IDENTIFICATION OF GAS-DIFFUSION PROCESS IN A THICK AND POROUS CATHODE SUBSTRATE OF SWPC TUBULAR SOFC USING AC IMPEDANCE METHOD

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ABSTRACT

The effects of cathodic DC bias, bulk P02 and effective O2-diffusivity on AC impedance spectrum of SWPC's cathode-supported SOFCs were studied over a temperature range of 800 to 1000°C. It was found that the activation process, identified as ionic transfer and O' surface diffusion, dominated the overall electrode kinetics at 800°C. The applied DC bias reduced the electrode resistance considerably. With increasing the temperature to above 900°C, the activation process became effectively activated, leading to a visible contribution of the pore gas-diffusion at the lowest frequency on the impedance spectrum. Under this circumstance, lower bulk P02 and lower effective O2-diffusivity increase pore gas-diffusion polarization as predicted by the gas-diffusion theory. DC bias also increased gas-diffusion as a result of increased DC current. At any circumstance, no pore gas-diffusion was found in pure O2 atmosphere.

INTRODUCTION

The process of oxygen reduction taking place at the cathode of a SOFC has been an active subject for many years. The significance of this study lies in helping understand the underlying oxygen-reduction mechanism and develop catalytically active cathode materials for SOFCs. Generally speaking, there are two major types of electrochemical polarizations associated with the cathodic kinetics, namely activation and concentration, which account for the majority of voltage loss at the cathode during operation of a SOFC. The activation polarization is usually referred as a series of physicochemical processes involving O2 adsorption/dissociation, O' surface diffusion, ionization at Triple-Phase-Boundary (TPB) and ionic transfer across the cathode/YSZ interface. Due to the nature of solid state diffusion, these processes in principle have greater temperature dependence (higher activation energy). In other words, the oxygen reduction kinetics becomes sluggish with lowering temperatures. On the other hand, concentration polarization resulting from concentration gradient of reactive species across the thickness of the cathode is most likely caused by limited gas diffusion. The gas diffusion through pores in the cathode at a given cell current, therefore, determines largely the magnitude of concentration (or "pore") polarization. For planar, anode-supported SOFCs, the concentration polarization at the cathode is negligible compared to its counterpart activation polarization, simply due to a much thinner cathode layer. However, this contribution could be significant for tubular, cathode-supported SOFCs. In fact, gas...
diffusion through a thick, porous cathode substrate has been proven to be one of performance-limiting factors for SWPC’s tubular SOFC. Therefore, a comprehensive understanding on gas diffusion and its resulting pore polarization in thick and porous cathode is beneficial and indispensable for increasing powder density of SWPC’s SOFCs.

Gas diffusion through pores in a solid is essentially a mass-transport and complex process (1). Under a constant system pressure, the mass flux through a porous solid is diffusive in nature and may involve only ordinary molecular diffusion, Knudsen diffusion and surface migration. The latter is negligible if no diffusing gases are adsorbed in a mobile layer. Depending on pore size, the overall mass transport can be either dominated by molecular or Knudsen diffusion or both in some cases. Based on well-developed capillary theories that are established on relatively simple pore structure, equations for predicting the concentration gradient across SWPC’s thick porous cathode substrate and the resulting pore polarization have been developed and given in one of SWPC’s internal technical reports (2). The calculations clearly showed that 1) Knudsen diffusion is negligible compared to molecular diffusion within a range of pore size ~10 μm in the cathode, 2) pore polarization strongly depends on cathode-substrate thickness, porosity, effective O₂-diffusivity and bulk P₀₂ whereas temperature has a smaller effect on the pore polarization. With increasing cathode-substrate thickness, decreasing porosity, effective O₂-diffusivity and bulk P₀₂, the pore polarization can be dramatically increased to an unacceptable level. In literature, direct observations of gas diffusion process using AC impedance technique have also been reported to occur at the lowest frequency range of AC impedance spectrum and may vary greatly with the microstructure and the thickness of the cathode (3-6). By simulating the spectrum with equivalent-circuit approach, the electrode resistance related to the gas-diffusion can sometimes be extracted from other process (3).

