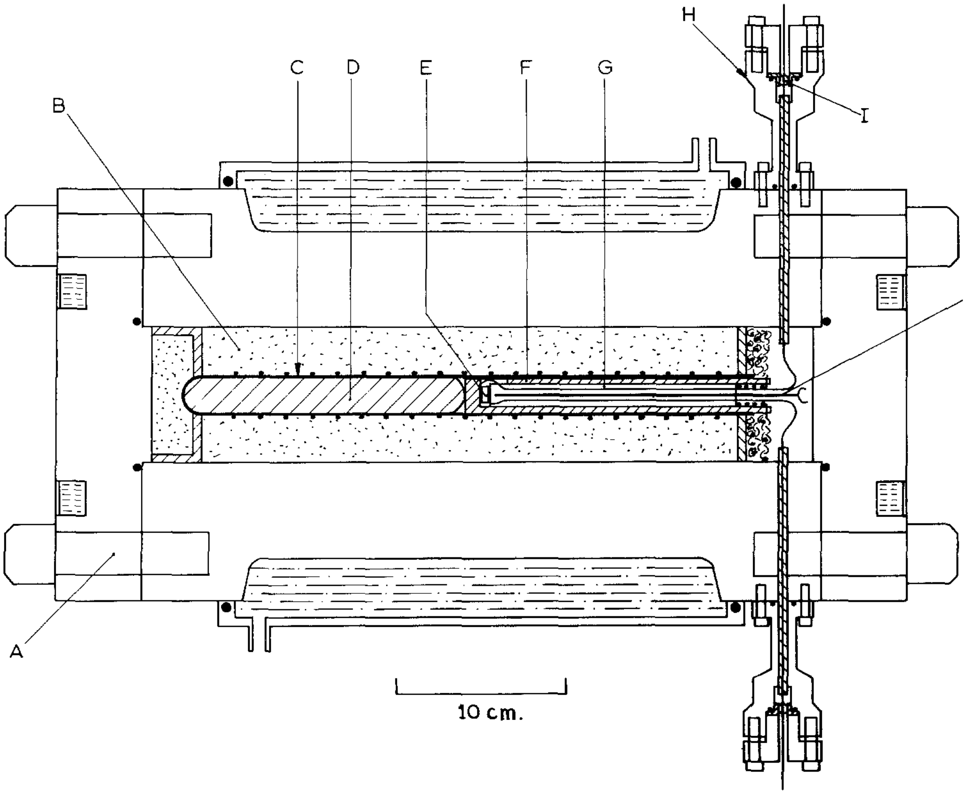

Figure 1 Internally heated pressure vessel with water cooling. A, High tensile bolts (9); B, alumina powder; C, Nichrome-wound furnace; D, alumina block; E, ceria pellet between Pt or Au plates; F, alumina sleeve; G, alumina insulator (spring-loaded); H, phosphor-bronze assembly for electrical leads; I, metal-ceramic seal; J, thermocouple sheath.

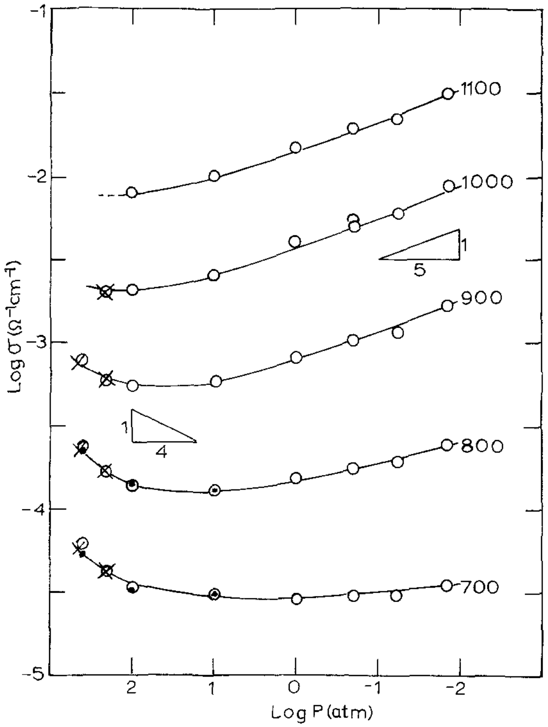

Figure 2 Total a.c. conductivity isotherms for high purity ceria. (o) Pt contacts; (•) Au contacts; (X) fugacities. Temperature (° C).

