Evaluation of Diffusion Coefficient of Oxygen in Liquid Silver from AC Impedance of an Electrochemical Cell based on Solid Electrolyte and Molten Silver Electrode

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The diffusion coefficient of oxygen in liquid silver was evaluated by analyzing the relaxation process of the electrode reaction of an AC-polarized solid galvanic cell employing stabilized zirconia as the solid electrolyte and liquid silver as the electrode. The AC impedance of the cell was measured for various amounts of oxygen at the silver electrode in the frequency range from 1 mHz to 1000 mHz at temperatures of 1273–1373 K. The well-defined Warburg impedance, which was expected when the overall electrode reaction rate was controlled by the diffusion of oxygen in liquid silver, was obtained for a certain limited condition. The diffusion coefficients determined from this impedance agreed fairly well with those reported by other authors. The factors causing errors in the evaluation of the diffusion coefficient were examined.

(Received March 13, 2001; Accepted April 3, 2001)

Keywords: diffusion, silver, polarization, electrochemistry, oxygen electrode, zirconia

1. Introduction

Electrochemical measurement using a solid electrolyte is a powerful technique for investigating the transport phenomena of atomic species taking place at high temperatures. By use of this method, the concentration of the species of interest could be measured as the electrical potential and its flux as the electrical current both of which are usually measured easily with high accuracy. Based on this technique, the diffusion of oxygen dissolved in liquid metals has been studied employing stabilized zirconia as the electrolyte and the liquid metals as the electrodes.^{1–10)} In these studies, all the measurements and the analyses were done on the relaxation phenomena of a single step response. If oxygen was released from the electrolyte or permeated electrochemically through the electrolyte, the data obtained by the single relaxation processes would contain systematic errors. By utilizing an alternating relaxation method,¹¹⁾ however, we may estimate the effect of these errors by analyzing the frequency dependencies of the measured value.

Furthermore, in the investigation of the bulk properties of the solid electrolyte by AC methods, utilizing a liquid metal as the electrode is more useful than a porous electrode of solid metals. The problems caused by the uncertainty of the morphology of the electrode which could not be avoided with solid electrodes are fully eliminated when a liquid metal electrode is used. The geometrical conditions of the electrode can be defined more simply with liquid electrodes. For such purposes, the behavior of a liquid electrode in AC measurements must be studied in more detail.

In the present report, the AC polarization of the galvanic cell employing stabilized zirconia as the electrolyte and molten silver as the electrode was analyzed theoretically, and the performance of the method to evaluate the diffusivity of oxygen in molten silver was examined.

Fig. 1 Schematic view of experimental cell.

2. Theoretical

Consider the asymmetrical galvanic cell represented in Fig. 1, which is based on an oxide ion-conducting electrolyte with a reversible electrode of constant oxygen activity ($p_{O_2} = 0.21$)¹²⁾ on the left side and an irreversible (closed) liquid silver electrode on the right side. When a constant potential E_0 is applied to this cell, a current is observed to flow and to decay gradually to a constant value, and finally the Hebb-Wagner polarization state^{13,14)} is obtained. The concentration of the oxygen in liquid silver in moles per unit volume is then set at a constant value c_0 , which is given as

$$c_0 = \frac{1}{V} \frac{\sqrt{0.21}}{\gamma_0} \exp\left(\frac{2FE_0}{RT}\right) \quad (1)$$

where γ_0 is the activity coefficient of oxygen in liquid silver defined by mole fraction X_O and activity p_{O_2} as $X_O = \gamma_0 p_{O_2}^{1/2}$, V is the molar volume of liquid Ag, F the Faraday constant, R the gas constant and T the absolute temperature.

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When an AC voltage,

$$v(t) = v'_0 \cos(\omega t + \beta) \quad (2)$$

was superimposed on the E_0 , a steady AC current should be observed to flow through the cell. We consider the case when the resulting overpotential at the liquid silver electrode $\eta(t)$ is represented as

$$\eta(t) = v_0 \cos(\omega t). \quad (3)$$

We then calculate the value of the current through the circuit assuming that the overall rate-determining step is the diffusion process of oxygen through the molten silver used as the electrode and assuming that the thickness of the layer of the molten silver is large enough to be regarded as semi-infinite media.

