Journal of the European Ceramic Society **19** (1999) 807–810

PII: S0955-2219(98)00320-3
0955-2219/99/$ - see front matter

Electron Hole Conductivity of Gadolinia Doped Ceria

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Abstract

The electron hole conductivity of gadolinia doped ceria (GCO) was estimated from electrochemical permeability measurements, at temperatures in the range of 800 to 1000°C. The transient behaviour of the cell (while recovering from reducing to oxidising conditions) was used to assess the accuracy of the experimental procedure, and some of these results still suggested the presence of leaks in the sealings. However, the temperature dependence of steady state results indicates that electrochemical permeability prevails, and these results were thus used to estimate the hole conductivity. These results showed that the hole conductivity of GCO at 1000°C is about two orders of magnitude higher than reported for yttria stabilized zirconia, and the activation energy (129 kJmol^{-1}) is slightly lower. © 1999 Elsevier Science Limited. All rights reserved

Keywords: electromechanical permeability, electrical properties, electrical conductivity, CeO_2, fuel cells.

1 Introduction

Gadolinia doped ceria (GCO) is considered to be one interesting alternative to yttria stabilised zirconia electrolytes (YSZ) for applications at intermediate temperature (800°C or lower). Several studies demonstrated the superior ionic conductivity of GCO with respect to YSZ, and the activation energy is lower.[1,2] GCO is thus more promising for current carrying devices operating at lower temperatures.

The main drawback of GCO is related to the onset of electronic conduction at low oxygen partial pressures (Po_2).[3] This electronic contribution will lower the open circuit electromotive force (emf) of the cell, yielding a decrease in the nernstian efficiency. Significant amount of work was thus dedicated to studying the lower limit of the electrolytic domain of these electrolytes. The p-type conductivity is poorly known but may still play a significant effect on the cell oxygen permeability under open circuit conditions. Furthermore, the hole conductivity may determine the electrolyte/electrolyte interfacial conditions (Po_2) in the case of cells with double-layer electrolytes.[4]

The evaluation of electronic conductivities of solid electrolytes can be made by a variety of dc techniques such as emf, ion blocking and electrochemical permeability measurements.[5] However, the use of these techniques is far from trivial due to a requirement of a gas tight sealing which must be stable at high temperature, and compatible with the materials being studied. Otherwise, the interpretation of results may be misleading. Noble metals (e.g., Au) have been used for this purpose but they are also a pathway for the transport of electrons, and local short circuit conditions cannot be avoided.[6] Glass seals have low ionic and electronic conductivities, but reaction with many materials may be a serious drawback.

A simple device for oxygen permeability measurements was presented in a previous work;[7] this consisted of a closed chamber with two electrochemically active components. The authors discussed the experimental constraints associated with leaks in the seals, and suggested criteria for validating the experimental procedure, based on a careful analysis of the cell steady state behaviour and transient response. This technique was now used to estimate the p-type conductivity of GCO.

2 Experimental

GCO and YSZ disks were prepared from commercially available powders (GCO with 20 mol% Gd_2O_3 from SSC, Inc., and YSZ with 8 mol% Y_2O_3 from Tosoh, respectively). The powders were uniaxially pressed and the resulting disks were fired at 1500°C for 2 h. The sintered materials were all inspected by SEM to check for the presence of open porosity, and the density was also evaluated from measurements of weight and dimension. The samples used in this work were at least 93% dense.

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The experimental set-up is shown in Fig. 1. The cell includes one CSZ tube (from Degussa) covered by two disks (YSZ and GCO). The CSZ electroded tube was used to pump the oxygen from the cell chamber and the electroded YSZ disk to monitor the Po_2 inside this chamber. One d.c. source and one multimeter were used to drive the oxygen pump and to monitor the current flowing through the pump and the sensor emf. The system was sealed with Pyrex 'O' rings.

The relation between the steady state current flowing through the pump, and the sensor open circuit emf were used to estimate the electrochemical permeability of GCO in the range 850 to 1000°C. After reaching a sensor voltage in the order of 200 mV, the pump was deactivated and the transient response of the cell was recorded in closed circuit conditions. This transient recovery was used to detect significant leaks in the seals.