In this paper, we report direct experimental observations on the gas-diffusion process through SWPC’s thick and porous cathode substrate using AC impedance spectroscopy technique. To illustrate the effects of oxygen partial pressure and effective oxygen diffusivity on the gas-diffusion process, three levels of oxygen ranging from 100% to 5% in mixtures of O₂-N₂ and O₂-He were used during impedance measurements. In addition, DC bias applied over AC signal was also employed to distinguish the gas-diffusion process from activation polarization. Another benefit from using DC bias is the ability to determine the rate-limiting step for oxygen reduction at the cathode.

**EXPERIMENTAL PROCEDURE**

**Sample Preparation**

Samples that were used in this study include only cathode substrate and electrolyte thin-film (~ 40 μm) made from EVD (Electrochemical Vapor Deposition) process; a tube section of 20 mm was used. Figure 1 showed a schematic of the studied cell. On the top of the YSZ (ZrO₂+8mol%Y₂O₃) electrolyte, Pt-paste (Haeraus CL11-5100) was used as the counter electrode together with Pt-mesh as the current collector whereas the Pt-paste and Pt-mesh were used inside the tube only as the current collector since the thick porous cathode substrate was considered as the working electrode. The curing condition for the
Pt-paste was 800°C for 30 minutes. For convenience, the electrode current collector and the underlying Pt-paste in this study were all made into 1 cm² in area.

![Diagram](image_url)

**Figure 1. A schematic of studied half-cell.**

**AC Impedance Measurement**

The aforementioned half-cell was then connected to a high-temperature test rig, which links to impedance analyzer. After loading the test rig into a furnace, the temperature was ramped to 800°C at a rate of 3°C/min with flowing air. The formal experiment was normally started from 800°C after the cell was equilibrated overnight and continued to 1000°C in an interval of 50°C. To study the Po₂ effect, various gases with known Po₂ varying from 1 to 0.05 atm were used during the experiment. To study the O₂-diffusivity effect, mixtures of O₂+N₂ and O₂+He were chosen based on the fact that O₂-diffusivity in He+O₂ mixture is greater than that in N₂+O₂ mixture. All gases had a fixed flow of 100 ml/min for any individual experiment.

The AC impedance measurements were conducted with Solartron 1250 Frequency Response Analyzer and 1286 Electrochemical Interface. The frequency was swept from 65,000 to 0.1 Hz with an AC amplitude of 10 mV. To study the DC current effect on the concentration and activation polarizations, two levels of DC bias were chosen to overlay on AC signal during impedance measurement: -100 mV and -200 mV, in comparison with that without DC bias. The negativity of the applied DC bias, as defined by the instrument, assures the DC current flowing from air-electrode towards YSZ, in analogy to that in a practical SOFC. Most of interested processes such as pore gas-diffusion and charge-transfer can be resolved on the impedance spectrum within the swept frequency range.

**RESULTS AND DISCUSSION**

**DC Bias Effect**

Figure 2 showed the impedance spectra under two levels of DC bias taken at 800°C and in three different atmospheres (a) pure O₂ (b) air and (c) 5%O₂-N₂. It is evident that the DC bias has reduced the electrode resistance (R_{DC}) in all three atmospheres. The observation suggests that the activation process, which is a strong function of applied...
external electrical field, dominate the overall electrode kinetics at 800°C. In addition, with increasing DC bias level, two semicircles can be justified to evolve from one big semicircular arc at zero DC bias (see solid lines), indicating that the actual electrode process could possibly consist of two elemental steps. As suggested in literature (3, 4), these two semicircles are most likely associated with $O^2-$ transfer from TPB to YSZ electrolyte at higher frequency range and O' diffusion along LaMnO$_3$ surface at lower frequency range. At this temperature, no gas-diffusion impedance is appreciable enough to be observable on the spectra.

Figure 2. AC Impedance spectra taken at 800°C and DC bias.
(a) pure O$_2$; (b) air; (c) 5%O$_2$ + N$_2$.

The overall electrode resistance $R_{dc}$ at a given DC bias was also shown in Figure 2 to decrease with increasing P$_{O_2}$. This is understandable in that the electrode resistance
associated with $O^-$ surface diffusion has a strong dependence on $P_{O_2}$ as expressed as $1/R_{DC} \propto P_{O_2}^{1/m}$, $m>0$.

