

DC Electrical Current Behavior of Calcia Doped Zirconia Under Various Oxygen Containing Gases

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The DC current variation of calcia doped zirconia single crystal was measured under various oxygen containing gases at high temperatures. The DC current was influenced by the gas species for oxygen activity establishment. Also, strong non-ohmic characteristics were observed in the CO/CO₂/N₂ gas mixtures. Based on the experimental data obtained by introducing the non-buffering gas N₂ into the CO/CO₂ mixtures, the processes occurring at the gas/solid interface during a defect relaxation process are discussed

Key words : Calcia doped zirconia, DC current, Solid electrolyte

I. Introduction

Stabilized zirconia has historically received the greatest attention as a solid electrolyte membranes in electrochemical devices, such as oxygen sensor cells for metals processing or for combustion control, fuel cells for electricity generation, and oxygen pump cells for partial pressure regulation. The introduction of di- or trivalent oxides, such as CaO, Y₂O₃, MgO that are added to stabilize the zirconia into the cubic structure occurs oxygen ion vacancies as charge-compensating effects, and the resulting high oxygen ion diffusion coefficient imparts good ionic conductivity. Stabilized zirconia acts as a predominantly ionic conductor over a wide range of oxygen partial pressures. These features make it suitable for a variety of device applications.

When a DC voltage is applied to the oxide solid electrolyte consisting a porous Pt electrode under oxygen containing gases, current would be transferred by the following two steps. The steps are i) transport processes in the electrolyte, i.e. migration of O²⁻ ions, and ii) a charge transfer reaction at the gas/solid interfaces, i.e. O₂(gas) + 4e(metal) ⇌ 2O²⁻(electrolyte).

The first step of reaction may cause changes in the homogeneity and/or microstructure within the electrolyte which may correspond to a partial demixing.^{1,2)} Although demixing has been observed in other systems, such as the (Co,Mg)O system,³⁾ it is still unknown whether any significant demixing occurs in doped zirconia. Electrical and/or oxygen potential gradients, which is existed in operating of device, act as driving forces for the drift of point defects as well as ions. If two cations present in the doped oxide have different mobilities, one type of ion will move faster than the other one. This should cause a partial demixing. The expected partial demixing of the

electrolyte may change its electrical resistance with time until a steady state is reached after a sufficiently long time.

The second step of reaction lead to interface polarization phenomena. The interfacial reactions will most easily occur at the three phase boundary of electrode, electrolyte, and gas phase.⁴⁾ It is necessary to maximize the effective three phase boundary region, therefore, porous Pt electrodes are generally employed. However, the electrode reaction may not be limited to precise three phase boundary region. The reaction takes place more or less along the entire metal-electrolyte contact area, involving gas permeation through the metal and/or surface diffusion of adsorbed gas along the metal-electrolyte interface. A limited degree of reaction at the gas-electrolyte interface is in principle possible if the electrolyte has some electronic conductivity.

If all of above two steps could be very fast, no overpotential would be induced at the gas/solid interfaces. In reality, this not the case, and polarization voltages is to be built up. Some review articles⁵⁻⁸⁾ and general articles⁹⁻¹⁷⁾ supply the importance of gas/solid interfaces reaction for oxide ion conductors.

Yanagida *et al.*¹²⁾ measured the direct current-voltage characteristics of a symmetrical cell Pt₁Po₂(I)/Zr_{0.85}Ca_{0.15}O_{1.85}/Pt₁Po₂(II), with Po₂(I)=Po₂(II) at 560°C under oxygen pressures from 1 to 10⁻²⁰ atm. Marked non-ohmic characteristics were observed in his experiment using the Pt paste electrode sintered at 800°C for 0.5 hr. The low voltage region of <2 V showed an oxygen pressure dependence, and the rate-determining process was the diffusion of oxygen atoms through the Pt electrode. The high field region showed practically no Po₂ dependence and the rate-determining step was the direct oxygen moving from the gas phase into the zirconia.

