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Gas-Diffusion Process in a Tubular Cathode Substrate of a SOFC

II: Identification of Gas-Diffusion Process Using AC Impedance Method

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The effects of cathodic dc bias, bulk p_{O_2} , and effective O_2 -diffusivity on ac impedance spectra of Siemens Westinghouse Power Corporation's cathode-supported solid oxide fuel cells were systematically studied over a temperature range of 800 to 1000°C. It was found that the activation process dominated the overall electrode kinetics at 800°C, by which 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 arc at the lowest frequency on the impedance spectrum, which is relevant to the pore gas-diffusion process. Under this circumstance, lower bulk p_{O_2} and lower effective O_2 diffusivity were shown in ac impedance spectra to increase pore gas-diffusion polarization as predicted by the gas-diffusion theory shown in part I of this paper. DC bias was also found to greatly affect the gas-diffusion process as a result of increased dc current.

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Direct observation of the gas-diffusion process using ac impedance spectroscopy has been reported in the literature.¹⁻⁴ It was generally found that the gas-diffusion process occurred at the lowest frequency range of an ac impedance spectrum and may vary greatly with the condition of how the cathode was prepared (microstructure)^{3,4} and the thickness of the cathode layer. Other common features of the gas-diffusion process found by the ac impedance technique include insensitivity to temperature (low activation energy)^{1,3} and a strong function of bulk p_{O_2} and oxygen diffusivity.¹ By going to an extreme condition, Van Herle⁴ demonstrated even further with a dense strontium-doped lanthanum manganite (LSM) cathode that a large gas-diffusion arc occurred at the lowest frequency range and the electrode overpotential was sharply increased as approaching to a constant current density (limiting current density). With correctly identifying the gas-diffusion process on an ac impedance spectrum, the electrode resistance and peak frequency related to the gas-diffusion have also been quantified by simulating the spectrum with equivalent-circuit method.^{1,2}

As the second part of a two-part paper, direct experimental observation on the gas-diffusion process through Siemens Westinghouse Power Corporation's (SWPC's) thick and porous cathode substrate using ac impedance spectroscopy technique is reported. To better understand the gas-diffusion process, temperature, oxygen partial pressure, the effective oxygen diffusivity and dc bias were systematically varied to investigate the effect on the pore polarization and the results can be interpreted well with the theory presented in part I of this paper. In addition, the relationship between activation and concentration polarizations (gas-diffusion) is also discussed as a function of temperature and partial pressure of oxygen.

Experimental

Sample preparation.—Samples that were used in this study include only the cathode tubular substrate and electrolyte thin film. The cathode tubular substrate is made of Ca-doped $LaMnO_3$ with a porosity of ~30% and a wall thickness of ~2 mm. The electrolyte YSZ ($ZrO_2 + 8 \text{ mol } \% Y_2O_3$) in a thickness of ~40 μm was made from the EVD (electrochemical vapor deposition) process. Figure 1 shows a cross section schematic of a studied cell, which has been cut into a typical length of 20 mm for the schematic measurement. On the top of the YSZ electrolyte, Pt paste (Haeraus CL11-5100) was used as the counter electrode together with Pt mesh as the

current collector. However, Pt paste and Pt mesh used inside the tube serve only as the current collector because the cathode substrate is considered as the working electrode. The curing condition for the Pt paste is 800°C for 30 min. For convenience, the electrode current collector and the underlying Pt paste in this study were all made into 1 cm^2 in area.

It is to be noted that the studied cell is not symmetrical as is normally used for ac impedance measurement. Therefore, two electrodes are expected to contribute differently to the measured spectrum. However, it is reasonable to assume that the major contributor is the thick cathode substrate due to a thin and porous film on the platinum counter electrode.

