Electronic Conductivity Measurement of Yttria-Stabilized Zirconia Solid Electrolytes by A Transient Technique

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Abstract

A new oxygen permeation technique is developed to measure the electronic conductivity of yttria-stabilized zirconia (YSZ). The permeation cell is a YSZ disc with an embedded Pt probe and a cavity at the center. Two porous platinum electrodes are applied on the disc surfaces. By applying a small DC bias (0.03V) across one surface electrode and the embedded probe, oxygen is pumped into the YSZ disc and stored in the cavity. In steady state, a stable Nernst potential is developed between the cavity and the outer surfaces. The Nernst voltage is very close to the applied voltage since YSZ is essentially an ionic conductor. When the DC bias is removed, oxygen permeates out of the cavity leading to a decay of the Nernst potential. Electronic conductivity of YSZ corresponding to the ambient oxygen pressure (~0.21 atm) is determined by analyzing the time dependence of

the decay of Nernst potential. The measured electronic conductivity is in good agreement with values reported in the literature.

Key Words: Electronic conductivity, transient technique, oxygen permeation, YSZ.

Introduction

Predominantly ionic conductors and mixed ionic and electronic conductors (MIEC) have numerous applications in gas permeable membranes, solid oxide fuel cells (SOFC), solid oxide electrolysis cells (SOEC) to name a few. Both ionic and electronic conductivities of MIEC are of interest.

The most commonly used technique to measure partial conductivity is the Hebb-Wagner polarization method [1-3]. In the original work by Hebb [1], electronic partial conductivity of Ag_2S was determined by measuring the electron electrochemical potential, $\tilde{\mu}_e$, (the measurable electric potential being $\varphi = -\frac{\tilde{\mu}_e}{F}$ where F is the Faraday constant) as a function of position and the net current in steady state. The derivative of the electric potential as a function of position, $\frac{\partial \varphi}{\partial x}$, allows for the estimation of the local electronic partial conductivity, σ_{elec} . Wagner suggested a different but a more convenient method, especially useful for anion conductors such as YSZ, which involves the measurement of steady state current as a function of the applied potential [2]. The

derivative of current with respect to the applied potential gives the partial conductivity at the blocking electrode. Wagner also expressed the electronic current as a function of the applied potential by considering both electron and hole transport. This expression since has been known as the Hebb-Wagner polarization equation. The application of the Hebb-Wagner method to materials such as YSZ involves fitting to the Hebb-Wagner equation [3] since in most studies the position-dependent electric potential cannot be easily measured. Many of the measurements are made under an applied voltage large enough so that parts of the sample exhibit n-type and p-type conduction as well as the intrinsic region in which the electronic conductivity is exceptionally low.

Another approach to measure the electronic conductivity of YSZ is the oxygen permeation method, which was discussed in detail by Heyne [4,5]. Oxygen permeation through a dense solid has been studied as early as the 1930s [6-8]. However, at the time the mechanism was not clear. Heyne explained oxygen permeation in terms of ambipolar transport. This method requires a permeation cell which consists of a gas-tight YSZ tubular cylinder and two YSZ discs. One disc is used to pump oxygen into the chamber; the other disc serves as the oxygen permeation path, although permeation can occur through all exposed YSZ surfaces. Heyne provided a detailed discussion on the steady state data analysis based on ambipolar transport [5]. Insofar as the non-steady state process is concerned, Fick's law of diffusion has been used to obtain diffusivity of electrons and holes in solid electrolytes [6]. Park and Blumenthal conducted both steady state and non-steady state measurements to investigate electronic transport in 8YSZ by using an oxygen permeation cell [9]. Over the past four decades, electronic conductivity

of many oxygen ion conductors such as YSZ, rare earth oxide doped ceria, pyrochlores, etc. has been measured using Hebb-Wagner and permeation methods [10-17].

In the present work, we propose a new oxygen permeation technique using a YSZ disc with an embedded Pt probe and a cavity (volume $\sim 0.25 \text{ mm}^3$) at the center of the disc. The non-steady state (or transient process) is analyzed in terms of ambipolar transport.

