COMPLEX IMPEDANCE ANALYSIS OF SOFC CATHODE AND ITS APPLICATION TO INVESTIGATE THE Cr-POISONING

Yoshio Matsuzaki, Masakazu Hishinuma and Isamu Yasuda
Fundamental Technology Research Laboratory
Tokyo Gas Co. Ltd.
1-16-25 Shibaura, Minato-ku, Tokyo, 105-0023 Japan

ABSTRACT

By making clear the relationship between the cathodic limiting current density and R-type Warburg impedance used in the Randles type equivalent circuit, the limiting current density as well as the exchange current density of a porous La$_{0.6}$Sr$_{0.4}$MnO$_{3+\delta}$ (LSM)/YSZ electrode has been successfully estimated from a complex impedance spectrum measured at an equilibrium potential. A steady-state polarization calculated from these current densities gave a good agreement with the measured one, which indicates that even at equilibrium potential, the limiting current density can be obtained with a high precision from the complex impedance. Investigation of the Cr-poisoning using this analysis method made clear that the Cr$_2$O$_3$ deposition at the interface between the LSM and the YSZ electrolyte causes an increase in both diffusion and charge-transfer resistances.

INTRODUCTION

The perovskite-type oxides such as La$_{1-x}$Sr$_{x}$MnO$_{3+\delta}$ are used as the cathode material of solid oxide fuel cells (SOFCs) because of their high activity for oxygen reduction (1), electrical conductivity (2) and chemical compatibility with YSZ (3). For use as the SOFC cathode, one of the most important properties required for the electrode is the steady-state polarization which is characterized mainly by the parameters such as the exchange current density and the limiting current density. In most of the preceding works, electrode reaction mechanisms were discussed on the basis of kinetic parameters related to charge-transfer reaction process such as the exchange current density and the electrode interface resistance (4-9). As for the limiting current density, measurements were conducted under a DC polarization, but it is difficult to obtain the polarization data with good reproducibility due to the difficulty in maintaining a constant electrode microstructure at relatively high current densities (10). Methods to determine the limiting current density of the SOFC cathode with good reproducibility without DC polarizations have not been proposed.

Several arcs are known to appear in a complex impedance curve of a SOFC electrode, and an equivalent circuit with as many RC (resistance and capacitance) parallel circuits connected in series as the number of the arcs is typically used to simulate the impedance curve (11,12). But the physical meaning of the equivalent circuit is not clear. The use of a finite-length diffusion impedance (R-type Warburg impedance), on the other hand, was
shown to be effective to express a mass transfer in the reaction process of the electrode (13). A Randles type equivalent circuit (14) which includes the R-type Warburg impedance was then shown to be able to well simulate the complex impedance curve (15-17). But the kinetic parameters calculated by fitting the impedance spectrum to the equivalent circuit were not able to explain steady-state polarization characteristics of the electrode, and the limiting current density has not been obtained from the fitted parameters.

For the interconnects of a planar type SOFC, ceramic materials based on doped LaCrO₃ have been widely used. Because of higher thermal conductivity, lower costs and higher strength compared with ceramic interconnects, metallic interconnects have been expected to be applicable, particularly for a substrate-type SOFC which can be operated under 1073 K. However, CrO₂(OH)₂ vapor generated from the oxide scale (Cr₂O₃) formed on most high temperature oxidation-resistant alloys degrades the performance of the cathode (18-20). The CrO₂(OH)₂ vapor is assumed to be generated by the following reaction:

\[
\text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CrO}_2(\text{OH})_2
\]  

[1]

The CrO₂(OH)₂ vapor pressure calculated by using the thermodynamic data (21) is lower at a lower oxygen partial pressure. Since the oxygen partial pressure at the interface between the cathode and the electrolyte is lowered by an electrode polarization, the CrO₂(OH)₂ vapor generated from the alloy surface is reduced to precipitate Cr₂O₃ preferentially at the interface where electrochemical reactions take place. The mechanism of the Cr₂O₃ precipitation in the electrode has thus been known, but the electrochemical properties of the electrode affected by the Cr-poisoning have not been made clear.

In this study, we tried to obtain the limiting current density as well as the exchange current density by analyzing the complex impedance spectrum of the SOFC cathode measured at an equilibrium potential using the Randles type equivalent circuit. We then calculated the steady-state polarization of the electrode from the obtained exchange and limiting current densities, which was compared with the measured value to examine the validity of the determined parameters. The effect of the Cr₂O₃ precipitation on the electrochemical properties of the cathode was also studied by using the same analysis.

