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Oxygen semipermeability and electronic conductivity in calcia-stabilized zirconia

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The oxygen semipermeability of calcia-stabilized zirconia tubes has been studied up to 2073 K, by determination of the oxygen flow through the electrolyte tube and it is found to be in good agreement with the theoretical expression for the oxygen electrochemical transport in these materials. The parameter $p\ominus$, at which the ionic transference number is equal to 0.5, has been deduced from the oxygen permeability measurements and is compared with different results obtained by various techniques.

1. Introduction

Stabilized zirconias belong to the group of good oxygen ion conductors and may be used in electrochemical cells to perform oxygen titration, for instance in liquid steel [1]. However, at high temperature and low oxygen activities, these materials are characterized by a mixed conductivity, both ionic and electronic in nature, that is responsible for deviations from the ideal behaviour of a purely anionic sensor. At very low oxygen activities, the e.m.f. of the cell is lowered since the ionic transference number becomes smaller than unity [2], but even under moderately reducing conditions, electrochemical semipermeability of the electrolyte may also result in electrode polarization that affects the response of the cell [2].

In a recent work [3], we attempted to use the semipermeability process to produce hydrogen from thermal dissociation of water. Basically, oxygen arising from the thermal dissociation is allowed to diffuse *in situ* through a stabilized zirconia membrane under the driving force of a gradient in the oxygen chemical potential, without any need of external electrodes. The amount of collected hydrogen can be directly related, up to very high temperature, to the electrochemical transport inside the solid material, thus making this technique suitable for the determination of the partial electronic conductivity of the solid electrolyte. The purpose of this paper is to describe and discuss results obtained with such an arrangement.

2. Equation of electrochemical transport in stabilized zirconia

The partial current density, j_k, connected with the flow of particles k, may be derived from the general equations describing the diffusion of a mobile species k through an electrolyte located in a chemical potential gradient. It is given by the following relationship [4]:

$$j_k = -\frac{\sigma_k}{Z_k q}\nabla\eta_k \qquad (1)$$

where σ_k is the partial conductivity associated with particles k, Z_k their valency, q the electron charge and $\nabla\eta_k$ the gradient in the electrochemical potential.

In the case of stabilized zirconia at high temperature, both electron and O^{2-} ion displacements may contribute to the electrochemical transport [5]. The total current density, j_t, is then the sum of the electronic j_e and the ionic $j_{O^{2-}}$ partial currents. On applying Equation 1, it follows:

$$j_t = \frac{\sigma_e}{q}\nabla\eta_e + \frac{\sigma_i}{2q}\nabla\eta_{O^{2-}}, \qquad (2)$$

where σ_i and σ_e are the partial anionic and electronic conductivities and where $\nabla\eta_e$ and $\nabla\eta_{O^{2-}}$ denote the electrochemical potential gradients relative to electrons and O^{2-} ions.

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It is more expedient to relate j_t to the chemical potential of oxygen, μ_{O_2}, on assuming that the thermodynamic equilibrium between electrons and O^{2-} ions remains locally undisturbed by the partial current flows:

$$O^{2-} \rightleftharpoons 1/2\,O_2 + 2\,e^-.$$

Then, it may be shown that the total current j_t may be rewritten as [6]:

$$j_t = \frac{\sigma_t}{q}\nabla\eta_e + \frac{\sigma_i}{4q}\nabla\mu_{O_2}, \qquad (3)$$

where σ_t is the total conductivity ($\sigma_t = \sigma_i + \sigma_e$).

The gradient of oxygen chemical potential $\nabla\mu_{O_2}$ may be ensured in intercalating a stabilized zirconia sample between two regions where the oxygen partial pressures are kept constant (Fig. 1). Without any external electrical contacts between the two boundaries of the sample, which are assumed to be in equilibrium with the respective oxygen partial pressures, $p_{O_2,I}$ and $p_{O_2,II}$, the local total current, j_t, is zero under stationary conditions. The partial current densities j_e and $j_{O^{2-}}$ are deduced from Equation 3 under the condition $j_t = 0$:

$$j_{O^{2-}} = -j_e = \frac{\sigma_e}{4q}\, t_i\, \nabla\mu_{O_2}, \qquad (4)$$

where t_i denotes the ionic transference number ($t_i = \sigma_i/\sigma_t$).

