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Electronic Transport Properties and Electrically Induced *p–n* Junction in $ZrO_2 + 10$ m/o Y_2O_3

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Through the application of voltages to cubic ZrO_2, stabilized by 10 m/o Y_2O_3, using a nitrogen/Ag and an air/Pt electrode, concentration gradients of the electronic species and *p–n* junctions in the sample have been created. The transient relaxation of the voltage is investigated and is interpreted in terms of the mobilities of both excess and defect electrons between 700 and 900°C. The movement of the *p–n* junction is characterized by a shoulder-type voltage–time relation. At 900°C the mobilities of the electrons and holes are 2.3×10^{-2} and 1.5×10^{-4} cm²/Vsec, respectively. The activation energy of transport is much smaller for the excess electrons than the holes. The electronic conductivities are determined from the steady-state polarization current.

1. Introduction

Since Nernst's investigations in 1899 on the replacement of the carbon filament used at that time as a light source, zirconia doped with several mole percent yttria (or some other lower valent oxides) has been known to exhibit high ionic conductivity at high temperatures (*1*). Later this was determined to be exclusively oxygen ion movement via oxygen vacancies (*2–4*).

In addition to the ionic conductivity, a small contribution from electronic species[1] has been detected. The amount and character of the electronic conductivity is dependent on the equilibrium oxygen partial pressure. The material behaves like an amphoteric semiconductor with respect to the electronic conductivity. At high oxygen partial pressure ($p_{O_2} \gtrsim 10^{-10}$ atm at 900°C) *p*-type conduction occurs while at low oxygen partial pressure *n*-type conductivity ($p_{O_2} \lesssim 10^{-10}$ atm at 900°C) is found (*5–22*).

So long as the ionic conductivity is large compared to the electronic conductivity, the electronic properties may be changed in a simple manner by applying a voltage to the material. Thus, in a purely electrical manner a *p–n* junction may be created by producing a stoichiometry inhomogeneity in the sample. This is another way to create a *p–n* junction besides the known homo- and hetero-junctions.

2. p_{O_2} Dependence of the Electronic Properties

The concentration of electrons and holes is dependent on the defect structure and is variable with the partial pressure of one component, in this case oxygen. By doping zirconia with 10 m/o (mole%) yttria, first the cubic fluorite phase is stabilized to lower temperatures, and second a large number of oxygen vacancies is produced (*3*, *4*). The following equations describe the incorporation of oxygen from the gas phase into the vacancies using defect structure elements:[2]

$$\tfrac{1}{2}O_2(g) + V_O^{\cdot\cdot} = 2h^{\cdot}, \qquad (1)$$

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[1] For brevity, in this paper, the term "electronic" refers to both *n*- and *p*-type carriers.

[2] Defect structure elements (DSE) are the structure elements in the sense of Kröger–Vink (*23–25*) neglecting the regular structure lattice elements of the ideal crystal. In this manner, the elements are independent of each other, and the chemical potentials may be defined for them. The DSE's have the meaning of the Schottky building units (*26*), but also have the intuitive appeal of the Kröger–Vink elements.

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and similarly

$$\tfrac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2e' = 0. \qquad (2)$$

$V_O^{\cdot\cdot}$ is the (compared to the perfect lattice) doubly positive charged oxygen ion vacancy, e' and $h^{\cdot}$ are the electrons and holes, respectively. In thermodynamic equilibrium the following equations are valid:

$$\tfrac{1}{2}\mu_{O_2}(g) + \mu_{V_O^{\cdot\cdot}} = 2\mu_{h^{\cdot}}, \qquad (3)$$

and

$$\tfrac{1}{2}\mu_{O_2}(g) + \mu_{V_O^{\cdot\cdot}} + 2\mu_{e'} = 0, \qquad (4)$$

where μ is the chemical potential. The concentration of the oxygen vacancies is strictly dependent upon the oxygen partial pressure, but may be considered as approximately constant, since the concentration is essentially fixed by the high dopant concentration to about 5%.

The chemical potential of oxygen (related to one molecule) can be expressed by $\mu_{O_2} = \mu^0_{O_2} + kT\ln p_{O_2}$. Furthermore, so long as the electrons and holes at low concentrations show ideal behaviour (or the activity coefficient is independent of the concentration) a similar relation holds: $\mu_{e,h} = \mu^0_{e,h} + kT\ln c_{e,h}$ and the following equations are valid for a given fixed temperature:

$$c_{h^{\cdot}} \propto p_{O_2}^{1/4}, \qquad (5)$$

and

$$c_{e'} \propto p_{O_2}^{-1/4}. \qquad (6)$$

Both equations are valid at the same time. But depending on the oxygen partial pressure, one or the other of the two conditions may be dominant and determine the electronic properties of the material.