Similar measurements using Pt electrodes of various types were performed at 500–700°C under $P_{O_2}=1\sim 10^{-4}$ atm by Brook *et al.*¹³ For applied voltages of 0–3 V, sputtered or porous paste electrode fired at 800°C were found to have an ohmic I-V characteristics with a resistance equal to the bulk ionic resistance. Thus the rate-controlling mechanism with electrodes of these types were ionic conduction through the zirconia. The I-V characteristics of the other Pt electrodes, such as foil, fluxed paste, and non-fluxed paste fired at higher temperatures (1300°C), showed markedly non-ohmic behavior. The rate-determining step responsible for this behavior was confined to the cathode area. Several different rate-limiting mechanism were proposed for the various types of Pt electrodes, depending on the value of the applied field.

These experiments show that the rate of take up of oxygen at the cathode may be limiting. The magnitude of the effect depends strongly on the electrode preparation routes, and it is only present at relatively high applied voltages. These experiments were all performed in air having higher oxygen pressure. Other experimental variables, such as gas atmosphere, may also be in a matter of concern and interest.

Binder *et al.*⁹ measured I-V characteristics of 15 mol% CaO doped ZrO_2 with porous Pt electrodes under H_2 - H_2O and CO - CO_2 gas mixtures at 900–1000°C. For H_2 - H_2O mixtures negligible polarization were observed, but a considerable polarization was found for CO - CO_2 mixtures of lower ratio. These results suggested a competitive adsorption process, where CO_2 was more readily adsorbed at comparable CO and CO_2 pressures. However, the work of Karpachev *et al.*¹⁰ showed the much less pronounced effect of the CO/CO_2 ratio. Considerable polarization was found even at high CO/CO_2 ratios. Like these, there are many discrepancies in the same system.

Similar gas phase dependence on DC polarization was performed at 800°C using air and CO - CO_2 mixtures of ratio 1 by Möbius and Rohland.¹¹ They also investigated various electrodes effect. For Pt electrode, CO - CO_2 mixtures showed much more polarization than air, and a pronounced effect of the electrode material was observed.

The problems of kinetics for when a DC voltage is applied to the oxide solid electrolyte are obviously complex and there is still scope for careful experimentation in order to determine unambiguously the mechanisms which are operating under given conditions. To simplify the complex structures, using CaO doped ZrO_2 single crystal attached the sputtered Pt electrode, the DC current behaviour is measured as a function of time at 1300°C under various oxygen containing gases.

II. Experimental Procedures

Single crystals of 14 mol% CaO doped ZrO_2 with about 10 mm diameter and 0.5–0.8 mm thickness (Ceres Corporation) were used as the sample. The experimental ar-

rangment for electrical measurements is schematically shown in Fig. 1. Each sample was coated on both side with sputtered platinum (2×10^{-6} Torr argon, 50 Å/sec). The sputtered Pt electrode consisted of about 6 mm diameter and 200 Å thickness. The 80-mesh Pt10Rh gauzes (Johnson Matthey Inc.) were pressed between the spring-loaded alumina tubes. Jagged edges were made in the alumina tube to facilitate the gas flow. On the side of each sample, a Pt10Rh electric leadwire was connected to the gauzes so that the sample data could be taken. Temperature measurements were taken with a Pt 30Rh-Pt6Rh thermocouple.

Constant DC voltages operated in voltage source (Keithley 230 programmable voltage source) were applied to the sample using a circuit consisting of a resistor. Potential reading between the resistor was taken with a digital multimeter (Keithley 195 system DMM). The potential reading was recorded by a plotter, and converted into current. Applied voltage range was 0.2–1 V.

Various oxygen containing gases were made from air,

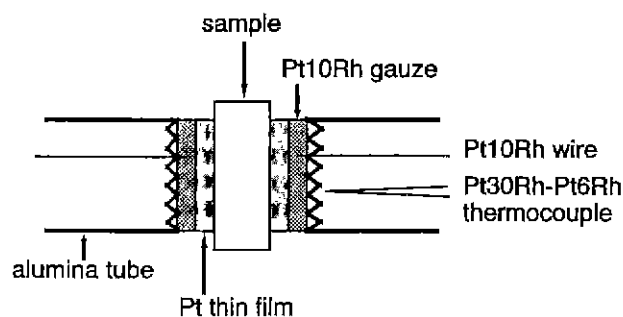


Fig. 1. Schematic configuration of sample for electrical measurements.