Experimental Details

Disc samples of 8YSZ with an embedded Pt probe without a cavity were made using the procedure described elsewhere [18]. A sample with an embedded Pt probe and a cavity at the center was made by pressing two powder pellets in each of which a removable metal disc was pressed in. After removing the metal discs the two powder pellets with surface recesses were pressed against each other (with the recesses facing each other), with a platinum wire placed in between, to create a YSZ disc with a cavity and an embedded Pt probe. The disc was then sintered at 1500°C for 5 h. Two porous platinum electrodes were symmetrically applied on the two circular surfaces of the disc and fired at 900°C for 2 h. All other exposed surfaces of the disc were coated with a glass and fired at 900°C for 2 h.

All tests were conducted in air over a range of temperatures from 550°C to 800°C by heating the sample in a tubular furnace. The disc sample was placed in a sample holder made of alumina. Each of the two porous Pt electrodes (II and III) was covered with Pt

mesh, and Pt leads were connected to the two meshes and to the embedded Pt probe (I).

A DC voltage (~ 0.03 V) was applied across electrodes I and II using a constant voltage power source (National Instruments), and was monitored by a voltmeter (Keithley 2000). The positive of the voltage source was connected to the embedded electrode (I). The charging current from electrode I to electrode II and the Nernst potential between electrodes I and III were monitored both by a low speed multimeter (Keithley 2000) and a high speed multimeter (National Instrument PXI-4065).

Theoretical Model

Charging Stage: When a DC voltage is applied across electrodes I and II with the positive connected to electrode I (the embedded Pt electrode), oxygen ions migrate from electrode II to electrode I through the 8YSZ electrolyte as shown in Figure 1(a). Electrons migrate from electrode I to electrode II through the external circuit. At electrode II neutral oxygen molecules (at triple phase boundaries) are reduced to oxygen ions. At electrode I oxygen ions are oxidized to neutral oxygen molecules and stored in the cavity. Figure 1(c) shows the equivalent circuit for the charging step. In the equivalent circuit, R_i' denotes the ionic resistance of the YSZ disc between II and I, and R_e' denotes the electronic resistance of the YSZ disc between II and I. Note that $R_e' \gg R_i'$. Thus, the charging current is dictated by the ionic resistance, R_i' , between the surface electrode II and the embedded probe I. It is assumed that much of resistance is associated with the YSZ electrolyte and electrode

polarizations are much smaller. This assumption was verified in an earlier study by the authors [18]. If the electrode polarization resistances cannot be neglected, the equivalent circuit will have three separate segments connected in series, as shown previously by one of the authors [19].

As the oxygen partial pressure in the cavity increases, the Nernst potential between the embedded Pt probe and the two porous Pt electrodes increases. The Nernst potential drives the dissipation current of oxygen ions from electrode I to electrode II and from electrode I to electrode III through the 8YSZ electrolyte. The balancing electron (hole) flow through the YSZ electrolyte occurs in the opposite direction – from II & III to I for electrons (in the same direction – from I to II & III for holes). The dissipation current eventually rises to the same value as the charging current so that the oxygen pressure in the cavity is maintained constant. The state in which the dissipation current equals the charging current is the steady state. Thus, during dissipation, the oxygen reduction reaction occurs at I and the oxygen evolution reaction occurs at II and III. A detailed analysis of the steady state was presented elsewhere [18].

Discharging Stage: The DC voltage is removed after the establishment of steady state. Oxygen molecules that are stored in the cavity continue to migrate from electrode I through YSZ to electrodes II and III driven by the Nernst potential. This occurs as a coupled transport of oxygen ions and electrons (and holes) through YSZ. However, due to the absence of a DC bias there is no charging current any more. As a result, the amount of oxygen in the cavity decreases leading to a decrease in the Nernst potential. The

dissipation current and the redox reactions are shown in Figure 1(b).