3. Electronic Conductivities

If the electronic mobilities u are independent of the concentration c (as is observed in many cases), then the partial conductivities $\sigma = cuq$ of the electrons and holes show the same p_{O_2} dependence as given in Eqs. (5) and (6). This has been directly verified in some cases with CaO-stabilized ZrO_2 (*12*, *16*, *20*). Supporting evidence is provided by the observation of the exponential dependence of the current density i on the applied voltage E under conditions of blocked ionic current (*12*, *19–21*) as in Hebb–Wagner polarization experiments (*27–29*); specifically

$$i = -(kT/qL)\,[\sigma_e{}^R(e^{qE/kT} - 1) + \sigma_h{}^R(1 - e^{-qE/kT})]. \qquad (7)$$

In this diffusion equation the electronic conductivity at the blocking electrode merely changes with the quarter of the power of the oxygen partial pressure $p_{O_2} = p^R_{O_2}\exp(-4qE/kT)$. k is Boltzmann's constant, T the absolute temperature, q the elementary charge, L the sample thickness; and $\sigma_e{}^R$ and $\sigma_h{}^R$ are the electron and hole conductivities at the reversible reference electrode at the right-hand side of the cell.

In Fig. 1 the electronic partial conductivities as a function of the oxygen partial pressure are shown for ZrO_2 + 10 m/o Y_2O_3 at 700, 800, and 900°C. According to the Hebb–Wagner dc polarization technique (*27–29*), the conductivities were determined by comparison of the experimental *i–E* curve with Eq. (7) using a reversible air electrode. The activation energies for the conductivities of 4.1 eV for the electrons and 1.85 eV for the holes agree within 10% with other measurements (*12*, *18*, *19*) and are not very sensitive to the amount and type of dopant. In comparison, the ionic conductivity between 700 and 900°C is about 10^{-3} to 10^{-2} Ω^{-1} cm^{-1}. Because of the lower activation energy of the conductivity of the holes compared to the electrons, the oxygen partial pressure for the transition from *p*- to *n*-type conductivity increases with increasing temperature.

4. Electronic Mobilities

The traditional steady-state polarization technique used for the determination of Fig. 1 only allows the determination of the partial conductivities. Therefore, further investigations have been made in order to analyze the contribution of the concentration and the mobility of the charge carriers to the conductivity. Transient voltage type experiments (*19*, *30–34*) have been carried out in order to separate the two parts.

A voltage less than the decomposition voltage (2.23 V relative to air at 900°C (*35*))

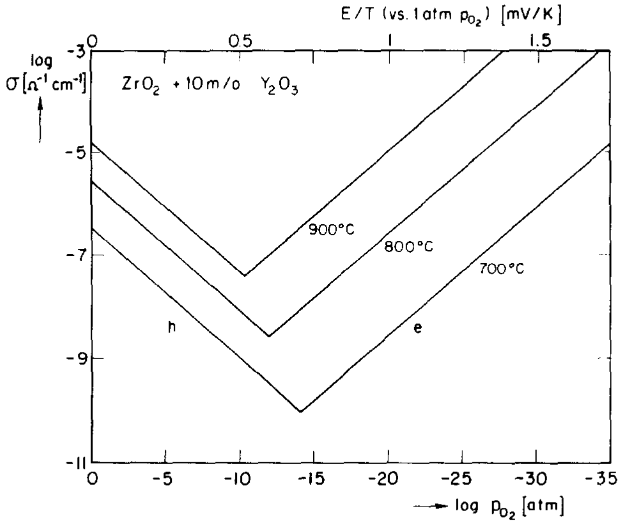

FIG. 1. The dependence of the partial conductivities of electrons (e), and holes (h) in ZrO_2 + 10 m/o Y_2O_3 the oxygen partial pressure.

was applied to the sample. Porous platinum in contact with air has been used as the positive reversible electrode, while a thin silver layer in contact with a chemically inert material like nitrogen gas has been used as the negative electrode:

(−) Inert material (e.g., N_2 gas), (I)

′ ″

Ag | ZrO_2 + 10 m/o Y_2O_3 | Pt, Air(+)

E

0 L x

Pt may not be used at the low oxygen partial pressure of the inert electrode because of the formation of Pt–Zr compounds (*35–37*), which thermodynamically influence the voltage of the cell. Most other suitable metals show similar effects (*36*); in the case of silver, however, the formation of AgZr is not expected below about 1.92 V at 955°C (*36*).

During a transient period, negative oxygen ions are drawn out of the sample to the right. But in steady state, no ionic current exists since the inert material cannot supply oxygen ions; only a small electronic current will be observed.