The trend remained same at higher $P_{O_2}$ range as the temperature was increased to 900°C. In Figure 3 (a) and (b), it has shown that increasing DC bias continued to decrease the electrode resistance $R_{DC}$, implying that the activation process still dominated the overall electrode kinetics. However, a careful examination of the spectra, Figures 3 (b) and (c), revealed that a small tail at the lowest frequency begun to emerge. This effect became more explicit at the lowest $P_{O_2}$, see Figure 3 (c). In addition, a striking difference in Figure 3 (c) from Figure 2 and Figures 3 (a) & (b) is that $R_{DC}$ at DC bias -200 mV is no longer the smallest. It exceeded that of at -100 mV with a visible growing third semicircle, which was later identified to be the gas-diffusion impedance.

**Figure 3.** AC impedance spectra taken at 900°C and DC bias. (a) pure $O_2$; (b) air; (c) 5% $O_2 + N_2$.  

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At 1000°C, the third semicircle was seen at even higher $P_{O_2}$, i.e., in air. In Figure 4(b), the impedance spectrum at $-200$ mV completely surpassed that of at $-100$ mV with a clear semicircle at the tail. In atmosphere of 5% $O_2$ - $N_2$, the semicircles at the lowest frequency for both DC bias $-200$ mV and $-100$ mV were enlarged further and higher than that of without DC bias. At DC bias of $-200$ mV, the low-frequency semicircle became extremely large.

![Figure 4](image_url)

**Figure 4.** AC impedance spectra taken at 1000°C and DC bias. (a) pure $O_2$; (b) air; (c) 5% $O_2$ + $N_2$.

The above observations provided good examples to illustrate the relationship between activation and pore polarizations. It is well known that the electrode kinetics is mostly dominated by the activation process at lower temperatures. This infers that applying cathodic DC bias would show lowered electrode resistance $R_{DC}$ as a result of improved...
electrode kinetics, which has been demonstrated in Figure 2. Due to the high cell resistance, the DC current resulting from DC bias was relatively low. Therefore, no gas-diffusion process could be manifested on the impedance spectrum at these temperatures within a fixed frequency-domain (0.1 to 65000 Hz) of the AC impedance measurement. With increasing temperature, however, a considerable reduction in activation electrode resistance dramatically lowered the total cell resistance, leading to a noticeable increase in cell current upon applying DC bias. As a result, the pore-diffusion resistance was increased, making the pore diffusion a dominating process. As shown in Figure 4 (c), it appeared to approach the limiting current density.

It is also evident that lower bulk oxygen partial pressure favored pore polarization, particularly at higher temperature range. This observation is a direct experimental proof for the calculations made in the SWPC internal report (2), in which low bulk P02 in surrounding environment was concluded to increase the pore diffusion polarization remarkably.

Theoretically speaking, no pore diffusion polarization in pure oxygen should be encountered in the impedance spectrum. Therefore, the applied cathodic DC bias should only have one effect on $R_{\text{DC}}$, i.e., $R_{\text{DC}}$ decreases as the DC bias increases. This assertion has been clearly proven in the temperature range of 800 to 1000°C by Figures 2(a), 3(a) and 4(a) with the smallest $R_{\text{DC}}$ occurred at DC bias -200 mV.

### O2- Diffusivity and Bulk Po2 Effects

A set of impedance spectra taken from 800 to 1000°C in different gas mixtures with various oxygen partial pressures were shown in Figure 5. Note that no DC bias was applied in this study. In general, the electrode resistance $R_{\text{DC}}$ at every temperature decreased as the bulk partial pressure of oxygen increased. This trend agrees well with that observed in Figure 4, in which it was ascribed to the relationship of $1/R_{\text{DC}} \propto P_{O2}^{1/m}$, $m > 0$. At 800°C, Figure 5(a), replacement of N2 with He in N2-O2 mixture did not lead to any appreciable difference in the spectra as the oxygen content was varied from 100% to 2%. The spectra for both gas mixtures with the same oxygen content remained essentially unchanged. Theoretically speaking, a smaller pore diffusion resistance shall be observed with He-O2 as opposed to N2-O2 simply because of a higher effective O2-diffusivity in He-O2 mixture than that in N2-O2 mixture. Failure to see this difference on the spectra at 800°C implies the domination of a process (activation) other than pore-diffusion within a fixed frequency-domain of the impedance analyzer. This conclusion is also in agreement with what have been found in the DC-bias study. With an increase in temperature, it is expected that the pore diffusion begin to play a role in the overall electrode kinetics as activation polarization reduces.