As shown by various authors [5, 7], in large ranges of temperature and oxygen partial pressure, the anionic conductivity for stabilized zirconia remains much higher than the electronic one and the ionic transference number is close to unity. Moreover, for small values of oxygen partial pressure, any contribution of electron holes may be reasonably neglected and the electronic conductivity is given by [8]:

$$\sigma_e = \sigma_e^0 \exp\left(-\Delta E_e/kT\right) p_{O_2}^{-1/4}, \qquad (5)$$

where σ_e^0 is a constant and ΔE_e the corresponding activation energy. ΔE_e is generally reported to amount to ~ 4 eV in the case of calcia-stabilized zirconia [8].

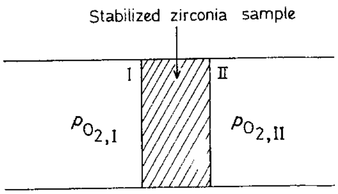

Figure 1 Schematic illustration of a stabilized zirconia membrane located in a gradient of oxygen chemical potential.

Inserting these conditions into Equation 4, it follows that:

$$j_{O^{2-}} = \frac{\sigma_e^0}{4q} \exp\left(-\Delta E_e/kT\right) p_{O_2}^{-1/4} \nabla\mu_{O_2}.$$

Integration over the sample thickness l, between the boundaries of the zirconia wall, yields:

$$J_{O^{2-}} = \frac{kT}{ql}\,\sigma_e^0 \exp\left(-\Delta E_e/kT\right) \times \left[p_{O_2,II}^{-1/4} - p_{O_2,I}^{-1/4}\right].$$

The flow J_{O_2}, expressed in terms of oxygen mole units, is then derived from $J_{O^{2-}}$, which denotes a flow of electrical charges, by:

$$J_{O_2} = \frac{J_{O^{2-}}}{4F},$$

where F is the Farady's constant, so that finally:

$$J_{O_2}\ (\text{mol cm}^{-2}\,\text{sec}^{-1}) = \frac{kT}{4qFl}\,\sigma_e^0 \exp\left(-\Delta E_e/kT\right) \times \left[p_{O_2,II}^{-1/4} - p_{O_2,I}^{-1/4}\right]. \qquad (6)$$

3. Experimental procedure

The schematic arrangement of the experimental apparatus is depicted in Fig. 2. A stabilized zirconia membrane, which consists of a closed-ended tube of calcia-stabilized zirconia, with a chemical composition $0.9\,ZrO_2$–$0.1\,CaO$, is located in a laboratory-built high-temperature furnace [9]. The latter, in which the heating elements are made of partially stabilized zirconia, allows the zirconia membrane to be heated up to 2100 K.

Water is injected into the zirconia tube, in compartment I, as vapour diluted in argon purified from traces of oxygen, the flow-rate of which is 3.4 litre h^{-1}. The steam partial pressure in argon is 0.2 atm. The oxygen partial pressure in the inner part of the zirconia tube, $p_{O_2,I}$ is related to the water dissociation equilibrium occurring at high temperature, according to:

$$H_2O \rightleftharpoons H_2 + 1/2\,O_2.$$

Without any oxygen transfer through the membrane, the value of $p_{O_2,I}$ should be given by the following expression:

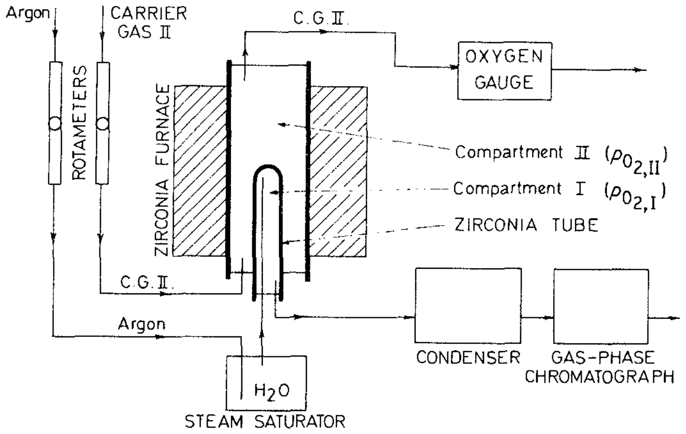

Figure 2 Schematic illustration of the arrangement of the experimental apparatus.

$$p_{O_{2,I}} = K^2 p^2_{H_2O} p^{-2}_{H_2}, \qquad (7)$$

where K is the equilibrium constant for steam dissociation and p_{H_2O} and p_{H_2} are the water and hydrogen partial pressures in compartment I.