At the inert electrode side, the activity and the equilibrium partial pressure of the oxygen are given by the applied voltage. The energy $4qE$ (q is the elementary charge) necessary to transport two oxygen ions from one side of the sample to the other is equal to the "chemical" energy necessary to transfer an oxygen molecule from the inert material to the air (assuming prevailing ionic conductivity)

$$4qE = (\mu''_{O_2} - \mu'_{O_2}) = kT \ln (p''_{O_2}/p'_{O_2}). \quad (8)$$

μ'_{O_2} and μ''_{O_2} are the chemical potentials of the neutral oxygen (per molecule) at the left- and right-hand sides, respectively. Due to the difference in μ_{O_2} there is a difference in the concentration of electrons and holes between the two phase boundaries. This concentration gradient is the reason for the slight steady-state electronic current after the ionic current is blocked. The current density is then given by Fick's first law

$$i = q\left(D_e \frac{\partial c_e}{\partial x} - D_h \frac{\partial c_h}{\partial x}\right), \quad (9)$$

where D is the diffusion coefficient. An electric field does not exist in the sample. The high ionic conductivity allows for ionic defect redistribution so that the formation of an electric field is precluded. The main part of the voltage drop occurs at the phase boundary between the silver at the inert material side and the sample, which acts as a capacitor in the case discussed here. However, it should be mentioned that different potential distributions can occur in situations in which the electronic transference numbers are significant (*38, 39*).

Because in steady state i is independent of the position, according to Eq. (9), $D_e c_e - D_h c_h$ has to be linear throughout the sample. If either electrons or holes have a much larger conductivity than the other, the concentration gradient is linear and the slope is inversely proportional to the diffusion coefficient. This is evident in Fig. 2. A *p–n* junction is induced within the sample at the cross point of the two concentration curves by the applied voltage only.

After the steady-state concentration profile is produced, determined by the constancy of the electric current, the external voltage is removed, and the transient voltage is studied. As shown below, the time dependence is determined by the mobility (or the diffusion coefficient) of the electronic species.

After the voltage is removed, an equilization process begins. The concentrations at the right-hand phase boundary are presumed to remain fixed by equilibrium with the reference electrode, and eventually these electron and hole concentrations are communicated to all other regions of the sample. The transport of electrons moving to the right and of the holes moving to the left is electrically compensated by an equivalent current of oxygen incorporated into the crystal lattice at the air electrode. In the incorporation process, the oxygen accepts two electrons or donates two holes. The *p–n* junction moves through the sample and leaves at the left-hand phase boundary.

As in the steady-state condition, during the transient period the movement of the electrons is exclusively a concentration gradient-driven diffusion process. The highly mobile internal ionic defects, as evidenced by the high ionic conductivity, again prevent the formation of an internal electric field due to the movement of the electrons.

One boundary condition of the diffusion problem is the fixed concentration of electrons and holes at $x = L$ and the other boundary condition is that no oxygen leaves the electrolyte at the inert electrode $x = 0$. In fact a certain amount of oxygen will be dissolved in the silver electrode and the inert gas chamber. But this effect is negligible as long as this amount is much smaller than the changes of the electronic concentrations in the electrolyte, as will be justified later. Therefore, the point $x = 0$ is assumed to be impermeable to the electrons and holes which may here not be delivered to or taken off from the oxygen vacancies.

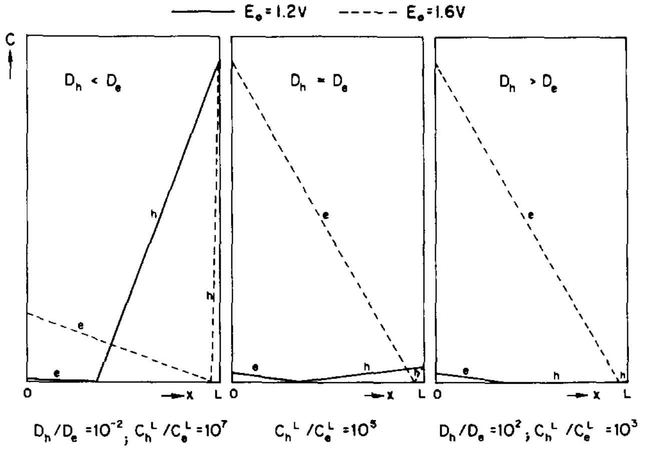

FIG. 2. Initial conditions of the concentrations of electrons (e) and holes (h) for two higher polarization voltages with an identical conductivity ratio $\sigma_h^R/\sigma_e^R = 10^5$ at the reference electrode but different ratios of the diffusion coefficients of the electronic species.