We represent the instantaneous concentration of oxygen in liquid silver at the distance x from boundary and at time t as $c(x, t)$. The concentration at the boundary facing the electrolyte, $c(0, t)$, is determined by the oxygen activity corresponding to the electrical potential of the electrode. If the absolute value of $\eta(t)$ is sufficiently small compared to that of E_0 , it can be represented from eq. (1) as follows,

$$c(0, t) = c_0 + kv_0 \cos(\omega t) \quad (4)$$

where $k = Fc_0/RT$. On the other hand, based on the assumption of semi-infinite media,

$$c(\infty, t) = c_0 \quad (5)$$

Solving the second Fick's law under the above boundary conditions, we obtain¹⁵⁾

$$c(x, t) = c_0 + kv_0 \times \exp\left(-\left(\frac{\omega}{2\tilde{D}}\right)^{\frac{1}{2}} x\right) \cos\left(\omega t - \left(\frac{\omega}{2\tilde{D}}\right)^{\frac{1}{2}} x\right). \quad (6)$$

From this concentration profile, the flux of oxygen $J(t)$ at the electrode-electrolyte interface can be determined by Fick's first law below.

$$J(t) = -\tilde{D} \left(\frac{\partial c(x, t)}{\partial x} \right)_{x=0} = kv_0(\tilde{D}\omega)^{\frac{1}{2}} \cos\left(\omega t + \frac{\pi}{4}\right) \quad (7)$$

When the electrode reaction is assumed to be perfectly controlled by the diffusion of oxygen in the electrode, the electrical current can be represented by the flux of oxygen using Faraday's law as below.

$$i(t) = 2FSJ(t) = 2FSkv_0(\tilde{D}\omega)^{\frac{1}{2}} \cos\left(\omega t + \frac{\pi}{4}\right), \quad (8)$$

where S is the contact area of the electrode-electrolyte interface.

The AC component of the imposed voltage $v(t)$ contains not only the overpotential at the molten metal electrode but also that induced by the impedance of the bulk electrolyte and

the counter electrode. It may be written as

$$v(t) = \eta(t) + Z'(t) \bullet i(t) \quad (9)$$

where $Z'(t)$ means the sum of these impedances.

If the complex notations familiar to the analysis of such a sinusoidal steady state are employed, $v(t)$ and $i(t)$ are represented as $\dot{v}$ and $\dot{i}$ as below,

$$\dot{v} = v_0 + \dot{Z}\dot{i} \quad (10)$$

$$\dot{i} = \sqrt{2}FSkv_0(\tilde{D}\omega)^{\frac{1}{2}}(1 + j) \quad (11)$$

where j is the notation representing $\sqrt{-1}$.

Therefore, the whole impedance of the cell to be observed is represented below,

$$\begin{aligned} \dot{Z} = \frac{\dot{v}}{\dot{i}} &= \frac{1}{2\sqrt{2}FSk(\tilde{D}\omega)^{\frac{1}{2}}}(1 - j) + \dot{Z}' \\ &= A(1 - j)\omega^{-1/2} + \dot{Z}' \end{aligned} \quad (12)$$

where

$$A = \frac{1}{2\sqrt{2}FSk\tilde{D}^{1/2}} = \frac{RT}{4\sqrt{2}F^2Sc_0\tilde{D}^{1/2}} \quad (13)$$

The first term of eq. (12) is known as the Warburg impedance¹⁶⁾ and is easily deduced from the complex impedance plot (Cole-Cole plot) because the second term $Z'(t)$ may be taken as a constant real value at low frequencies such as those used mainly in this experiment. If the conditions of the experiment really fulfill the above assumptions, we should obtain a cell impedance whose Cole-Cole plot is represented as shown in Fig. 2. The diffusion coefficient of oxygen in the liquid metal then can be determined by the coefficient of the Warburg impedance of the experimental cell using eq. (13).

3. Experimental

The schematic view of the cell assembly except for a heating furnace is shown in Fig. 3. The electrolyte was a flat bottom-type polycrystalline sintered 8 mol% Y_2O_3 -doped zirconia tube, 15 mm OD by 11 mm ID by 450 mm long. Silver melted in the zirconia tube was used as the irreversible electrode. A porous platinum layer prepared on the outside of the bottom of zirconia tube by applying a platinum paste

Fig. 2 Cole-Cole plot expected for the impedance of experimental cell.

