WATER EFFECT ON OXYGEN REDUCTION IN MOLTEN CARBONATES

Isamu Uchida, Tatsuo Nishina, Shinji Ohuchi, and Kohta Yamada
Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University
Aramaki-Aoba, Aoba-Ku, Sendai 980, Japan

ABSTRACT

The effect of water on electrode kinetics and mechanism of the oxygen reduction at the fully immersed flag type Au electrode in (62+38)mol% (Li+K)CO₃ melt at 650°C have been investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and the digital simulation of the single scan voltammograms. The cyclic voltammograms of the oxygen reduction under P₀₂:P₃ₐ₀₂ = 0.9:0.1 atm with 2.9~15.4 mmHg H₂O vapor showed more reversible waves than that obtained under a dry atmosphere. The EIS spectra at the open circuit potential for the oxygen reduction also showed distinctly reduced impedance values by the presence of water. From the analysis of both data, it was found that the apparent mass transfer parameter CV was increased by the presence of water, indicating that water can act as an acid species in the neutralization reaction of the oxide ion according to the reaction H₂O + O²− ⇌ 2OH⁻.

INTRODUCTION

The molten carbonate fuel cell (MCFC) is expected to be one of the most promising power generation systems for the coming century due to the high energy conversion efficiency, the excellent characteristics to the environment and the ability to utilize a wide variety of fuels. In the MCFC power generation plant, CO₂ from the anode exhaust is recycled to the cathode gas inlet, and this may introduce certain amount of H₂O to the cathode gas stream.

The overall oxygen reduction in the carbonate melt is

\[
\frac{1}{2}O₂ + CO₂ + 2e \rightarrow CO₃^{2-}
\]  

[1]

For the past 20 years, many efforts have been made to elucidate the oxygen electrode reaction in molten alkali carbonates (1-19). Recently, Nishina et al. (12,13) have investigated the reaction order of the oxygen reduction with respect to the partial pressures of O₂ and
CO$_2$ using the Warburg coefficients. They concluded that the process proceeds via the mixed diffusion of superoxide ion O$_2^-$ and CO$_2$ in Li/K carbonate melts at 888-1027K at the moderate O$_2$ and CO$_2$ partial pressures (0.9-0.1 atm):

\[ \frac{3}{4}O_2 + \frac{1}{2}CO_3^{2-} \rightleftharpoons O_2^- + \frac{1}{2}CO_2 \]  

where the recombination reaction [6] of the oxide ion with CO$_2$ is the reverse reaction of the dissociation reaction of carbonate ion CO$_3^{2-}$, which controls the acid–base property in molten salts of the Lux-Flood type, where the oxide ion acceptor CO$_2$ is an acid, and the oxide ion donor CO$_3^{2-}$ is a base (20).

However, all the studies mentioned above were carried out under the dry atmospheres, and the effect of H$_2$O impurity on the electrode kinetics and mechanisms of the oxygen reduction have not been well understood despite of the probable existence of certain amount of H$_2$O impurity gas in the cathode gas stream. This paper reports the effect of H$_2$O in O$_2$+CO$_2$ mixed gases on the electrode kinetics and mechanisms of the oxygen reduction at gold electrodes.

**EXPERIMENTAL**

Figure 1 shows the schematics of the electrochemical cell assembly. An alumina crucible containing (62+38)mol% (Li+K)CO$_3$ was placed in the gas-tight quartz vessel. The working electrode was fully immersed flag type electrode of gold (0.39 cm$^2$). All the potentials were referred vs (0.33+0.67)atm (O$_2$+CO$_2$)/Au reference electrode which is denoted as (1:2 O$_2$/CO$_2$)/Au in this paper. The experimental temperature was fixed at 650°C.

The mixed gases of O$_2$:CO$_2$=9:1, 5:5, and 1:9 were supplied to the cell via a humidifier as shown in figure 2. The water vapor pressures applied in this work were 2.9, 6.2 and 15.4 mmHg. They were obtained by controlling the concentration of H$_2$SO$_4$ aqueous solution and the temperature of the humidifier (21,22). The electrode kinetic data were measured using cyclic voltammetry (CV), AC impedance (or electrochemical
impedance spectroscopy (EIS). The experimental techniques, melt purification, apparatus and cell assembly were similar as described in a previous paper (6).