An additional constraint on the diffusion is that in thermodynamic equilibrium the product of the concentration of electrons and holes is constant. Especially in the region of the *p–n* junction, recombination or formation of electron–hole pairs is superposed on the diffusional change in the concentration of the electrons and holes according to Fick's second law. But these additional terms for electrons and holes cancel out if we write the concentration difference of the two types of electronic species

$$\frac{\partial}{\partial t}(c_h - c_e) = D_h \frac{\partial^2 c_h}{\partial x^2} - D_e \frac{\partial^2 c_e}{\partial x^2}. \quad (10)$$

With the introduction of the new variable

$$C = (D_h/D_e)\, c_h - c_e \quad (11)$$

Eq. (10) becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad \text{with } D = \frac{D_h c_h + D_e c_e}{c_h + c_e}. \quad (12)$$

The rate-determining "effective diffusion coefficient" D is in general a function of position, and only in the case of equal electronic diffusion coefficients ($D_h = D_e$) is it a constant.

With the new variable, the boundary and initial conditions are

$$\begin{aligned} &C = \text{const} && \text{at } x = L, t \geqslant 0; \\ &\partial C/\partial x = 0 && \text{at } x = 0, t > 0; \\ &C = C(x=0, t=0) + \frac{C(x=L) - C(x=0,t=0)}{L} x && \text{at } t = 0. \end{aligned} \quad (13)$$

Under the condition of equal diffusion coefficients, $D_e = D_h$, the solution of the differential Eq. (12) is known *(40, 41)*:[3]

$$C(x=0,t) = C(x=0,t=0) - \frac{2(Dt)^{1/2}}{L}[C(x=0,t=0) - C(x=L)] \times \left[\frac{1}{\pi^{1/2}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\frac{nL}{(Dt)^{1/2}}\right] \quad (14)$$

or

$$C(x=0,t) = C(x=L) + \frac{8}{\pi^2}[C(x=0,t=0) - C(x=L)] \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-D(2n+1)^2\pi^2 t/4L^2}. \quad (15)$$

The connection with the measured voltage E is given by Eq. (8) using the equilibrium condition

$$\mu_{O^{2-}} - 2\mu_{e^-} = \mu_{O^{2-}} + 2\mu_{h^+} = \tfrac{1}{2}\mu_{O_2}. \quad (16)$$

Because of the high disorder of the crystal lattice due to the large amount of dopant, the chemical potential $\mu_{O^{2-}}$ may be regarded as equal at both phase boundaries. This leads to

$$C(x=0,t) = \frac{D_h}{D_e} c_h(x=L)\, e^{-Eq/kT} - c_e(x=L)\, e^{Eq/kT}. \quad (17)$$

For the ratio 10^{-5} of the conductivities of electrons and holes at $x = L$ (a value approximately valid for zirconia in contact with air) at 900°C the calculated decay of the voltage is shown in Fig. 3. This solution is exactly valid only in the case of $D_h = D_e$, but in general exhibits the characteristic properties of the transient voltage. At higher starting voltages, after a short period with the voltage decay proportional to the square root of time, a slow linear decay follows with the slope

$$dE/dt = D\pi^2 kT/4qL^2. \quad (18)$$

This value is independent of the applied polarizing voltage. The transition voltage to a relatively fast decay at longer times is also independent of the initial voltage. The physical interpretation of the shoulder-like behavior is that at high voltages the relaxation process is determined by the diffusion of the electrons which dominate at the inert side, or, in the diffusion Eq. (17) the term with the positive exponent dominates. The motion of the holes is negligible by comparison, and their concentration increases to maintain equilibrium with the electrons, as required by the mass action law. After a transitional period, the holes will dominate and determine the relaxation process, i.e., the term with the negative exponent in Eq. (17) dominates. Similarly, the concentration of the electrons is now

[3] ierfc $x = (1/\pi^{1/2})e^{-x^2} - x + (2x/\pi^{1/2}) \int_0^x e^{-\xi^2} d\xi$.

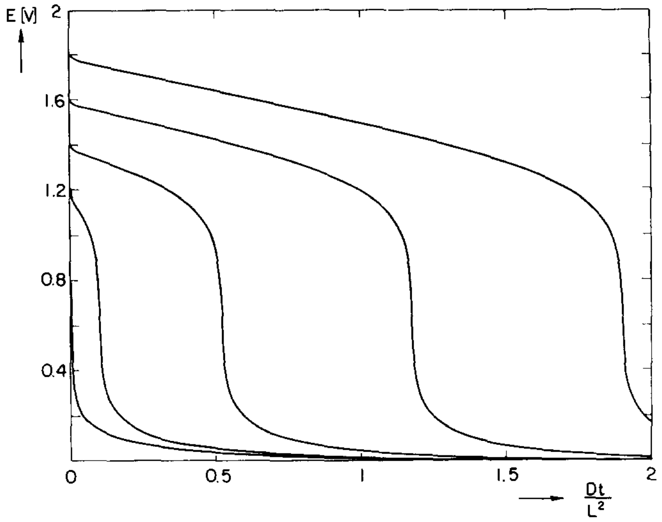

FIG. 3. Theoretical dependence of the relaxing voltage as a function of time t (multiplied by D/L^2) for different polarization voltages assuming equal diffusion coefficients of both electronic species.

determined through equilibrium with the holes.