AC impedance measurement.—The aforementioned half-cell was then connected to a high-temperature test rig, with links to the 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 experiment was normally started from 800°C after the cell was equilibrated overnight and continued to 1000°C in intervals of 50°C. To study the p_{O_2} effect, various gases with known p_{O_2} varying from 1 to 0.05 atm were used during the experiment. To study the O_2 diffusivity effect, mixtures of $O_2 + N_2$ and $O_2 + He$ were chosen based on the fact that O_2 diffusivity in the $He + O_2$ mixture is greater than that in the $N_2 + O_2$ mixture. All gases had a fixed flow rate of 100 mL/min for any measurement.

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 at the cathode/electrolyte interface, two levels of dc bias were chosen to overlay with the ac signal during impedance measurement, -100 and -200 mV, in comparison with that of zero dc bias. The negativity of the applied dc bias, as defined by the instrument, assures the dc current flowing from cathode toward YSZ, is analogous to that in a practical SOFC. Most processes of interest, such as pore gas diffusion and charge-transfer processes can be convoluted from the impedance spectrum within the range of sweeping frequency.

Results and Discussion

DC bias effect.—Figure 2 shows the impedance spectra under two levels of dc bias taken at 800°C and in three different atmospheres: (a) pure O_2 , (b) air, and (c) 5% O_2-N_2 . It is evident that the dc bias has reduced the electrode resistance (R_{DC} , the difference in low-frequency and high-frequency intercepts on a real-axis) in all three atmospheres. This observation suggests that the activation pro-

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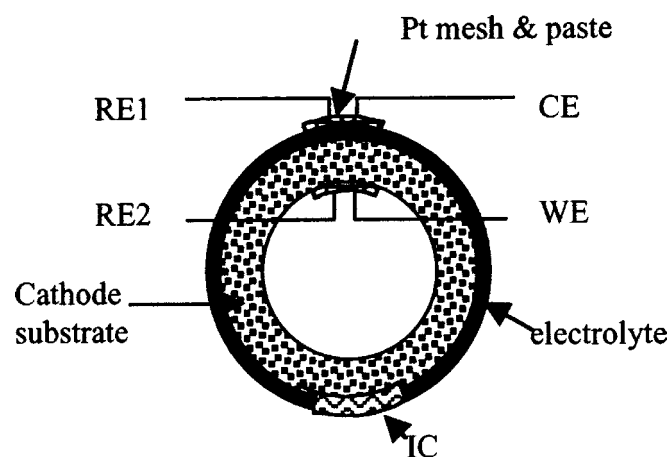


Figure 1. A cross section schematic of studied cell. IC means interconnection.

cess, which is a strong function of the external electrical field, dominates 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 at least two elemental steps. As suggested in the literature,^{1,2} these two semicircles are most likely associated with O^{2-} transfer from three-phase boundary (TPB) to YSZ electrolyte at the higher frequency range and O^- diffusion along $LaMnO_3$ surface at the lower frequency range. At this temperature, no gas-diffusion impedance is appreciable enough to be observable on the spectra.

The overall electrode resistance R_{DC} at a given dc bias is also shown in Fig. 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 remains the same at the higher p_{O_2} range as the temperature is increased to 900°C. In Fig. 3a and b, it is shown that increasing dc bias continued to decrease the electrode resistance R_{DC} , implying that the activation process still dominates the overall electrode kinetics. However, a careful examination of the spectra, Fig. 3b and c, revealed that a small tail at the lowest frequency began to emerge. This effect became even more visible at the lowest p_{O_2} , see Fig. 3c. In addition, a striking difference in Fig. 3c from Fig. 2 and Fig. 3a and b is that R_{DC} at dc bias of -200 mV is no longer the smallest. It exceeded that of at -100 mV with a visibly growing third semicircle, which was later identified to be the gas-diffusion impedance.

At 1000°C, the third semicircle is seen at even higher p_{O_2} , *i.e.*, in air. In Fig. 4b, the impedance spectrum at -200 mV completely surpasses that at -100 mV with a clear semicircle at the tail. In the atmosphere of 5% O_2 - N_2 , the semicircles at the lowest frequency for both the dc bias -200 mV and -100 mV are enlarged further and much higher than that of at zero dc bias. At a dc bias of -200 mV, the low-frequency semicircle becomes extremely large.