Compartment II of the reaction cell is fed with an equimolar CO–CO$_2$ mixture with a flow-rate of 18.5 litre h^{-1}. The buffer capacity of this mixture is large enough to preserve in this chamber an oxygen partial pressure $p_{O_{2,II}}$ lower than $p_{O_{2,I}}$. The oxygen pressure gradient thus produced allows the oxygen arising from the steam decomposition to diffuse through the zirconia wall. The resulting oxygen flow can be measured by means of an oxygen gauge. However, it can be also checked with a better accuracy by determining the amount of hydrogen evolved from compartment I with the aid of a gas-phase chromatograph. Owing to stoichiometric considerations, under stationary conditions, the hydrogen flow, D_{H_2}, evolved from the reactor is twice the oxygen flow, D_{O_2}, through the effective permeation area, S, of the zirconia tube:

$$D_{H_2} = 2D_{O_2} = 2J_{O_2}S, \qquad (8)$$

where S in the present conditions amounts approximately to 20 cm^2 [10].

4. Results and discussion

The hydrogen flow D_{H_2} at the gas outlet of compartment I has been measured as a function of the cell temperature between 1673 and 2073 K. The oxygen pressure $p_{O_{2,I}}$, which is in fact smaller than the value directly fixed by the water dissociation equilibrium (Equation 7), has been calculated by taking the transfer of the oxygen arising from the steam decomposition to compartment II into account. The oxygen pressure, $p_{O_{2,II}}$ is not affected by the oxygen flow through the membrane owing to the high buffer capacity of the CO–CO$_2$ mixture. The deduced values of the semipermeability coefficient, which is defined as the ratio of the oxygen flow D_{O_2} to the difference $[p^{-1/4}_{O_{2,II}} - p^{-1/4}_{O_{2,I}}]$, are plotted on Fig. 3 against the cell temperature T_c.

The temperature dependence of the oxygen semipermeability coefficient obeys an Arrhenius law, the activation energy of which is 4.0 eV. Such

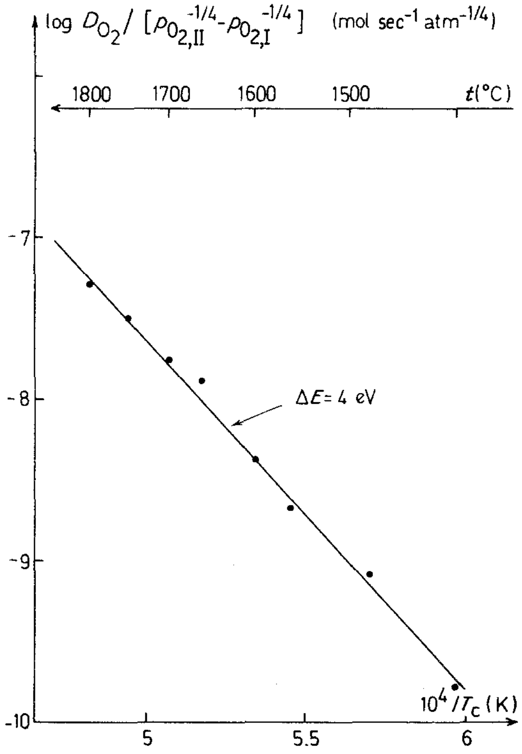

Figure 3 Temperature dependence of the ratio of the oxygen flow D_{O_2} through the zirconia wall to the difference $[p^{-1/4}_{O_{2,II}} - p^{-1/4}_{O_{2,I}}]$.

a value is in good agreement with the published data for the activation energy of electronic conductivity in stabilized zirconia [8]. This result suggests that the thermal variation of the electrochemical semipermeability is indeed controlled by the dependence of electronic conductivity on temperature. Furthermore, it has been shown elsewhere [10] that under isothermal conditions the theoretical dependence of the oxygen flux against $[p_{O_2,II}^{-1/4} - p_{O_2,I}^{-1/4}]$, predicted by Equation 6, is well observed. Thus it was attempted to use such an experiment to determine the partial electronic conductivity, commonly characterized at a given temperature by an oxygen partial pressure $p\Theta$, at which n-type electronic conductivity and ionic conductivity become virtually equal. So that for $p_{O_2} = p\Theta$:

$$\sigma_i = \sigma_e^0 \exp\left(-\Delta E_e/kT\right) p\Theta^{-1/4}. \tag{9}$$