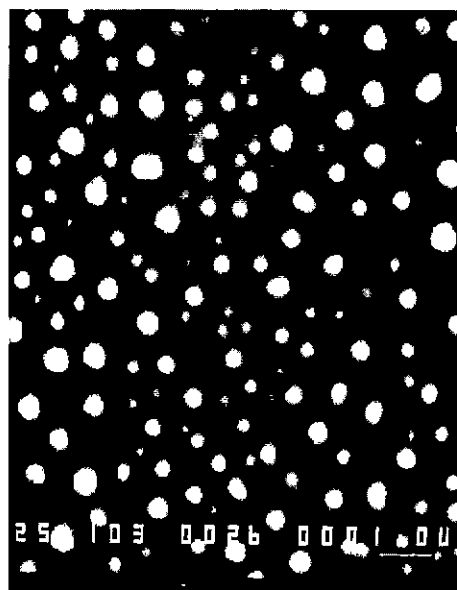


Fig. 2. Scanning electron micrograph of sample measured at 1300°C for 141 hr under $CO/CO_2/N_2$ mixture gas. Sintered small Pt particles were scatterly shown.

N_2 , and gas mixtures of air and N_2 , of CO and CO_2 , and of CO, CO_2 and N_2 with different mixing ratios using special gas mixing pumps (H. Wösthoff GmbH). All experiments were carried out with flowing gases at a total pressure of about 0.5 atm. An EMF zirconia cell was used to monitor the gas mixing ratios and/or the oxygen contents supplied by the gas mixing pump. The discrepancy between the measured value of an EMF cell and the theoretical value is within a few per cent.

Electrode of all samples was sintered at 1300°C in air for 3 hr. Figure 2 shows scanning electron micrograph of sample measured at 1300°C for 141 hr under $CO/CO_2/N_2$ mixture gas. Sintered small Pt particles of $0.1\text{--}0.5\ \mu\text{m}$ diameter scatterly exist on stabilized zirconia matrix up to for a long time.

III. Results and Discussion

As an example of the oxide MO with completely reversible electrodes we can consider the two cases.⁵⁾ One case is that the sample is in equilibrium with the electrodes consisting of the metal component M. The other case is that it is in equilibrium with the oxygen present in the surrounding atmosphere through the porous inert electrodes. In above situation, since the reversibility of the electrodes is assumed, the sample is in equilibrium everywhere and no concentration gradients are formed. This means that the chemical potential gradient term becomes zero in flux equation of conducting species i . Therefore, the electrical current density is proportional to electrical potential gradient (i.e. applied voltage). This shows the Ohm's law behavior.

DC electrical current versus time curve as a function of applied voltage was measured in 20% CO in CO_2 diluted with 95% N_2 at 1300°C , as shown in Fig. 3(a). With increasing voltage current non-linearly flows much more. It shows that the sample has a non-ohmic behaviour (Fig. 3(b)). Also, at high applied voltages current is much changed with time, and it takes many time to obtain a steady state. Similar behaviour was observed in air. However, non-ohmic characteristics in air is weaker than in CO/CO_2 gas mixture. Time dependence between high voltage and low voltage regions is different. In the case of both atmosphere, current gradually tends to decrease with time at low voltage region (0.2 V) and then is reached in the steady state. However, with increasing voltage current increases with time probably as a result of the increasement of the electronic component of the current. Similar time dependence of current was observed by Heyne^{5,18)} and Yanagida *et al.*¹²⁾ even though having the higher voltage region of 2~3 V. Heyne confirmed the increasement of the electronic component by a determination of the amount of oxygen transported. The amount of oxygen transported showed a corresponding decrease in time as did the resistance.