**EXPERIMENTAL**

Dense pellets (20 mm in diameter and 2 mm in thickness) of 3 mol% or 8 mol% yttria-doped zirconia were used as the electrolytes of electrochemical cells. The oxide electrode material, La₀.₆Sr₀.₄MnO₃+δ (LSM) powder with an average grain size of 2 μm purchased from Nihon Kenmazai Kogyo was dispersed in hexylene glycol and then screen-printed onto one side of the electrolyte pellet before firing at 1423 K for 2 hrs. to prepare a porous LSM electrode. The thickness and porosity of the LSM electrode was about 30 μm and 40 %, respectively. For the counter electrode, Pt paste (Tokuriki Kagaku, 8103) was painted symmetrically to the LSM electrode on the other side of the pellet and fired at 1273 K for 2 hrs. For the reference electrode, Pt paste was painted at the perimeter of the pellet and fired at 1273 K for 2 hrs.
Figure 1 shows the test geometry used in the electrochemical measurements. Two Sr-doped LaCrO$_3$ plates with grooves were used as both manifolds and current collectors. Air was fed into the doped LaCrO$_3$ plates from the top and bottom of a furnace and supplied over the reference, counter, and the LSM working electrodes. Platinum wires were used as voltage terminals for the working and reference electrodes. For the investigation of the Cr-poisoning, an Inconel 600 plate was used instead of the doped LaCrO$_3$ plate on the side of the LSM working electrode.

The complex impedance measurements were made over the frequency of 1 mHz-100 kHz with an applied amplitude of 10 mV using the three-terminal method at 1073 K in air. The system for the impedance measurements was composed of a frequency response analyzer (Solartron 1260), a potentiostat (Solartron 1287) and a personal computer (Compac Armada 1120T). The measured spectra were fitted to the equivalent circuit by using the nonlinear least square fitting software, EQUIVCRT, developed by Boukamp (18). Steady-state polarization was measured by a current interruption method using a current-pulse generator (Hokuto Denko HC-110).

RESULTS AND DISCUSSION

Complex Impedance

The frequency dispersion diagram of the complex impedance of the LSM/3YSZ electrode measured under the open circuit condition is shown in Fig. 2 with the simulated one. Two arcs seem to be overlapped in the impedance plot. In the case of a cathode reaction, oxygen is regarded to be reduced in the flowing process as illustrated in Fig. 3. Oxygen molecules are dissociatively adsorbed on LSM surface, then the adsorbed oxygen atoms (O$_{ad}$) diffuse over a characteristic length $\delta$ from $x=\delta$ to the triple phase line at $x=0$. The O$_{ad}$ is further reduced to O$_2^-$ at the triple phase line by the charge-transfer reaction. Figure 4 shows the Randles type equivalent circuit used to represent the electrochemical behavior of the electrode: $R_e$ is the resistance of charge-transfer reaction, $Z_d$ is the R-type Warburg impedance, $R_b$ is the ohmic resistance of electrolyte and lead wires, $W$ is a semi-infinite length diffusion impedance known as Warburg impedance, $C_{dl}$ is double layer capacitance, and $L$ is the inductance of lead wires. The closed symbols in Fig. 2 were plotted by fitting the observed impedance spectrum to the equivalent circuit. A good fit can be seen between the experimental result and the calculation.

Steady-State Polarization

The values of the exchange current density, $I_o$, and the cathodic limiting current density, $I_{L,C}$, have to be determined before calculating the steady-state polarization. The exchange current density, $I_o$, is related to $R_e$ by

$$I_o = \frac{RT}{nFSR_e}$$  \[2\]
where \( n \) is the number of electrons which contribute to the charge transfer reaction, \( F \) is the Faraday constant and \( S \) is the electrode area. The limiting current density, \( I_{L,C} \), should be related to \( Z_d \). The calculation of the R-type Warburg impedance is given by Broers (19) for an electrode in aqueous solutions and molten salts as summarized below.

