Electrochemical Transient Investigations of the Diffusion and Concentration of Electrons in Yttria Stabilized Zirconia-Solid Electrolytes

W. Weppner

Center for Materials Research, Stanford University, Stanford, California

(Z. Naturforsch. **31 a**, 1336–1343 [1976]; received September 25, 1976)

The voltage relaxation of galvanic cells with zirconia electrolytes polarized between an inert silver electrode and an Fe+FeO electrode has been analyzed to obtain the diffusion coefficient of the electronic minority charge carriers in the temperature range between 700 and 900 °C. The method has been examined by using different thicknesses of the sample. At 800 °C the diffusion coefficient of the electrons is 1.4×10^{-3} cm^2/sec, i. e., about two orders of magnitude higher than that for the holes, 4.5×10^{-6} cm^2/sec. The activation energy 0.55 eV is obtained for the electrons, compared to 1.4 eV for the holes. From conductivity data, the concentrations of electrons and holes at 800 °C and 1 atm oxygen partial pressure are calculated to be 1×10^9 and 4×10^{17} cm^{-3}, respectively. The electronic band gap is evaluated to be 4.1 eV.

1. Introduction

At high temperature, ZrO_2 stabilized in the cubic CaF_2 structure by the incorporation of a few mole percent of a second oxide, e. g., Y_2O_3 or MgO is known to exhibit high ionic conductivity. This property was already recognized by Nernst[1] at the end of the last century, but it was not before 1943 that Wagner[2] identified the electrolytic conductivity as oxygen ion conductivity. Later investigations by Hund[3, 4] proved the existence of vacancies in the oxygen sublattice through whose motion the transport of oxygen ions occurs.

Doped ZrO_2 has important scientific and technical applications, and a comprehensive review is given in the literature[5]. Important examples are the use of zirconia to determine the thermodynamic quantities for oxides by the measurement of electrical quantities[5–8], and the investigation of kinetic phenomena, e. g., the mobility of oxygen in metals[9–11], or the chemical diffusion in metal oxides[12, 13]. In practical applications, the electrolyte can serve as a probe to measure and adjust the oxygen content in gases, as a monitor during reduction of ores, and as a membrane in high temperature fuel cells[5, 14–18].

In all cases, it is important that the electronic portion of the electrical conductivity be negligible compared to the ionic portion in order to avoid internal short circuiting of the cell. To study the partial conductivities of the electrons and holes in doped ZrO_2, the steady state polarization method of Hebb[19] and Wagner[20, 21] has been applied in several investigations[22–27]. From these experiments the product of the electrical mobility u and the concentration c (in particles/cm^3) of the charge carriers may be determined because of the following relation with the conductivity σ

$$\sigma = q\, c\, u \tag{1}$$

where q is the elementary charge.

Only little information exists on the separation of the two contributions c and u to the electronic conductivity. Results differ widely, and were mainly derived from the observation of oxygen permeation velocities[28–30, 51] with possible other rate determining steps involved. But this knowledge is of special interest because in its general feature ZrO_2 is not a particularly good ionic conductor, but is a very poor electronic conductor. The reason for the latter may be due to either low mobility or low concentrations of electronic species, or it may be due to both. Resolution of this question may also provide hints for other suitable materials with similar electronic properties and possible dominant ionic conduction.

The electronic properties of zirconia are dependent on the oxygen partial pressure. From the incorporation reaction of neutral oxygen from an adjacent gas phase into the lattice by the annihilation of a doubly positive (relative to the neutral lattice) oxygen vacancy and the creation of two holes, we find that the concentration of the holes is directly and the concentration of the electrons is inversely

Reprint requests to Dr. W. Weppner, Center for Materials Research, McCullough Building, Stanford University, *Stanford*, California 94305, USA.

proportional to the 4th root of the oxygen pressure p_{O_2}[22–24].

A method that has been developed to determine the concentration separately is the charge transfer technique suggested by Raleigh[31] and first applied by Wagner and Joshi[32–35]. The principal advantage is the elimination of the double layer charge by measuring the difference in charge that is pumped in or out of two electrolytes of different thicknesses after changing the applied voltage. In such experiments, the time integral of the current from one steady state to the next for each sample has to be determined very accurately.

In the case of doped ZrO_2 it has been observed that this determination is difficult because of a very slow transient process and because of unavoidable fluctuations in the final steady state current. Even though the latter may be small they become important because of their integration over long periods of time.

Therefore, it seems to be desirable to explore other methods that are suitable to separately determine either the mobility or concentration of the electronic species in zirconia and other electrolytes. In this paper the relaxation of the voltage previously applied to the sample is studied and analyzed in order to obtain the electron diffusion coefficient. Besides the specific application to doped zirconia the general features of the method are treated. The general fact that transient voltages may be determined by the mobilities of certain mobile species has already been recognized in a number of papers[36–39, 23, 24, 27, 31] before.