3 Steady State Behavior

When the cell (Fig. 1) attains steady state the current supplied to the CSZ pump (I_{pump}) must be balanced by the electrochemical permeability of the GCO disk, J_p:

$$S_{GCO}.J_p = I_{pump} \qquad (1a)$$

where S_{GCO} is the surface area of the GCO sample. The permeability of the YSZ sensor is presumably much lower than J_p. Gas leaks are also neglected, and the detection of gas leaks is thus crucial for the proper use of this technique.

In oxidising conditions the hole conductivity must prevail over the n-type electron conductivity, but must still remain much lower than the ionic conductivity. In this case, $J_{p,}$ reduces to:

$$J_p = (RT/FL_{GCO})\cdot\sigma_p^0\cdot(P_1^{1/4} - P_2^{1/4}). \qquad (2a)$$

where σ_p^0 is the p-type electronic conductivity of GCO at unit Po_2, L_{GCO} is the thickness, $P_1 = 0{\cdot}21$ atm is the reference Po_2, and P_2 the Po_2 inside the chamber. R, T and F have their usual meaning.

The ionic and n-type conductivities have been evaluated by alternative techniques,[3] and those results may be used for a suitable correction. For example, on introducing the n-type conductivity one expects:

$$J_p = (RT/FL_{GCO})\cdot[\sigma_p^0\cdot(P_1^{1/4} - P_2^{1/4}) + \sigma_n^0\cdot P_2^{-1/4}] \qquad (2b)$$

where σ_n^o is the n-type electronic conductivity of GCO at unit Po_2. In addition, the accuracy of eqn (2a) may be affected by overpotentials (caused by slow surface reactions), but these terms are much more difficult to evaluate.[8]

When leaks do occur, the mass balance is no longer described by eqn (1a), and an additional leak current I_{leak} must be considered:

$$I_{leak} + J_p\cdot S_{GCO} = I_{pump} \qquad (1b)$$

The leak current is related to an oxygen gas phase flux through the leaks, $I_{leak} = \mathrm{Flux}/(4F)$, and its temperature dependence should thus be determined by the diffusion coefficient of oxygen in the gas phase. This dependence is very weak. On the contrary, the hole conductivity is thermally activated, and the activation energy of the electrochemical permeability should be identical to that expected for σ_p^0. The temperature dependence of the current (for a given Po_2 gradient) is thus a strong indication of the quality of the sealings.

Figure 2 shows the ionic current crossing the electrochemical pump plotted as a function of the oxygen pressure inside the cell. These results show an important temperature dependence which can be interpreted as a result of the thermally activated σ_p^0, rather than a negligible temperature dependence expected for gas phase diffusion; this suggests that the

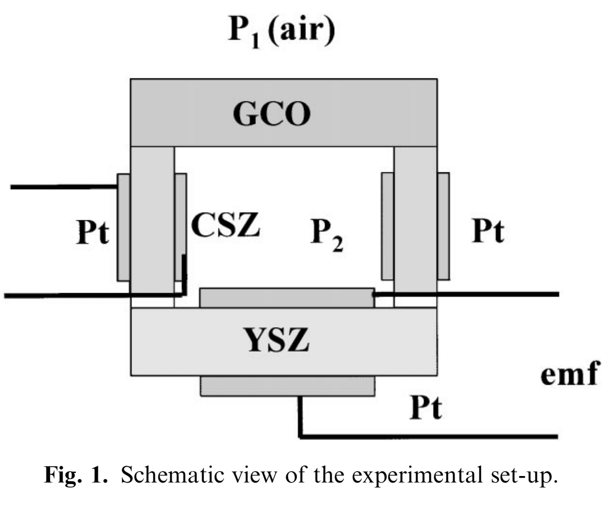

Fig. 1. Schematic view of the experimental set-up.