and then sintering in air was used as the reversible electrode. The oxygen activity of the reversible electrode was kept constant by the air flow on the electrode. The area of the outer electrode was adjusted to that of the bottom of the cylinder of liquid silver. The depth of the liquid silver was 40 mm. This depth is assumed to be large enough for the liquid Ag electrode to be regarded as a semi-infinite media under the present experimental conditions ($\geq \sqrt{2D/\omega}$). Two platinum wires are attached to the outer electrode by sintering and are used as the lead wires for potential sensing and current passage, respectively. On the other hand, two platinum wires installed with iridium tips on the top ends were used as the sensing and the current passing lead wires, respectively. With this four-lead system, an accurate voltage could be imposed on the cell using a potentiostat and a variable frequency oscillator. A schematic view of the circuit connection is shown in Fig. 4. The current was measured by the potential drop across a standard resistance placed in the circuit. The atmosphere at the silver electrode is inert Ar gas, but air is used when the applied constant voltage is 0 mV. An electric resistance furnace and an electronic control system were used to keep the temperatures at 1273–1373 K within ± 1 K. Silver was heated with the inner chamber of the electrolyte under vacuum, and Ar was introduced immediately when it melted. Subsequently, it was heated to a given temperature by applying 300 mV between the electrodes in the direction to pump out the oxygen from the liquid silver to the outside. Using this method, it was found that the formation of gas pores in the liquid silver could be perfectly prevented. The temperature profile of the cylinder of liquid silver was controlled as keeping the top end slightly hotter (about two degrees) than the bottom end in order to eliminate the effect of convection flow.

In the experiment, the initial composition of oxygen in liquid silver was set by applying a constant voltage E_0 ranging from -300 mV to 0 mV and holding for more than 12 h. Then, an alternating voltage whose amplitude ranged from

Fig. 3 Schematic diagram of cell assembly.

5 – 15 mV and a frequency 1 – 1000 mHz was superimposed on E_0 . After 10 cycles, the voltage across the electrodes and the current were measured simultaneously by two computer-controlled digital voltmeters, and the values were recorded at an appropriate time interval. The amplitude ratio and phase shift were determined by analyzing the Lissajous' figure plotted by the measured voltage and current values. The same procedures were done at various frequencies, and the Cole-Cole plots on a complex impedance plane were obtained.

4. Results

A typical example of the relation between the imposed voltage and the electrolytic current is shown in the Lissajous' plot in Fig. 5. In this measurement, the constant voltage was set at -100 mV versus the reference electrode. According to the thermodynamic data for the solubility of oxygen in liquid silver,¹⁷⁾ the corresponding concentration of dissolved oxygen was calculated to be 0.157 mol%. An AC voltage of the amplitude of 10 mV and an angular velocity of 0.008π rad/s was then superimposed on the constant voltage. A well-defined Lissajous' figure was obtained as shown in the figure. The current offset observed in the figure shows that a steady current flows at the DC polarization state with a constant offset voltage. The amount of this current was found to be larger than that estimated from the electronic conductivities of the electrolyte used. Some part of the current is, therefore, thought to be the oxide ion current to pump out the oxygen

Fig. 4 Schematic view of the circuit connection of the experimental arrangement.

Fig. 5 Typical example of the relation between current and applied voltage.

Fig. 6 Effect of oxygen concentration in liquid silver electrode on impedance of experimental cell. The frequency is changed from 1 mHz to 1000 mHz for every measurement.

permeated electrochemically through the side wall of the electrolyte. The value of this current was found to vary with each run and with their histories, which has been frequently observed in these measurements. However, the reproducibility of the Lissajous' figures in every measurement was excellent. The locus in Fig. 5 is a duplicate plot based on data from two cycles of measurement. The fluctuations in each cycle were within 2% of the absolute values. Therefore, only the relative deviation from the steady constant current was taken as the electrolytic current. In other words, the current offset resulting from the DC polarization was ignored because it could be regarded to be constant for such a small amplitude oscillation of the applied voltage and for the short period of the measurement. The absolute value of the impedance was then determined from the ratio of the amplitude of the AC voltage to that of the observed AC current. The phase shift was determined by the standard procedure of analyzing the Lissajous' plot. Based on these values, the complex impedance for each measurement was determined.

The amplitude of the imposed ac voltage was tested for ± 5 mV, ± 10 mV and ± 15 mV. For a value of more than 15 mV, a slight distortion of the Lissajous' figure was observed. For a value of less than 5 mV, the signal is small and accurate measurement was not possible.