The observed non-ohmic characteristics in this ex-

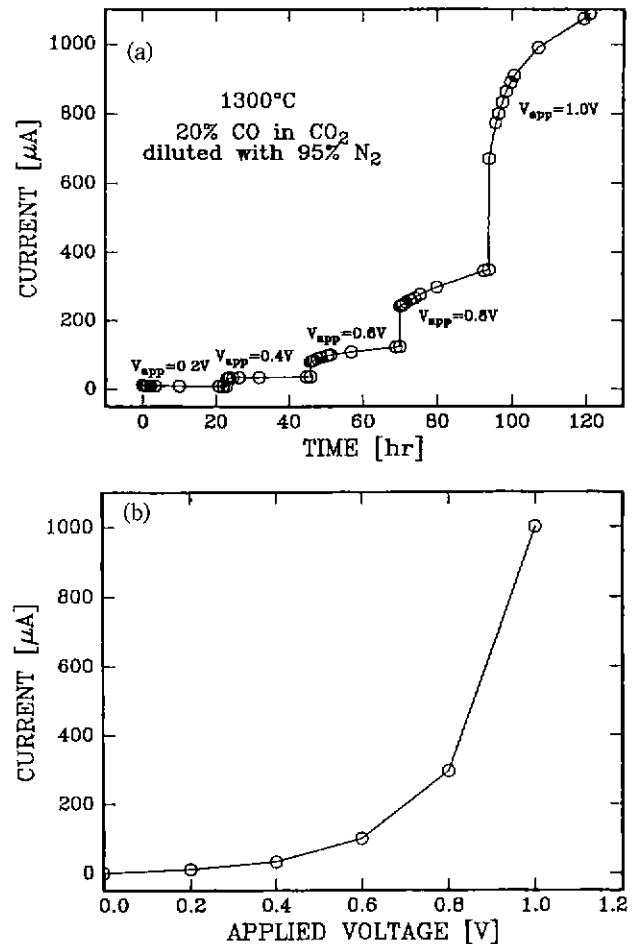


Fig. 3. (a) DC electrical current vs. time curve as a function of applied voltage measured in 20% CO in CO_2 diluted with 95% N_2 at 1300°C . (b) DC electrical current vs. applied voltage curve measured in above condition. Non-ohmic characteristics were shown seriously.

periment indicate that the boundary regions are not in exact equilibrium with the gas phase. Slow gas diffusion into three phase boundary of electrode, electrolyte, and gas phase causes the overpotential voltages, the lower is the gas pressure and the higher is the current density.⁶⁾ The effect is clearly evident from this experimental results: $CO/CO_2/N_2$ mixture gas, which has the lower oxygen partial pressure, has more non-ohmic characteristics; with increasing voltage current non-linearly flows much more.

Figure 4 shows the DC electrical current behaviour under various oxygen containing gases. Experiment was done at 1300°C with an applied voltage of 0.4 V. We can easily see the fact that current is strongly influenced by the gas species for oxygen activity establishment. This is in contrast with the oxygen partial pressure independence in the electrical conductivity of doped zirconia.

In the case of doped zirconia, variation in the concentration of oxygen ion vacancies due to variations in oxygen partial pressure may be neglected in comparison with the vacancy concentration caused by doping. There-

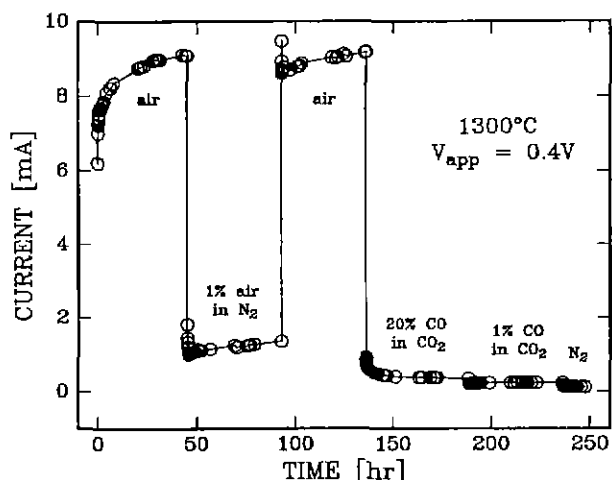


Fig. 4. DC electrical current under various oxygen containing gases.

