

## Characteristics of cathodic polarization at Pt/YSZ interface without the effect of electrode microstructure

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### Abstract

The characteristics of cathodic polarization at the Pt/yttria stabilized zirconia (YSZ) interface have been evaluated with different electrode microstructures by ac impedance analysis. The measurements were carried out at the temperatures of 873–1273 K and oxygen partial pressure ( $P_{O_2}$ ) in the range of 0.01–1 atm. From the results of impedance analysis, it was found that gas phase diffusion can be involved in two different ways, such as boundary-layer diffusion and pore diffusion. When the gas phase diffusion was effectively eliminated from the total electrode resistance ( $R_{e1}$ ), we observed the same dependences of temperature and oxygen partial pressure regardless of their different electrode microstructures.

In the high temperature (1073–1273 K) and low oxygen partial pressure regions (<0.01 atm  $P_{O_2}$ ), the cathode reactions included two major reactions: gas phase diffusion and direct adsorption reaction. In direct adsorption reaction oxygen molecules are directly adsorbed from the gas phase and dissociate on oxygen vacancies, which are located at the triple phase boundaries (TPB). In the low temperature (<973 K) and high oxygen partial pressure region ( $\sim 1$  atm  $P_{O_2}$ ), the cathode reaction is dominated by the dissociation of oxygen molecules at the Pt/YSZ interface.

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**Keywords:** Solid oxide fuel cell; Pt/YSZ interface; Cathode reaction; Electrode microstructure; Impedance analysis

### 1. Introduction

There is a considerable interest in yttria stabilized zirconia (YSZ) as a solid electrolyte for use in oxygen sensors, oxygen pumps, and solid oxide fuel cells (SOFCs) [1,2]. In the application of SOFCs, YSZ has been widely studied and used because of its high ionic conductivity and stability [2,3]. The thermodynamic and kinetic properties of YSZ have been well researched in the development of SOFCs [1–3]. However, the kinetics of the electrode process, especially for cathode reactions, is quite controversial even today. It is one of the reasons that the measurements have been performed at different operating temperature, oxygen partial pressure ( $P_{O_2}$ ), types of supplied gases and with microstructure of the electrodes [4–6]. Recently, many researchers have agreed that mass-transfer and charge-transport reactions are in competition in the electrode reactions and the rate determining step (RDS) can be affected by

temperature, oxygen partial pressure, electrode overpotential, and the microstructure of electrodes [7–10]. Most of all, it is believed that a different electrode microstructure can result in different behavior of the electrode reactions due to mass-transfer. Therefore, experimental data on cathode reactions should be carefully analyzed at low oxygen partial pressure.

In this study, we have tried to eliminate the effect of the electrode microstructure on the cathode reactions by analyzing impedance spectra of the electrodes with different microstructures at various operating temperatures and oxygen partial pressures. With these experimental results and the data from literature, we have proposed a cathode reaction model, which can reasonably well explain the dependences of temperature and oxygen partial pressure.

### 2. Experimental

#### 2.1. Preparation of the electrodes

The solid electrolyte was prepared with 8 mol%  $Y_2O_3$ -stabilized zirconia powder (Tosoh Co. Ltd., TZ-8Y) by uni-

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Table 1  
Summary of preparation method for the various electrodes

Sample	Materials	Sintering temperature (K)	Modification method
#1	Pt gauze	1673	No
#2	Pt paste	1373	No
#3	Pt paste + graphite	1373	Addition of pore-former
#4	Pt paste + YSZ sol	1373	YSZ sol-gel coating

axial pressing and sintered at 1773 K for 2 h into pellets of 25 mm in diameter and 1 mm in thickness with a relative density of more than 98%. This electrolyte was polished with SiC paper (#1000) and washed with isopropyl alcohol in an ultrasonic cleaner. All electrodes had a 1 cm × 1 cm area and were symmetrically applied to the center of the electrolyte. The #1 electrode was sintered with Pt gauze supplied from Alfa (52 mesh, 0.1 mm wire) under a load of 100 g/cm<sup>2</sup> at 1673 K for 2 h. The #2 electrode was prepared with Pt paste (TR-7060, Tanaka) by the tape-casting method. The #3 electrode was made with a mixture of Pt paste (#2 electrode) and pore-former (graphite, particle size 2 μm, Aldrich) to obtain a large porosity. The #4 electrode was prepared by the same method as the #2 electrode except that it was modified with YSZ sol. The dip coating of YSZ sol within the pores of cathode produced a thin-film of YSZ, leading to an increase of the triple phase boundary (TPB) length or electrochemical reaction site (ERS) [11–13]. All the electrodes were sintered at 1373 K for 2 h except the #1 electrode. The preparation method of the each electrode is summarized in Table 1.

## 2.2. Measurement of ac impedance

The schematic design of electrochemical cell is shown in Fig. 1. Pt gauze applied to the #1 electrode was used as a current collector for the other electrodes (#2, #3, and #4). The current collectors were spring loaded, as depicted in Fig. 1. Measurements were performed at temperatures from 873 to 1273 K and in the  $P_{O_2}$  range of 0.01–1 atm. The electrodes were equilibrated for 2 or 3 days at 1273 K until the ac admittances were stable. Since the long term operation of the electrodes at the high temperature can alter the morphology of the electrodes during the experiments, the usual operating temperature was maintained below 1073 K and the maximum operating temperature (1273 K) was kept as short as possible. Gas flows were regulated with a mass flow controller (Unit instruments Inc., URS-8100) and control units (Unit instruments Inc., URS-100-5). The gas flow rate was in the ranges of 100–400 cm<sup>3</sup>/min. A Pt–(Pt + 13% Rh) thermocouple was placed near the electrodes to measure the temperature. The complex impedance measurement was conducted with a Solatron 1260 (frequency analyzer) and 1287 (electrochemical interface). The ac impedance spectra in the frequency ranges of 0.01 to