To determine the effect of oxygen composition of the liquid silver electrode, impedance measurements were performed on the cells by applying several values of constant voltages at 1273 K. The results are shown as Cole-Cole plots in Fig. 6. We could obtain plots similar to that illustrated in Fig. 2 in the theoretical sections. For higher constant voltages, however, a clear Warburg impedance (a linear relationship between the imaginary and the real part of the impedance with a slope of $\pi/4$) was not obtained. As is mentioned later, this is estimated due to the effect of the permeation of oxygen from the other part of the cell and the release of the oxygen from the electrolyte. When the constant voltage is 100 mV (corresponding concentration of oxygen in Ag is 0.157 mol%), a linear relationship with a slope of almost $\pi/4$ was obtained. With a constant voltage of 0 mV, reproducible measurement was not possible because the value of impedance was very small. Therefore, the rest of the measurements were performed with the constant voltage set at 100 mV.

The Cole-Cole plot for the measurement with an applied

Fig. 7 Typical impedance plot when a well-defined Warburg impedance was observed.

Fig. 8 The coefficients of Warburg impedance determined from the values of an imaginary part of the impedance given in Fig. 7 as a function of angular velocity.

constant voltage of 100 mV at 1273 K is replotted in Fig. 7. It is seen that a Warburg impedance was obtained for low frequencies. The coefficient of the Warburg impedance, A , calculated from the imaginary part of the impedance is plotted as a function of $\omega^{-1/2}$ in Fig. 8. In a moderate frequency range, a constant value was obtained. This shows that, under these conditions, a situation is attained where the rate of the electrode reaction is practically controlled by the diffusion of oxygen in liquid silver. At frequencies higher than 10 Hz, a different relaxation process accompanying a larger phase shift was observed, which was probably due to a relaxation process at the counter electrode. At frequencies lower than 10 mHz, meanwhile, the phase shift was observed to decrease slightly.

The above measurements were performed at 1273, 1323 and 1373 K, and the diffusion coefficients of oxygen in liquid silver at each temperature were determined. The results are shown in Fig. 9 with reported values by other authors.^{1-4, 8, 18-20} The present value is substantially in agreement with the reported ones. The absolute values are, however, slightly higher than the others. The temperature dependence of the diffusion coefficient was determined with the least squares method as shown below,

$$\tilde{D}/\text{cm}^2 \text{ s}^{-1} = 7.26 \times 10^{-3} \times \exp \left(-\frac{40600}{(R/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(T/\text{K})} \right). \quad (14)$$

Fig. 9 Diffusion coefficient of oxygen in liquid metal as a function of temperature. Individual data points in the present data represent the difference in employed amplitude; Δ 5 mV, $\circ$ 10 mV, $\square$ 15 mV.

5. Discussion

The experimental setting is not as ideal as assumed in the theoretical section. In the following, the factors disturbing the measurement in the real experiment are analyzed and the performance of this method is discussed.

In order to determine whether the experimental conditions mentioned in the theoretical section are satisfied, the frequency dependence of the concentration distribution in liquid silver was examined based on eq. (6) using the diffusion coefficient determined above. Figure 10 represents the concentration profiles calculated for the measurement at the frequency of 1 mHz and for that at 40 mHz, which frequencies cover the conditions selected to determine the diffusion coefficient. These profiles are at the timing when the concentrations deviate the most from the value set at infinity (at the phase $\pi/4$). As seen in the figure, the depth of 4 cm is adequate for semi-infinite assumption even for the lowest frequency used in the present measurement. On the other hand, even at the highest frequency, the extent of the distribution is far larger than the size of the roughness of the electrolyte/electrode interface which is estimated to be about several μm . Therefore, it was concluded that the assumption of a flat interface and of semi-infinite media is satisfied under the present experimental conditions.

Taking into account the deviations from ideality of the experimental cell due to the existence of the impedance of the counter electrode, the electronic conduction in the electrolyte, the compositional change in the electrolyte on polarization, and the geometrical deviation from the ideal design of the liquid silver electrode, the overall impedance for the real experimental cell should be represented by the equivalent circuit

Fig. 10 Variation in concentration profile with frequency of superimposed AC voltage.

Fig. 11 Equivalent circuit assumed for real experimental cell.

shown in Fig. 11.

