ELECTROCHEMICAL CHARACTERIZATIONS ON CATHODE AND ITS INTERFACE WITH ELECTROLYTE OF CATHODE-SUPPORTED SOFCs

Keqin Huang
Siemens Westinghouse Power Corporation
1310 Beulah Road, Pittsburgh, PA 15235, USA

ABSTRACT

AC impedance spectroscopy and DC polarization techniques have been used to characterize the cathode/YSZ interface of SWPC's cathode-supported SOFCs. Examples from plasma-sprayed YSZ/cathode interface are given to demonstrate how to identify activation and pore diffusion processes with varying DC bias, surrounding P02 and O2-diffusivity. Equations for quantifying diffusion resistance and activation polarization are also given. In addition, DC polarization method has been shown to be a useful and convenient approach for screening the quality of the cathode/YSZ interface.

INTRODUCTION

The performance of SWPC's cathode-supported SOFCs is knowingly limited by the properties of the cathode. The voltage loss at 1000°C resulting from the cathode accounts for more than 50% of the total loss in standard CeO2 interlayer SOFCs, and further increases up to 70% at 900°C. To further breakdown the voltage loss within the cathode, it was found that the activation and concentration (hereinafter referred as "pore") polarizations comprise of the majority whereas the associated ohmic IR loss of the electrolyte and cathode substrate only contributes a small portion. In other words, the electrochemical catalytic activity for oxygen reduction and gas (air) mass transport property of the cathode substrate need to be improved in order to enhance cell electrical performance.

To achieve this goal, the concept of applying two-phase interlayer material at the interface of cathode and electrolyte, which has been widely accepted by the SOFC community as an effective means to increase the triple phase boundary length (oxygen reactive sites) necessary for reducing the activation polarization, has been practiced over the past several years in SWPC. This concept also offers a viable engineering solution to dealing with potential thermal expansion mismatch between the cathode interlayer and cathode or electrolyte as shown in many other excellent single-phase mixed conductors (such as doped LaCoO3), particularly under the condition of thermal cycling during the operation of a fuel cell. In an effort to reduce the pore diffusion polarization, the sintering condition of two-phase interlayer cells has been maintained moderate. As a result of both efforts, the performance of SWPC's SOFCs has been increased by 5-10% at 1000°C, and 30-50% at 900°C.
The emphasis of present paper is, however, to demonstrate several electrochemical techniques developed in SWPC for characterizing the cathode and electrolyte interface. These techniques include AC impedance spectroscopy and DC polarization. The benefit of using these methods is manifested by their capability of identifying and quantifying polarization processes of the cathode so that the dominant resistance contributor can be correspondingly addressed in the process of development. With utilizing fundamental theories of electrochemistry and gas mass transport, some equations that formulate the correlation between current density and polarizations are also described in this paper.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples used in this study consisted of cathode substrate, interconnection, and YSZ thin-film (~50-60 μm) made by Atmospheric Plasma Spray (APS) process. The presence of the interconnection is a part of process and not being investigated in this study. After APS process, the YSZ film together with the cathode substrate was subsequently sintered at a higher temperature in order to achieve an acceptable gas tightness. To conduct the electrochemical measurements, the cathode substrate was made as the working electrode (WE) whereas Pt paste/Pt mesh was used as counter electrode (CE) and current collectors for both WE and CE. A detailed description on how to make such a cell is given in Ref. (1).

AC Impedance Measurement

The above electrochemical cell was then installed into a high-temperature test rig, which connects to an impedance analyzer (Solartron 1252 Frequency Response Analyzer and 1286 Electrochemical Interface System), followed by loading the test rig into a horizontal tubular furnace. The furnace temperature was ramped to 800°C at a rate of 3°C/min with flowing air at a rate of 100 ml/min. The experiment was normally started from 800°C after the cell was equilibrated overnight and ramped up to 1000°C in an interval of 50°C. The frequency of impedance measurements was swept from 65,000 to 0.1 Hz with an amplitude of 10 mA (Galvanostatic mode). To study the DC current effect on the pore and activation polarizations, four levels of DC bias were imposed on AC signal during impedance measurement: -100, -200, -250 and -300 mA/cm². The negativity of the applied DC bias, as regulated by the instrument, assures the DC current flowing from air-electrode towards YSZ, in analogy to that in a practical SOFC.

To study the Po₂ effect, gas mixtures of O₂-N₂ with a known Po₂ varying from 1 to 0.02 atm were used. In addition, transition from O₂+N₂ to O₂+He was implemented at a given temperature and DC bias, by which a number of gas diffusion properties of the cathode substrate can be determined. All gases had a fixed flow rate of 100 ml/min for any individual experiment.