The above observations provided a good example for illustrating the relationship between activation and concentration polarizations. It is well known that the electrode kinetics is primarily dominated by the activation process at lower temperatures. This infers that applying cathodic dc bias would introduce a lowered electrode resistance R_{DC} as a result of improved electrode kinetics, which has been demonstrated in Fig. 2. Due to the high cell resistance, the dc current resulting from dc bias is 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 65,000

Hz) of the ac impedance measurement. With increasing temperature, however, a considerable reduction in activation resistance lowers the total cell resistance, leading to a noticeable increase in cell current upon applying a dc bias. As a result, the pore-diffusion resistance is increased, making the pore diffusion a dominating process. As shown in Fig. 4(c), the limiting current density of the cathode substrate appears to be approached. On the other hand, the time constant of the activation relaxation process is also reduced as the temperature is increased. The implication of such a reduction for fixed frequency-domain ac impedance spectroscopy is a shift of the activation process toward the higher frequency region and therefore leaves the low-frequency spectrum available for depicting the low-frequency gas-diffusion process.

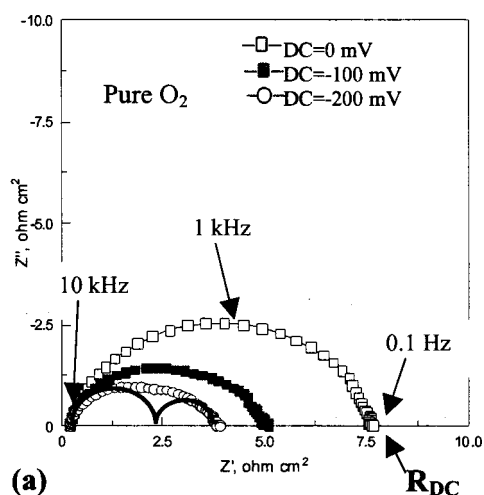
It is also evident that lower bulk p_{O_2} favored pore polarization, particularly at a higher temperature range. This observation is a direct experimental proof of the calculations made in part I of this paper, in which low bulk p_{O_2} in surrounding environment was concluded to increase the pore-diffusion 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_{DC} , *i.e.*, R_{DC} decreases as the dc bias increases. This assertion has been clearly proven in the temperature range of 800 to 1000°C by Fig. 2a, 3a, and 4a with the smallest R_{DC} occurring at a dc bias -200 mV.

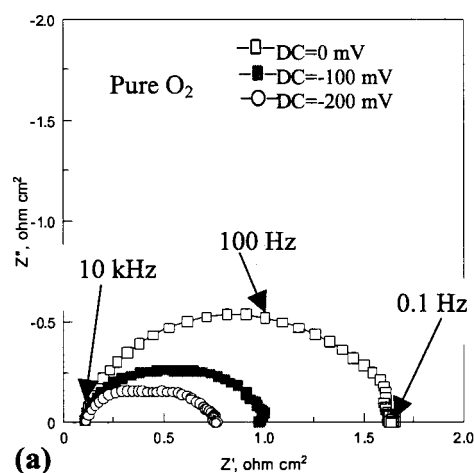
O₂ diffusivity and bulk p_{O_2} effects.—A set of impedance spectra taken from 800 to 1000°C in different gas mixtures with various oxygen partial pressures are shown in Fig. 5. Note that no dc bias was applied for this study. In general, the electrode resistance R_{DC} at every temperature decreases as the bulk partial pressure of oxygen increases. This trend agrees well with that observed in Fig. 4, in which it was ascribed to the relationship of $1/R_{DC} \propto p_{O_2}^{1/m}$, $m > 0$. At 800°C, Fig. 5a, replacement of N_2 with He in a N_2 - O_2 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 remains essentially unchanged. In principle, a smaller pore diffusion resistance shall be observed with He- O_2 as opposed to N_2 - O_2 simply because of a higher effective O_2 diffusivity in the He- O_2 mixture than that in the N_2 - O_2 mixture. Failure to see this difference on impedance 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 was found in the aforementioned dc-bias study. With an increase in temperature, it is expected that pore diffusion begins to play a role in the overall electrode kinetics as activation polarization reduces.