As an essentially oxygen ion conductor, the ionic conductivity of 8YSZ is much larger than its electronic conductivity. Therefore, the measured potential between electrode I and electrode III during the dissipation stage nearly equals the Nernst potential given by

$$E_N(t) \cong -\frac{\Delta\tilde{\mu}_e(t)}{F} = \Delta\varphi(t) = \frac{\Delta\mu_{O_2}(t)}{4F} \quad (1)$$

where $\tilde{\mu}_e(t)$ is the electrochemical potential of electrons, $\mu_{O_2}(t)$ is the chemical potential of oxygen, F is the Faraday constant, $\Delta\tilde{\mu}_e(t)$ is the difference in electrochemical potentials of electrons between I & II and between I & III, and $\Delta\mu_{O_2}(t)$ is the difference in oxygen chemical potentials between I & II and between I & III. The electrochemical potential of electrons is given by

$$\tilde{\mu}_e = \mu_e - F\Phi \quad (2)$$

where μ_e is the Fermi level and Φ is the electrostatic potential. The measurable electric potential is

$$\varphi = -\frac{\tilde{\mu}_e}{F} = -\frac{\mu_e}{F} + \Phi \quad (3)$$

The Fermi level in YSZ is different (and is lower) than the Fermi level in Pt. Electron hole flux occurs down the gradient of φ (electron flow occurs up the gradient of φ). As a result, the Φ increases in YSZ from I to II and from I to III with abrupt changes occurring across all interfaces such that Φ is higher at I in YSZ than at II and III in YSZ. The transport of O^{2-} ions, which occurs as migration flux, can be viewed as going up the gradient of Φ through the YSZ with the oxygen reduction reaction occurring at I and the oxygen evolution reaction occurring at II and III. The variation of φ from I to II and

from I to III, however, is a monotonic decrease with step changes occurring at the interfaces as previously shown in [19].

The oxygen partial pressure in the cavity at time t is given by

$$P_{O_2}^I(t) = P_{O_2}^{III} \exp\left(\frac{4FE_N(t)}{RT}\right) \quad (4)$$

As oxygen molecules continue to dissipate from the cavity near electrode I to electrodes II and III, oxygen content in the cavity decreases leading to a reduced oxygen partial pressure at electrode I. From the ideal gas law

$$P_{O_2}^I(t)V = n(t)RT \quad (5)$$

where V is the volume of the cavity and $n(t)$ is the number of moles of oxygen in the cavity at time t . The dissipation flow of oxygen molecules from electrode I to electrodes II and III can be defined as

$$Flow = -N_A \frac{dn(t)}{dt} \quad (6)$$

where N_A is Avogadro's number. Units of flow are s^{-1} .

Since the solid electrolyte is dense, there is no gas leakage. Oxygen permeation through the dense electrolyte is realized by ambipolar transport [4]. Oxygen ions migrate from electrode I to electrodes II and III, and electrons (holes) migrate in the opposite (same) directions. This process can be understood by the equivalent circuit in Figure 1(d). Therefore the dissipation flow of oxygen molecules is proportional to the dissipation current given by

$$Flow = \frac{N_A}{4F} I^{diss}(t) \quad (7)$$

Combining Equations (6) and (7) the dissipation current can be expressed as

$$I^{diss}(t) = -4F \frac{dn(t)}{dt} \quad (8)$$

Together with Equation (4) and Equation (5) the dissipation current can be further expressed as

$$I^{diss}(t) = -\left(\frac{4F}{RT}\right)^2 P_{O_2}^{11} V \left[\exp\left(\frac{4FE_N(t)}{RT}\right) \right] \frac{dE_N(t)}{dt} \quad (9)$$

The dissipation current is also given by

$$I^{diss}(t) = \frac{E_N(t)}{R_e + R_i} \approx \frac{E_N(t)}{R_e} \quad (10)$$

where R_i is the total ionic resistance and R_e is the total electronic resistance with $R_e \gg R_i$. Note that the geometry factors for the charging and the discharging steps are different. Thus, R_i is different from the ionic resistance during charging, R_i' , and R_e is different from the electrolyte electronic resistance during charging, R_e' . Note also that the R_e' is not reflected in the charging current measurement since $R_e' \gg R_i'$ (Figure 1(c)).