DC Polarization Measurement

The DC polarization measurement was performed with Solartron 1287 only. The polarization was applied on the aforementioned cell in the mode of potentiostatic from 0
to -1 volt. The resulting current was then measured and plotted as a function of the applied polarization. Based on the fundamentals of electrochemistry, the measured V-I curves were interpreted into regions that are related to activation polarization, ohmic IR loss, mass transfer and electronic leakage.

THEORETICAL BASIS

In this section, we discuss some fundamentals that laid the foundation for the techniques described in this paper.

Gas Diffusion Resistance – Pore Polarization

As described in a separate paper (2), the partial pressure of oxygen, $P_2$(atm), at the cathode/YSZ interface under cylindrical coordinate is governed by:

$$P_2 = P_{\text{total}} - (P_{\text{total}} - P_1) \exp \left[ \frac{R T r_2}{4 F D^{\text{eff}}_{O_2} P_{\text{total}}} J \ln \left( r_2 \right) r_1 \right]$$

where $P_{\text{total}}$ is the system total pressure in atm; $P_1$ is the bulk P02 of air in atm; $r_1$ and $r_2$ are the inner and outer radii of the cathode tube, respectively; $D_{O2}^{\text{eff}}$ is the effective oxygen diffusivity at temperature $T$, including microstructure factor of the cathode tube; $J$ is the cell current density.

The corresponding pore polarization $\eta^p_{CA}$ (V) is, therefore, written by:

$$\eta^p_{CA} = \frac{RT}{4F} \ln \frac{P_1}{P_{\text{total}} - (P_{\text{total}} - P_1) \exp \left[ \frac{R T r_2}{4 F D^{\text{eff}}_{O_2} P_{\text{total}}} J \ln \left( r_2 \right) r_1 \right]}$$

At extreme condition where $P_2\rightarrow0$, the cell current density $J$ approaches to the so-called “limiting current density” $J_L$ (A/cm²), which is given by:

$$J_L = \frac{\ln(1-x) \times 4F D^{\text{eff}}_{O_2}}{R T r_2} \times P_{\text{total}}$$

where $x=P_1/P_{\text{total}}$.

The gas diffusion resistance $R_d$ (Ωcm²), which is the focal interest of this study, is accordingly yielded from combining equations [2] and [3]:

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\[ R_d = \frac{RT}{4F} \times \frac{\ln(1-x)}{J_L} \times \frac{1}{1 - (1-x)^{(J/L-1)}} \]  

The significance of the Equation [4] is to allow the determination of \( R_d \) through measuring the change of \( R_d, \Delta R_d \), after the surrounding gas is transited from one to another. At a given \( T \) and \( x \), \( R_d \) is the function of \( J \) and \( J_L \). The latter varies primarily with the effective oxygen diffusivity \( D_{O_2}^{\text{eff}} \), which can be simply expressed by:

\[ D_{O_2}^{\text{eff}} = m \times D_{O_2} \]  

where \( D_{O_2} \) is the molecular diffusivity of oxygen, which can be readily calculated using Chapman-Enskog equation (3) for specific gas mixtures, and \( m \) is a factor that is strongly dependent on the microstructure of the cathode tube (porosity and tortuosity).

Application of equations [4] and [5] to a case with transition from air to a mixture of He-O\(_2\), \( \Delta R_d \) is given by:

\[ \Delta R_d = A \left( \frac{1}{J_L^{O_2N_2}} \times \frac{1}{1 - (1-x)^{(J/L^{O_2N_2})}} - \frac{1}{J_L^{O_2He}} \times \frac{1}{1 - (1-x)^{(J/L^{O_2He})}} \right) \]  

\[ A = \frac{RT}{4F} \ln(1-x) \]  

The implication of equation [6] is significant as the microstructure factor, \( m \), can be obtained by a measurable \( \Delta R_d \) resulted from the above transition. The attainment of \( m \) can be further utilized to calculate \( R_d^{O_2N_2} \), which is a direct measure of gas diffusion properties.