RESULTS AND DISCUSSION

Cyclic Voltammetry

Figure 3 shows the effect of water vapor pressures on single scan voltammograms for the oxygen reduction at $P_{O_2}:P_{CO_2}=0.9:0.1$ atm. The single peak which resembles the constant activity case (23) was observed. The peak potential $E_p$ was independent of the scan rate up to 10 V/s, and the peak current density $i_p$ was proportional to the square root of the scan rate as shown in figure 4, indicating that the reaction is reversible and diffusion controlled. The increase in the water vapor pressure appeared not only in increasing $i_p$ but also in the peak shape which becomes sharper.

According to the voltammetric theory of the constant activity case for a single redox species (23), the following equations were derived.

$$i_p = 0.6105 \frac{n^{1.5}F^{1.5}}{R^{0.5}T^{0.5}} C_{ox}^{\frac{1}{2}}D_{ox}^{\frac{1}{2}} \sqrt{v}$$  \[7\]

$$|E_p - E_i| = 0.8540 \frac{RT}{nF}$$  \[8\]

The equation [7] predicts that the slope of the $i_p-v$ plot is proportional to the apparent value $C_{app}^{\frac{1}{2}}D_{app}^{\frac{1}{2}}$ of the electrochemically active species. Thus, the apparent electron number $n_{app}$ transferred through the reaction and $C_{app}^{\frac{1}{2}}D_{app}^{\frac{1}{2}}$ values were calculated and shown in table 1. The $n_{app}$ increased with increasing water content, and the $C_{app}^{\frac{1}{2}}D_{app}^{\frac{1}{2}}$ values, which were calculated using $n_{app}$, were decreased with increasing water content. This result is inconsistent because the peak current increased with increasing water content. This means that the equations [7] and [8] are not applicable directly to this case. As discussed later, in the "digital simulation of single scan voltammograms" section, the oxygen reduction path is complicated by "mixed" diffusion of $O_2$ and $CO_2$.

Generally, the slope of the $i_p-v$ plot is proportional to the apparent value $C_{app}^{\frac{1}{2}}D_{app}^{\frac{1}{2}}$ of the electrochemically active species and this enables us to perform the reaction order analysis vs the water vapor pressure. Unfortunately, it is impossible to analyze the true reaction order on the water vapor pressure in this case because the $n_{app}$ varies as discussed above. However, the slope $i_p/v$ is an experimental parameter related to the mass transfer, and we tried to construct the reaction order plot as shown in figure 5. In this figure, we showed the similar reaction order plot using the Warburg coefficients obtained from the EIS data as discussed later. Two plots gives similar dependency on $P_{H_2O}$.

According to our earlier works (12,13), the oxygen reduction process in this melt...
proceeds via the mixed diffusion of superoxide ion \( O_2^- \) and \( CO_2^- \) under the dry condition as follows:

\[
O_2^- + 3e \rightarrow 2O^{2-} \quad [5]
\]

\[
O^{2-} + CO_2 \rightleftharpoons CO_3^{2-} \quad [6]
\]

When \( P_{O_2}:P_{CO_2} = 0.9:0.1 \) atm, \( CO_2 \) diffusion dominates the overall reaction process of the oxygen reduction, \( CO_2 \) being depleted in the electrode surface. If the water vapor exists in the cathode gas, it may act as an additional oxide ion acceptor (24):

\[
O_2^- \rightarrow H_2O \rightarrow 2OH^- \quad [9]
\]

When reaction [9] is relatively fast than reaction [6], part of \( O^{2-} \) ion can be consumed by \( H_2O \) in a reaction layer adjacent to the electrode surface. The recovery of \( H_2O \) may occur outside the reaction layer according to reaction [10] as follows (20):

\[
2OH^- + CO_2 \rightleftharpoons CO_3^{2-} + H_2O \quad [10]
\]

Thus, the apparent diffusion resistance of \( CO_2 \) can be decreased by coexistence of the additional acid-base reaction [9] and reaction [6].

In this context, the water effect may disappear if the \( CO_2 \) concentration in the melt is larger than the \( O_2^- \) concentration, i.e., under high \( CO_2 \) partial pressures. To confirm this, we performed single scan voltammetric experiments as shown in figure 6 for \( P_{CO_2} = 0.5 \) atm and figure 7 for \( P_{CO_2} = 0.9 \) atm. Clearly, the water effect disappeared even when the 15.4 mmHg of the water vapor was introduced to the cathode gas of the \( P_{O_2}:P_{CO_2} = 0.5:0.5 \) and 0.1:0.9 atm. Therefore, it can be concluded that the water impurity in the cathode gas stream of MCFC has no negative effect on the oxygen reduction kinetics.