Combining Equations (9) and (10) the electronic resistance can be expressed as

$$R_e = -\frac{E_N(t)}{\left(\left(\frac{4F}{RT}\right)^2 P_{O_2}^{11} V \left[\exp\left(\frac{4FE_N(t)}{RT}\right) \right] \frac{dE_N(t)}{dt}\right)} \quad (11)$$

There are two methods to calculate the electronic resistance using Equation (11). The first method involves calculating the derivative of the Nernst potential with respect to time and inserting all of the measured values into Equation (11). The obtained result may fluctuate due to any noise in the data. The second method is to obtain a maximum likelihood estimate as suggested by Smith [8]. It requires expressing the Nernst potential

as a function of time by integrating Equation (11) and then fitting to the measured Nernst potential. A least squares fit gives the maximum likelihood estimate of the electronic resistance. However, since Equation (11) cannot be integrated without approximation only the first method will be used to calculate the electronic resistance.

Volume of the Cavity: In Equation (11) the only unknown parameter is the volume of the cavity. The cavity volume can be measured directly on SEM by measuring the cavity dimensions. The cavity volume can also be estimated by integrating the charging current. The method of charging current integration is discussed first.

The charging current was measured using both low speed and high speed ammeters. The measured charging current at 650°C is plotted (the red curve) in Figure 2(a) as a function of time. In Figure 2(a), the dissipation current is also plotted (the blue curve). The Nernst potential was measured between the embedded Pt electrode and electrode III (Equation (10)). The dissipation current is linearly proportional to the Nernst potential. Thus, the dissipation current should exhibit the same shape as the measured Nernst potential. In steady state the dissipation current equals the charging current. As a result the curves for the two currents eventually merge as seen in Figure 2(a). Once the steady state value of the dissipation current is known from the charging current, the dissipation current can be calculated at any time, which is plotted in Figure 2(a).

Initially before applying a DC bias there is no excess oxygen in the cavity. As a result, the Nernst potential is zero and the dissipation current is also zero. Immediately after the

DC voltage is applied, the charging current reaches the corresponding maximum value. As the Nernst potential increases, the charging current decreases gradually and merges with the corresponding dissipation current. The area under the charging current vs. time curve corresponds to the total amount of oxygen pumped into the sample. The area under the dissipation current vs. time curve corresponds to the amount of oxygen removed by permeation. The difference of the two areas corresponds to the maximum amount of stored oxygen in the cavity at the given temperature and under the applied potential in steady state and is given by

$$n_{O_2} = \frac{1}{4} n_e = \frac{1}{4F} \int_0^\infty (I_{ch} - I_{diss}) dt \quad (12)$$

From Equations (4) and (5) the volume of the cavity can be estimated as

$$V = \frac{n_{O_2} RT}{P_{O_2}^{III}} \exp\left(-\frac{4FE}{RT}\right) \quad (13)$$

Results and Discussion

Glass Sealing: All samples were coated with a glass on all surfaces except the surfaces with the porous platinum electrodes as shown in Figure 3(a). Glass Sealing has two roles: (1) It prevents oxygen permeation through the bare YSZ surfaces to ensure a well-defined geometry, and (2) prevents any possible gas leakage along the embedded probe. Also, as pointed out elsewhere [18], oxygen permeation out of the sample occurs through all surfaces exposed to the atmosphere. As shown in Figure 3(b), during charging oxygen ions migrate from the porous Pt electrode I to the embedded Pt probe. However, out permeation of oxygen from the cavity to the exposed surfaces (electrodes II and III) occurs from the entire cavity surface. The ionic resistance for charging can be calculated

using the method discussed elsewhere [18] and is given by

$$R_i' \cong \frac{(E_A - E_N(t))}{I_A(t)} \quad (14)$$

where $I_A(t)$ is the measured charging current at time t . Figure 4 shows a plot of $(E_A - E_N(t))$ vs. $I_A(t)$ at 650°C. Note that the plot is linear. Table I lists the measured R_i' over a temperature range from 550°C to 800°C. The ionic resistivity of 8YSZ, ρ_i , at 800°C was assumed as 25 Ωcm based on prior work [18]. The measured ionic resistance during charging, R_i' , at 800°C is 49 Ω (Table I). The ionic resistance is related to the ionic resistivity by

$$R_i' = g' \rho_i \quad (15)$$

where g' is the geometry factor in units of cm^{-1} . Thus, g' is estimated as 1.96 cm^{-1} . Using this value of the geometric factor, the ionic resistivity of 8YSZ was determined at all other temperatures from the measured values of R_i' (Table I).