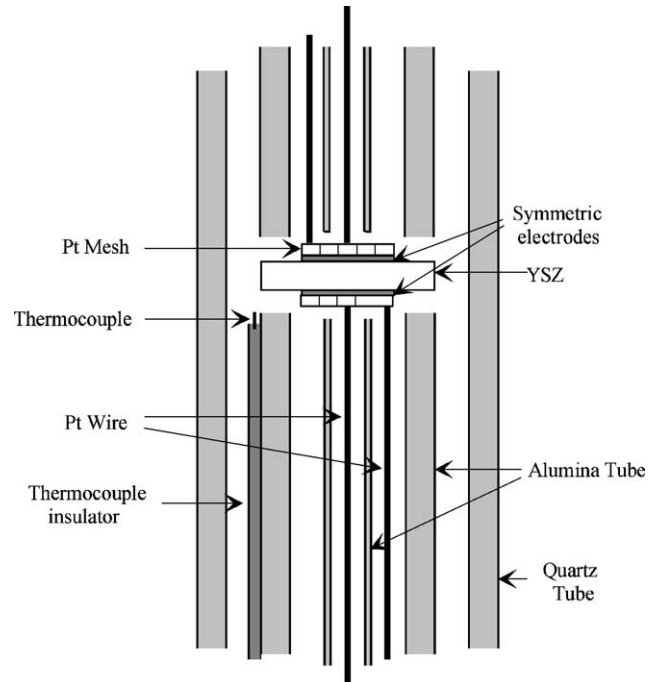
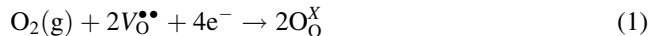


Fig. 1. Configuration of a symmetric cell.

10<sup>3</sup> kHz, with an excitation voltage of 10 mV, were taken to ensure a linear response.

## 3. Possible cathode reactions

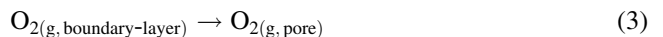
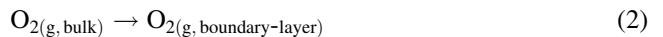
In general, the exchange of oxygen between the gas and the electrolyte can be described with the following overall reaction [14,15]:



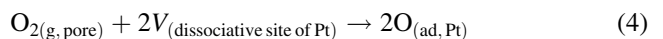
where in Kröger–Vink notation,  $V_{O}^{\bullet\bullet}$  is an oxygen vacancy and  $O_O^X$  is a normal oxygen ion in the YSZ lattice. This overall reaction (1) can be divided into largely three steps: adsorption and dissociation, diffusion, and charge-transfer reaction.

In view of preceding consideration, the possible cathode reactions can be summarized as follows [14–16]:

*Gas phase diffusion:*



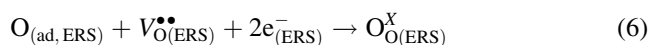
*Adsorption and dissociation:*



*Surface diffusion:*



*Charge-transfer reaction:*



Other reactions:



The reaction (2) has no relation to the electrode performance itself because the boundary-layer diffusion is only a function of the apparatus geometry and the gas flow rate [5,17]. The reaction (3) represents the gas phase diffusion through the pores of electrode which is strongly related with electrode microstructure [18]. If the reaction (2) and (3) is the rate determining step (RDS), the electrode resistance ( $R_{\text{el}}$ ) should be directly proportional to oxygen partial pressure and independent of temperature [4,5,17]. This reaction mechanism is strongly influenced by the morphology of electrodes. Reaction (4) represents the dissociative adsorption of oxygen on the surface of Pt electrodes. It is possible that the adsorption can occur associatively or dissociatively. On the Pt surface, however, the adsorption associatively occurs as oxygen molecules only under 150 K and, in the temperature of >400 K, dissociative adsorption is predominant [19]. In that case, the oxygen atoms adsorbed can participate in the cathode reaction by the surface diffusion on Pt electrode like reaction (5) [20–24] or by the bulk diffusion through Pt electrode [25,26]. In this study, however, the oxygen supply to the reaction site by diffusion through Pt-bulk can be neglected due to the low diffusivity and high activation energy of oxygen in Pt [27–29]. On the other hand, the surface diffusion of oxygen on Pt occurs at low surface coverage in the temperature of >500 K and its activation energy is 142 kJ/mol [30]. Mizusaki et al. [23,24] studied the reaction kinetics of Pt electrode at the temperature of 643–1073 K and in the  $P_{\text{O}_2}$  range of  $10^{-4}$  to 1 atm. They concluded that the charge-transfer kinetics could not be the RDS of the electrode reaction. Therefore, below 773 K, the possible RDS was dissociative adsorption of oxygen molecules on the Pt surface and, above 873 K, the surface diffusion of oxygen atoms adsorbed ( $O_{\text{ad}}$ ). Kuzin and Komarov [16] also reported that the electrode reaction rate near the equilibrium potential was limited by the diffusion rate of atomic oxygen over the Pt electrode to the triple phase boundary (TPB) line. In the surface coverage range ( $\theta$ ) of 0.05–0.5 and at the temperature of 825–1031 K, the activation energy of electrode resistance,  $R_{\text{el}}$ , was  $145 \pm 5$  kJ/mol which is very close to that (142 kJ/mol) of surface diffusion measured by Lewis and Gomer [30].