In a preceding paper[27] the transient voltage of a galvanic cell using an air reference electrode where both electrons and holes are involved and the movement of induced pn-junctions have been investigated. Because of experimental limitations the thickness of the electrolyte could not be changed over a considerable range. However, the dependence of the voltage relaxation on the thickness is a very important indication of the applicability of the method, since for a diffusion determined process a typical velocity proportional to the square of the thickness is expected. Furthermore, it is of interest to operate exclusively in a region of prevailing electron conduction (compared to hole conduction) and, therefore, lower polarization voltages and concentration gradients. These experiments give information about the electron properties, which are even less known than hole properties determined from permeation experiments.

From the knowledge of the temperature dependence of the calculated electron and hole concentrations it is possible to evaluate the electronic band gap. Thus, by the use of only electrochemical tools it is possible to determine important properties of the electrons and holes in the solid ionic conductor.

2. General Technique

In contradistinction to the charge transfer method[31–35], the mobilities u of the electronic charge carriers can be directly measured and the concentration calculated according to Eq. (1) using known values of the conductivities.

The voltage relaxation technique used to experimentally determine the electronic mobilities employs the same type of galvanic cells used in measurements of conductivities according to the Hebb-Wagner method:

$$\begin{array}{l}(-)\ \text{Inert Material}\\ \qquad (\mathrm{N_2}),\ \mathrm{Ag}\ \big|\mathrm{Zr_9Y_2O_{21}}\big|\ \mathrm{Fe+FeO,\ Pt}\,(+)\,.\\ \qquad\quad -\big|\text{————}\big|\!\rightarrow x\\ \qquad\qquad 0 \qquad\quad\ \ L\end{array} \qquad \text{(I)}$$

The two phase, two component mixture of Fe and $Fe_{1-\delta}O$ serves as a highly nonpolarizable source of oxygen with a defined reference partial pressure. Usually, purified nitrogen has been used as the inert material. Pt may not be used for the electronic lead on this side because of the formation of Pt-Zr compounds, influencing the voltage of the cell[40–43]. Therefore, silver has been used, for which formation of similar intermetallic compounds is not expected below the decomposition voltage of zirconia, according to data from the literature[40].

By applying a voltage lower than this limiting value (about 2.2 V versus air at 800 °C[43]) in the polarity indicated in (I) no steady state oxygen flux is possible, because no replenishment takes place at the inert electrode. The remaining current is due to the product of the concentration and mobility of the electrons.

Since (in steady state) there is no flux of ions, the force acting on the ions has to vanish. This means that the gradient of the electrochemical potential for the ions is zero:

$$\operatorname{grad} \eta_{O^{--}} = 0\,. \tag{2}$$

In the usual manner, the electrochemical potential η may be replaced by the chemical (μ) and the electrostatic potential (Φ)*

$$\eta_{O^{--}} = \mu_{O^{--}} - 2\,q\,\Phi\,. \tag{3}$$

Because of the high degree of disorder in the crystal lattice (approximately 5% oxygen ion vacancies) the change in the concentration of defects with oxygen partial pressure may be neglected. The chemical potential of the oxygen ions is then independent of position in the sample, and in view of Eq. (2) the gradient of the electrostatic potential disappears, i.e., Φ is constant throughout the sample. The transport of the electrons then takes place only under the influence of a concentration gradient, which has to be linear if we assume the independence of the mobility upon the oxygen partial pressure. The behavior of the chemical potentials of the neutral oxygen, the oxygen ions and the electrons, and the electrostatic potential within the sample and the electrodes are shown in Figure 1.

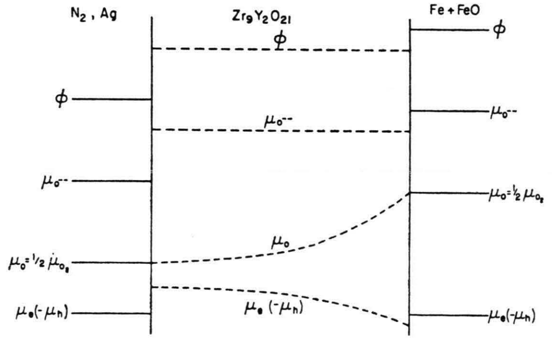

Fig. 1. Local dependence of the chemical potentials μ of the oxygen ions O^{--}, the neutral oxygen O and the electrons e and holes h as well as the electrical potential Φ under steady state polarization conditions of cell (I) within the electrolyte and the electrodes.

After steady state conditions are established, the external voltage is switched off. The concentration gradients decay until the equilibrium stoichiometry, as fixed by the reference electrode, is established throughout the entire sample. The voltage of the galvanic cell is observed as a function of time. If the movement of both electrons and holes is involved in the process, the mathematical treatment is complicated by the annihilation and formation of electrons and holes to establish thermodynamic equilibrium[27]. This change is superposed on the diffusion of the species. The analysis and the application of the voltage relaxation method are more direct if the concentration of either the electrons or holes prevails, which eventually occurs because of the nature of the sample or by using suitable reference electrodes, e. g., Fe + FeO, for the adjustment of a stoichiometry with prevailing electron concentration in the case of doped zirconia.