In the figure, C_{Pt} and R_{Pt} are the elements relating to the porous platinum electrode. The parallel connection of these elements corresponds to the relaxation process of the electrode reaction at the counter electrode. The elements, R_{ion} , $R_{electronic}$ and $Z_{nonstoichio}$ are related to the bulk of stabilized zirconia used as the electrolyte and represent the resistance to ionic conduction, the resistance to electronic conduction and the impedance due to the compositional change in the electrolyte, respectively. The current through $R_{electronic}$ is electronic current and does not accompany any electrode reaction. $R_{electronic}$ is therefore connected directly between the outer and inner lead wires. The compositional change indicates the change in oxygen content due to the formation of electronic defects and also due to the redox reactions of impurity elements upon the change in the potential profile of oxygen in stabilized zirconia.²¹⁾ The current through this impedance is thought to flow as the electronic current at the irreversible electrode but as the oxide ion current at the reversible electrode; therefore, the circuit containing this impedance should be connected directly only to the inner lead wire as shown in the figure. The impedance Z_{WAg} is the Warburg impedance in question and corresponds to the diffusion of oxygen in the liquid silver electrode. Differing from the ideal design of the irreversible electrode, the liquid silver is in contact with the electrolyte not only at the bottom but also at the side wall of the electrolyte tube. A small amount of electrode reaction may take place at the fringe of the upper surface of the electrode. The oxygen permeated electrochemically through the

upper part of the zirconia tube should be pumped out by this electrode reaction regardless of the diffusion in liquid silver. The element R_{geo} represents the resistance of this electrode reaction. The impedance Z_{wAg} is then thought to be short-circuited through this resistance as shown in the figure. According to this equivalent circuit, the phenomena observed in the experiment are explained below.

When the concentration of oxygen in the liquid silver electrode is high, the value of Z_{wAg} is small according to eq. (13). The current then flows mainly through Z_{wAg} . In other words, the total current through the cell is substantially controlled by the diffusion of oxygen dissolved in the liquid silver electrode. For an extremely high concentration, however, the measurement of its impedance becomes difficult because the value of the impedance is so small relative to that of the platinum electrode and the resistance of the bulk electrolyte. Actually, when the applied constant voltage is selected to be 0 mV, accurate determination of Z_{wAg} was not possible under the present experimental conditions. On the contrary, when the concentration of oxygen in the liquid electrode is very low, Z_{wAg} increases and the effect of the current through R_{geo} , $Z_{\text{nonstoichio}}$, and R_{electron} on the total current cannot be ignored. The Cole-Cole plot was then affected by these currents. In Fig. 6, we can see that the bend from the linear line with a slope of $\pi/4$ becomes larger with the increase in the value of applied constant voltage. From the analysis of the equivalent circuit, the main reason for this bend is attributed to the existence of a bypass resistance R_{geo} . The small contributions of $Z_{\text{nonstoichio}}$ and R_{electron} , however, may not be ignored.

At a moderate concentration such as that at an offset of 100 mV, nearly ideal plots were obtained. Even under this condition, when the measuring frequency is high, the dispersion due to the impedance of the platinum electrode becomes remarkable as is seen in Fig. 7. On the other hand, when the measuring frequency is very low, the deflection from Warburg impedance was also observed. This may be attributed to the existence of the bypass impedance $Z_{\text{nonstoichio}}$, because the current through it should increase with the decrease in frequency.

Under the limited conditions given above, it was found that the diffusion coefficient calculated from the cell impedance agreed substantially with that of oxygen in liquid silver reported by other investigators as represented in Fig. 9. The slightly higher value of the present method might come from the fact that the disturbing effects mentioned above could not be eliminated completely. However from these results it was found that the electrochemical properties of liquid silver as an oxygen electrode are characterized precisely from the diffusion process of the dissolved oxygen. Therefore, it be

used conveniently as the electrode for AC measurements in research on the bulk properties of oxide-ion conductors.

6. Summary

The diffusion coefficient of oxygen in liquid silver was evaluated by measuring the AC impedance of a solid cell using stabilized zirconia as the electrolyte and liquid silver as the electrode. By this method, the origin of the factors disturbing the measurement and their extent could be estimated from the analysis of the frequency dependency of the complex impedance of the cell. By selecting an appropriate oxygen concentration in the electrode and measuring frequencies, the diffusion coefficient of oxygen in liquid silver substantially consistent with those reported by others was obtained by the present relatively simple cell assemblies. The usefulness of the liquid silver as a well-defined oxygen electrode for oxide ion solid conductors was demonstrated.

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