The one-dimensional diffusion equation is given by

\[
\frac{\partial \Delta C}{\partial t} = D \frac{\partial^2 \Delta C}{\partial x^2}
\]  

where \( \Delta C = C(x,t) - C_0 \) and \( C_0 \) is the equilibrium concentration. The boundary conditions are given by

\[
\text{at } x = \delta, \quad \Delta C = 0 \quad [4]
\]

\[
\text{at } x = 0, \quad D \left( \frac{\partial \Delta C}{\partial x} \right)_{x=0} = \frac{i}{nF} \quad [5]
\]

Using the boundary conditions Eqs. [4] and [5] and the additional condition,

\[
|\Delta C| \ll C_0 \quad [6]
\]

the solution of Eq. [3] is given by

\[
Z_d = R_d \frac{\tanh[(1 + j)\delta \sqrt{2D_o}]}{(1 + j)\delta \sqrt{2D_o}} \quad [7]
\]

where \( R_d \) is the diffusion resistance given by

\[
R_d = \frac{RT\delta}{n^2F^2C_0D_oS} \quad [8]
\]

Using this equation we have derived the following relationship between the cathodic limiting current density and the diffusion resistance.

\[
I_{L,c} = nFC_0D/\delta = RT/nFSR_d \quad [9]
\]

Using the values of \( R_e \) and \( R_d \) determined from the impedance measurements into Eqs. [2] and [8], \( I_e \) and \( I_{L,C} \) at 1073 K were calculated to be 0.21 and 0.53 A cm\(^{-2}\), respectively. To examine the validity of the parameters, a steady-state polarization of the electrode was then calculated by substituting the \( I_e \) and \( I_{L,C} \) into the following generalized equation which expresses the relationship between the current density \( i \) and the polarization \( \theta \).
\[ \frac{i}{I_o} = (1 - \frac{i}{I_{La}}) \exp\left(-\frac{\alpha_a F \eta}{RT}\right) - (1 - \frac{i}{I_{La,a}}) \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \]  

[10]

where \( \alpha_a \) and \( \alpha_c \) are anodic and cathodic transfer coefficients, respectively and \( I_{La,a} \) is an anodic limiting current density. \( \alpha_a \) and \( \alpha_c \) were regarded as constant at 0.5 (20), and for \( I_{La,a} \) \( i \ll I_{La,a} \) was assumed in the current range of 0 to 0.3 Acm\(^{-2}\). The calculated results are compared with the measurements in Fig. 5. It can be seen that the calculated and measured polarizations show close correspondence without using arbitrary fitting parameters. This indicates that the limiting current density as well as the exchange current density can be determined at high precision by the complex impedance measurements without DC polarizations.

**Cr-Poisoning**

The analysis method given above was used to evaluate the effect of using the chromium-containing alloy, Inconel 600, on the electrochemical properties of the LSM/8YSZ electrode. Figure 6 shows the overvoltage of the electrode (including the IR loss) as a function of time under the current density of 0.3 Acm\(^{-2}\) at 1073 K. The broken line indicates the overvoltage when using an Inconel 600 plate as a current collector, and the solid line indicates the overvoltage for a doped LaCrO\(_3\) current collector. With the doped LaCrO\(_3\), the overvoltage decreased with time, which is attributed to the improvement in the electrode performance due to the current flow. This effect is considered to be caused by a change in the microstructure of the electrode (22), but the details for the mechanism have not been clarified. With the alloy current collectors, however, the electrode performance degraded and the overvoltage increased with time rapidly. During the test, the current was switched off several times to measure the AC impedance spectra under the open circuit condition, and the current was switched on again. The degraded performance recovered for a short period of current interruption, but degraded rapidly again when the current was switched on. The transient recovery of the electrode performance after a current interruption was reported also by Badwal et al (20) for a current collector of a Cr-based alloy.

The complex impedance spectra measured under the open circuit condition are shown in Fig. 7. With the doped LaCrO\(_3\), the size of impedance arcs decreased with time, which corresponds to the decrease in the overvoltage. With the alloy plate, the size of the arcs decreased during the initial 10 hrs, but the degree of the decrease was smaller than in the case with the doped LaCrO\(_3\). The arcs then turned to expand with time. The impedance spectra thus obtained were analyzed with the equivalent circuit described in Fig. 4 to separate the individual resistance components, and the results are shown in Fig. 8. In the case of using the doped LaCrO\(_3\) plate, \( R_b \), \( R_e \) and \( R_d \) all decreased with time, with the transition time to reach a steady level of about 1 hr. for \( R_b \) and 20 hrs. for both \( R_e \) and \( R_d \). In the case of the alloy, \( R_b \) decreased for about 1 hr. and then maintained a constant value. In contrast, \( R_e \) and \( R_d \) decreased initially and then increased with time. These results
suggest that the increase in the overvoltage caused by the Cr-poisoning is due to the increase in the charge-transfer resistance and the diffusion resistance, not in the ohmic resistance.