It is shown below how the mobilities of the minority charge carriers may be determined from the voltage-time observations.

3. Theory

At first it will be proved mathematically that the relaxation process is exclusively controlled by the diffusion of the electronic species as long as the O_2 partial pressures everywhere in the electrolyte are of such a magnitude that the electronic conductivity is low compared to that of the ions.

When the external voltage is switched off, because of electroneutrality the electron current density (i_e, i_h) is coupled with the oxygen ion current density ($i_{O^{--}}$) so that the net charge transport is zero at every point in the electrolyte:

$$i_{O^{--}} + i_e + i_h = 0\,. \tag{4}$$

The expressions for the individual particle current densities are

$$i_e = c_e\,u_e \operatorname{grad} \eta_e\,, \tag{5}$$

$$i_h = -\,c_h\,u_h \operatorname{grad} \eta_h\,, \tag{6}$$

$$i_{O^{--}} = c_{O^{--}}\,u_{O^{--}} \operatorname{grad} \eta_{O^{--}}\,. \tag{7}$$

The electrochemical potentials may be replaced by the chemical and electrostatic potentials, $\eta = \mu + z\,q\,\Phi$. Eliminating the electrostatic potential Φ and recalling that the ionic conductivity is always much greater than that of the electrons and holes, and that the chemical potential of the oxygen ions is locally independent, Eqs. (4) – (7) become

$$i_e = c_e\,u_e \operatorname{grad} \mu_e\,, \tag{8}$$

$$i_h = -\,c_h\,u_h \operatorname{grad} \mu_h\,. \tag{9}$$

These are the common transport equations for diffusion in an activity gradient. The motion of the electrons and holes, therefore, is given by the influence of the activity gradient, whereas, the transport of the ions to maintain charge neutrality is

---

* The chemical potential μ and the electrochemical potential η are related to one particle.

caused only by a very weak electric field. The electrical force acting on the electrons is smaller than the effect of the concentration gradient by the ratio of the electronic to ionic partial conductivities.

The mathematical treatment of the relaxation process as a pure diffusion problem must lead to a solution in terms of experimentally accessible quantities. This is primarily the emf of cell (I) as a function of time. If oxygen conduction prevails everywhere in the electrolyte, the emf is given by the difference of the oxygen chemical potentials μ_O at both boundaries of the electrolyte divided by the charge transferred by one oxygen ion, $2\,q$.

In equilibrium between neutral oxygen, oxygen ions, electrons and holes, the chemical potential μ_O of oxygen may be expressed by $\mu_{O^{--}} - 2\,\mu_e$ or $\mu_{O^{--}} + 2\,\mu_h$. Due to the local independence of $\mu_{O^{--}}$, the voltage is therefore determined by the difference of the chemical potentials of the electrons or (with the reverse sign) the holes at both sides of the electrolyte, divided by q. If ideal behavior may be assumed, the chemical potential $\mu_{e,h}$ can be expressed by $\mu^0_{e,h} + k\,T \ln c_{e,h}$, in which $\mu^0_{e,h}$ is related to standard conditions, and the final result is

$$E = -\frac{k\,T}{q} \ln \frac{c_e\,(x=0)}{c_e\,(x=L)} = +\frac{k\,T}{q} \ln \frac{c_h\,(x=0)}{c_h\,(x=L)} \tag{10}$$

where k is Boltzmann's constant. As seen in these equations, the voltage E measures the ratio of the electron and hole concentrations at both the phase boundaries. The concentration at $x=L$ is fixed by equilibrium with the reference electrode.

Because of the recombination or production of electrons and holes, generally Fick's second law can only be written for the difference in concentration of both types of electronic carriers. If one of the electronic species dominates, however, this effect may be neglected:

$$\partial c_{e,h}/\partial t = D_{e,h}\, \partial^2 c_{e,h}/\partial x^2 \tag{11}$$

where $D_{e,h}$ is the diffusion coefficient of the electrons and holes, respectively, and is related to the electrical mobility $u_{e,h}$ according to the Nernst-Einstein equation

$$D_{e,h} = (k\,T/q)\, u_{e,h}\,. \tag{12}$$

The boundary conditions of the differential Eq. (11) are given by the constant concentrations c_e and c_h at the reference electrode ($x=L$) at all times, and by the suppression of exchange of oxygen and electrons with the inert electrode at all times, i. e., $\partial c_{e,h}/\partial x = 0$ at $x=0$. As the initial concentration dependence, the linear behavior resulting from the previous steady state polarization, as described in Sect. 2, is assumed.