**Electrochemical Impedance Spectroscopy**

Figure 8 shows the effect of water vapor pressure on the EIS data of oxygen reduction at the rest potential. The frequency range was 6 kHz to 1 Hz. The absence of a semicircular arc indicates a fast charge transfer process. These plots show linear behavior with a slope close to 45 degrees, indicating a mass transfer limited process, that is, the
diffusion (Warburg) impedance prevails over the entire frequency range used in this study. Again, the diffusion impedances at lower frequency region were reduced with increasing water vapor pressure, which is similar to the CV behavior.

These EIS data were analyzed using the Randles–Ershler equivalent circuit shown in figure 8, where $R_a$ is the charge transfer resistance, $C_d$ is the double layer capacitance, the $R_s$ is the solution resistance and $\sigma$ is the Warburg coefficient.

$$\sigma_{app} = \frac{RT}{n_{app}F^2/2C_{app}} \left[ \frac{1}{D_{app}} \right]$$  \[11\]

These parameters were determined by the non-linear parameter fitting (Simplex method) over the whole frequency range. The results are listed in table 2. In this table, we neglected $R_a$ because it was such small that it was difficult to obtain its reliable values. Clearly, the $\sigma$ values decreased with increasing water vapor pressure.

According to the theory of EIS (25), the apparent value of the Warburg coefficient $\sigma_{app}$ for the reactions [5], [6] and [9] under the semi-infinite diffusion condition may be expressed as following:

$$\sigma_{app} = \frac{RT}{3^2F^2/2C_{O_2}} \left[ \frac{1}{D_{O_2}} \right] + \frac{RT}{1.5^2F^2/2} \left[ \frac{1}{(C_{CO_2}F^2D_{CO_2} + C_{H_2O}F^2D_{H_2O})} \right]$$  \[12\]

In this equation, $\sigma_{H_2O}$ and $\sigma_{CO_2}$ are connected in parallel, because the water effect appears as an additional oxide ion acceptor according to the reaction scheme [5], [6] and [9]. Thus, it can be explained that the presence of water vapor in the cathode gas decreases the $\sigma_{app}$ according to the equation [12]. In addition, this equation may be used to explain the water effect which disappears at high CO₂ concentration as shown in figures 6 and 7. In such the extreme case, we can assume that $C_{CO_2}F^2D_{CO_2}$ so that the second term of the right hand side of equation [12] is negligibly small compared to the first term, i.e., only the $O_2$ diffusion dominates the diffusion impedance.

**Digital Simulation of Single Scan Voltammograms**

To elucidate the above reaction schemes, the digital simulation of the single scan voltammograms was carried out. Since there are no data for the solubility and diffusivity of H₂O in molten carbonates, we applied the following simplified reaction scheme.
\[ O_2 + 3e \rightarrow 2O^{2-} \quad [5] \]
\[ O^{2-} + CO_2 \rightarrow CO_3^{2-} \quad [6'] \]

where

\[ K_d = \frac{k_b}{k_f} \quad [13] \]

According to the equation [12], the effect of water vapor in the cathode gas appears as an similar effect for increasing CO\(_2\) concentration. Therefore, It may be possible to simulate the water effect using the reaction scheme [5] and [6'] with an increased CO\(_2\) concentration, and the following simultaneous partial differential equations have been solved with the appropriate boundary conditions and initial conditions.

\[ \frac{\partial C_{O_2^-}}{\partial t} = D_{O_2} \frac{\partial^2 C_{O_2^-}}{\partial x^2} \quad [14] \]
\[ \frac{\partial C_{CO_2^-}}{\partial t} = D_{CO_2^-} \frac{\partial^2 C_{CO_2^-}}{\partial x^2} - k_f C_{O_2^-} C_{CO_2} + k_b C_{CO_3^-} \quad [15] \]
\[ \frac{\partial C_{CO_2}}{\partial t} = D_{CO_2} \frac{\partial^2 C_{CO_2}}{\partial x^2} - k_f C_{O_2^-} C_{CO_2} + k_b C_{CO_3^-} \quad [16] \]

