
Kevin Huang
University of South Carolina - Columbia, huang46@cec.sc.edu

Follow this and additional works at: https://scholarcommons.sc.edu/emec_facpub

Part of the Mechanical Engineering Commons

Publication Info
© The Electrochemical Society, Inc. 2004. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Journal of The Electrochemical Society.
Publisher’s Version: http://dx.doi.org/10.1149/1.1688339

This Article is brought to you by the Mechanical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.
Gas-Diffusion Process in a Tubular Cathode Substrate of a SOFC

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

Keqin Huang

Siemens Westinghouse Power Corporation, Pittsburgh, Pennsylvania 15235, USA

The effects of cathode 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.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1688339] All rights reserved.

Manuscript submitted August 4, 2003; revised manuscript received November 17, 2003. This was in part Paper 1868 presented at the Paris, France, Meeting of the Society, April 27-May 2, 2003. Available electronically April 12, 2004

Direct observation of the gas-diffusion process using ac impedance spectroscopy has been reported in the literature. 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) 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) and a strong function of bulk $p_{O_2}$ and oxygen diffusivity. By going to an extreme condition, Van Herle demonstrated even further with a dense strontium-doped lanthanum manganese (LSM) cathode that a large gas-diffusion are 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.

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 mol% Y$_2$O$_3$) 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-
A cross section schematic of studied cell. IC means interconnection.

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 in 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 an effect $R_{DC}$, 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.

$O_2$ 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 expected 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 dominance of a process (activation or electrochemical) 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.
Based on the above observations in Fig. 5, it is clear that lower bulk $p_{O_2}$ and effective $O_2$ 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.

Figure 2. AC impedance spectra taken at 800°C and with dc bias: (a) pure $O_2$, (b) air, (c) $5\% O_2 + N_2$.

Figure 3. AC impedance spectra taken at 900°C and with dc bias: (a) pure $O_2$, (b) air, (c) $5\% O_2 + N_2$. 
Conclusions

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

Figure 4. AC impedance spectra taken at $1000^\circ\text{C}$ and with dc bias: (a) pure $O_2$, (b) air, (c) $5\% O_2 + N_2$.

Figure 5. Impedance spectra in He-$O_2$ and $N_2-O_2$ mixtures with varied $p_{O_2}$: no dc bias was applied; (a) 800, (b) 900, (c) $1000^\circ\text{C}$. 
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.

Acknowledgments

The author thanks the U.S. Department of Energy, National Energy Technology Laboratory for financial support under Cooperative Agreement DE-FC26-97FT34139 and SECA program DE-FC26-02NT41247. Larry Paulukonis is also thanked for his assistance in preparing samples and conducting ac impedance measurements.

Siemens Westinghouse Power Corporation assisted in meeting the publication costs of this article.

References