Moreover, in a very large range of oxygen partial pressure, the ionic conductivity for stabilized zirconias does not depend on the oxygen activity [4]. In the oxygen pressure range of interest the ionic transference number is close to unity and the ionic conductivity may be confused, in a first approximation, with the total conductivity σ_t. Equation 6 is then rewritten as:

$$J_{O_2} = \frac{kT}{4qFl}\sigma_t p\Theta^{1/4}\left[p_{O_2,II}^{-1/4} - p_{O_2,I}^{-1/4}\right]. \tag{10}$$

The total conductivity of a sample cut from the zirconia tube has been measured by a standard four-probe d.c. method (Fig. 4). The values of the parameter $p\Theta$ calculated from Equation 10 are plotted as a function of temperature on Fig. 5, with the results of other authors [7, 11–13], who used diversified techniques on samples of calcia-stabilized zirconias with different nominal compositions. Janke and Fischer [7] deduced $p\Theta$ from a modified polarization technique on a material containing 14 mol% CaO, while Scaife *et al.* used coulometric titration on samples with dope contents ranging from 13.1 to 16.6 mol% [12]. Etsell and Flengas [11] also used coulometric titration at lower temperatures on tubes with a calcia content of 10 mol%, and more recently Iwase and Mori [13] determined the oxygen semipermeability of zirconia tubes containing 12 mol% CaO.

Similar trends are found for the various sets of data (Fig. 5), that show general agreement. However, some discrepancies are observed, since at a given temperature, points are distributed over two decades of magnitude for the oxygen partial pressure. In the temperature range investigated by Etsell and Flengas, the concentration of 10 mol% CaO may be too low to achieve complete stabilization of zirconia under the cubic form [14], and this could explain higher $p\Theta$ values owing to the probable presence of a tetragonal phase with a higher electronic conductivity. For other works, according to the phase diagram proposed by Stubican and Ray [14], all the compositions should fall in the cubic-phase field and discrepancies should be looked for elsewhere. Apart from experimental errors, some disagreements may arise from differences in (i) nominal composition, (ii) impurity content, (iii) techniques and derivations of $p\Theta$. As pointed out by Scaife and co-workers, the dependence of $p\Theta$ on the stabilizer content is expected to be small and dispersion of results on samples with variable composition is of the same order of magnitude as the dispersion of repetitive measurements on samples with compositions which are *a priori* similar. It is therefore not possible at the present time to conclude the

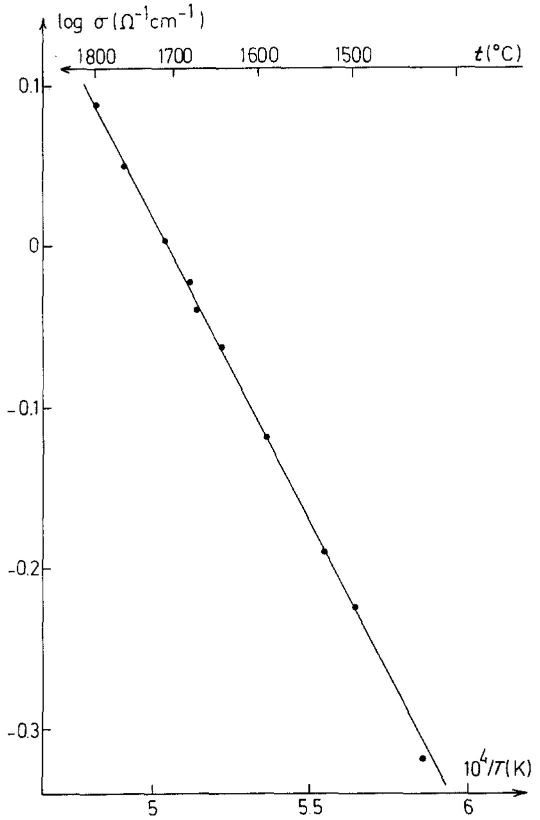

Figure 4 Electrical conductivity in air of the calcia-stabilized zirconia tube.