where \( C_{CO_3^-} \) is constant \((C_{CO_3^-}) \) \( C_{O_2^-} \) \( C_{CO_3^-} \) \( C_{CO_3^-} \) \( C_{CO_3^-} \). To solve the above simultaneous partial differential equations, equations [14]-[16] were converted to the finite difference equations and then calculated numerically using the explicit calculation method (26). In the numerical calculation, we assumed the followings:

i) \( D_{O_2} = D_{O_2^-} = D_{CO_2} = D_{H_2O} = 7.8 \times 10^{-6} \text{ cm}^2/\text{s} \) (27) to simplify the calculation according to the Feldbergh's notation (26),

ii) Reaction [5] (charge transfer process) is very rapid and reversible so that the Nernst equation for reaction [5] is always fulfilled.

The actual calculations were carried out for the following three cases.
Under Dry Pure O\textsubscript{2} Atmosphere
In this procedure, we fitted the experimental single scan voltammograms with calculated one to obtain the C\textsubscript{O\textsubscript{2}}- and C\textsubscript{O\textsubscript{2}}\textsuperscript{2-} as shown in figure 9 and to calculate K\textsubscript{d} and K\textsubscript{f} values. In this case, we supplied pure oxygen gas to the cell, but small amount of CO\textsubscript{2} exists due to the decomposition of carbonate ion according to the reaction [6]. At first, we estimate the dissociation pressure of CO\textsubscript{2} from the equilibrium potential as P\textsubscript{CO\textsubscript{2}}=0.0012 atm and P\textsubscript{O\textsubscript{2}}=0.9988 atm. Since P\textsubscript{CO\textsubscript{2}} was very small, we can neglect the reaction [6], and only the O\textsubscript{2} and O\textsubscript{2}\textsuperscript{2-} diffusions were considered with taking k\textsubscript{f} as zero. Thus determined values were C\textsubscript{O\textsubscript{2}}\textsuperscript{2-} = 1.9 x 10^{-4} mol/cm\textsuperscript{3}, K\textsubscript{d} = P\textsubscript{CO\textsubscript{2}}C\textsubscript{O\textsubscript{2}}\textsuperscript{2-} / C\textsubscript{CO\textsubscript{2}}\textsuperscript{2-} = 1.1 x 10^{-7} atm, and K\textsubscript{f} = 6.6 x 10^{-3} mol·cm\textsuperscript{-3}·atm\textsuperscript{-0.25}. These values were used in the following simulations.

Under Dry P\textsubscript{O\textsubscript{2}}:P\textsubscript{CO\textsubscript{2}}=0.9:0.1 Atm
Using the above estimated values, the concentrations of diffusing species were calculated as C\textsubscript{O\textsubscript{2}}\textsuperscript{2-} = 1.93 x 10^{-7} and C\textsubscript{O\textsubscript{2}}\textsuperscript{-} = 2.15 x 10^{-8} mol/cm\textsuperscript{3} respectively, and C\textsubscript{CO\textsubscript{2}} was calculated as C\textsubscript{CO\textsubscript{2}} = 7.16 x 10^{-7} mol/cm\textsuperscript{3} by using the data from the literature (27) of the Henry's constant of CO\textsubscript{2} dissolution (K\textsubscript{h} CO\textsubscript{2} = 7.16 x 10^{-6} mol·cm\textsuperscript{-3}·atm\textsuperscript{-1}). Then, the single scan voltammograms were simulated for the following three cases as shown in figure 10.

a) Assuming the polarographic case, only the reaction [5] was considered with taking k\textsubscript{f} = 0 cm\textsuperscript{3}·mol\textsuperscript{-1}·s\textsuperscript{-1}.

b) Assuming the mixed diffusion of O\textsubscript{2} and CO\textsubscript{2}, the reaction [5] and [6'] were considered where k\textsubscript{f} was the fitting parameter.

c) Assuming the constant activity case which corresponds to the direct reduction of O\textsubscript{2} to CO\textsubscript{3}\textsuperscript{2-}, i.e., the case of C\textsubscript{CO\textsubscript{2}} \rightarrow C\textsubscript{O\textsubscript{2}}\textsuperscript{2-}, only the diffusion of O\textsubscript{2} was taken into account in the calculation.