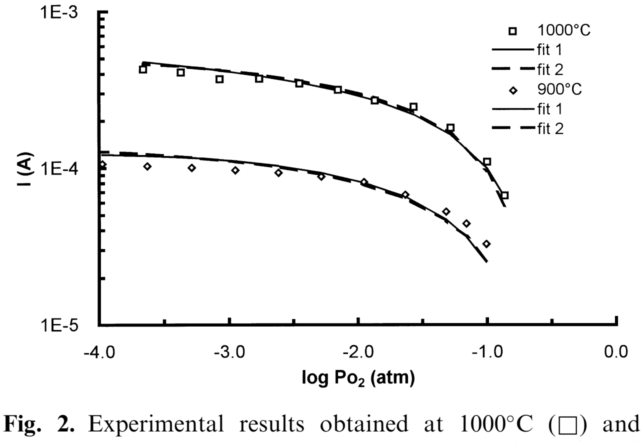

Fig. 2. Experimental results obtained at 1000°C (□) and 900°C (◇).The solid line represents eqn (2a) and the dashed line represents eqn (2b).

electrochemical permeability prevails. Equation (2a) was thus used to fit the experimental results (Fig. 2), and to obtain the fitting parameter σ_p^0. The estimates of σ_p^0 are shown in Fig. 3, and the activation energy is about 129 kJ mol^{-1}.

Actually, the fitting obtained for some of the data shown in Fig. 2 is somewhat poor, and an alternative fitting was attempted by adding the n-type conductivity [eqn (2b)]. However, the differences between eqns (2a) and (2b) are negligible, and do not contribute to improve the fitting shown in Fig. 2. The differences between the values of σ_p^0 obtained with and without the n-type conductivity are also relatively small (Fig. 3).

Relatively slow surface reactions may contribute to the differences between experimental data and model behaviour. The importance of surface reactions on transport processes involving GCO has been recently addressed by IEDP/SIMS,[9] and these studies indicated that the activation energy for the tracer diffusion coefficient D^* (0·9 eV) is lower than for the surface exchange coefficient (3·3 eV). In this case, the effective driving-force may be significantly lower than measured by the YSZ sensor, and the low temperature data are more likely to be affected by a significant overpotential term. Gas phase concentration overpotentials are less likely to explain the deviations observed at low temperature because the permeability drops with decreasing temperature while the diffusion coefficient in the gas phase remains nearly unchanged.

3.1 Transient behaviour

The transient behaviour was recorded after switching off the pump ($I_{\text{pump}} = 0$). In this case, the cell recovers spontaneously from reducing to oxidising conditions and on inserting the leak current I_{leak} one obtains the mass balance:

$$I_{\text{leak}} + J_p \cdot S_{\text{GCO}} = (4FV/RT)\mathrm{d}P_2/\mathrm{d}t \qquad (3)$$

where V is the volume of the chamber. The transient behaviour may then be useful to detect leaks.

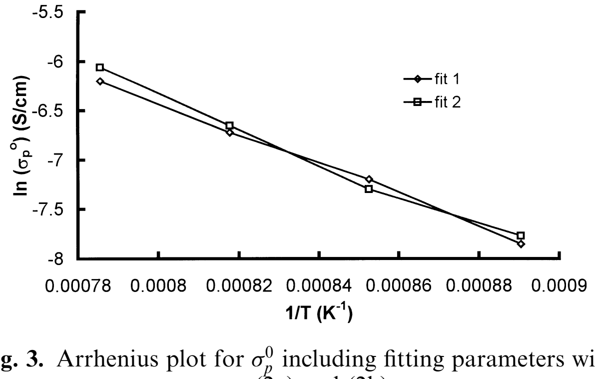

Fig. 3. Arrhenius plot for σ_p^0 including fitting parameters with eqns (2a) and (2b).

Equation (3) can be used to compare the time dependence of P_2 for two limiting cases:[7] (i) when physical leaks dominate over cell permeability; (ii) when the cell permeability dominates over physical leaks. However, these solutions contain a significant number of unknown parameters (e.g. dimensions of the leaks), and may be poorly suited to fit the type of experimental data shown in Fig. 4. It is thus preferable to resort to a reduced time t/t_5, (where t_5 is the time required to reach 5% of the final reading). The corresponding solutions for the limiting cases are shown in Fig. 5.