In fact, as the temperature is increased to 900°C, Fig. 5b, a small semicircle begins to be visible at the lowest frequency, and becomes more pronounced as the bulk p_{O_2} is decreased. Moreover, among the mixtures of He- O_2 and N_2 - O_2 with the same level of oxygen, the N_2 - O_2 mixture has a tendency of yielding a higher electrode resistance than the He- O_2 mixture. The difference shown suggests the appearance of an extra semicircle at the lowest frequency, indeed, relevant to the pore-diffusion process in the cathode.

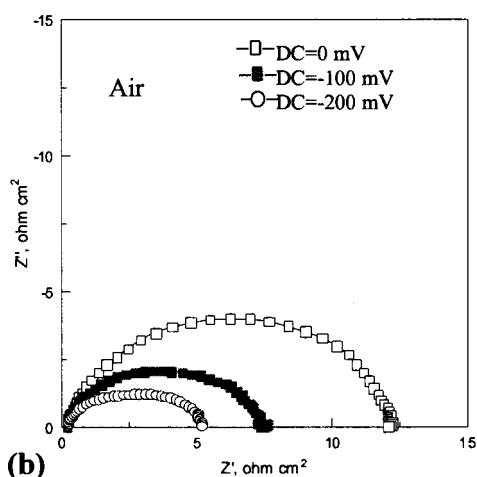
The above hypothesis is further supported by the impedance spectra measured at 1000°C with the same gas condition. In Fig. 5c, the low-frequency semicircles are clearly shown to be different between He- O_2 and N_2 - O_2 mixtures and become more evident for those containing 2% O_2 . The difference exclusively reflects the difference in effective O_2 -diffusivity among two gas mixtures, *i.e.*, higher effective O_2 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% O_2 gas mixtures, are virtually overlapping, implying that these two semicircles are unrelated to the gas-diffusion process and likely link to the activation polarization.



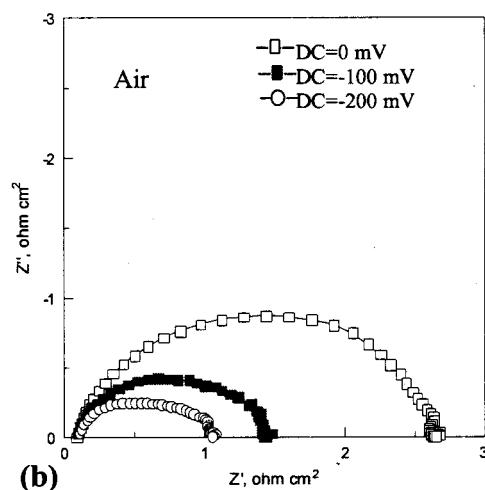
(a)



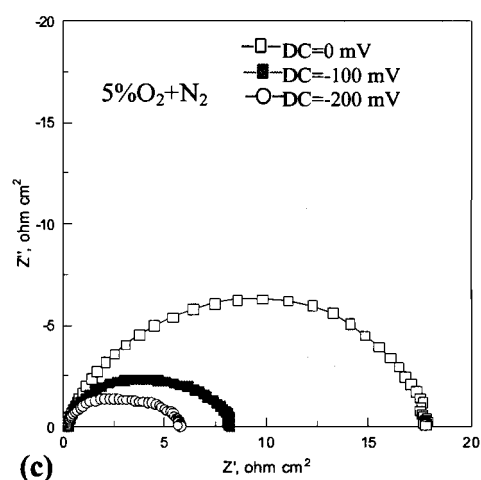
(a)