As seen in the figure 10, the measured single scan voltammograms was well simulated only in case the mixed diffusion of O\textsubscript{2} and CO\textsubscript{2} was assumed (case b) with taking k\textsubscript{f} = 10\textsuperscript{10} cm\textsuperscript{3}·mol\textsuperscript{-1}·s\textsuperscript{-1}, i.e., the reaction [6'] is very rapid. Some difference in peak current between the calculated value and the measured value is noted in the figure 10. Since there are some uncertainties in literature values, and also the diffusion coefficients of all species are assumed to be equal in this calculations, it is reasonable to conclude that the simulated single scan voltammograms agree well with the measured one.

Under P\textsubscript{O\textsubscript{2}}:P\textsubscript{CO\textsubscript{2}}=0.9:0.1 Atm With 15.4 mmHg H\textsubscript{2}O
Using the above estimated values, the single scan voltammograms with and without 15.4 mmHg H\textsubscript{2}O were simulated as shown in figure 11, where C\textsubscript{CO\textsubscript{2}} was the fitting parameter in this case to examine the water effect and the Y axis was normalized by the peak current under the dry conditions. As shown in figure 11, the simulated voltammograms fit well with the measured one, indicating that the constant activity case could not be applied to the oxygen reduction at these conditions. The obtained values for C\textsubscript{CO\textsubscript{2}} were C\textsubscript{CO\textsubscript{2}} = 7.16 x 10^{-7} mol/cm\textsuperscript{3} at dry
condition under $P_{CO_2} = 0.1$ atm, and $C_{CO_2} = 3.5 \times 10^{-6}$ mol/cm$^3$ under 15.4 mmHg $H_2O$. It was found that $C_{CO_2,wet}/C_{CO_2,dry} = 5$, that is, the effective concentration of CO$_2$ increased by a factor of 5 in the presence of water ($P_{H_2O}$=15.4 mmHg). If we may assume the followings:

i) the water dissolves into the carbonate melt physically;

ii) the equation [12] can be applied;

iii) $D_{H_2O} = D_{O_2} = D_{O_2^-} = DCO_2 = 7.8 \times 10^{-6}$ cm$^2$/s can be applied.

Then the Henry's coefficients for CO$_2$ and H$_2$O is estimated. The estimated values were $Kh_{CO_2} = 7.16 \times 10^{-6}$ mol·cm$^{-3}$·atm$^{-1}$ and $Kh_{H_2O} = 1.37 \times 10^{-4}$ mol·cm$^{-3}$·atm$^{-1}$. Using these parameters, the $\sigma_{app}$ values were calculated using the equation [12] and the results were shown in table 2. Although the calculated $\sigma_{app}$ were a little bit smaller than that of the experimental values, the data showed fair agreement.

CONCLUSIONS

The effect of water on electrode kinetics and mechanisms of oxygen reduction at the fully immersed flag type Au electrode in (62+38)mol% (Li+K)CO$_3$ melt at 650°C have been investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and the digital simulation of the single scan voltammograms, and the following conclusions were obtained.

i) The presence of 2.9–15.4 mmHg H$_2$O vapor to the $P_{O_2}/P_{CO_2} = 0.9$ atm lowered the apparent diffusion resistance of oxygen reduction.

ii) The apparent mass transfer parameters, $i_{p}/V$ and $1/\sigma_{app} = C_{app}/D_{app}$, were increased by the presence of water, indicating that water can act as an acid species in the neutralization reaction of oxide ion, $H_2O + O^{2-} \rightarrow 2OH^-$.

iii) Single scan voltammograms of oxygen reduction in this melt was simulated using finite difference method with assuming the reaction path as the mixed diffusion of O$_2$ and CO$_2$. Also the condition $D_{H_2O} = D_{O_2} = D_{O_2^-} = DCO_2 = 7.8 \times 10^{-6}$ cm$^2$/s was assumed in the numerical calculations. The simulated voltammograms agreed well with the observed ones, and the following parameters were obtained with the above assumptions: $K_i = 6.6 \times 10^{-6}$ mol·cm$^{-3}$·atm$^{-0.25}$, $K_d = P_{CO_2}C_{O_2^-}/C_{CO_3^{2-}} = 1.1 \times 10^{-7}$ atm, $k_r = 10^{10}$ cm$^3$·mol$^{-1}$·s$^{-1}$, $K_h, CO_2 = 7.16 \times 10^{-6}$ mol·cm$^{-3}$·atm$^{-1}$ and $K_h, H_2O = 1.37 \times 10^{-4}$ mol·cm$^{-3}$·atm$^{-1}$.

iv) The water impurity in the cathode gas stream of MCFC has no negative effect on the oxygen reduction kinetics.
ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research of the Ministry of Education, Science, and Culture of Japan.