For different mobilities, $D = D_e$ in the region of prevailing electron conductivity and concentration, and $D = D_h$ in the region of prevailing hole conductivity and concentration. This is schematically shown in Fig. 4.

In the case of smaller hole than electron mobility, first a relaxation of the electrons will occur, while the concentration of the holes will hardly be affected. For this homogenization in the left-hand region Eqs. (14) and (15) are valid if the sample length L is replaced by L' and the right-hand boundary value $C(x = L)$ by C' (at high polarization voltages the values are almost identical). At later times, the slow equilibration of the hole concentration determines the time dependence of the voltage. The solution of the diffusion problem is closely related to Eqs. (14) and (15) (*40*, *41*), and the slope of the voltage–time curve at later times is given by Eq. (18). Besides this possibility, information on D_h is available from the time τ of the appearance of the steep decrease of the voltage as a function of the previously applied polarization E_0:

$$dE_0/d\tau = D_h \pi^2 kT/4qL^2. \qquad (19)$$

In the case of $D_e < D_h$ a similar treatment is applicable, but is not discussed here because of the observed experimental results.

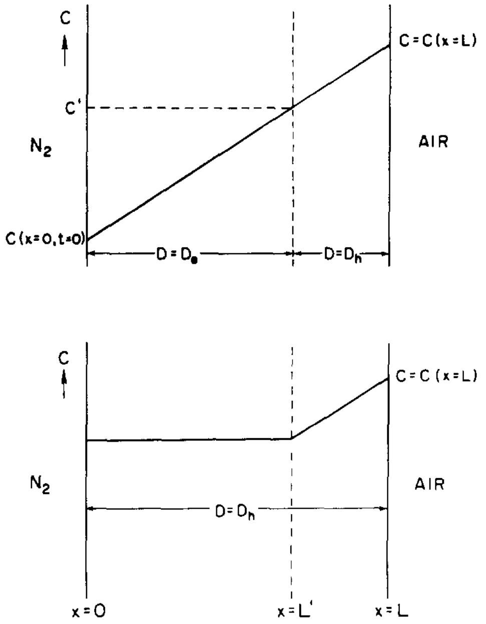

FIG. 4. Initial condition of the concentration C for the total relaxation (top) and the equilibration of the holes (below), and the different regions of the diffusion coefficient D in the case of $D_h \ll D_e$.

5. Experimental Considerations

Flat-ended tubes of $ZrO_2 + 10$ m/o Y_2O_3 with about 1-cm outer diameter and 0.16-cm wall thickness (Zircoa, Zirconium Cor-

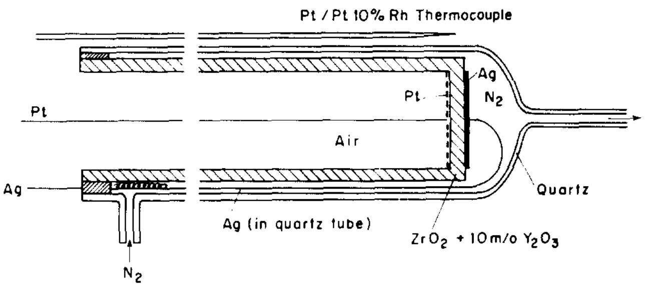

FIG. 5. Schematical representation of the experimental arrangement of cell (I).

poration of America, Cleveland, Ohio) were used as the ionic conductor. The experimental arrangement is schematically shown in Fig. 5. The bottoms of the tubes were polished to a final thickness of 1–2 mm and served as the electrolyte. The interior of the tubes were in contact with the atmosphere which served as the reference electrode. Porous electrodes were made by painting platinum paste (Degussa, Hanau, Germany) on the surfaces. The outside of the tubes were in a nitrogen (or helium) atmosphere which had been carefully purified. The space between the zirconia tube and the protecting quartz tube was made as small as possible. The silver contacts at the inert electrode were prepared by sputtering. Their thickness was about 1 μm.