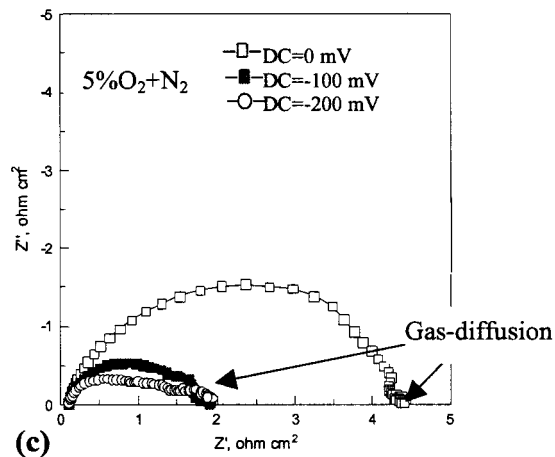
(b)



(b)



(c)



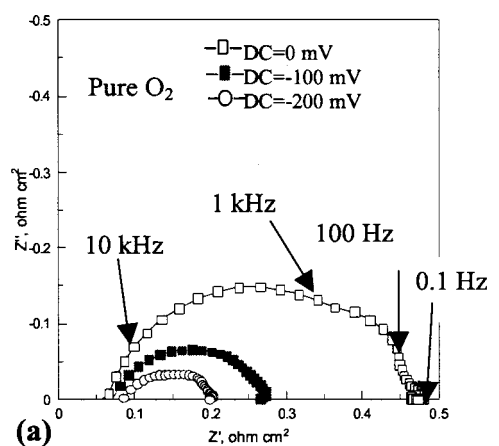
(c)

Figure 2. AC impedance spectra taken at 800°C and with dc bias: (a) pure O₂, (b) air, (c) 5% O₂ + N₂.

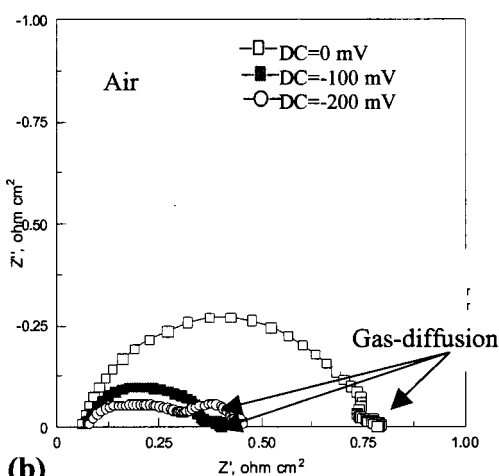
Figure 3. AC impedance spectra taken at 900°C and with dc bias: (a) pure O₂, (b) air, (c) 5% O₂ + N₂.

Based on the above observations in Fig. 5, it is clear that lower bulk p_{O_2} and effective O₂ diffusivity favor the domination of the gas-diffusion process on impedance spectra at higher temperatures. Absence of the gas-diffusion semicircle at lower temperatures does not necessarily infer that pore gas diffusion is not existent or negligible under given conditions. The reason for being unable to discern the pore-diffusion process from others on the impedance spectra is attributed to the relative magnitudes of time constants common to

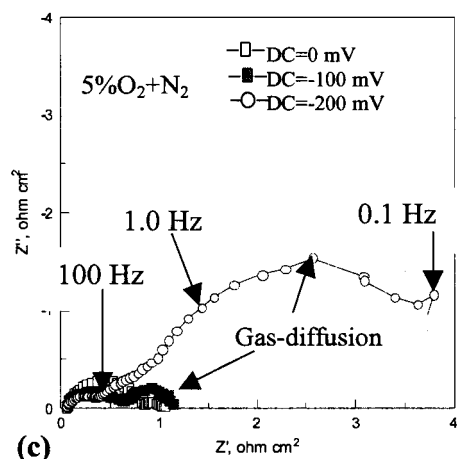
these relaxation processes. For instance, at lower temperatures the activation process dominates the overall electrode kinetics due to its relatively wider and larger time constant. As a result, the pore diffusion could not be manifested on a fixed frequency-domain impedance spectrum because of an even larger time constant. With increasing the temperature and the activation process being thermally activated, the pore diffusion process begins to appear on the impedance spectra.