It is also suggested that the oxygen molecules, atoms, or ions adsorbed on electrolyte can participate in the cathode reaction and one of these reactions can be considered to be the RDS. For example, the equilibrium adsorption of oxygen molecules on undoped  $\text{ZrO}_2$  has been studied by Smith [31,32] at temperatures from 673 to 1173 K and in the  $P_{\text{O}_2}$  range of  $1.3 \times 10^{-8}$  to 1 atm. The author concluded that primary adsorption of molecular oxygen is stabilized by

receiving an electron from the conduction band of  $\text{ZrO}_2$  and then dissociates into atoms. The activation energies for the reversible adsorption of molecular oxygen and the irreversible adsorption of atomic oxygen are 146 and 242 kJ/mol, respectively. More recently, Meas et al. [33] observed that the amount of oxygen molecules adsorbed on YSZ was roughly equivalent to the number of anionic vacancies at the temperature of 648–973 K and in the  $P_{\text{O}_2}$  range of  $2.6 \times 10^{-7}$  to  $2.6 \times 10^{-3}$  atm. Although these results reveal the associative or dissociative adsorption on oxygen vacancies of YSZ, it is insufficient to conclude participation in the cathode reactions.

A charge-transfer reaction like reaction (6) can be also considered as the RDS. As mentioned above, both the mass-transfer reaction and charge-transport reaction can be involved in electrode reactions so that the RDS can be affected by temperature, oxygen partial pressure, electrode overpotential, and microstructure of an electrode [7–10]. However, this is not sufficient to explain the overall electrode reaction of Pt/YSZ system. For example, the Pt/YSZ system shows a low activation energy of  $80 \pm 5$  kJ/mol that is comparable to that of ionic conductivity at the high temperature and low oxygen partial pressure regions, and an abrupt increase of activation energy at the low temperature and high oxygen partial pressure regions. Therefore, we separated the experimental conditions into two parts,  $T > 1073$  K and  $P_{\text{O}_2}^{\text{low}}$ , and  $T < 973$  K and  $P_{\text{O}_2}^{\text{high}}$ .

## 4. Result and discussion

### 4.1. In the high temperature ( $T > 1073$ K) and low oxygen partial pressure ( $P_{\text{O}_2}^{\text{low}}$ ) region

The Arrhenius plots of  $R_{\text{el}}$  of the electrodes #1, #2, #3, and #4 in the temperature range of 1073–1273 K and at a  $P_{\text{O}_2}$  of 0.01 atm are shown in Fig. 2. Except for the #4 electrode

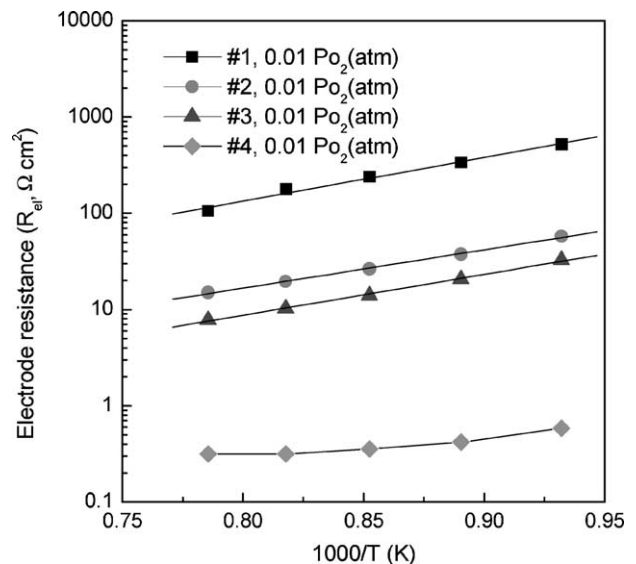


Fig. 2. Arrhenius plots of  $R_{\text{el}}$  for various electrodes in the  $P_{\text{O}_2}$  of 0.01 atm.

having an activation energy of 20 kJ/mol, all electrodes showed the same activation energy of about  $80 \pm 5$  kJ/mol. Similarly way, only the  $P_{O_2}$  dependence of the #4 electrode was larger than the others (Fig. 3). In order to find the reason for this discrepancy, we analyzed the impedance spectra of the #4 electrode under this experimental condition.

The ac impedance spectra of the #4 electrode measured at the temperature of 1273 K and in the  $P_{O_2}$  range of 0.01–0.1 atm are plotted in Fig. 4. The impedance measurements were analyzed by means of an equivalent circuit which consists of an inductance ( $L$ ) originating from the leads and the equipment, resistance ( $R$ ), and CPE (constant phase elements), as shown in Fig. 5. This overall circuit was analyzed by a complex non-linear least square (CNLS) fitting program [34]. The electrochemical components of the #4 electrode calculated by the equivalent circuit (Fig. 5) are plotted as a function of oxygen partial pressure in Fig. 6 and the Arrhenius plots of the each component are shown in Fig. 7. In general, if the electrode reaction is limited by gas diffusion through the boundary-layer, the limiting current

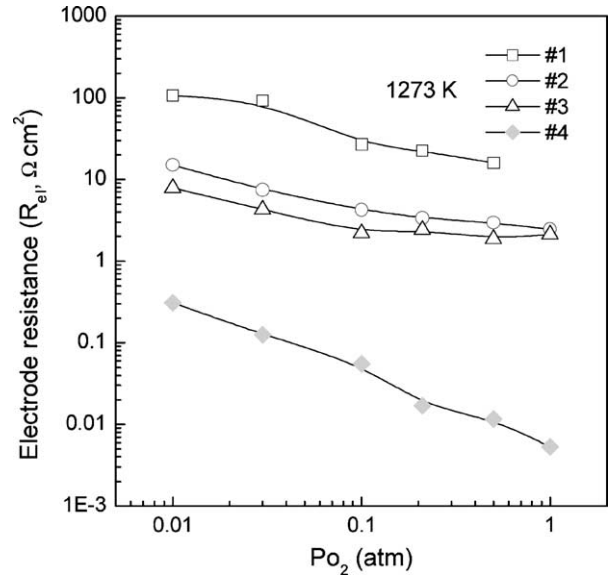


Fig. 3. Log-log plots of  $R_{ei}$  vs. oxygen partial pressure at 1273 K.