Ni–Cr resistance heaters with stabilized dc supplies were used, and were carefully isolated. The experiments were predominantly carried out in the temperature range from 700 to 900°C. Voltages were applied potentiostatically and measured during the transient period with a high resistance millivolt meter ($R \simeq 2 \times 10^{14}$ Ω, Keithley, Cleveland, Ohio), the output of which was further processed. For the initial voltage drops a two-channel oscilloscope was used. The current measurements for the steady-state polarization experiments were made with a Keithley 410 microammeter.

6. Results and Discussion of the Transient Measurements

Some results of typical transient experiments at 900°C with $L = 0.15$ cm are shown in Fig. 6 for several low initial polarization voltages with mainly hole conduction prevailing, and for some voltages between 1.4 and 2 V in Fig. 7. For applied voltages up to about 1 V, a rather rapid drop is seen. The shape of the curves is in good agreement with that calculated from Eqs. (15) and (17) assuming values of the diffusion coefficient of the holes that are either determined from the last slope of the shoulder (before the fast voltage decrease) or the time dependence for the appearance of the steep voltage steps. At about 1 V, a shoulder is beginning to form. At higher initial voltages, the shape of the shoulder becomes more marked and longer. For very short times there is a rapid initial decrease observed.

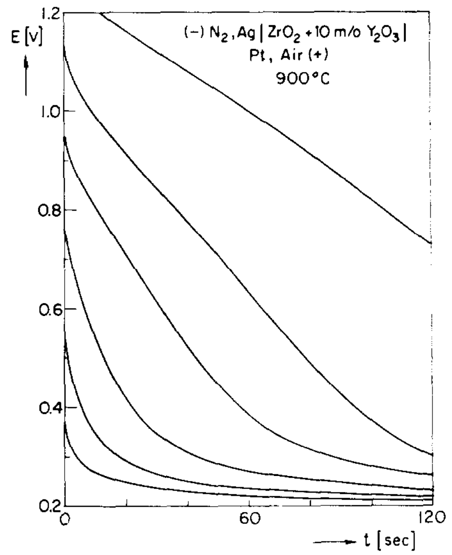

FIG. 6. The time dependence of the voltage relaxation after lower polarization voltages, $T = 900°C$.

The appearance of the shoulder in the transient voltage characteristics is similar to the theoretical curves previously derived for

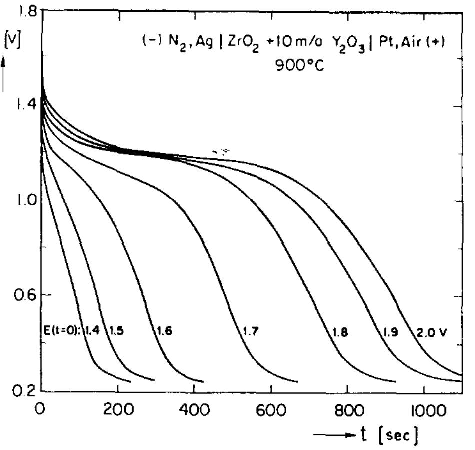

FIG. 7. The total voltage relaxation behavior for higher polarization voltages between 1.4 and 2 V, at $T = 900°C$.

the assumption $D_h = D_e$. An important difference, however, is the initial voltage behavior at high polarization voltages. In order to determine the diffusion coefficient of the electrons quantitatively, the initial time dependence of the voltage at some higher initial polarizations is plotted in Fig. 8. In agreement with the upper part of Fig. 3, or Eqs. (14)–(16), after a short curved portion a linear dependence is seen. This is attributed to the relaxation of only the electrons, and D_e may be calculated from the slope according to Eq. (18). At 900°C D_e has a value of 2×10^{-3} cm^2/sec, equal to an electric mobility of 2×10^{-2} cm/Vsec.

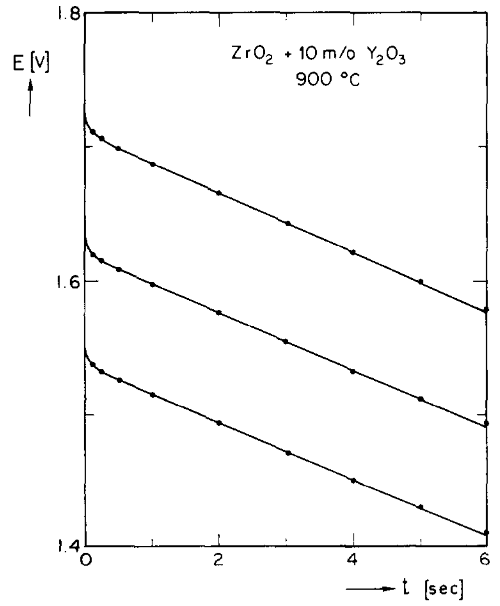

FIG. 8. Voltage–time dependence in the beginning of the relaxation at high initial polarizations, at $T = 900°C$.