(a)



(b)

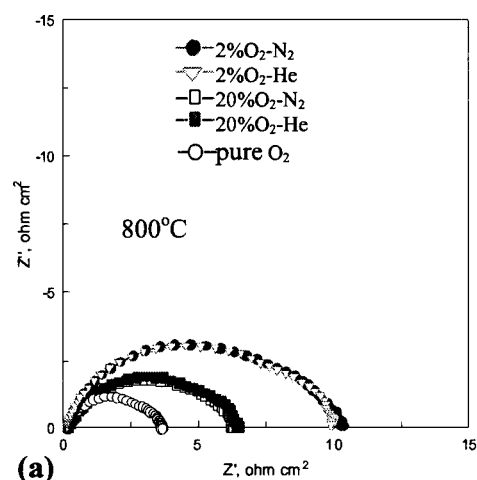


(c)

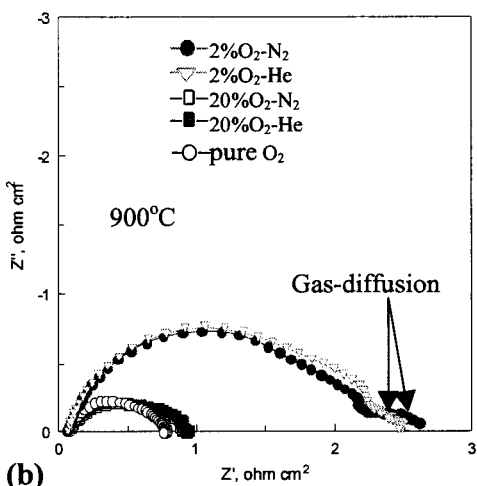
Figure 4. AC impedance spectra taken at 1000°C and with dc bias: (a) pure O₂, (b) air, (c) 5% O₂ + N₂.

Conclusions

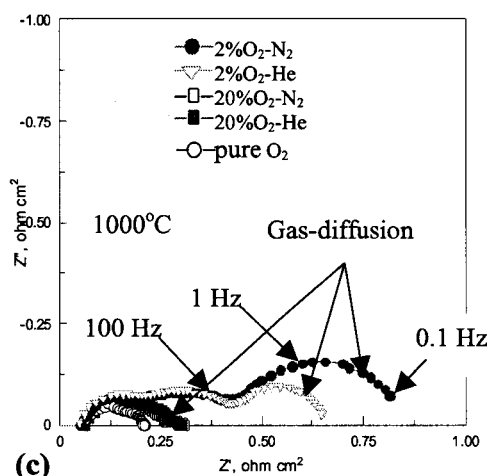
Generally speaking, no pore gas-diffusion process can be found on the impedance spectra at lower temperatures regardless of dc bias (down to -200 mV), bulk p_{O_2} , and effective O₂ diffusivity. This observation suggests the domination by the activation process associated with the cathode at low temperatures, which has been indirectly verified by the reduction in electrode resistance with increasing cathodic dc bias. With increasing temperature to above 900°C, the pore gas-diffusion process became visible as a semi-circle at the lowest frequency on the impedance spectra. The shown



(a)



(b)



(c)

Figure 5. Impedance spectra in He-O₂ and N₂-O₂ mixtures with varied p_{O_2} ; no dc bias was applied; (a) 800, (b) 900, (c) 1000°C.

gas-diffusion impedance became even more pronounced as the bulk p_{O_2} and effective O₂ diffusivity were decreased. Similarly, as the applied cathodic dc bias and the resulting dc current increased, the gas-diffusion process was promoted. In no circumstance, was gas-diffusion impedance observable in a pure O₂ atmosphere.

It was also found that there are two semicircles at high and intermediate frequency related solely to the activation process, most likely O^{2-} 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 elucidate 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 the SWPC cathode-supported SOFCs due to the dominance by the activation polarization. As temperature increases and the activation process becomes thermally activated, the pore gas-diffusion comes into play and quickly becomes dominated at higher current density, low bulk p_{O_2} and effective O_2 -diffusivity.

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