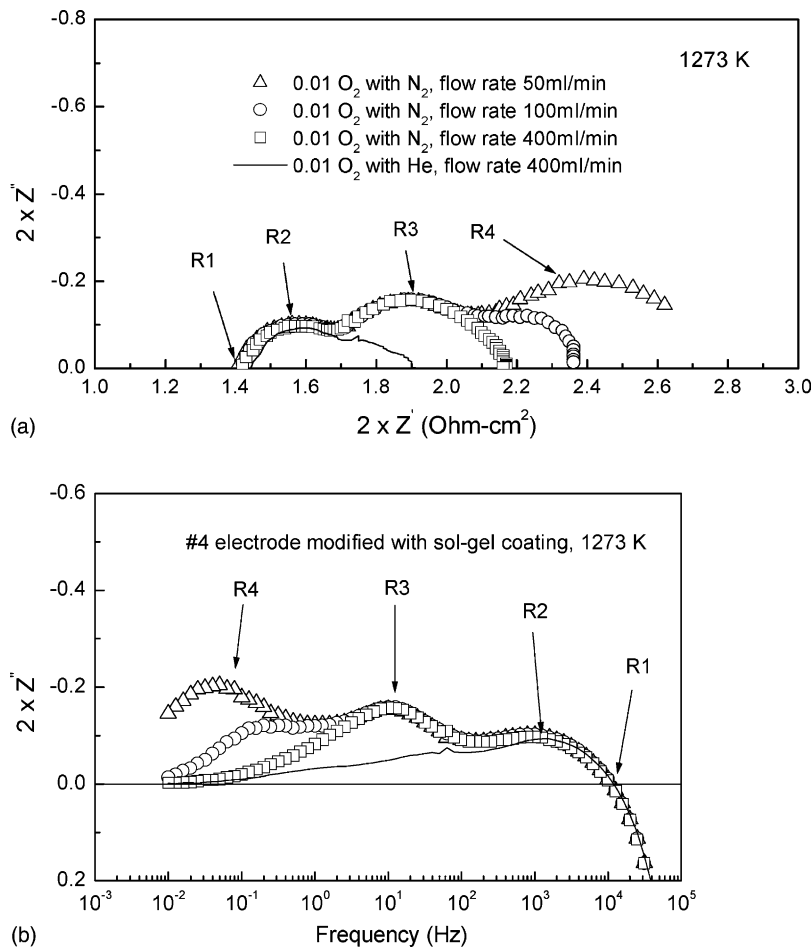


Fig. 4. Effects of gas flow rate and gas component on  $R_{component}$  of the #4 electrode at 1273 K and in 0.01atm  $P_{O_2}$ : (a) Nyquist plot; (b) comparison of spectra with frequencies.

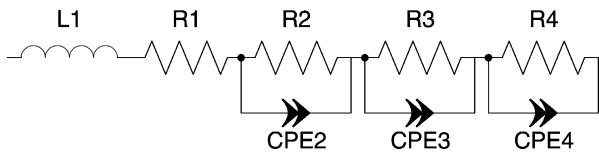


Fig. 5. Equivalent circuit used in the non-linear least square fitting of impedance diagrams.

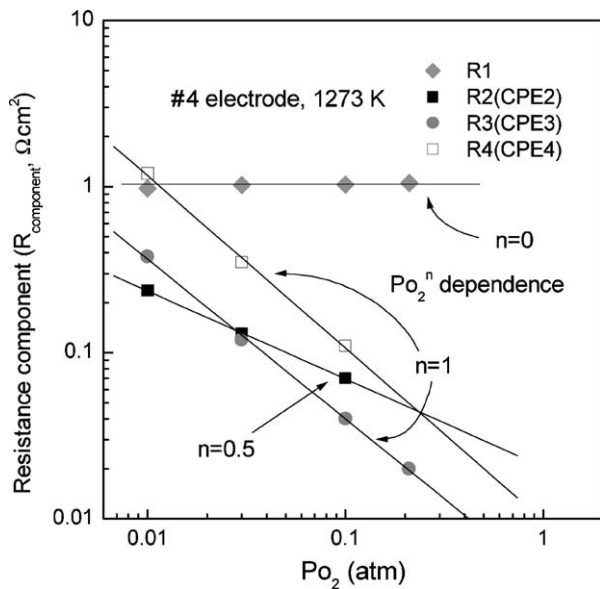


Fig. 6. Log–log plots of  $R_{\text{component}}$  of the #4 electrode vs. oxygen partial pressure at 1273 K.

( $I_{\text{lim}}$ ) and  $R_{\text{el}}$  should be dependent on the first power of the oxygen partial pressure and the gas flow rate, and exhibit no temperature dependence like a non-thermally activated process [5,35]. The R4(CPE4) in low frequency ranges (<1 Hz)

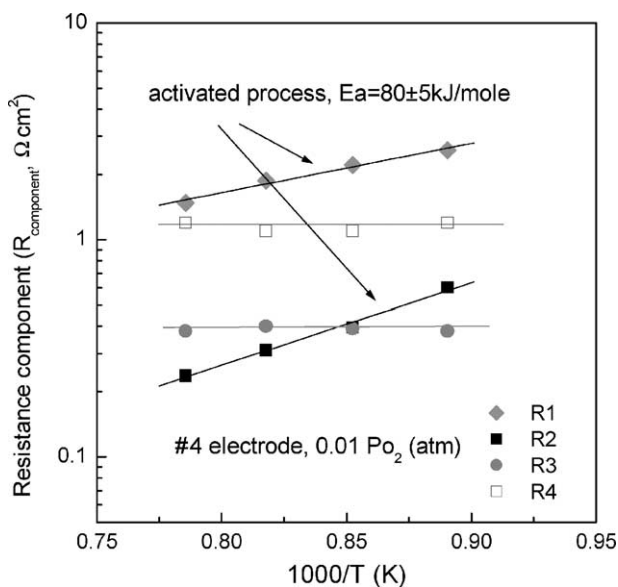


Fig. 7. Arrhenius plots of  $R_{\text{component}}$  of the #4 electrode in the constant 0.01 atm  $P_{\text{O}_2}$ .