Volume of the Cavity – Charging Current Integration: Figure 2(a) shows plots of both the measured charging current (red curve) and the estimated dissipation current (blue curve) at 800°C under an applied DC bias of 0.03V. Using Equations (12) and (13), the cavity volume is estimated as 0.26 mm^3 .

The charging current measured by both the high speed ammeter and the low speed ammeter are plotted in Figure 2(b). The high speed ammeter has a sampling rate of 3000 s^{-1} , while the low speed ammeter has a sampling rate of 1 s^{-1} . It is clear that the very

initial value of the charging current captured by the high speed ammeter is much higher than that captured by the low speed meter. However, the high speed data rapidly converged with the low speed data in a fraction of a second. The difference in the calculated number of oxygen molecules stored in the cavity using the data from the fast meter and the slow meter is only 2.4%. Therefore, the sampling rate is not that critical for the accurate determination of the cavity volume.

Volume of the Cavity – Direct Observation: The disc sample was cut and ground to the center of the cavity to measure the cavity dimensions. The cavity had a uniform thickness in the middle part with a width of about 2.05 mm with a slight tapering near the edges. The average thickness of the cavity was measured to be $\sim 75 \mu\text{m}$. Ignoring the edge of the cavity the volume of the uniform region is calculated to be 0.246 mm^3 . This value does not include the volume near the edge and does not exclude the volume of the Pt probe inside the cavity. However, the value of 0.246 mm^3 is a good approximation and it is very close to the value calculated by the charging current integration method.

Oxygen Storage – Cavity vs. Stoichiometry Change: The transient technique is based on the assumption that the oxygen pumped into the sample is stored as gaseous oxygen in the cavity. Equation (3), the ideal gas law, is used to relate the number of oxygen molecules in the cavity to the measured Nernst potential. However, when a DC bias is applied between the embedded Pt probe I and electrode II the stoichiometry of the 8YSZ electrolyte can also change to some extent [18]. In order to verify the assumption made in this transient technique that most of the pumped oxygen is stored in the cavity, samples

without cavity were also made using the procedure described elsewhere [18]. The measured charging current and the measured Nernst potential on the sample with and without cavity are plotted in Figure 5.

Both sets of measurements were made at 800°C. For the sample without a cavity, the applied DC bias was 0.05V and as a result the Nernst potential was close to 0.05V. However, to compare the two sets of measurements the data on the sample without the cavity was normalized to that of the sample with the cavity insofar as the voltage is concerned. Figure 5(a) shows that the charging current for the sample with the cavity is much greater than the sample without a cavity and maintains for a long time. Also, Figure 5(b) shows that the measured Nernst potential on the sample without a cavity sharply rises to the steady state value compared to the sample with a cavity. Eventually the two merge consistent with the attainment of steady state in both experiments. These observations are consistent with the assumption made that most of the pumped oxygen was stored in the cavity.

The Geometry Factor during Dissipation: Figures 3(b) shows a schematic of the oxygen permeation path from the cavity to the exposed surfaces. Figure 3(c) shows the geometry of dissipation current path used in the calculation. This assumes that the current path is a truncated cone. This assumption is deemed satisfactory since the sample thickness is much smaller than the diameter. The geometry factor on one side is given by

$$g_1 = \int_0^h \frac{dx}{\pi \left(\left(\frac{R-r}{h} \right) x + r \right)^2} \quad (16)$$

where R is the radius of the porous electrodes, r is the radius of the cavity, and h is the distance between the cavity and the surface electrodes (about half the disc thickness). Equation (16) integrates to

$$g_1 = \frac{h}{\pi r R} \quad (17)$$

Since permeation occurs towards both surfaces the actual geometry factor is half the above value namely

$$g = \frac{g_1}{2} = \frac{h}{2\pi r R} \quad (18)$$

For the sample with the cavity geometry in this work the value of g is estimated as 0.47.

