EFFECT OF O₂/CO₂ GAS PARTIAL PRESSURES ON OXYGEN REDUCTION KINETICS IN MOLTEN CARBONATE

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ABSTRACT

The effect of O₂ and CO₂ gas partial pressures on oxygen reduction path at Au flag electrode has been investigated in a (62+38)mol% (Li+K)CO₃ melt at 600-800°C. We carried out precise measurements of the Warburg coefficient of the ac impedance at the rest potential, using a Randles'-Ershler equivalent circuit. Taking into account three possible diffusing species, i.e., O₂⁻, O₂²⁻ and CO₂, a graphical reaction order analysis was made, using the Warburg coefficients. Only the case of mixed diffusion of O₂⁻ and CO₂ was found to result in a satisfactory linear relationship. Therefore, we conclude that simultaneous diffusion of O₂⁻ and CO₂ is the dominant feature of the oxygen reduction process in bulk (Li+K)CO₃ melt.

INTRODUCTION

Recent work has shown that the exchange current density, \( i_0 \), of oxygen reduction in molten carbonate at 650°C is of the order of 10 mA/cm². However, the reaction mechanism is still not well understood. According to Appleby and Nicholson (1-3), the oxygen reduction follows the superoxide path(SOP) or the peroxide path(POP), where these oxygen species are chemically formed in the carbonate melts as follows.

(A) Superoxide Path(SOP)

\[
3O_2 + 2CO_3^{2-} = 4O_2^{-} + 2CO_2 \\
[O_2^{-}] = K_1P_{O_2}^{0.75}P_{CO_2}^{-0.5} \\
O_2^{-} + 2CO_2 + 3e = 2CO_3^{2-} 
\]

(B) Peroxide Path(POP)

\[
O_2 + 2CO_3^{2-} = 2O_2^{2-} + 2CO_2 
\]
\[ [O_2^{2-}] = K_2P_{O_2}^{0.5}P_{CO_2}^{-1.0} \]  
\[ O_2^{2-} + 2CO_2 + 2e = 2CO_3^{2-} \]

It has been pointed out that experimental \( O_2 \) and \( CO_2 \) reaction orders in (Li+K)CO_3 melt do not agree with the predictions according to the SOP and POP mechanisms (4). Also, it has been demonstrated that the rate at which oxide ion, which is an intermediate reduction product of peroxide or superoxide according to Equations [3] and [6], is neutralized by \( CO_2 \) may be limiting the overall reduction process (5). This neutralization rate in turn may be limited by \( CO_2 \) diffusion.

In this work, a reaction order analysis is applied to ac impedance results obtained for moderate partial pressures (0.1-0.9 atm) at temperatures of 600-800°C. The objective is to elucidate the reaction mechanism by identifying the species which dominate the mixed diffusion process, i.e., any or all of the following: \( O_2^{2-}, O_2^{2+} \) and dissolved \( CO_2 \).

**EXPERIMENTAL**

(62+38)mol% (Li+K)CO_3 melt was used as solvent. Electrochemical cell assembly, melt purification and gas handling have been described previously (4). The working electrode was a fully-immersed Au flag electrode (0.4 cm\(^2\)). In the present study, we concentrated precise measurements of the Warburg coefficient at the rest potential, using an ac impedance analysis based on the Randles'-Ershler equivalent circuit, and we present a reaction order analysis based on these coefficients. Impedance measurements were carried out using a Solartron 1250 frequency response analyzer (FRA) coupled with the Solartron 1186 (or 1286) electrochemical interface. Frequencies were varied from 1 Hz to 60 kHz and the signal amplitude was 5 mV rms. Data were transferred to microcomputers (Hewlett Packard 85 and NEC PC-9800) for faradaic impedance analysis.

**ANALYSIS ON WARBURG COEFFICIENT**

In the present study, the precise measurements of \( CD^{1/2} \) is the most important things to be done. This may be done using standard electrochemical methods such as cyclic voltammetry, potential step, chronopotentiometry and chronocoulometry. However, these methods require relatively higher overvoltage than ac impedance method, and this may changes the local basicity of carbonate melt at the electrode surface (5). On the other hand, ac impedance method uses small perturbation amplitude (5 mV rms) at the rest potential in the measurement, the local basicity change may be negligibly small. Furthermore, it is possible to obtain quite reliable impedance data over a wide frequency range (1 Hz to 60 kHz), because well-designed electronic apparatus, e.g., a recent FRA, are available and this can lead to a detailed view of the electrode process together with interfacial parameters such as the double layer capacitance, using well-established impedance theory. Thus, the ac impedance method seems to be most promising method.
for our purpose and applied to this study. Details of the analysis on impedance data were described in the previous paper (4).