is supposed to represent gas phase diffusion through the boundary-layer because of its first power dependence of  $P_{\text{O}_2}$  (Fig. 6), no dependence of temperature (Fig. 7), and dependence of gas flow rate and gas component (Fig. 4). On the other hand, the R3(CPE3) also showed a first power dependence of  $P_{\text{O}_2}$  (Fig. 6), dependence of gas component (Fig. 4), but no dependence of temperature (Fig. 7) and gas flow rate (Fig. 4). Therefore, we concluded that the R4 and the R3 are the boundary-layer diffusion resistance (reaction (2)) and the pore diffusion resistance (reaction (3)), respectively. Since the boundary-layer diffusion is only a function of the apparatus geometry and gas flow rate, we excluded the R4(CPE4) from the characterization of the electrode performances [17]. Consequently, the #4 electrode exhibited much lower activation energy (20 kJ/mol) and higher  $P_{\text{O}_2}^n$  dependence ( $n = 0.75$ ) than the others ( $80 \pm 5$  kJ/mol and  $n = 0.55 \pm 5$ ) because the large value of R3 related to the gas phase diffusion was involved in the cathode reactions. This is attributed to the quite different microstructure of the #4 electrode. In Fig. 8b, the surface of Pt particles was covered with porous YSZ film so that the TPB length can be enlarged [11–13]. Therefore, this electrode microstructure may be more susceptible to gas phase diffusion due to micro-pores at the additional TPB especially under the low  $P_{\text{O}_2}$  condition. Consequently, in the experimental conditions of high temperature and low oxygen partial pressure, the RDS of the #4 electrode is controlled by gas phase diffusion.

As shown in Figs. 6 and 7, the  $P_{\text{O}_2}$  dependence and the activation energy of the R2(CPE2) are similar to the  $R_{\text{el}}$  of the other electrodes (Figs. 2 and 3). The value of activation energy and  $P_{\text{O}_2}^n$  dependence were  $80 \pm 5$  kJ/mol and  $n = 0.5$ , respectively. When the gas phase diffusions were effectively eliminated from the total electrode resistance ( $R_{\text{el}}$ ), we observed the same dependences of temperature and oxygen partial pressure regardless of the electrode microstructures.

In the high temperature and low oxygen partial pressure region, the activation energy of  $R_{\text{el}}$  or exchange current density ( $I_0$ ) was widely reported as 75–100 kJ/mol [6,14,15]. Gür et al. [15] studied the polarization behavior of Pt/8 mol%  $\text{Sc}_2\text{O}_3$ - $\text{ZrO}_2$  by use of ac impedance techniques. They also reported that the bulk electrolyte and  $R_{\text{el}}$  had a similar activation energy above 973 K. But this was not clearly explained in their work. Recently, Mitterdorfer and Gauckler [36] reported that above  $\sim 1073$  K and at high oxygen partial pressures, the charge-transfer is in competition with surface diffusion. Under high temperature and low oxygen partial pressure, however, it is not supposed that the values of activation energy for the R2 (#4 electrode) and the  $R_{\text{el}}$  (#1, #2, and #3 electrodes) represent the surface diffusion of oxygen atoms on the Pt surface as compared to the values of surface diffusion given by Lewis and Gomer [30]. They reported that the activation energy of surface diffusion of oxygen atom on Pt(1 1 1) was 113 kJ/mol at high surface coverage and in the temperature ranges between 723 and



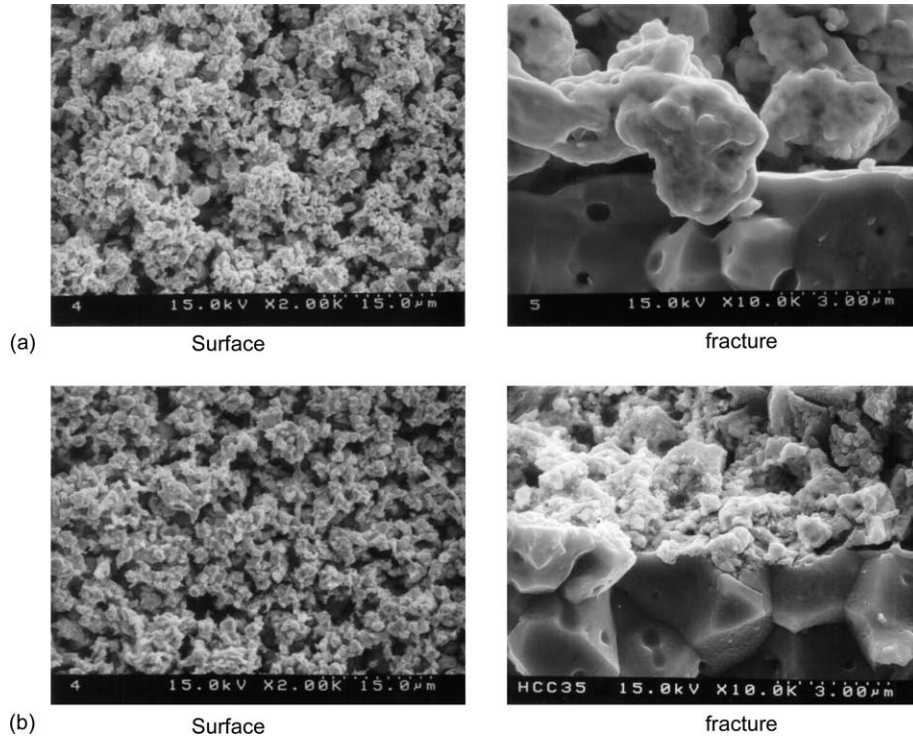


Fig. 8. SEM images of surface and fracture of the electrodes on YSZ electrolyte: (a) #2 electrode (porous Pt electrode); (b) #4 electrode (#2 electrode modified by sol-gel coating).