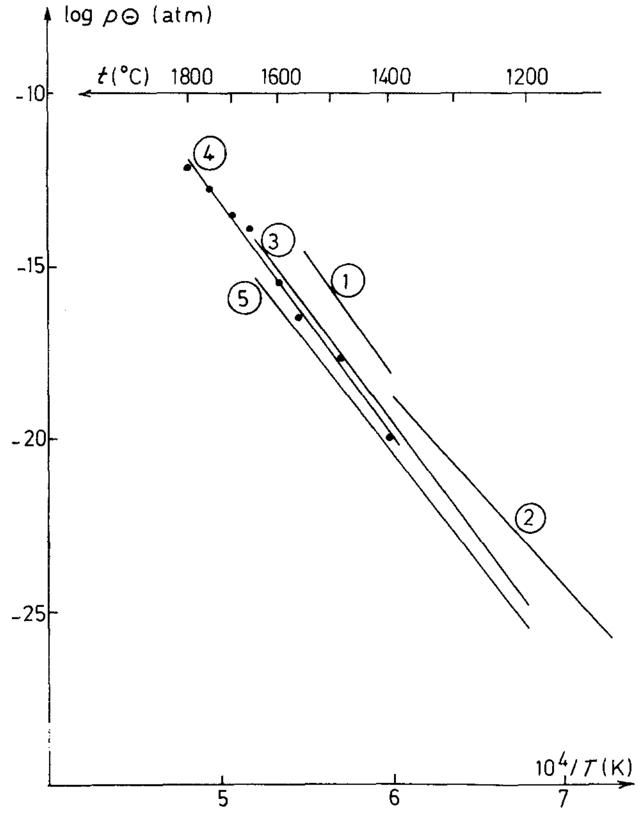

Figure 5 Variation of the oxygen partial pressure $p\Theta$ against temperature. Results of: (1) Iwase and Mori [13]; (2) Etsell and Flengas [11]; (3) Janke and Fischer [7]; (4) our results; (5) Scaife *et al.* [12].

exact role of the dope content. Influence of impurities is also often invoked to explain discrepancies between authors [13], but no explicit model is available to account for such an effect. It is worthwhile finally to mention that, in spite of a careful characterization, the results arrived at on the basis of various approaches need not be in good agreement, since the derivations of $p\Theta$ lie on assumptions that are different. For instance, the polarization technique involves e.m.f. measurements, the interpretation of which rests on the assumptions suggested by Schmalzried [15]. According to this author, the e.m.f. E of a concentration cell reads:

$$E = \frac{RT}{F}\ln\frac{p\Theta^{1/4}+p_{O_2,II}^{1/4}}{p\Theta^{1/4}+p_{O_2,I}^{1/4}}. \qquad (11)$$

As a matter of fact, Equation 11 is appropriate only in the case of a small electronic concentration, to which the Henry's law of ideal dilute solutions may be applied [16]. But significant departures from the Nernst law, obtained by putting $p\Theta = 0$ in Equation 11 are likely to be observed only when the electronic concentration is large enough to make this hypothesis not strictly valid. In such a case, the results are expected to be different from ours, since $p\Theta$ was here defined as the oxygen partial pressure where extrapolations of $p_{O_2}^{-1/4}$, dependent electronic conductivity and constant ionic conductivity as actually observed under less reducing conditions, intersect.

It is then difficult to conclude the respective advantages of the techniques mentioned. Let us only emphasize that no electrodes are needed in permeation experiments and that $p\Theta$ can be measured easily up to 2073 K without any specific limitation other than the measurement of the ionic or total conductivity itself under an oxidizing atmosphere.

5. Conclusion

Oxygen semipermeability measurements developed here allowed an estimation of the parameter $p\Theta$ for a calcia-stabilized zirconia material up to 2073 K. The results are in fair agreement with other data published in the literature that were obtained by other techniques at lower temperatures. A practical application of the method described in this paper is to reach the partial electronic conductivity in oxygen ion conductors under severe temperature conditions, and also to determine the parameter $p\Theta$ in mixed conductors for which e.m.f. measurements are rather inaccurate, owing to some polarization phenomena attributable to oxygen transfer through the electrolyte.

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