Although thoria and thoria–yttria have similar coefficients of expansion to ceria, this cracking was not observed with these materials; the reason for this behaviour with ceria is unclear.

3. Results and discussion

3.1. Results of conductivity measurements

Values of the total a.c. conductivity for high-purity ceria in the temperature range 700 to 1100° C at pressures up to 400 atm are shown in Fig. 2. A similar series of plots for the impure ceria at pressures up to 100 atm are shown in Fig. 3. At pressures above 100 atm, non-ideal behaviour of oxygen becomes significant so that the results should be interpreted in terms of the fugacities. The latter have been obtained by graphical integration of the relation

$$\ln \frac{P}{P^1} = -\frac{1}{RT}\int_0^{P^1} \alpha \, dP^1$$

where $\alpha = RT/P^1 - V$ and P^1 is the observed pressure. Values of α, the deviation factor have been derived at each temperature from the pressure–volume data compiled by Vaserman *et al.* [10]. In Fig. 2 the lines at the highest observed pressures have been drawn with respect to the fugacities marked (*X*). It is convenient to use the symbol *P* to represent the pressure at lower observed pressures and the fugacity at the higher pressures.

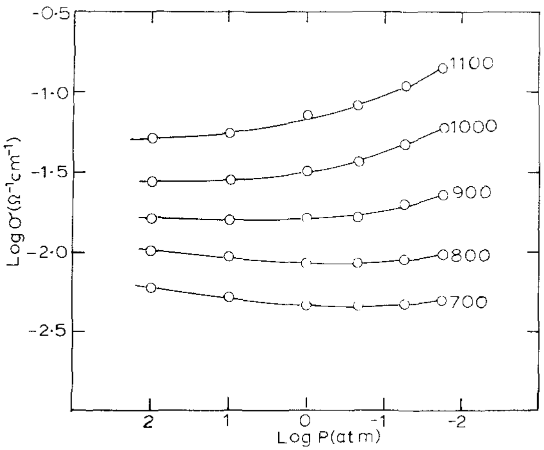

Figure 3 Total a.c. conductivity isotherms for impure ceria with Pt contacts. Temperature (° C).

The results with gold and platinum contacts are similar, which suggests that the electrode–electrolyte interface plays no significant role in the conduction process. The plots show some similarity to those obtained by Kevane *et al.* [1] at lower temperatures and pressures, having flattish minima with conductivity increasing with diminishing pressure as the material becomes increasingly n-type, and increasing with rising pressure (fugacity) as it becomes increasingly p-type. At the conductivity minima, the ionic contributions to σ will be a maximum.

Dissociation of ceria increases with temperature so that the pressure required to bring the conductivity into the plateau region must correspondingly increase with temperature. This accounts for the shift to the left of the minima in Figs. 2 and 3 with increasing temperature.

3.2. The n-type conduction region

In this region the plots for the high purity ceria at the higher temperatures (Fig. 2) show a dependency of conductivity of $P^{-1/5}$. This dependency has been found for undoped ceria to be maintained at pressures down to about 10^{-4} atm, and mechanisms based on generation of charged cerium interstitials and also on formation of anion vacancies have been proposed [3, 5, 6]. In this region where departure from stoichiometry is small, Panlener *et al.* [11] from thermogravimetric studies find that the results rather support a mechanism based on the formation of a doubly ionized oxygen vacancy, i.e. $V_{\mathrm{O}}^{2\cdot}$, but one based on the formation of a quadruply ionized double vacancy, i.e. $(V_{\mathrm{O}}V_{\mathrm{O}})^{4\cdot}$ is not excluded. The difficulty is that a $P^{-1/5}$ dependence of conductivity is not readily rationalized in terms of a single vacancy, but it is in terms of a double vacancy by simple electrical neutrality considerations involving the equilibrium.

$$2\mathrm{O}_{\mathrm{O}} \rightleftharpoons (V_{\mathrm{O}}V_{\mathrm{O}})^{4\cdot} + 4e' + \mathrm{O}_2(\mathrm{g})$$

where e' is the electronic charge.