773 K, whereas the activation energy was 142 kJ/mol at low surface coverage and temperatures above 773 K. In our experiments, we eliminated the influences of the gas phase diffusion on the resistance of the #4 electrode, which had additional micro-pores between the TPB by sol-gel coating [11–13]. Consequently, the R2(CPE2) of the #4 electrode showed the same dependences of temperature and oxygen partial pressure as those of the others, which were not affected by the gas phase diffusion (#1, #2, and #3). In many of our experiments at high temperatures and low oxygen partial pressures, when we removed the effect of gas phase diffusions, the values of activation energy of the electrode resistance were between 70 and 80 kJ/mol. Fig. 7 clearly indicates that the electrode resistance component, the R2, has an activation energy comparable to the bulk electrolyte at the high temperature ( $T > 1073$  K) and low oxygen partial pressure ( $P_{O_2}^{low}$ ). Bauerle [37] explained that the electrolyte polarization behavior, corresponding to the electrode and the higher frequency dispersion, resulted from the blocking of the oxygen ion conduction at the grain boundaries. Although the high frequency dispersion, the R2, has the same activation energy as the ionic conductivity of YSZ like the  $R_{e1}$  of the other electrodes, it seems not to be the effect of the grain boundaries or pores due to its high operation temperature of 1273 K. Therefore, we supposed that oxygen molecules are directly adsorbed from the gas phase and dissociate on the oxygen vacancies at the TPB. In the high temperature and low oxygen partial pressure region, the surface coverage ( $\theta$ ) of Pt electrode is so low that the

cathode reactions can occur without surface diffusion on Pt electrode because there is little chance that the pre-adsorbed oxygen atoms on the Pt electrode would hinder the oxygen molecules from being adsorbed directly on the oxygen vacancies at the TPB. In addition, as compared with the values for the diffusion coefficient of atomic oxygen on Pt surface ( $D = 4.1 \times 10^{-6}$  to  $1.1 \times 10^{-7}$  cm<sup>2</sup>/s at 975 K) [38], the gas phase diffusion coefficient in O<sub>2</sub>/N<sub>2</sub> mixture is larger by several orders of magnitude at the same condition. For example, the diffusion coefficient of oxygen in air can be calculated by the following empirical Eq. (10) [39].

$$D_{AB} = \frac{0.001T^{1.75}}{P(V_A^{1/3} + V_B^{1/3})} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (10)$$

where the molecular diffusion coefficient is expressed in cm<sup>2</sup>/s,  $V_A$  and  $V_B$  are the diffusion volumes of molecules A and B, and  $M_A$  and  $M_B$  are their respective molecular weight, and  $P$  and  $T$  are their usual meanings. In general, the electrodes of fuel cells are micro-porous so that we may consider the diffusion through the micro-pores, such as Knudsen diffusion [35].

$$D_K = 9700r \left( \frac{T}{M_g} \right)^{1/2} \quad (11)$$

where  $r$  is the pore radius (cm) and  $M_g$  is the molecular weight of the gas. From Eqs. (10) and (11), the diffusion coefficient of oxygen can be obtained from  $5 \times 10^{-2}$  to 1.6 cm<sup>2</sup>/s at 975 K. So, it is reasonable that the direct

cathode reaction is predominant in the high temperature and low oxygen partial pressure regions. Consequently, if the charge-transfer reactions are infinitely fast and adsorption and dissociation process are also quite fast, the RDS should be the migration of oxygen vacancies to the TPB line in this experimental region. Thus, the R2 of the #4 electrode and the  $R_{el}$  of the other electrodes showed the same activation energy of ionic conductivity of YSZ (Figs. 2 and 7). van Hassel et al. [40] and Nguyen et al. [9] also observed that the activation energy of  $R_{el}$  at Au/YSZ interface was equal to that of the ionic conductivity of the YSZ. This is the reason that the direct reaction is predominant in the wide range of temperatures and oxygen partial pressures because of the low catalytic activity of the Au electrode in the oxygen exchange reaction. However, the R2 of the #4 electrode and the  $R_{el}$  of the other electrodes showed linear dependence of  $P_{O_2}$  in this experimental condition (Figs. 3 and 7). This is attributed to the effect of surface diffusion (reaction (5)), which is more predominant in higher oxygen partial pressure or at higher surface coverage ( $\theta$ ).

#### 4.2. In the low temperature ( $T < 973$ K) and high $P_{O_2}$ ( $P_{O_2}^{high}$ ) region

Fig. 9 shows the Arrhenius plots of  $R_{el}$  with different microstructures of the electrodes (#1, #2, #3, and #4) at the low temperature and high oxygen partial pressure. The activation energy values of the  $R_{el}$  of all the electrodes were between 200 and 240 kJ/mol. In this experimental region, there was no gas phase diffusion resistance even in the impedance spectra of the #4 electrode. Moreover, in the oxygen partial pressure of 0.01 atm, the RDS of the #4 electrode was no longer the gas phase diffusion because the other electrode reactions increased exponentially while the gas phase diffusion was almost constant with decreasing the operating temperature.