According to these conditions the solution of the differential Eq. (11) may be derived from the literature[44, 45]:

$$\begin{aligned} c_{e,h}\,(x=0\,,t) \\ = c_{e,h}\,(0, t=0) - \frac{2}{L}\,[c_{e,h}\,(0, t=0) - c_{e,h}\,(L)] \\ \times \sqrt{D_{e,h}\,t} \left\{ \frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{n\,L}{\sqrt{D_{e,h}\,t}} \right\} \end{aligned} \tag{13}$$

Table I. Time dependence of the EMF relaxation of cell (I) if the concentration and conductivity of either the electrons or holes is dominant.

Prevailing Electronic Species	Period of Validity	Time Dependence	Determination of the Diffusion Coefficient	
Electrons (e)	$t \ll L^2/D_e$ $E_0 > R\,T/F$	$E_e\,(t) = E_0 + \frac{R\,T}{F} \ln \left(1 - \frac{2}{L} \sqrt{\frac{D_e\,t}{\pi}}\right)$ $\cong E_0 + \frac{2\,R\,T}{F\,L} \sqrt{\frac{D_e\,t}{\pi}}$	$D_e = \frac{\pi}{4} \left(\frac{F\,L}{R\,T}\right)^2 \left(\frac{dE}{d\sqrt{t}}\right)^2$	(A)
	$t \gg L^2/10\,D_e$ $E_0\,, E\,(t) > R\,T/F$	$E_e\,(t) = E_0 + \frac{R\,T}{F} \ln \frac{8}{\pi^2} - \frac{\pi^2\,R\,T\,D_e}{4\,F\,L^2}\,t$	$D_e = -\frac{4\,F\,L^2}{\pi^2\,R\,T} \frac{dE}{dt}$	(B)
Holes (h)	$t \ll L^2/D_h$ $E_0 > R\,T/F$	$E_h\,(t) = E_0 - \frac{R\,T}{F} \ln \left[1 + \exp\left(\frac{E_0\,F}{R\,T}\right) \frac{2\,\sqrt{D_h\,t}}{L\,\sqrt{\pi}}\right]$	$D_h = \frac{\pi\,L^2}{4} \left(\frac{d \exp(-E\,F/R\,T)}{d\sqrt{t}}\right)^2$	(C)
	$t \gg L^2/10\,D_h$	$\log E_h\,(t) = \log \left\{\frac{8\,R\,T}{\pi^2\,F} \left[1 - \exp\left(-\frac{E_0\,F}{R\,T}\right)\right]\right\}$ $- \frac{0.1086\,\pi^2\,D_h}{L^2}\,t$	$D_h = -\frac{L^2}{0.1086\,\pi^2} \frac{d \log E}{dt}$	(D)

$$= c_{e,h}(L) + \frac{8[c_{e,h}(0, t=0) - c_{e,h}(L)]}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\{-D_{e,h}(2n+1)^2 \pi^2 t/4L^2\} . \quad (14)$$

The time dependence of the voltage of the galvanic cell is found by substituting the solutions of Fick's law given above into Equation (10). The concentrations at time $t = 0$ are known from the applied polarization voltage.

From a practical point of view, the approximate solutions for different time ranges with their simpler functional forms are of more interest. These solutions, for short times, $t \ll L^2/D$, and for longer times, $t \gg L^2/10\,D$, are summarized for electrons and holes in Table I.

4. Experimental Arrangement

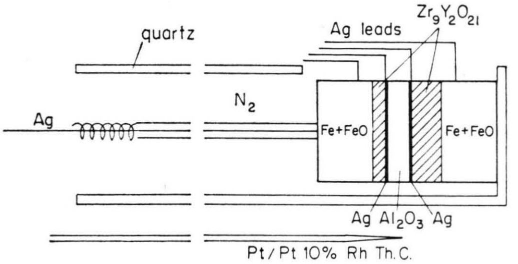

Fig. 2. Schematical representation of the experimental arrangement of cell (I) for measuring the diffusion coefficient of electrons in doped zirconia.

The experimental arrangement is shown schematically in Figure 2. Pellets of $ZrO_2 + 10$ m/o Y_2O_3 of about 1 cm diameter commercially made by the Zirconium Corporation of America (Cleveland, Ohio) were used. The thickness of the pellets was varied between 0.06 and 0.23 cm by abrading and polishing. The Fe + FeO electrodes were made by powder pressing (p. a. substances, 12 t/cm^2) with a surplus of metal, sintered for 24 hr at 1000 to 1100 °C in a small stream of purified nitrogen, and finally polished.

The silver electrodes were sputtered on the surface and were of a thickness of 1 μm. Silver wires were used as the leads.