REFERENCES

1. A.J. Appleby and S.B. Nicholson, *J. Electroanal. Chem.*, **53**, 105(1974).
2. A.J. Appleby and S.B. Nicholson, *J. Electroanal. Chem.*, **83**, 309(1977).
3. A.J. Appleby and S.B. Nicholson, *J. Electroanal. Chem.*, **112**, 71(1980).
4. W.M. Vogel, S.W. Smith, and L.J. Bregoli, *J. Electrochem. Soc.*, **130**, 575(1983).
5. S.H. White and U.M. Twardoch, *Electrochim. Acta*, **27**, 1599(1982).
6. I. Uchida, T. Nishina, Y. Mugikura and K. Itaya, *J. Electroanal. Chem.*, **206**, 229(1986).
7. I. Uchida, Y. Mugikura, T. Nishina and K. Itaya, *J. Electroanal. Chem.*, **206**, 241(1986).
8. I. Uchida, T. Nishina, Y. Mugikura and K. Itaya, *J. Electroanal. Chem.*, **209**, 125(1986).
9. T. Nishina and I. Uchida, *Denki Kagaku*, **56**, 111(1988).
10. T. Nishina and I. Uchida, *Denki Kagaku*, **56**, 419(1988).
11. I. Uchida and T. Nishina, *Nippon Kagaku Kaishi*, **1988**(8), 1297(1988).
12. T. Nishina and I. Uchida, *Proceedings of the 2nd symposium on Molten Carbonate Fuel Cell Technology*, PV90-16, The Electrochem. Soc., Pennington, 1990, p.438-453.
13. K. Yamada, T. Nishina and I. Uchida, *Proceedings of the 3rd symposium on Carbonate Fuel Cell Technology*, PV93-3, The Electrochem. Soc., Pennington, 1993, p.368-384.
14. M. Takahashi, *Extended Abstract of 21st Symposium on Molten Salt Chemistry*, Yamanashi, JAPAN, 1989, p.51.
15. G.B. Dunks and D. Stelman, *Inorg. Chem.*, **22**, 2168(1983).
16. D.A. Tryk and E.B. Yeager, *Proceedings of the Second Symposium on Molten Carbonate Fuel Cell Technology*, PV90-16, The Electrochemical Society, Inc., 1990, p.395-404.
17. S.H. Lu and J.R. Selman, *J. Electrochem. Soc.*, **137**, 1125(1990).
18. S.H. Lu and J.R. Selman, *J. Electroanal. Chem.*, **333**, 257(1992).
19. P. Tomczyk and L.K. Bieniasz, *J. Electroanal. Chem.*, **304**, 111 (1991).
20. B.K. Andersen, *Doctorate Thesis*, Tech. Univ. of Denmark, Lyngby, Denmark, 1975.
21. F.C. Blake and C.H. Grenewalt, *International Critical Tables*, **Vol.3**, McGraw-Hill, New York, 1928, p.302.
22. J.H. Perry, *Chemical Engineers' Handbook*, McGraw-Hill, New York, 1963, p.3-65.
23. T. Berzins and P. Delahay, *J. Am. Chem. Soc.*, **75**, 555 (1953).
24. J.R. Selman and H.C. Maru in G. Mamantov and J. Braunstein (Eds.), *Advances in Molten Salt Chemistry*, **Vol.4**, Plenum Press, New York, 1981, p.231-218.
25. M. Sluyters-Rehbach and J.H. Sluyters in A.J. Bard (Ed.), *Electroanalytical Chemistry*, **Vol.4**, Marcel Dekker, New York, 1970, p.16.
26. S.W. Feldberg in A.J. Bard (Ed.), *Electroanalytical Chemistry*, **Vol.3**, Macel Dekker, New York, 1969, p.199.
27. T. Nishina, Y. Masuda and I. Uchida, *Proceedings of the International Symposium on Molten Salt Chemistry and Technology*, **PV93-9**, The Electrochemical Society, Inc., 1993, p.424-435.
Figure 1  Schematics of the electrochemical cell assembly used in the experiment. R; reference electrode, W; working electrode, C; counter electrode, B; gas bubbler, T; thermocouple, V; quartz vessel and Pyrex™ top lid, J; cooling jacket, G; splash guard, O; outer alumina crucible, I; inner alumina crucible, H; electrical furnace.