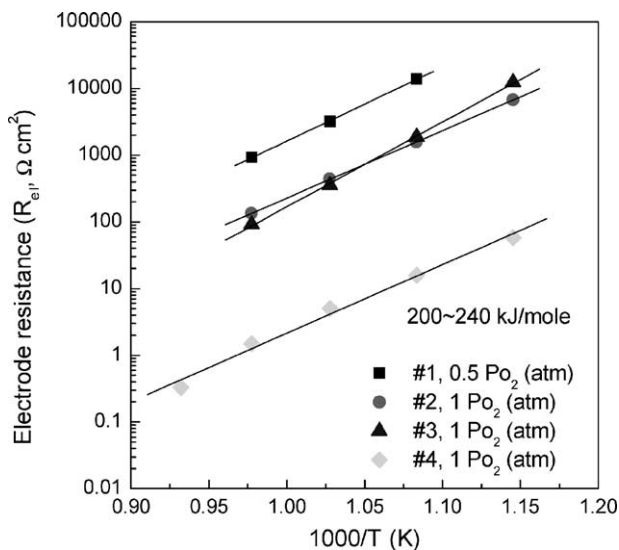
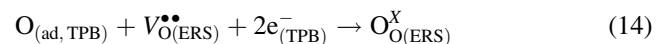
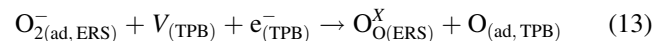
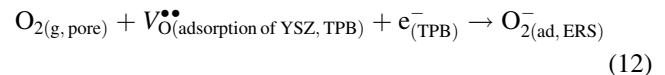


Fig. 9. Arrhenius plots of  $R_{el}$  for various electrodes in the high oxygen partial pressure.

Literature [6,15,37] reports that a high activation energy of  $R_{el}$  or  $I_0$  (200–250 kJ/mol) was observed at low temperature ( $T < 973$  K). One of the hypotheses for such a high activation energy is the surface reconstruction of Pt or the formation of Pt oxide [9,16,41]. For example, above 973 K the work function of Pt surface is lowered by approximately 116 kJ/mol [42]. In particular, Badwal and de Bruin [43] reported that at the temperature immediately below the thermodynamic formation temperature of PdO, the  $R_{el}$  abruptly increased due to a cathodic charge-transfer reaction, which was blocked by the formation of PdO. Similarly, Pt oxide, such as PtO<sub>2</sub>, can be formed in low temperature ( $T < 973$  K) and high  $P_{O_2}$  ( $P_{O_2} \sim 1$  atm) [44,45] so that it can prevent electrons from diffusing into the ERS. Provided that the formation of Pt oxides occurs and the oxygen atoms strongly chemisorbed are immobile under the experimental conditions, the Pt oxide may interrupt surface diffusion of oxygen atoms on the Pt electrode and the RDS is believed to be the dissociative adsorption of oxygen molecules on Pt oxide/YSZ interface. In this case, we can also consider the direct adsorption of oxygen molecules on Pt oxide/oxygen vacancy sites. From the results of Smith [31,32] and Meas et al. [33], it is clear that the oxygen vacancies on the YSZ surface can be provided as adsorption sites for the cathode reactions. However, the adsorption process is different at the high temperature and low oxygen partial pressure. For example, the emission of electrons to the new ERS (Pt oxide/YSZ/gas) needs much higher energies because of the oxygen atoms strongly chemisorbed on the Pt surface [42,43]. With regard to the electron affinity for various oxygen species [46], it is highly probable that oxygen first adsorbs as  $O_2^-$  by attracting an electron from Pt electrode in TPB line and dissociates to enter an oxygen vacancy. By the reaction model proposed above, one of the following reactions (12)–(14) can be also expected to be the RDS. In this study, we defined the ERS as the oxygen vacancy at the TPB.



Since the contribution of surface diffusion can be involved with a change of temperature and oxygen partial pressure, various values of the  $P_{O_2}^n$  dependence on  $R_{el}$  were reported in literature and also observed in our experiment ( $0.2 < n < 0.5$ ). However, it is supposed that in the low temperature ( $T < 973$  K) and high  $P_{O_2}$  region, if the reactions from (12) to (14) occur, the reaction (13) can be considered as the RDS from the activation energy value, which is similar to the heat of molecular dissociation of oxygen on undoped zirconia (242 kJ/mol) involving charge-transfer [31,32]. Since there were no precise data on the reaction (13) in the literature, further studies on various charge-transfer reactions remain to be done to understand

the exact electrode reactions that can be applied to this region.

## 5. Conclusion

The characteristics of electrode resistance ( $R_{el}$ ) at the Pt/YSZ interface have been studied as a function of the microstructure of electrodes. When the gas phase diffusion was effectively eliminated from the total electrode resistance, we observed the same dependences of temperature and oxygen partial pressure regardless of the electrode microstructures. Therefore, among the electrode reactions, only the gas phase diffusion was affected by electrode microstructure. From the analysis of ac impedance spectra, the Pt,  $O_2$ /YSZ system was examined at two distinctive reaction regimes at the temperature between 873 and 1273 K and in the  $P_{O_2}$  ranges of 0.01–0.1 atm. The main results can be summarized as follows:

### 5.1. In the high temperature ( $T > 1073$ K) and low $P_{O_2}$ ( $P_{O_2}^{low}$ ) region

In this range, the oxygen molecules can be directly adsorbed from gas phase and dissociate on the oxygen vacancies at the TPB. The RDS is migration of oxygen vacancies to the TPB line, assuming that the charge-transfer reactions are infinitely fast and adsorption and dissociation process are also quite fast. Consequently, the activation energies of  $R_{el}$  ( $80 \pm 5$  kJ/mol) of various electrodes are equal to that of ionic conductivity of YSZ.

### 5.2. In the low temperature ( $T < 973$ K) and high $P_{O_2}$ ( $P_{O_2}^{high}$ ) region

Since the surface diffusion can be restricted by the formation of Pt oxide, the RDS is supposed to be the dissociation of oxygen molecules involving a charge-transfer on Pt oxide/YSZ interface. The formation of Pt oxides makes the electron transfer difficult to diffuse from Pt electrode to EDS so that the value of activation energy can increase to 200–240 kJ/mol.