Analysis of the Steady State Data: The data measured at 650°C with the low speed meter are plotted in Figure 6. E_A is the applied DC voltage between the embedded Pt probe and the porous Pt electrode II (Figure 6(a)); E_N is the measured Nernst potential between the embedded Pt probe and the porous Pt electrode III (Figure 6(b)); I_A is the charging current (Figure 6(c)). At $t = 300$ s a DC bias of 0.0296V was applied. Within one second E_N rose to 0.0245 V and I_A reached a maximum value of 9×10^{-6} A. The steady state was established at around $t = 1400$ s. During this period the I_A decreased with time while the E_N increased with time.

In steady state the E_N was 0.0293V and I_A was 2.9×10^{-7} A at 650°C. The electronic resistance can be calculated using [18]

$$R_e^{steady} = \frac{3E_A}{I_A^{steady}} \quad (19)$$

where R_e^{steady} is the electronic resistance obtained in steady state and I_A^{steady} is the charging current measured at steady state. The total electronic resistance at 650°C is estimated as 0.15 MΩ. The measured values of R_e^{steady} at various temperatures are given in Table II. At $t = 3910$ s the applied DC voltage was removed and the charging current instantaneously dropped to zero. However, the Nernst potential decayed slowly with time as the dissipation (permeation) is governed by the electronic resistance.

Analysis of the Transient State Data: Equation (11) is used to calculate the electronic resistance using the transient technique. The derivative of the measured Nernst potential with respect to time can be easily obtained by differentiation. However, differentiating discrete data set introduces significant noise. Thus the measured Nernst potential vs. time data were fitted to a polynomial. Figure 7(a) shows the measured Nernst potential in black and the fitted polynomial in red. The derivative of $E_N(t)$ with respect to time was obtained by differentiating the fitted polynomial. The cavity volume of 0.26 mm³ was used in the calculations, which was obtained by integration of the charging current. With these data the electronic resistance at 650°C was calculated and is plotted in Figure 7(b) which is a double y-axis plot. The red curve shows the electronic resistance and the grey curve shows the measured Nernst potential. Most of the potential decay occurs immediately after the DC bias is removed and the large slope gives a better signal-to-noise ratio. Therefore only the measurements made during this fast decay period were used for data analysis. At 650°C the electronic resistance is calculated to be about 0.14

M Ω , which is very close to the value obtained using the steady state technique [18]. Both steady state and transient state measurements were conducted over a temperature range from 550°C to 800°C. The estimated values of the electronic resistance at various temperatures are listed in Table II.

Summary of the Electronic Resistance and the Ionic Resistance: The electronic resistance measured either by the steady state method or the transient method is related to the electronic resistivity through the geometry factor given by equation (18). As stated earlier, for the sample and the cavity geometry the value of g is 0.47. The estimated electronic resistivities are listed in Table III. The estimated values of the electronic resistivities by both techniques are in good agreement. The ionic transference number at 800°C is estimated as 0.998 and higher at lower temperatures. This is again consistent with YSZ being an essentially ionic conductor. Figures 8(a) and 8(b) show the Arrhenius plots of the electronic conductivity measured by the steady state technique and the transient technique, respectively. The corresponding estimated activation energies for electronic transport are 2.2 eV and 2.1 eV, respectively. Figure 8(c) shows an Arrhenius plot of the measured ionic conductivity. The corresponding activation energy is 1.1 eV. Heyne [4] measured the activation energy in calcia-stabilized zirconia as 1.9 eV for hole conduction, 3.7 eV for electron conduction, and 1.1 eV for oxygen ion conduction [4]. Since our experiments were carried out in air, the electronic conduction is p-type. Therefore, the activation energies of 2.2 eV and 2.1 eV agree quite well with Heyne's results.