The impedance measured under the open circuit condition does not, however, fully correspond to the actual change in the overvoltage because of the partial recovery of the electrode performance after repeated interruptions of the current. The overvoltage of the electrode was therefore measured under continuous current without interruptions, and the complex impedance spectra were measured under DC polarizations. Figure 9 shows the time change of overvoltage under the continuous current flow. Continuous curves were obtained this time for both electrodes with the doped LaCrO$_3$ and the alloy as the current collectors. The complex impedance spectra measured under polarization at the current density of 0.3Acm$^{-2}$ are shown in Fig. 10. Comparing the spectrum after 30 minutes with the initial one, the size of the arcs decreased for the doped LaCrO$_3$ but increased for the alloy, which corresponds to the change in the overvoltage with time. By analyzing the impedance spectra using the equivalent circuit, it was found that $R_b$ slightly decreased, while $R_e$ and $R_d$ greatly increased with time when the alloy was used as current collectors. It was therefore concluded that the degradation in the electrode caused by the Cr-poisoning is due to the increase in charge-transfer resistance and surface diffusion resistance.

CONCLUSIONS

The relationship between the cathodic limiting current density of the LSM/YSZ electrode and R-type Warburg impedance has been derived, and the limiting current density as well as the exchange current density was obtained by analyzing the complex impedance spectra measured at an equilibrium potential on the basis of a Randles equivalent circuit. The steady-state polarization of the electrode calculated using the parameters obtained by fitting the impedance spectrum to the equivalent circuit showed a good agreement with the measured one. This analysis method has also been used to evaluate the electrochemical properties of the cathode with the current collector made of a chromium-containing alloy. It was found that the Cr-poisoning is caused by increase of the charge-transfer and surface diffusion resistance.

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Fig. 1. Test geometry used in the electrochemical measurements. A: working electrode, B: reference electrode (Pt), C: counter electrode (Pt), D: YSZ pellet, E: Pt mesh for current collection, F: Sr-doped LaCrO₃ plate or Inconel 600 plate for current collection and manifold, G: Al₂O₃ plate for manifold, H: Gasket (Pt), I: glass seal and J: pushrod.

Fig. 2. A typical complex impedance plot measured at 1073 K under Po₂ of 0.21 atm.
Fig. 3. Schematic view of the oxygen reduction process at LSM/YSZ interface.

Fig. 4. Randles type equivalent circuit. Zd: finite-length diffusion impedance (R-type Warburg impedance), Re: charge-transfer resistance, Rb: ohmic resistance of electrolyte and lead wires, W: Warburg impedance, C<sub>dl</sub>: double layer capacitance and L: inductance of lead wires.

Fig. 5. Steady-state polarization of the electrode at 1073 K. A broken line shows the calculated polarization curve by Eq. [10] using I<sub>0</sub> and I<sub>Lc</sub> determined by fitting the complex impedance spectrum to the Randles type equivalent circuit.

Fig. 6. Plots of overvoltage at the current density of 0.3Acm<sup>2</sup> versus time for the LSM/8YSZ electrode with doped LaCrO<sub>3</sub> or alloy plates for current collection. Arrows indicate the points when the complex impedance measurements were conducted under the open circuit condition.
Fig. 7. Complex impedance spectra of the electrode measured under the open circuit condition at the times indicated with arrows in Fig. 6. The inset shows an expanded view of the high frequency end of the spectra. (a) with the doped LaCrO$_3$ and (b) with the alloy for current collection.

Fig. 8. Plots of ohmic, charge-transfer and diffusion resistance of the electrode estimated from the complex impedance spectra shown in Fig. 7. (a) with the doped LaCrO$_3$ and (b) with the alloy for current collection.
Fig. 9. Plots of overvoltage versus time with continuous current for the LSM/8YSZ electrode with the doped LaCrO$_3$ or the alloy for current collection.

Fig. 10. Complex impedance spectra of the electrode measured under polarization at the current density of 0.3Acm$^{-2}$. (a) with the doped LaCrO$_3$ and (b) with the alloy for current collection.