Since this region has been well studied, it is of less concern here than the high pressure region, but the values of σ at the lowest pressures in Fig. 2 show a fair agreement with those found elsewhere for undoped ceria.

3.3. Suggested p-type conduction mechanisms

For the high-purity ceria, positive holes ($\oplus$) could be generated by the formation of negatively charged vacancies of the type $V_{\mathrm{Ce}}^{\nu'}$ and lattice oxygen (O_{O}), where ν is the number of charges. The equilibrium would, therefore, be

$$\mathrm{O}_2(\mathrm{g}) \rightleftharpoons 2\mathrm{O}_{\mathrm{O}} + V_{\mathrm{Ce}}^{\nu'} + \nu\oplus \qquad (1)$$

where $K = [\mathrm{O}_{\mathrm{O}}]^2[V_{\mathrm{Ce}}^{\nu'}][\oplus]^{\nu}/P$

for electrical neutrality $[V_{\mathrm{Ce}}^{\nu'}] = [\oplus]/\nu$ so that

$$K = \frac{[\mathrm{O}_{\mathrm{O}}]^2[\oplus]^{\nu+1}}{\nu P}\,.$$

Since $[\mathrm{O}_{\mathrm{O}}]$ embraces all the structural oxygen sites, it can be considered constant, so that assuming the mobilities to be independent of temperature, then

$$\sigma \propto [\oplus] \propto P^{1/(\nu+1)}\,.$$

Powers of P ranging from $\frac{1}{5}$ to $\frac{1}{2}$ would theoretically be possible.

With impure ceria, the presence of low valency cations, means that there will be significant amounts of anion vacancies at the higher fugacities so that positive holes could be produced by a vacancy-filling process such as

$$\tfrac{1}{2}\mathrm{O}_2(\mathrm{g}) + V_{\mathrm{O}}^{2\cdot} \rightleftharpoons \mathrm{O}_{\mathrm{O}} + 2\oplus \qquad (2)$$

where

$$K = \frac{[\mathrm{O}_{\mathrm{O}}][\oplus]^2}{P^{\frac{1}{2}}[V_{\mathrm{O}}^{2\cdot}]}$$

$[\mathrm{O}_{\mathrm{O}}]$ can be considered constant and $[V_{\mathrm{O}}^{2\cdot}]$ will be fairly large so that it can be regarded as effectively constant. Again assuming the hole mobilities to be independent of temperature then

$$\sigma \propto [\oplus] \propto P^{\frac{1}{4}}.$$

At the highest fugacities a proportionality of σ to $P^{\frac{1}{4}}$ would theoretically be exhibited.

At the highest fugacity of 440 atm (corresponding to an observed pressure of about 400 atm), the conductivity at the lower temperatures in Fig. 2 shows an approximate proportionality to $P^{\frac{1}{4}}$; at higher fugacities a higher power of P might be found. At the higher temperatures, much higher fugacities would be required to resolve the p-type conduction properly. The flattening of the plots for the impure ceria in Fig. 3 resulting from a greater ionic contribution, indicates that with heavily doped ceria, any p-type conduction might be difficult to observe.

Conductivity measurements only give a guide to the possible mechanisms involved, but it is reasonable to attribute the p-type conduction in impure or doped ceria mainly to vacancy filling mechanisms such as Reaction 2, whilst in high purity ceria where anion vacancies will be few at the higher fugacities, the p-type conduction can be attributed mainly to generation of charged vacancies of the type $V_{\mathrm{Ce}}^{\nu'}$ as in Reaction 1.

At an oxygen fugacity of about 500 atm, thoria containing small amounts of yttria exhibits a p-type dependence of $\sigma \propto P^{\frac{1}{2}}$, and with thoria itself this proportionality is also neared [9]. It is unlikely that with further increases in pressure, higher dependencies of P would be obtained. At pressures above ~ 1000 atm, the fugacities become markedly greater than the pressures, also there is clearly a limit, particularly in the case of thoria itself, to the amount of oxygen that can be absorbed, so that the slope of the log conductivity–log fugacity plot would be expected subsequently to diminish. It is reasonable to suppose that the high-purity ceria would also show this behaviour at very high fugacities.