Two galvanic cells of type (I) with electrolytes of different thicknesses have always been used together in one arrangement. The pellets were spring loaded with ceramic pistons and supported by quartz devices in a purified nitrogen atmosphere. In some experiments purified helium was used instead of nitrogen. Electrical resistance heaters with stabilized a c supplies and grounded metallic shields were used, and were carefully isolated. The temperature was measured with Pt-Pt 10% Rh thermocouples. The cell voltages were measured with high resistance millivoltmeters ($R > 2 \times 10^{14}\,\Omega$, Keithley, Cleveland, Ohio), and for short times with a two channel storage oscilloscope.

5. Results

Some typical examples of transient relaxation curves at 825 °C using zirconia pellets of 0.106 and 0.218 cm thickness are shown in Fig. 3 for a series of initial polarization voltages. First, a fast decay, corresponding to the square root law of the voltage-time relationship for short times is observed, followed by a linear voltage decay. For longer times the decay becomes gradually slower and finally approaches zero voltage.

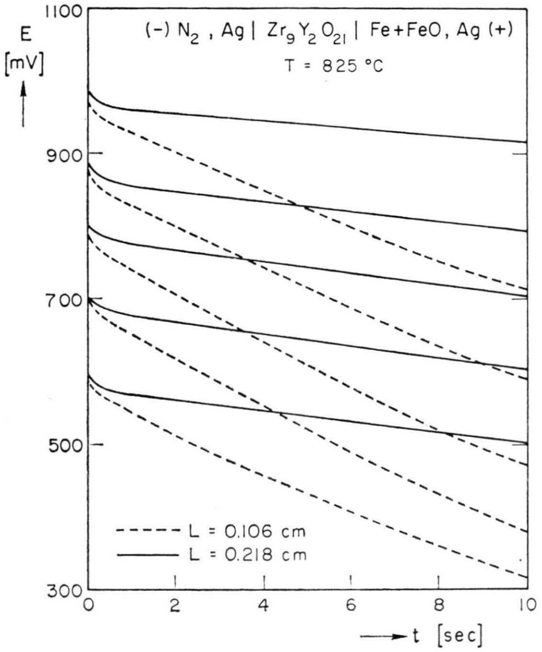

Fig. 3. Voltage of cell (I) as a function of time for several previous steady state polarization voltages and two different sample thicknesses (0.106 and 0.218 cm) at 825 °C.

The ratio of the slopes for the different thicknesses is 3.9, close to the ratio of the square of the thicknesses of both pellets, 4.2, as expected for an electron bulk diffusion ratedetermining process. From the slopes of the straight lines the diffusion coefficient of the electrons is determined, $D_e = 1.4 \times 10^{-3}$ cm^2/sec at 825 °C, according to Eq. (B) in Table I. The corresponding electrical mobility is $u_e = 1.5 \times 10^{-2}$ cm²/Vsec.

Analysis of the transient voltage relaxation has been undertaken for a large number of experiments in the temperature range between 700 and 900 °C. The resulting electron diffusion coefficients are plotted in Fig. 4 as a function of $1/T$. From the slope an activation energy of 0.56 ± 0.15 eV is determined. This value is much smaller than 1.4 ± 0.3 eV calculated from the temperature dependence of the hole diffusion coefficient as determined from voltage relaxation experiments with an air reference electrode[27] and also plotted in Figure 4. The results of other authors are shown for comparison.

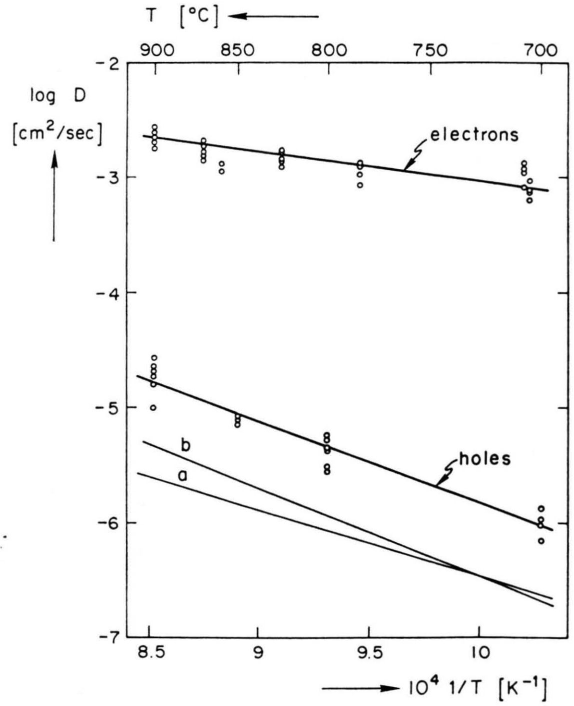

Fig. 4. Diffusion coefficient of the electrons and holes in $Zr_9Y_2O_{21}$ as a function of the reciprocal temperature between 700 and 900 °C. The results for the hole diffusion coefficient from permeation experiments are plotted for comparison: a: Heyne and Beekmans[30], b: Kitazawa and Coble[51].