fore, the concentration of oxygen ion vacancies may be considered as being approximately constant over a wide range of oxygen partial pressures i.e. the total conductivity which the partial conductivity of oxygen ions plays a main role becomes constant. On the other hand, the concentration of electron and hole obtained with the aid of equation which describes the incorporation of oxygen into the lattice shows the partial pressure dependence. At lower oxygen partial pressures electronic conductance becomes dominant, at higher oxygen partial pressures hole conductance. The partial pressure and temperature region over which the electronic contribution is less than 1%, i.e. the electrolytic domains, is of common knowledge.^{19,20} The oxygen partial pressures of the gas species used in this experiment are within the electrolytic domains. Therefore, the total conductivity measured by the use of a four point method or alternating current method is expected to be a constant under the oxygen partial pressures and temperatures used in this experiment.

In Fig. 4 different oxygen partial pressures were established by using air, N_2 , and gas mixtures of air and N_2 , of CO and CO_2 with different mixing ratio. Air and 1% air in N_2 include the oxygen partial pressures of 2.1×10^{-1} atm and 2.2×10^{-3} atm, respectively. Gases of 20% CO in CO_2 and 1% CO in CO_2 have the oxygen partial pressures of 10^{-4} atm and 10^{-5} atm at $1300^\circ C$, respectively. Also, the oxygen content of pure nitrogen gas was typically 10^{-4} atm according to the measured value by an EMF cell. The current in air atmosphere was abruptly decreased with changing into gas atmosphere of 1% air in N_2 . Air was used over again in order to confirm the reproductivity of current variation. The initial current response has roughly similar value as before, but there is appreciable difference and instability.

The CO/CO_2 mixing ratio dependence of current was also shown in Fig. 4. In lower mixing ratio more overpotential behaviour was observed. These results is qual-

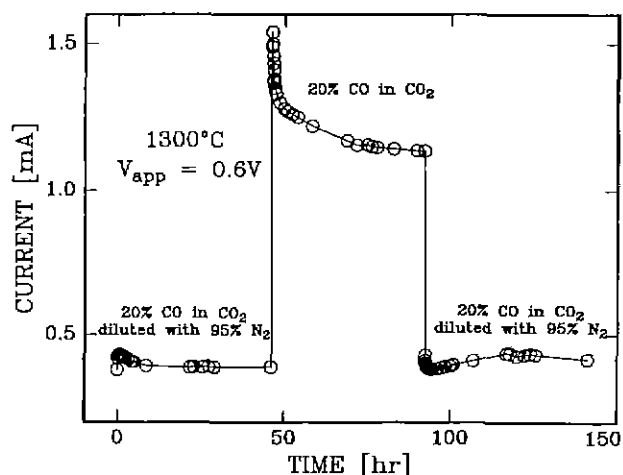


Fig. 5. Variation of DC electrical current under different mixture gases containing almost same oxygen partial pressure.

itatively consistent with the work of Binder *et al.*⁹ They found no appreciable polarization with $CO/CO_2=9$, but a considerable amount was found for $CO/CO_2=1$ and considerable more for $CO/CO_2=0.1$. Comparison of current between in gas mixtures of CO and CO_2 and in pure N_2 shows that there is no oxygen partial pressure dependence for this case. Oxygen partial pressure of CO/CO_2 gas mixtures is less than one of N_2 , but current flows much more.

Similar effect is well shown in another experimental data. Figure 5 shows the variation of current under different mixture gases containing almost same oxygen partial pressure. Current versus time were recorded, and sample was run until the current reach a steady state. Gas mixtures of 20% CO and 80% CO_2 have an oxygen partial pressure of about 10^{-4} atm at $1300^\circ C$. If we dilute the mixtures of 20% CO and 80% CO_2 with the nitrogen gas, the oxygen in nitrogen gas having the oxygen partial pressure of about 10^{-4} atm may be assumed to react with CO to form CO_2 . This may have influence on the CO/CO_2 ratio in the $CO/CO_2/N_2$ mixtures. However, the oxygen partial pressure may be almost same due to the small variation of CO/CO_2 ratio. That was confirmed by an EMF cell.