**Activation Polarization**

The activation polarization (no mass transport effect) of an electrochemical cell is expressed by the Butler-Volmer equation (4):

\[ J = J_o \left[ e^{-\alpha \eta} - e^{(1-\alpha) \eta} \right] \]  

where \( J \) and \( J_o \) are the cell current density and exchange current density, respectively; \( \alpha \) is the transfer coefficient, \( 0<\alpha<1 \); \( f = nF/RT \); \( \eta \) is the activation polarization or overpotential. At large \( \eta \) (\( \eta<0 \)) and oxygen reduction electrode reaction, the equation [8] becomes

\[ \eta = \frac{RT}{4\alpha F} \ln J_o - \frac{RT}{4\alpha F} \ln J \]  

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RESULTS AND DISCUSSION

Identification of Activation Polarization and Pore Diffusion Processes

In order to quantify the activation and pore polarization processes, the first step is to identify these processes by a certain technique. The method of choice in this study is the AC impedance spectroscopy, with which DC bias, P02 and O2-diffusivity are varied to facilitate the identification process during impedance measurement. The guidance used in this study is based on the fact that the activation polarization reduces and the pore polarization elevates as the DC bias increases. On the other hand, the change of P02 should alter both activation and pore polarizations. However, it is believed that the best approach to separate the above two processes is to compare the spectra obtained from using air and He-20% O2 under a given temperature and DC bias. Due to a fixed O2 content in both cases, the activation polarization and ohmic IR loss remain unchanged so that the observed change in spectra is solely attributed to the pore polarization. In the following discussion, we demonstrate the effectiveness of this approach.

Figure 1. The DC bias effect on the AC impedance spectra measured at 1000°C and in air.

**DC Bias Effect** The DC bias effect on the impedance of one two-phase cathode interlayer cell was studied at 1000°C and in air, and is shown in Figure 1. As expected, the DC current has reduced the total electrode resistance without affecting the ohmic resistance as indicated by the common interception of the spectrum with the real axis at high frequency end. However, the relative magnitude of the resistance of the first arc to the second arc varies considerably with the DC bias. As the DC bias increases, for
example from $-100$ to $-300$ mA/cm$^2$, the first arc shrinks as the second arc increases moderately. This trend appears to suggest that the first arc is related to the activation process whereas the second arc is associated with the pore diffusion process. The shift in the peak frequency towards higher value ($650\rightarrow818$ Hz) for the first arc implies that the DC bias improves the electrode kinetics. The positive $Z''$ at high frequency range in Figure 1 as well as Figures 2 and 3 was the result of induction originated from the measuring leads.

Figure 2. The $\text{Po}_2$ effect on the AC impedance spectra measured at 1000°C and $J = -300$mA/cm$^2$.

**The $\text{Po}_2$ Effect** To further confirm the above assertion, the $\text{Po}_2$ in the surrounding atmosphere was varied among pure $\text{O}_2$, air and $\text{N}_2$-$2\%\text{O}_2$. Figure 2 shows the spectra of another interlayer cell measured at 1000°C with a DC bias of $-300$mA/cm$^2$. The ohmic resistance at high frequency end is expectedly unchanged by the $\text{Po}_2$, indicating the effective conductivity of the electrolyte is a constant within the measured $\text{Po}_2$ range. A similar trend was also observed for the first arc, which is assumed to be related to the activation polarization. This is somewhat different from what observed in ref. (1), where a visible resistance shift upon change of $\text{Po}_2$ was seen. Note that the EVD cell studied in ref. (1) had CeO$_2$ interlayer. The presence of a two-phase interlayer material in this study is believed to help facilitate the electrode kinetics so that the $\text{Po}_2$-dependence of the activation process may become weaker. Despite of this, the peak frequency, a measure of time constant of the process, indeed decreased ($3257\rightarrow2587\rightarrow1296$ Hz) with $\text{Po}_2$, suggesting a slower kinetics at lower $\text{Po}_2$. The most dramatic changes are evidently found for the second arc, a process thought to be associated with the pore diffusion. According to ref. (2), the pore diffusion polarization is a strong function of partial pressure of oxygen. The lower the $\text{Po}_2$ is, the higher the resistance for $\text{O}_2$ diffusion would be, particularly under current loading condition. These findings also seem to support the previous assertion, *i.e.*, the first arc is due to the activation polarization and the second
one is associated with the pore diffusion polarization. It is worthy to mention that there should have no contribution from pore diffusion in pure O₂. The origin of a very small semicircle observed for the O₂-spectrum in Figure 2 is unclear. It may be the result of another hidden step that cannot be resolved because of overlapping when the pore diffusion polarization is present and overwhelming.