The experimental data for 850 and 1000°C follow the trend predicted for the true electrochemical permeability but the trend obtained for intermediate temperatures is closer to the solution predicted for the case when residual gas leaks prevail. However, the response times of experiments performed with poor seals are usually in the order of a few minutes, which is much smaller than the time scale in Fig. 4. One may thus assume that the electrochemical permeability plays a major role for response times

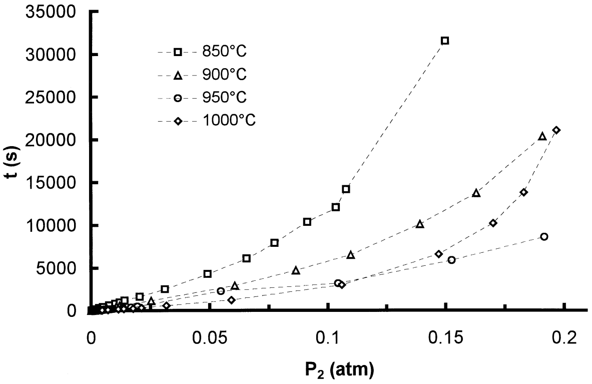

Fig. 4. Transient recovery of P_2 from reducing to oxidising conditions after deactivation of the YSZ pump.

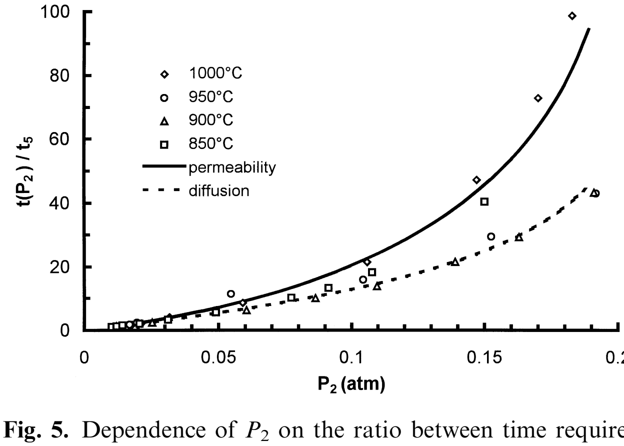

Fig. 5. Dependence of P_2 on the ratio between time required to reach a given P_2 and 5% of the final reading ($t(P_2)t_5$). The solid line represents the limiting solution for behaviour controlled by electrochemical permeability and the dashed line is the correspondent solution for dominant physical leaks.

of a few hours. Nevertheless, one cannot exclude the possibility of small leaks interfering with some of the results, especially when the values of Po_2 approach P_1. In this case minor leaks might still be effective. This is less likely in more reducing conditions because the electrochemical permeability flux varies as $(P_1^{1/14} - P_2^{1/4})$, and the gas phase flux is expected to vary as $P_1 - P_2$. The relative changes in electrochemical permeability should thus be 1:2·8:4·3 for $P_2 = P_1/2$, $P_2 = 0{\cdot}1P_1$ and $P_2 = 0{\cdot}01P_1$, while the changes in the gas leaks reduce to 1:1·8:1·98.

4 Conclusions

A simple set-up was used for the determination of oxygen permeation through GCO, and to evaluate its electron hole conductivity. The temperature dependence of these results ($\approx 1{\cdot}3$ eV), and the transient response were also used to detect leaks in the seals. Slight deviations from a model for the steady state behaviour suggests that slow surface exchange may still play a significant role, and the transient response suggests that minor leaks may affect some results. The values of electron hole conductivity obtained for GCO are about two orders of magnitude higher than reported for YSZ (at 1000°C), and the relative differences may even increase with decreasing temperature.

Acknowledgements

Work performed with financial support from FCT, Portugal (Programme PRAXIS and a grant).

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