Figure 2  Schematics of gas humidifier.
Figure 3  Single scan voltammograms of oxygen reduction as a function of water vapor pressures at a gold electrode in (62+38)mol% (Li+K)CO₃ melt at 650°C.

Figure 4  $i_p - \sqrt{v}$ plots obtained from the single scan voltammograms of oxygen reduction as a function of water vapor pressures at a gold electrode in (62+38)mol% (Li+K)CO₃ melt at 650°C.
Figure 5  Reaction order plots of water vapor pressure to the slope of ip-v plots (O) and the inverse of the Warburg coefficients (□) of oxygen reduction at a gold electrode under P_{O_2}:P_{CO_2} = 0.9:0.1 atm in (62+38)mol% (Li+K)CO_3 melt at 650°C.

Table 1  The effect of water vapor in the cathode gas stream to the kinetic parameters of oxygen reduction at a gold electrode under P_{O_2}:P_{CO_2} = 0.9:0.1 atm in (62+38)mol% (Li+K)CO_3 melt at 650°C obtained from the single scan voltammetry.

| P_{H_2O} mmHg | n_{app} | ip/v mA·cm⁻²·V⁻¹·s⁻⁰·⁵ | C_{app}D_{app} using n_{app} mol·cm⁻²·s⁻⁰·⁵ |
|----------------|---------|--------------------------|------------------------------------------|
| 0              | 0.89    | 0.434                    | 2.49 x 10⁻⁹                              |
| 2.9            | 1.57    | 0.526                    | 1.27 x 10⁻⁹                              |
| 6.2            | 1.60    | 0.563                    | 1.33 x 10⁻⁹                              |
| 15.4           | 2.00    | 0.587                    | 9.94 x 10⁻¹⁰                             |
Figure 6  The effect of water vapor pressures at a low $P_{O_2}/P_{CO_2}$ ratio (0.5/0.5) on cyclic voltammograms of oxygen reduction at a gold electrode in (62+38)mol% (Li+K)CO$_3$ melt at 650°C.

Figure 7  The effect of water vapor pressures at a low $P_{O_2}/P_{CO_2}$ ratio (0.1/0.9) on cyclic voltammograms of oxygen reduction at a gold electrode in (62+38)mol% (Li+K)CO$_3$ melt at 650°C.
Figure 8 The EIS spectra (6kHz – 1Hz) at an open-circuit potential of oxygen electrode reaction at an gold electrode as a function of water vapor pressures in (62+38)mol% (Li+K)CO$_3$ melt at 650°C.

Table 2 The effect of water vapor in the cathode gas stream to the kinetic parameters of oxygen reduction at a gold electrode under P$_{O_2}$:P$_{CO_2}$ = 0.9:0.1 atm in (62+38)mol% (Li+K)CO$_3$ melt at 650°C obtained from the EIS analysis.

| PH$_2$O mmHg | Experimental $\sigma_{pp}$ $\Omega \cdot cm^{-2} \cdot s^{0.5}$ | Calculated $\sigma_{pp}$ a) $\Omega \cdot cm^{-2} \cdot s^{0.5}$ | $C_d$ $\mu F \cdot cm^{-2}$ |
|--------------|-------------------------------------------------|-------------------------------------------------|------------------|
| 0            | 330                                             | 250                                             | 96               |
| 2.9          | 230                                             | 195                                             | 111              |
| 6.2          | 220                                             | 171                                             | 122              |
| 15.4         | 200                                             | 147                                             | 131              |

a) these values were calculated with equation [12] using the parameters obtained by the digital simulation of the single scan voltammograms.
Figure 9 Simulated single scan voltammograms of the oxygen reduction at a gold electrode under pure oxygen atmosphere without water traces at 650°C.

Figure 10 Simulated single scan voltammograms of the oxygen reduction at a gold electrode under $P_{O_2}:P_{CO_2} = 0.9:0.1$ atm without water traces at 650°C.

a) Polarographic case
b) Mixed diffusion of $O_2$ and $CO_2$ case
c) Constant activity case
Figure 11 Simulated single scan voltammograms of the oxygen reduction at a gold electrode under $P_{O_2}:P_{CO_2} = 0.9:0.1$ atm with and without 15.4 mmHg H$_2$O at 650°C. Y axis was normalized by the peak current of the dry condition.