In fact, as the temperature was increased to 900°C, Figure 5(b), a small semicircle appeared to be visible at the lowest frequency, and became more pronounced as the bulk P02 was decreased. Moreover, among the mixtures of He-O2 and N2-O2 with the same level of oxygen, the N2-O2 mixture had a tendency of yielding a higher electrode resistance than He-O2 mixture. The shown difference suggests the appearance of extra semicircle at the lowest frequency indeed relevant to the pore diffusion in the cathode.
The above hypothesis is further supported by the impedance spectra measured at 1000°C with the same gas condition. In Figure 5(c), the low-frequency semicircles were clearly shown to differentiate between He-O2 and N2-O2 mixtures and became more evident for those containing 2% O2. The difference explicitly reflected the difference in the effective O2-diffusivity among two gas mixtures, i.e., higher effective O2-diffusivity gives lower pore-diffusion resistance. On the other hand, it was also found that the high-frequency and intermediate-frequency semicircles, especially for 2%O2 gas mixtures, are virtually overlapping, implying that these two semicircles are gas-diffusion independent and likely linked to the activation polarization.

Figure 5. Impedance spectra in He-O2 and N2-O2 mixtures with varied Po2 (a) 800°C; (b) 900°C; (c) 1000°C.
Based on the above observations in Figure 5, it is clear that lower bulk $P_{O_2}$ and effective $O_2$-diffusivity favor the domination of gas-diffusion process on impedance spectra within a fixed frequency-domain. Absence of gas-diffusion semicircle at lower temperatures does not necessarily infer that pore gas-diffusion is not existent or negligible under given conditions. In fact, the pore polarization should be slightly higher at low temperature than at high temperature according to the pore-diffusion theory. The reason for being unable to distinguish the pore-diffusion process from others on the impedance spectra is attributed to the relative magnitudes of time constants owned by these processes. For instance, at lower temperatures the activation process dominates the overall electrode kinetics due to its relatively wider and larger time-constant. As a result, the pore-diffusion could not be manifested because of an even larger time-constant within a fixed frequency-domain. With increasing the temperature and the activation process being thermally activated, the pore diffusion process began to appear on the impedance spectra.

**CONCLUSIONS**

Generally speaking, no pore gas-diffusion process can be found on the impedance spectra at lower temperatures regardless of DC bias (down to $-200$ mV), bulk $P_{O_2}$ and effective $O_2$-diffusivity. This observation suggests the domination by the activation process associated with the cathode at low temperature, which has been indirectly verified by the reduction in electrode resistance with increasing cathodic DC bias. With increasing temperature to above $900^\circ$C, the pore gas-diffusion process became visible as a semicircle at the lowest frequency on the impedance spectra. The shown gas-diffusion impedance became more pronounced as the bulk $P_{O_2}$ and effective $O_2$-diffusivity decreased. Similarly, as the applied cathodic DC bias and the resulting DC current increased, the gas-diffusion process was promoted. In any circumstance, no gas-diffusion impedance was observable in pure $O_2$ atmosphere.

It was also found that there were two semicircles at high and intermediate frequency related solely to activation process, most likely ionic transfer and $O^-$ surface diffusion, respectively. These two semicircles were shown to strongly depend on the external DC bias.

The findings in this study clearly elucidated the relationship between concentration and activation polarizations as temperature, bulk $P_{O_2}$ and effective $O_2$-diffusivity vary. At low temperatures, pore diffusion (concentration polarization) does not play a role in SWPC cathode-supported SOFCs due to the dominance by the activation polarization. As temperature increased and the activation process became thermally activated, the pore gas-diffusion came into play and quickly became dominated at higher current density, low bulk $P_{O_2}$ and effective $O_2$-diffusivity.

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