Electronic conductivity of YSZ and zirconia containing other dopants has been measured by Hebb-Wagner and the permeation technique. Table III also lists the electronic conductivity and the activation energy from a number of reported studies. All of the literature data listed in Table III represented extrapolated values since all of these studies were conducted at a temperature typically higher than 700°C. Park and Blumenthal [9] measured electronic conductivity on 8 YSZ above 850°C. In the p-type regime they measured an activation energy of 1.67 eV. Their extrapolated value of the electronic resistivity in the p-type regime (air) at 550°C is $\sim 1.0 \times 10^8 \Omega\text{cm}$, which is about 7 times larger than in the present study. Kobayashi et al [20] studied electronic conduction in Ti-doped 8YSZ. Their measurements were all above 800°C. Extrapolated value of electronic resistivity in air at 550°C from the work of Kobayashi et al. is $3 \times 10^6 \Omega\text{cm}$, which is a factor of ~ 5 lower than the present work. Thus, the measured values of the electronic conductivities in the work of Park and Blumenthal [9], Kobayashi et al. [20] and the present work are within an order of magnitude. Valov et. al. [3] measured electronic conductivity on 8YSZ single crystals above 700°C. In the p-type regime (air), the extrapolated value of the electronic resistivity at 550°C was $\sim 8.2 \times 10^4 \Omega\text{cm}$, which is much lower than either the present work or the work of Park and Blumenthal [9] or the work of Kobaysahi et al. [20]. Han and Worrell [21] measured electronic conductivity in YSZ doped with terbia up to 30 mol.%. Their values of the electronic resistivity are about 3 orders of magnitude lower, which is attributed to the added terbia. These results show that the electronic resistivity measured on 8YSZ in the present work is comparable to other reported studies which have used either a permeation technique and/or the Hebb-Wagner method. The activation energy for oxygen ion conduction measured in the

present work also agrees well with the literature, especially with the results of Kobayashi et al. [20], Park and Bluemnthal [9] and Heyne and Beekmans [4].

In the present work, electronic conductivity of 8YSZ was measured by the embedded probe technique under a very small applied voltage. As the measurements were conducted in air, the measured electronic conductivity corresponds to $p_{O_2} \sim 0.21$ atm. The procedure for measurements at other oxygen partial pressures would consist of the following steps: (1) Equilibrate the sample in an atmosphere containing a given oxygen partial pressure, p_{O_2} . Low oxygen partial pressures can be obtained in the usual manner, such as by using H_2 - H_2O gas mixtures. (2) Once equilibration is achieved (which can be determined by measuring voltage between the surface electrode and the buried electrode), a small voltage is applied across the buried electrode and one of the surface electrodes. In this manner, electronic conductivity can be measured as a function of p_{O_2} at various temperatures. The measured electronic conductivity can then fitted to the Hebb-Wagner equation from which both the n-type and p-type contributions can be determined as a function of p_{O_2} .

Summary

A new oxygen permeation technique is developed to measure the electronic resistivity of 8YSZ using a sample with an embedded Pt probe and a cavity. When a DC bias is applied between the embedded Pt probe and the porous electrode II, oxygen is pumped into the cavity. Oxygen simultaneously permeates out by a coupled transport of oxygen

ions and electronic defects. When the DC bias is removed, the only remaining process is the permeation of oxygen out of the sample. The dissipation rate is determined by the electronic resistance which can be obtained from the measured time dependence of the Nernst potential decay. Charging current integration and SEM observations were used to estimate the cavity volume. The results from both the steady state technique and the transient technique are in good agreement. The activation energies are calculated to be around 2.0 eV for hole conduction and 1.1 eV for oxygen ion conduction. A potential attribute of the proposed method is the ability to measure electronic conductivity at very small applied voltages. It has been previously reported that the lower the temperature and the higher the applied voltage, the longer is the time required to achieve equilibration [22]. Weppner [22] investigated the effect of applied voltage on the kinetics of equilibration on YSZ. In his work, the applied voltage was varied over between 1 V and 2 V. The equilibration time was greater by more than one order of magnitude at an applied voltage of 2 V. The longer equilibration time was explained by the occurrence of n-p transition within the sample and the occurrence of a significant nonstoichiometry. In the present work, the applied voltage was only 0.03 V, and measurements can be conducted at even much lower applied voltages (e.g. 0.01 V). Thus no n-p transition occurs in the sample. In fact, under the very low applied voltage, the oxygen chemical potential within the sample is essentially unchanged, and negligible changes in stoichiometry occur. Also, the cavity volume was very small, which further increased the kinetics of equilibration and dissipation. The application of a very small applied voltage in the proposed method thus allows for rapid equilibration and facilitates the measurement of electronic conductivity of YSZ at relatively low temperatures, such as 550°C demonstrated in the

present work.