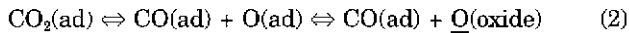
We can easily know from Fig. 5 that two different mixture gases have almost same oxygen partial pressures, but the currents have the different value. The current measured in 20% CO in CO_2 is much more higher than in 20% CO in CO_2 diluted with 95% N_2 . This means that the DC current of the zirconia solid electrolyte sample is strongly dependent on the gas species containing oxygen partial pressure. Especially, the nitrogen gas served as non-buffering gas plays an important role in decreasing the DC current as shown in Fig. 4 and Fig. 5.

The reactions between a CO/CO_2 gas mixture and an oxide solid electrolyte are considered in order to explain this behaviour as follows.

i) adsorption of CO₂ molecules



ii) conversion of adsorbed CO₂ molecules into CO molecules and oxygen incorporation into the oxide



iii) desorption of CO molecules



These reactions include adsorption/desorption of CO and CO₂ and reaction between the two gas species at the solid interface. If the processes occurring at the gas/solid interface during a defect relaxation process are very slow compared with the migration of oxygen ion in the oxide solid electrolyte, they may become the rate-controlling. Nevertheless each of these three processes may become the rate-controlling step, the same type of expression is obtained for the reaction rate in all three different cases. Eventually the equation for the rate of oxygen uptake of electrolyte $\frac{dnO}{dt}$ is induced as

$$\frac{1}{A} \cdot \frac{dnO}{dt} = k(a_{\text{O}_2}^* \cdot x_{\text{CO}_2} \cdot P_{\text{total}} [1 - (\frac{a_{\text{O}_2}^*}{a_{\text{O}_2}})^{1/2}]) \quad (4)$$

Where A is the area of the gas/solid interface. $k(a_{\text{O}_2}^*)$ represents the summarizing rate constant which depend on the oxygen activity ($=P_{\text{O}_2}/P^0$, where $P^0=1$ bar) established in the oxide at the gas/solid interface. x_{CO_2} is the mole fraction of CO₂ in the gas, P_{total} the total pressure in the gas. $a_{\text{O}_2}^*$ and a_{O_2} are the oxygen activity in the solid at the interface and in the gas, respectively.

From above eq. (4), the rate of oxygen uptake of zirconia electrolyte is proportional to the partial pressure of CO₂ in the gas. The partial pressure of CO₂ is determined by the surface concentration of adsorbed CO₂ molecules. After all, use of the diluted CO/CO₂ mixtures (20% CO in CO₂ diluted with 95% N₂ in Fig. 5) for oxygen activity establishment yields that the kinetics become slower with decreasing the partial pressure of CO₂ at constant CO/CO₂ mixing ratio. The slow kinetics cause a lowering of DC electrical current, as shown in Fig. 5.

IV. Conclusions

The current variation of CaO doped ZrO₂ single crystal attached the sputtered Pt electrode was measured under various oxygen containing gases at high temperatures.

The electric DC current was influenced by the gas species for oxygen activity establishment. This is in contrast with that the electrical conductivity of doped zirconia does not show the oxygen partial pressure dependence.

Also, as a result of the voltage-current characteristics measurement, strong non-ohmic behavior was shown in the CO/CO₂/N₂ gas mixture. Time dependence of current

was in the high voltages more strongly.

By introducing the non-buffering gas N₂ into the CO/CO₂ mixtures, we could easily understand the above phenomena. Use of diluted CO/CO₂ mixtures for oxygen activity establishment yields that the kinetics become slower with decreasing CO₂ partial pressure at constant CO/CO₂ mixing ratio.

The processes occurring at the gas/solid interface under various oxygen containing gases are stressed in order to understand DC electrical current behavior.

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