With known partial conductivities[23, 24, 27] of the electrons and holes and the results for the diffusion coefficients of these minority charge carriers, the concentrations of the electrons and holes can be determined from Eqs. (1) and (12). The result is graphically represented as a function of the oxygen partial pressure in Fig. 5 for the temperatures 700, 800 and 900 °C. Due to the higher activation energy of formation for electrons than holes, the intrinsic point of equal concentrations of electrons and holes moves markedly to higher oxygen partial pressures with increasing temperature.

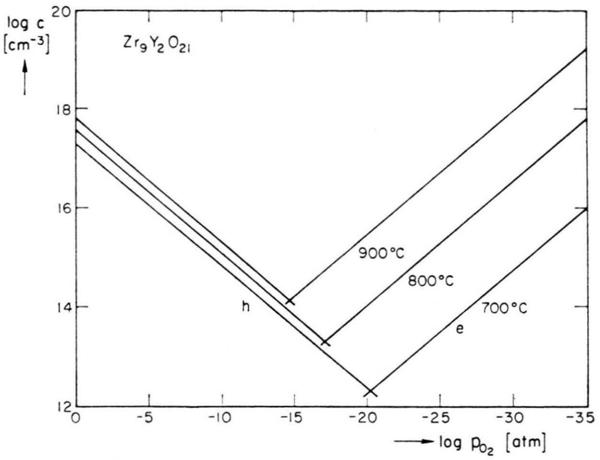

Fig. 5. Concentrations of electrons (e) and holes (h) in $Zr_9Y_2O_{21}$, calculated from conductivity data[27] and the measured diffusion coefficients of electrons and holes (Figure 4), as a function of the equilibrium oxygen partial pressure at 700, 800 and 900 °C.

From the temperature dependence of the product of the electron and hole concentrations, the electronic band gap E_g of $Zr_9Y_2O_{21}$ may by evaluated using the equation

$$c_e\, c_h = \left(\frac{kT}{2\pi\hbar^2}\right)^3 (m_e\, m_h)^{3/2} \exp\{-E_g/kT\} \quad (15)$$

where $\hbar$ is Planck's constant divided by 2π and $m_{e,h}$ are the effective electronic masses. According to the experimental results the band gap is found to be $E_g = 4.1$ eV.

6. Discussion

The measurements have clearly shown that low mobilities of the electrons and holes are the main cause of the low electronic conductivity of $Zr_9Y_2O_{21}$. Because of the low values of the mobilities it is assumed that the electrons and holes are partially trapped in the lattice and some kind of a hopping or small polaron mechanism occurs.

The magnitudes of the mobilities of the electronic species found in this investigation have also been observed in a number of closely related, as well as other, materials, e.g., in HfO_2[46] ($u_h = 3 \times 10^{-4}$

cm²/Vsec at 1000 °C; activation energy 0.7 eV below 1300 °C and 0.2 eV above 1300 °C), TiO_2 [47] ($u_e = 1 \times 10^{-1}$ cm²/Vsec at 1027 °C), and CeO_2 [47] ($u_e = 9.4 \times 10^{-3}$ cm²/Vsec at 800 °C). In particular, in monoclinic ZrO_2 the mobility of the holes has been estimated as 1.4×10^{-6} cm²/Vsec at 1000 °C and the p-n transition point has been found at an oxygen partial pressure of 10^{-16} atm at the same temperature [48]. This was generally confirmed by another investigator [49].

Some experimental errors limit the voltage relaxation method. First, an error may arise because of insufficient reversibility of the reference electrode due to a limited ability to deliver the oxygen necessary during the relaxation process. The maximum current, however, is obviously equal to the current passing through the galvanic cell during the preceding steady state polarization. From these measured values, and considering the decrease in the flux of the oxygen, no decisive influence is expected for reference electrodes with a high diffusivity of oxygen or metal, such as air, $Cu + Cu_2O$ or $Fe + FeO$. Also, if a totally non-reversible electrode is assumed in place of the reference electrode during the relaxation, a point with no change in concentration during the relaxation process will appear in the middle of the sample, this point working as an ideal "reversible electrode". The shape of the relaxation curve remains valid, and the maximum error for the calculated diffusion coefficient would be a factor of 4.