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## References

- [1] T.H. Etsell, S.N. Flengas, Chem. Rev. 70 (1970) 339.
- [2] N.Q. Minh, T. Takahashi, Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam, 1995, p. 69.
- [3] W.L. Worrell, Topic in Applied Physics, vol. 21, Springer, Berlin, 1977, p. 143.
- [4] T.H. Estell, S.N. Flengas, J. Electrochem. Soc. 118 (1971) 1890.
- [5] T.M. Gür, I.D. Raistrick, R.A. Huggins, J. Electrochem. Soc. 127 (1980) 2620.
- [6] M.J. Verkerk, M.W.J. Hammink, A.J. Burggraaf, J. Electrochem. Soc. 130 (1983) 70.
- [7] D.Y. Wang, A.S. Nowick, J. Electrochem. Soc. 128 (1981) 55.
- [8] D. Braunshtein, D.S. Tannhauser, I. Riess, J. Electrochem. Soc. 128 (1981) 82.
- [9] B.C. Nguyen, L.M. Rincon-Rubio, D.M. Mason, J. Electrochem. Soc. 133 (1986) 1860.
- [10] F.H. van Heuveln, H.J.M. Bouwmeester, J. Electrochem. Soc. 144 (1997) 134.
- [11] S.P. Yoon, S.W. Nam, T.-H. Lim, I.-H. Oh, H.Y. Ha, S.-A. Hong, Enhancement of the cathode performance by sol–gel coating of yttria-stabilized zirconia, in: Proceedings of Fuel Cell Seminar, Portland, OR, 2000, p. 611.
- [12] S.P. Yoon, S.W. Nam, T.-H. Lim, J. Han, S.-A. Hong, Improved performance of  $La_{0.85}Sr_{0.15}MnO_3$  cathode by sol–gel coatings, in: Proceedings of Solid Oxide Fuel Cells VII, Tsukuba, Ibaraki, 2001, p. 485.
- [13] S.P. Yoon, J. Han, S.W. Nam, T.-H. Lim, I.-H. Oh, S.-A. Hong, Y.-S. Yoo, H.C. Lim, J. Power Sources 106 (2002) 160.
- [14] D.Y. Wang, A.S. Nowick, J. Electrochem. Soc. 126 (1979) 1155.
- [15] T.M. Gür, I.D. Raistrick, R.A. Huggins, Solid State Ionics 1 (1980) 251.
- [16] B.L. Kuzin, M.A. Komarov, Solid State Ionics 39 (1990) 163.
- [17] S. Prindahl, M. Mogensen, J. Electrochem. Soc. 145 (1998) 2431.
- [18] J. Geyer, H. Kohmüller, H. Landes, R. Stubner, Investigation into kinetics of the Ni–YSZ cermet-anode of a solid oxide fuel cell, in: Proceedings of Solid Oxide Fuel Cells V, Aachen, 1997, p. 585.
- [19] J.L. Gland, Surf. Sci. 93 (1980) 487.
- [20] S. Pizzini, M. Bianchi, P. Colombo, S. Torchio, J. Appl. Electrochem. 3 (1973) 153.
- [21] F.K. Moghadam, D.A. Stevenson, J. Electrochem. Soc. 133 (1986) 1329.
- [22] N.L. Robertson, J.N. Michaels, J. Electrochem. Soc. 137 (1990) 129.
- [23] J. Mizusaki, K. Amano, S. Yamauchi, K. Fueki, Solid State Ionics 22 (1987) 313.
- [24] J. Mizusaki, K. Amano, S. Yamauchi, K. Fueki, Solid State Ionics 22 (1987) 323.
- [25] H. Yanagida, R.J. Brook, F.A. Kröger, J. Electrochem. Soc. 117 (1970) 593.
- [26] R.J. Brook, W.L. Pelzmann, F.A. Kroger, J. Electrochem. Soc. 118 (1971) 185.
- [27] L.R. Velho, R.W. Bartlett, Metall. Trans. 3 (1972) 65.
- [28] L.R. Velho, R.W. Bartlett, Metall. Trans. 3 (1972) 65.
- [29] F.J. Norton, J. Appl. Phys. 29 (1958) 1122.
- [30] R. Lewis, R. Gomer, Surf. Sci. 12 (1968) 157.
- [31] T. Smith, J. Electrochem. Soc. 111 (1964) 1020.
- [32] T. Smith, J. Electrochem. Soc. 111 (1964) 1027.
- [33] Y. Meas, J. Fouletier, D. Passelaigne, M. Kleitz, J. Chim. Phys. 75 (1978) 826.
- [34] Zview, Version 2.1b, Scribner Associates Inc.
- [35] H. Diets, Solid State Ionics 6 (1982) 175.
- [36] A. Mitterdorfer, L.J. Gauckler, Solid State Ionics 120 (1999) 211.
- [37] J.E. Bauerle, J. Phys. Chem. Solids 30 (1969) 2657.
- [38] A. Mitterdorfer, L.J. Gauckler, Solid State Ionics 117 (1999) 203.
- [39] Nickolas J. Themelis, Transport and Chemical Rate Phenomena, Gordon and Breach Publishers, New York, 1995, p. 210.
- [40] B.A. van Hassel, B.A. Boukamp, A.J. Burggraaf, Solid State Ionics 48 (1991) 155.
- [41] S. Pizzini, Fast Ion Transport in Solids, North-Holland, Amsterdam, 1973, p. 461.
- [42] R.J. Berry, Surf. Sci. 76 (1978) 415.
- [43] S.P.S. Badwal, H.J. de Bruin, J. Electrochem. Soc. 129 (1982) 1921.
- [44] T. Kenjo, Y. Yamakoshi, K. Wada, J. Electrochem. Soc. 140 (1993) 2151.
- [45] S.J. Schneider, C.L. McDaniel, J. Am. Ceram. Soc. 52 (1969) 518.
- [46] E.R.S. Winter, Advances in Catalysis, vol. X, Academic Press, New York, 1958, p. 214.