**Figure 3.** AC impedance spectra measured at 1000°C and J=300mA/cm² in air and He-20%O₂.

**The O₂-diffusivity Effect** To finally confirm that the first and second arcs on the AC impedance spectrum are corresponding to activation and pore diffusion polarizations, respectively, a gas mixture of He-20%O₂ was used in comparison to that is measured from using air. This selection of different O₂-diffusivity gas mixture avoids the potential interference from Po₂-dependent ohmic IR loss and activation polarization, and therefore it makes any shift in resistance shown on the spectrum by transiting from air to He-20%O₂ be caused solely by pore diffusion process. Figure 3 compares the spectra measured in both gases. Clearly, the only part changed on the spectrum was the second arc, favorably supporting the previous identification. More importantly, with the measurable shift, ΔRₐ, the air diffusion resistance Rₐ can be calculated by equation [6].

**Determination of Air Diffusion Resistance Rₐ**

According to equation [6], the resistance shift, ΔRₐ, shown in Figure 3 yields the microstructural parameter m= 0.121 and air diffusion resistance Rₐ= 0.032 Ωcm², which estimates a porosity of 34.8% in the cathode substrate for this specific sample.

**Activation Polarization**

With the activation process identified on the AC impedance spectrum, an estimation of the polarization resistance under various current densities is possible. Figure 4 shows the
Tafel plot of the activation polarization from another two-phase interlayer cell. With using equation [9], the least-square fitting yields \( J_0 = 0.020 \text{A/cm}^2 \) and \( \alpha = 0.98 \) at 1000°C.

**Figure 4. Plot of cathodic polarization as a function of current.**

**DC Polarization**

In addition to AC impedance method, a simple DC polarization was also performed on cells to quickly screen the cathode properties. Figure 5 illustrates three V-I polarization curves, measured from one EVD cell (CeO\(_2\) interlayer) and two APS cells (CeO\(_2\) interlayer). In general, each curve can be divided into four regions, as marked by the vertical lines, each of which has a unique shape and electrochemical meaning. The Region I, located at the lowest current density range (0-0.2A/cm\(^2\)), reflects the activation polarization. As the current density progresses into Region II, ohmic IR loss becomes dominant. Further increasing the current density into Region III, a sharp increase in polarization is clearly observed. This observation suggests that Region III be closely related to pore diffusion polarization as a result of approaching limiting current density. Lack of sharpness in two APS cells is probably caused by the presence of partial mixed conduction in the YSZ layer. As the polarization continues to rise and into Region IV, the measured residual current can only be the result of electronic leakage current since all the oxygen ions have been depleted at the cathode/YSZ interface at above the limiting current. By comparing three curves, a good APS cell exhibited the same order of magnitude of ohmic IR loss, activation and pore polarization resistance as the EVD cell. Furthermore, the leakage current in the EVD cell is clearly smaller (larger slope) than that in APS cells. This most likely resulted from a lower densification temperature for EVD cell than for APS cells.

**General Comments**

It is to be noted that the cells investigated in this study were not symmetrical in electrode configurations, *i.e.*, Pt/YSZ vs. cathode/YSZ. The measured impedance spectra, therefore, must contain the contribution from Pt/YSZ interface, which is not the interest...
of the study. The impedance from the Pt/YSZ interface is known non trivial. As a result, the Tafel plot of activation polarization shown in Figure 4 may well overestimate for the cathode/YSZ interface. Despite of this, a relative comparison from cells to cells that are measured with the same configuration is still valid, and in fact has been proven as a very useful and quick tool for quality control. It is the interference from Pt/YSZ interface that prevents the author from further extracting extensive electrochemical quantities of cathode/YSZ interface from measurements. The developed method in this paper is intended for using as a screening tool of cathode/YSZ quality control. An accurate determination of various polarization resistance of cathode/YSZ interface requires a knowledge of impedance contribution from Pt/YSZ interface. One exception from the influence of Pt/YSZ interface is the method to measure diffusion resistance $R_d$ by “resistance shift” as the gas diffusion contribution from Pt/YSZ is negligible due to a thin and porous Pt counter electrode.

**CONCLUSIONS**

The identification of activation and pore diffusion processes was demonstrated by AC impedance spectroscopy technique on two-phase cathode interlayer cells with varying DC bias, $P_{O_2}$ and $O_2$-diffusivity. It was found that applying DC bias reduces the activation polarization but increases the pore polarization. The variation of $P_{O_2}$ has a greater impact on the pore diffusion process than the activation polarization under a loading current condition. Use of He-20%$O_2$ mixture has been shown to be the best means of identifying and quantifying the pore diffusion related process since an identical $P_{O_2}$ level in air and He-20%$O_2$ mixture avoids the contribution from the activation polarization and ohmic IR loss. The equation for calculating the pore diffusion resistance based on the “resistance shift” created by transiting air to He-20% $O_2$ was also formulated. In addition, DC polarization technique has been demonstrated to be a useful and convenient tool for screening the quality of cathode/YSZ interface.
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