A more serious, fundamental limitation is the change of the charge in the electrical double layer that exists at the interface between the electrolyte and the inert electrode. Here, nearly the entire applied voltage drop appears. At very high double layer capacitances and low bulk concentrations of the electronic species the decay of the double layer charge may determine the transient voltage behavior. As shown by Raleigh [31], this process may also depend on the thickness of the sample, but inversely to the first power of the length. In order to estimate the magnitude of the possible error, it is assumed that the distribution of the equilibrium concentration of the electrons is fast compared to the change of the double layer charge. Therefore, between both electrodes a linear concentration gradient always exists. The electric current due to this gradient causes the change in the charge of the double layer and is given by the Hebb-Wagner voltage-current relationship [19–21] for the steady state polarization. Assuming an electron conductivity of $\sigma_e = 1.5 \times 10^{-7}$ $\Omega^{-1}\,cm^{-1}$ and a hole conductivity of $\sigma_h = 4 \times 10^{-11}$ $\Omega^{-1}\,cm^{-1}$ at 800 °C for zirconia in contact with $Fe + FeO$ ($p_{O_2} \approx 10^{-19}$ atm) [27] and a double layer capacitance of 100 μF/cm², the corresponding voltage relaxation due only to the double layer charge is calculated and plotted in Figure 6. This value of the double layer capacitance is reasonable in light of some experimental indications [50]. For other values the time axis is stretched or compressed linearly. As can be seen from the plot, for not too low cell voltages this double layer effect is much faster than the experimentally observed decay and is, therefore, not the rate-determining process in the described experiments. However, for small voltages its influence becomes important and, as can be seen experimentally from the curvature of the voltage versus time curves, influences the relaxation in this region. For experiments with air reference electrodes [27] also for low voltages the decay of the double layer charge is much faster, due to the much higher total electronic conductivity compared to that in equilibrium with $Fe + FeO$; the velocity here only

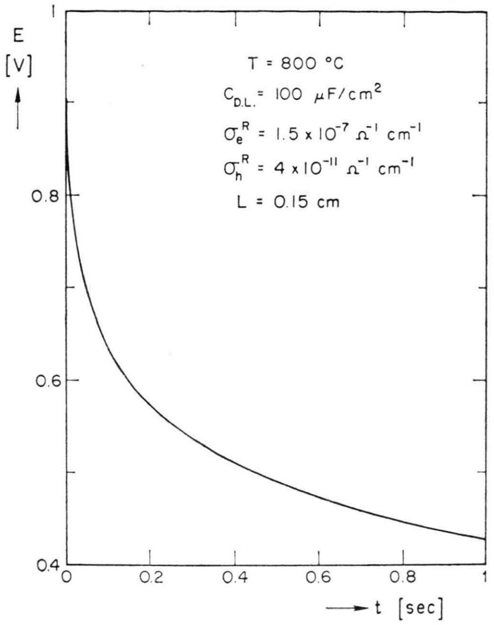

Fig. 6. Voltage relaxation of cell (I) if the change of charge of the double layer between electrolyte and inert electrode is the rate determining step. Assumed data: Electron conductivity $1.5 \times 10^{-7}\ \Omega^{-1}\,cm^{-1}$, hole conductivity $4 \times 10^{-11}\ \Omega^{-1}\,cm^{-1}$ double layer capacitane 100 μF/cm², sample thickness 0.15 cm; 800 °C.

slows down to a constant rate of about 15 mV/sec at 800 °C and 100 mV/sec at 900 °C when hole conduction predominates.

Another serious, but more or less avoidable error is that the inert electrode is not absolutely inert but is a small sink for oxygen and therefore a source for electrons. The error is smaller the more inert the gas and the lower the oxygen solubility and diffusion in the electrode metal, as well as when the volumes of the gas compartment and the metal are smaller. In this respect, silver is not very favorable, but at high polarizations the oxygen partial pressure, determined by the applied voltage is so small that the oxygen solubility or its change during the decay of the voltage is negligible. The voltage relaxation, calculated if the filling of the inert gas volume is the rate determining step, results in a very much faster decay than that for the double layer effect shown in Figure 6. Therefore, this error is of minor influence here.

In conclusion, the voltage relaxation method has been proven to be suitable for the determination of the minority charge carriers in solid electrolytes. However, in each case, possible limitations have to be considered carefully.

Acknowledgement

The author acknowledges helpful discussions with Professors R. A. Huggins, S. Miyatani, H. Rickert and Mr. E. Hellstrom. To the latter he is also indebted for help in preparing the English version of this paper.

[1] W. Nernst, Z. Elektrochem. **6,** 41 [1899].

[2] C. Wagner, Naturwiss. **31,** 265 [1943].

[3] F. Hund, Z. Elektrochem.**55,** 363 [1951].

[4] F. Hund, Z. physik. Chem. **199,** 142 [1952].

[5] T. H. Etsell and S. N. Flengas, Chem. Rev. **70,** 339 [1970].

[6] K. Kiukkola and C. Wagner, J. Electrochem. Soc. **104,** 308 [1957].

[7] Y. Matsushita and K. Goto, in: Thermodynamics, Proc. Symp. Thermodyn., Vol. **1**, p. 111, IAEA, Wien 1966.

[8] B. C. H. Steele, in: EMF Measurements in High Temperature Systems (C. B. Alcock, Ed.), p. 3, Institute of Mining and Metallurgy, London 1968.

[9] H. Rickert and R. Steiner, Naturwiss. **52,** 451 [1965].