After the short initial rapid decrease the voltage change slows down, indicating a much smaller diffusion coefficient for the holes. This is in accordance with the assumed model of $D_h \ll D_e$ as graphically shown in Fig. 4. When the voltage reaches about 1.1 V the decay begins to decrease rapidly again with a velocity independent of the initial polarization voltage. The width of the shoulder increases with the starting polarization corresponding to the changing initial position of the *p–n* transition point. At the lower investigated temperatures the shoulder becomes several times longer. As mentioned earlier the diffusion coefficient of the holes has been determined from the distance between two steep decreases and the last slope of the shoulder. The agreement is rather satisfactory. At 900°C for D_h a value of 1.5×10^{-5} cm^2/sec, equal to an electric mobility of 1.5×10^{-4} $cm^2/Vsec$, is obtained. This value is two orders of magnitude lower than that of the electrons. For this reason, the stoichiometric point with equal excess and defect electron concentrations corresponds to an oxygen partial pressure about 8 orders of magnitude lower than that at equal conductivities.

From the temperature dependence of the diffusion coefficients in the range between 700 and 900°C activation energies of 0.6 and 1.4 eV for electrons and holes, respectively, were evaluated. Because the movement is an activated process and has low values for the diffusion coefficients, the results fit the requirements of hopping conduction.

Compared to other measurements the diffusion coefficient of the holes determined in the present investigation is about three times larger than that derived from permeation experiments ($D_h = 4.5 \times 10^{-6}$ cm^2/sec) (*18*); the activation energy (1.24 eV) agrees within the limits of error. It is remarkable that for monoclinic zirconia similar low values have also been observed (*42*).

According to the knowledge that we now have of the electronic properties of doped ZrO_2 it may be stated that the general observation of low electronic conductivities is primarily due to very low electronic mobilities rather than low electronic species concentrations, but the dilute solution assumption can still be employed in this region of applied oxygen partial pressures.

An error in using the voltage relaxation method for the interpretation of the electronic bulk diffusivities might be related to the neglect of the solubility of oxygen in the silver electrode and in the inert gas compartment. If we assume that either of these processes were rate determining, the redistribution of the electrons and holes in the electrolyte would have to be assumed to be fast and that quasi-steady states exist. Then, the transport of oxygen would be equivalent to the electronic current according to the Hebb–Wagner Eq. (7). From the known electron and hole conductivities in the zirconia electrolyte (Fig. 1) and solubility data of oxygen in Ag (*43*), assuming Sievert's law, a calculation shows that in this case the relaxation should be several orders of magnitude faster than that observed experimentally. Therefore, the solubility of oxygen in silver and in the gas phase must have only a minor influence, and may be neglected. Also, the diffusion of oxygen in the inert electrode material cannot control the relaxation process because the diffusion time constant is very small compared to the measured relaxation time, according to known values of the diffusion coefficient of oxygen in silver (*43*). It can also be shown that the kinetics of the charging of the double layer at the electrolyte-inert electrode interface, assuming several hundred microfarads for its capacitance, cannot have a significant effect upon the measured results.

In some cases, when using polycrystalline materials, especially in the form of thin films with submicron grain size, electronic transport barriers have been observed at intercrystalline or grain boundaries, which has been reflected through low electronic mobilities rather than low carrier concentration, e.g., (*44–46*). If such an effect were to also dominate the transport in zirconia, Ohm's law would have to be observed for electronic conduction. However, previous polarization measurements using the Hebb–Wagner technique (*27–29*) have shown an exponential current–voltage dependence as described by Eq. (7). This indicates that the transport of the electrons and holes is determined by diffusion in the bulk of the grains, i.e., the electronic conductivity in the intercrystalline regions is better or at least comparable to the bulk. Also, the ionic conductivity at the intercrystalline contacts may be assumed to be comparable with the bulk. Otherwise, the polycrystalline nature of zirconia would markedly decrease the ionic conductivity of the material. Therefore, the relaxation which is determined by a coupling with the slowest species can be assumed to be fast enough in the intergrain regions, thus keeping the transport in the bulk rate-determining step. Of course, by the presence of grains a geometrical correction factor has to be considered for the determination of the electronic mobilities, but this factor is considered to fall within the range of the experimental error.