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Table I. Ionic Resistance and Ionic Resistivity

Temperature (°C)	R'_i (Ω)	ρ (Ωcm)
550	1.37×10^3	6.94×10^2
600	8.68×10^2	4.41×10^2
650	3.72×10^2	1.89×10^2
700	1.81×10^2	9.19×10^1
750	9.20×10^1	4.67×10^1
800	4.92×10^1	2.50×10^1

Table II. Electronic Resistance

Temperature (°C)	R_e (Ω) Transient	R_e (Ω) Steady State
550	6.66×10^6	4.74×10^6
600	8.46×10^5	6.20×10^5
650	1.40×10^5	1.54×10^5
700	3.95×10^4	4.26×10^4
750	1.52×10^4	1.49×10^4
800	7.18×10^3	7.05×10^3

Table III. Electronic Resistivity

Temperature (°C)	ρ_e (Ωcm) Transient	ρ_e (Ωcm) Steady State	ρ_e (Ωcm) Ref [3]	ρ_e (Ωcm) Ref [16]
550	1.42×10^7	1.01×10^7	8.19×10^4	5.10×10^5
600	1.80×10^6	1.32×10^6	3.52×10^4	2.01×10^5
650	2.98×10^5	3.28×10^5	1.67×10^4	8.79×10^4
700	8.40×10^4	9.06×10^4	6.73×10^3	4.20×10^4
750	3.23×10^4	3.17×10^4	5.07×10^3	2.16×10^4
800	1.53×10^4	1.50×10^4	2.93×10^3	1.18×10^4
E_a	2.1eV	2.1eV	1.12eV	1.23eV

Temperature (°C)	ρ_e (Ωcm) Ref [21]	ρ_e (Ωcm) Ref[20]	ρ_e (Ωcm) Ref [9]	ρ_e (Ωcm) Ref [4]
550	2.51×10^4	3.01×10^6	1.06×10^8	9.67×10^8
600	1.45×10^4	7.39×10^5	2.75×10^7	2.08×10^8
650	8.97×10^3	2.12×10^5	8.27×10^6	5.31×10^7
700	5.84×10^3	6.91×10^4	2.81×10^6	1.55×10^7
750	3.97×10^3	2.53×10^4	1.06×10^6	5.14×10^6
800	2.81×10^3	1.02×10^4	4.39×10^5	1.88×10^6
E_a	0.75eV	1.81eV	1.67eV	1.9eV

Figure Captions:

Figure 1: A schematic cross sectional view of the 8YSZ disc sample with an embedded Pt probe (grey line) and a cavity (white region). a) The charge migration path and electrode reactions (R1 and R2) during the charging stage. b) The charge migration paths and electrode reactions (R3 and R4) during the discharging stage. c) The equivalent circuit describing the charging stage. d) The equivalent circuit describing the discharging (permeation) stage.

Figure 2: a) Measured charging current (red) and calculated dissipation current (blue); b) Comparison of the charging current measured using the high speed ammeter (blue) and the low speed ammeter (red).

Figure 3: a) A photo of the glass sealed sample; b) Geometry of the charging current path (solid black arrows) and the dissipation current path (dashed red arrows) when all bare YSZ surfaces except the porous electrodes are sealed with glass. c) The geometry used to calculate the geometry factor during dissipation.

Figure 4: A plot of $(E_A - E_N(t))$ vs. $I_A(t)$ at 650°C. The slope gives the ionic resistance during charging, R_i' .

Figure 5: a) The measured charging currents on the samples with and without cavity; b) The measured Nernst potentials on the samples with and without cavity.

Figure 6: a) The applied DC voltage between electrodes I and II; b) The measured Nernst potential between electrodes I and III; c) The measured charging current.

Figure 7: a) Polynomial fitting of the measured Nernst potential; the black dots are the measured data and the red curve is the best fit. b) A double y-axis plot, with the left y-axis as the electronic resistance and the right y-axis as the measured Nernst potential.

Figure 8: a) Arrhenius plot of the electronic conductivity measured by the transient technique; b) Arrhenius plot of the electronic conductivity measured by the steady state technique described in [18]; c) Arrhenius plot of the oxygen ion conductivity.

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