[10] H. Rickert and R. Steiner, Z. physik. Chem. NF **49,** 127 [1966].

[11] H. Rickert, in: EMF Measurements in High Temperature Systems (C. B. Alcock, Ed.), p. 59, Institute of Mining and Metallurgy, London 1968.

[12] W. F. Chu, H. Rickert, and W. Weppner, in: Fast Ion Transport in Solids. Solid State Batteries and Devices (W. van Gool, Ed.), p. 181, North Holland Publ. Co., Amsterdam-London 1973.

[13] H. Rickert and W. Weppner, Z. Naturforsch. **29 a,** 1849 [1974].

[14] J. Weissbart and R. Ruka, in: Fuel Cells, Vol. II (G. J. Young, Ed.), Am. Chem. Soc. 140th Meeting, Chicago, Reinhold Publ. Corp., New York 1963.

[15] J. Weissbart and R. Ruka, J. Electrochem. Soc. **109,** 723 [1962].

[16] D. Yuan and F. A. Kröger, J. Electrochem. Soc. **116,** 594 [1969].

[17] W. Fischer, H. Kleinschmager, F. J. Rohr, R. Steiner, and H. H. Eysel, Chemie-Ing. Techn. **43,** 1227 [1971]; **44,** 726 [1972].

[18] W. Pluschkell, Arch. Eisenhüttenwes. **46,** 11 [1975].

[19] M. Hebb, J. Chem. Phys. **20,** 185 [1952].

[20] C. Wagner, Proc. 7th Meeting CITCE, Lindau, 1955, Butterworth, London 1957, p. 361.

[21] C. Wagner, Z. Elektrochem. **60,** 4 [1956].

[22] J. W. Patterson, E. C. Bogren, and R. A. Rapp, J. Electrochem. Soc. **114,** 752 [1967].

[23] R. Steiner, Thesis, Karlsruhe 1969.

[24] L. D. Burke, H. Rickert, and R. Steiner, Z. physik. Chem. NF **74,** 146 [1971].

[25] L. M. Friedman, K. E. Oberg, W. M. Boorstein, and R. A. Rapp, Met. Trans. **4,** 69 [1973].

[26] R. Hartung, Z. physik. Chem. Leipzig **254,** 393 [1973].

[27] W. Weppner, to be published.

[28] A. W. Smith, F. W. Meszaros, and C. D. Amata, J. Amer. Ceram. Soc. **49,** 240 [1966].

[29] R. Hartung and H. H. Möbius, Z. physik. Chem. Leipzig **243,** 133 [1970].

[30] L. Heyne and N. M. Beekmans, Proc. Brit. Ceram. Soc. **19,** 229 [1970].

[31] D. O. Raleigh, Z. physik. Chem. NF **63,** 319 [1969].

[32] A. V. Joshi, Ph. D. Thesis, Northwestern University, 1972.

[33] A. V. Joshi, in: Fast Ion Transport in Solids. Solid State Batteries and Devices (W. van Gool, Ed.), p. 173, North Holland Publ. Co., Amsterdam-London 1973.

[34] A. V. Joshi and J. B. Wagner, Jr., J. Phys. Chem. Solids **33,** 205 [1972].

[35] A. V. Joshi and J. B. Wagner, Jr., J. Electrochem. Soc. **122,** 1071 [1975].

[36] I. Yokota, J. Phys. Soc. Japan **8,** 595 [1953].

[37] S. Miyatani, J. Phys. Soc. Japan **10,** 786 [1955].

[38] K. Weiss, Z. physik. Chem. NF **59,** 242 [1968].

[39] K. Weiss, Electrochimica Acta **16,** 201 [1971].

[40] L. Brewer and P. R. Wengert, Met. Trans. **4,** 83 [1973].

[41] P. J. Meschter, Ph. D. Thesis, Univ. of Pennsylvania, Philadelphia 1974.

[42] P. J. Meschter and W. L. Worrell, to be published in Met. Trans.

[43] W. Weppner, to be published.

[44] H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, Oxford Univ. Press, London 1959.

[45] J. Crank, The Mathematics of Diffusion, Oxford Univ. Press, London 1967.

[46] N. M. Tallan, W. C. Tripp, and R. W. Vest, J. Amer. Ceram. Soc. **50,** 279 [1967].

[47] R. N. Blumenthal, J. Solid State Chem. **12,** 307 [1975].

[48] R. W. Vest, N. M. Tallan, and W. C. Tripp, J. Amer. Ceram. Soc. **47,** 635 [1964].

[49] M. M. Nasrallah and D. L. Douglass, J. Electrochem. Soc. **121,** 255 [1974].

[50] A. T. Filyaev, S. V. Karpachev, and S. F. Pal'guev, Dokl. Akad. Nauk SSSR **149,** 909 [1963].

[51] K. Kitazawa and R. L. Coble, J. Amer. Ceram. Soc. **57,** 360 [1974].