3.4. Determination of activation energies

In Fig. 4 are plotted values of log σ as a function of $1/T$ for the conductivity minima in Figs. 2 and 3. At the conductivity minima, the contribution of the ionic conductivity σ_{i} to the total conductivity σ, will be a maximum, but evaluation of the contribution requires emf data to yield values of

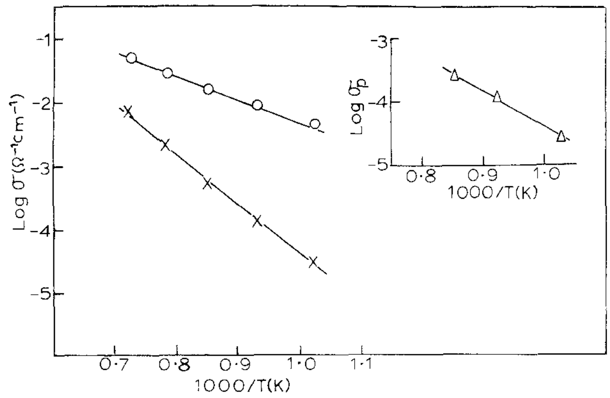

Figure 4 Conductivity-temperature relations. At conductivity minima: (○) impure ceria; (X) high purity ceria. Hole conductivity in high purity ceria, (△).

the anion transport number t_i, where $t_i = \sigma_i/\sigma$; such data are not available for the high pressure region.

For the impure ceria with its high aliovalent cation content, it is reasonable to assume that at the conductivity minima, $t_i \sim 1$, so that the corresponding plot in Fig. 4 is effectively log σ_i as a function of $1/T$; from its slope a value for the ionic activation energy E_i, of 0.85 eV, is obtained.

The data collected by Steele and Floyd [6] and the work of Tuller and Nowick [12] on ceria highly doped with calcium, show that, as expected, the conductivity rises with calcium content, but the value of E_i remains at about 0.9 eV. For the impure ceria used here in which the main impurity is calcium, the conductivity values and value of E_i are in reasonable accord with these authors' findings.

For the high-purity ceria, the plot, although quite linear, yields a higher value for the activation energy of 1.55 eV. At very low concentrations of anion vacancies, the restricted number of paths available for ionic transport might lead to a higher energy of activation, but a significant electronic contribution to the conduction which increases with temperature is a more likely factor. Without t_i data for the conductivity minima, the electronic contribution cannot be determined. Van Handel and Blumental [13] have obtained t_i values for undoped ceria at oxygen pressures less than 1 atm, but unfortunately, lengthy extrapolation of their data into the high pressure region introduces too many uncertainties to be of use; also their ceria was of much lower purity than that used here.

In the p-type conduction region, the total conductivity can be expressed as

$$\sigma = \sigma_i + \sigma_p \tag{3}$$

where σ_p is the conductivity due to positive holes. When there are well defined ionic plateaux where the conductivity is effectively independent of oxygen fugacity and t_i can be taken as unity, extrapolation of the σ_i values into the p-type region yields σ_p values from Equation 3 with a fair degree of certainty [9]. This naturally assumes that any vacancy filling does not significantly reduce σ_i as the oxygen fugacity is increased. In any case, the uncertain error associated with this effect becomes less important at the higher fugacities owing to σ_i being a small fraction of σ.

The case here with the high purity ceria is more difficult because at the highest fugacity of 440 atm, only the values at the three lower temperatures are amenable to treatment. Also, at the corresponding conductivity minima, some electronic conduction appears to be present. Although any n-type conduction would be expected to diminish as the p-type region is entered, nevertheless the best compromise seems to be, to regard the values of σ at the minima as being roughly "fixed contributions" and to subtract them from the values at 440 atm to obtain at least a measure of the fugacity-dependent hole conductivities. Values of σ_p thus obtained are plotted as a function of temperature in Fig. 4, and yield a value for the apparent activation energy E_p of $\sim$ 1.1 eV. Although this value is of uncertain accuracy, it is about the same as the value of E_p for hole conduction in thoria [9], namely 1.2 eV.

Clearly any improvement on the above approximate treatments cannot be made until ionic transport data are available for the high pressure region.

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