Acknowledgments

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References

1. W. Nernst, *Z. Elektrochem.* **6**, 41 (1899).
2. C. Wagner, *Naturwissenschaften* **31**, 265 (1943).
3. F. Hund, *Z. Elektrochem.* **55**, 363 (1951).
4. F. Hund, *Z. Phys. Chem.* **199**, 142 (1952).
5. H. Schmalzried, *Z. Phys. Chem. N.F.* **38**, 87 (1963).
6. B. C. H. Steele and C. B. Alcock, *Trans. Met. Soc. AIME* **233**, 1359 (1965).
7. R. W. Vest and N. M. Tallan, *J. Appl. Phys.* **36**, 543 (1965).
8. H. H. Möbius and R. Hartung, *Silikattechnik* **16**, 276 (1965).
9. A. W. Smith, F. W. Meszaros, and C. D. Amata, *J. Amer. Ceram. Soc.* **49**, 240 (1966).
10. H. H. Möbius, *Silikattechnik* **17**, 358 (1966).
11. Y. D. Tretyakov, *Inorg. Mat.* (*USSR*) **2**, 432 (1966).

12. J. W. Patterson, E. C. Bogren, and R. A. Rapp, *J. Electrochem. Soc.* **114**, 752 (1967).
13. H. Ullmann, *Z. Phys. Chem. (Leipzig)* **237**, 71 (1968).
14. W. A. Fischer and D. Janke, *Arch. Eisenhüttenw.* **39**, 89 (1968).
15. Y. D. Tretyakov and A. Muan, *J. Electrochem. Soc.* **116**, 332 (1969).
16. R. Hartung and H. H. Möbius, *Z. Phys. Chem. (Leipzig)* **243**, 133 (1970).
17. W. A. Fischer and D. Janke, *Z. Phys. Chem. NF* **69**, 11 (1970).
18. L. Heyne and N. M. Beekmans, *Proc. Brit. Ceram. Soc.* **19**, 229 (1970).
19. L. D. Burke, H. Rickert and R. Steiner, *Z. Phys. Chem. NF* **74**, 146 (1971).
20. L. M. Friedman, K. E. Oberg, W. M. Boorstein, and R. A. Rapp, *Met. Trans.* **4**, 69 (1973).
21. R. Hartung, *Z. Phys. Chem. (Leipzig)* **254**, 393 (1973).
22. D. Janke and W. A. Fischer, *Arch. Eisenhüttenw.* **45**, 477 (1975).
23. F. A. Kröger and H. J. Vink, *in* "Solid State Physics," Vol. 3 (F. Seitz and D. Turnbull, Eds.), p. 307, Academic Press, New York (1956).
24. F. A. Kröger and H. J. Vink, *J. Phys. Chem. Solids* **5**, 208 (1958).
25. F. A. Kröger, "The Chemistry of Imperfect Crystals," North Holland, Amsterdam (1964).
26. W. Schottky, *in* "Halbleiterprobleme," Vol. 4 (W. Schottky, Ed.), p. 235, Vieweg, Braunschweig (1958).
27. M. Hebb, *J. Chem. Phys.* **20**, 185 (1958).
28. C. Wagner, *in* "Proc. Int. Comm. Electrochem. Thermodyn. and Kinetics (CITCE)," p. 361, 7th Meeting, Lindau 1955, Butterworth, London (1957).
29. C. Wagner, *Z. Elektrochem.* **60**, 4 (1956).
30. I. Yokota, *J. Phys. Soc. Japan* **8**, 595 (1953).
31. S. Miyatani, *J. Phys. Soc. Japan* **10**, 786 (1955).
32. D. Heitkamp, *Z. Phys. Chem. NF* **25**, 108 (1960).
33. K. Weiss, *Z. Phys. Chem. NF* **59**, 242 (1968).
34. D. O. Raleigh, *Z. Phys. Chem. NF* **63**, 319 (1969).
35. W. Weppner *J. Electroanal. Interf. Chem.* (to appear).
36. L. Brewer and P. R. Wengert, *Met. Trans.* **4**, 83 (1973).
37. P. J. Meschter, Ph.D. Thesis, University of Pennsylvania, 1974.
38. N. S. Choudhury and J. W. Patterson, *J. Electrochem. Soc.* **117**, 1384 (1970).
39. N. S. Choudhury and J. W. Patterson, *J. Electrochem. Soc.* **118**, 1398 (1971).
40. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford Univ. Press, London (1959).
41. J. Crank, "The Mathematics of Diffusion," Oxford Univ. Press, London (1967).
42. R. W. Vest, N. M. Tallan, and W. C. Tripp, *J. Amer. Ceram. Soc.* **47**, 635 (1964).
43. T. A. Ramanarayanan and R. A. Rapp, *Met. Trans.* **3**, 3239 (1972).
44. R. L. Petritz, *Phys. Rev.* **104**, 1508 (1956).
45. L. L. Kazmerski, W. B. Berry, and C. W. Allen, *J. Appl. Phys.* **43**, 3515 (1972).
46. R. H. Bube, "Photoconductivity of Solids," p. 81, Wiley, New York/London/Sidney (1960).