According to the theory of ac impedance in the presence of semi-infinite diffusion, the Warburg coefficient, $\sigma$, is

$$\sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left( \frac{1}{C_O \sqrt{D_O}} + \frac{1}{C_R \sqrt{D_R}} \right)$$

[7]

In the case of reactions [3] and [6], $1/C_R D_R^{1/2}$ is negligible compared with $1/C_O D_O^{1/2}$, because the product is $CO_3^{2-}$, i.e., the melt itself, and $C_O < C_R$. When the electrode processes take place at the electrode surface simultaneously, we have to take into account three diffusing species, i.e., $O_2^-$, $O_2^{2-}$ and $CO_2$, in the interpretation of the reaction order. In the Randles-Ershler circuit adopted in this study, the diffusion impedance is simply represented by a single element, $W$, as shown in Figure 1.

$$W = (1 + j) \frac{\sigma_{app}}{\sqrt{\omega}}$$

[8]

However, in the case of multiple (parallel) reaction paths the observed $\sigma$ values are to be regarded as effective values, not necessarily reflecting the reaction orders deduced from either the SOP and POP mechanism. Considering that the $O_2^-$ and $O_2^{2-}$ reactions both involve $CO_2$, the apparent diffusion impedance can be divided into three components as illustrated in Figure 2. According to this scheme, the apparent $\sigma$ value may be expressed as follows.

$$\sigma_{app} = \frac{1}{A[O_2^-] + B[O_2^{2-}] + C[CO_4^{2-}]} + \frac{1}{D[CO_2]}$$

[9]

where A, B, C and D are constants, and [ ] means the bulk concentration of a species in the melt.

Using equations [2] and [5] for $[O_2^-]$ and $[O_2^{2-}]$ respectively, and Henry's law for $[CO_2]$,

$$[CO_2] = K_h P_{CO_2}$$

[10]
the apparent value of $\sigma$ may be expressed as a function of $P_O$ and $P_{CO_2}$. To simplify the analysis, three limiting cases are considered as follows.

(I). $A[O_2] > B[O_2^{2-}], C[CO_4^{2-}] ; O_2/CO_2$ mixed diffusion case.

$$
\sigma_{app} P_{CO_2} = a P^{1.5}_{O_2} P^{-0.75}_{O_2} + b \quad [11]
$$

$$
\sigma_{app} P^{-0.5}_{O_2} P^{-1}_2 = a + b P^{0.5}_{O_2} P^{-0.5}_{CO_2} \quad [12]
$$

(II). $B[O_2^{2-}] > A[O_2], C[CO_4^{2-}] ; O_2^{2-}/CO_2$ mixed diffusion case.

$$
\sigma_{app} P_{CO_2} = a P^2_{O_2} P^{-0.5}_{O_2} + b \quad [13]
$$

$$
\sigma_{app} P^{0.5}_{O_2} P^{-1}_{CO_2} = a + b P^{0.5}_{O_2} P^{-2}_{CO_2} \quad [14]
$$

(III). $D[CO_2] > A[O_2], B[O_2^{2-}] > C[CO_4^{2-}] ; O_2/CO_2$ mixed diffusion case.

$$
\sigma_{app} P_{CO_2} = a P^{-0.5}_{O_2} P^{0.5}_{CO_2} + b \quad [15]
$$

If any of these three limiting cases applies, it will show up as linear relationship of the Warburg coefficient in combination with the appropriate powers of $P_O$ and $P_{CO_2}$.

**REACTION ORDER PLOTS OF WARBURG COEFFICIENTS**

Based on the above analysis, we have made reaction order plots for the Warburg coefficients, obtained at 650°C, according to equations [11]-[15]. The results are shown in Figures 3-5.

(I). $A[O_2] > B[O_2^{2-}], C[CO_4^{2-}] ; O_2/CO_2$ mixed diffusion case.

Figure 3 shows the reaction order plot using equation [11]. The linearity was fairly good. This suggests that the oxygen reduction in (Li+K)CO$_3$ melt is dominated by the mixed diffusion of $O_2$ and $CO_2$.

(II). $B[O_2^{2-}] > A[O_2], C[CO_4^{2-}] ; O_2^{2-}/CO_2$ mixed diffusion case.
Figure 4 shows the reaction order plot using equation [13]. The plot did not show a linear relationship. This suggests that the oxygen reduction in \((\text{Li}+\text{K})\text{CO}_3\) melt is unlikely to involve mixed diffusion of \(\text{O}_2^{2-}\) and \(\text{CO}_2\).

(III). \(D[\text{CO}_2] > A[\text{O}_2^2], B[\text{O}_2^{2-}] > C[\text{CO}_4^{2-}]\); \(\text{O}_2/\text{O}_2^{2-}\) mixed diffusion case.

Figure 5 shows the reaction order plot using equation [15]. Again, the plot did not show a linear relationship. This suggests that the oxygen reduction in \((\text{Li}+\text{K})\text{CO}_3\) melt is unlikely to involve mixed diffusion of \(\text{O}_2^2\) and \(\text{O}_2^{2-}\).

Consequently, we find that only one case, i.e., mixed \(\text{O}_2/\text{CO}_2\) diffusion, results in a satisfactory linearity, and the other two cases do not produce a consistently linear dependence for bulk melt at 650°C. These results suggest that the simultaneous diffusion of \(\text{O}_2^2\) and \(\text{CO}_2\) in the melt is the dominant feature of the oxygen reduction process at the fully-immersed Au flag electrode.

EFFECT OF TEMPERATURE

The above results apply only at the temperature of 650°C. The concentrations of \(\text{O}_2^2\), \(\text{O}_2^{2-}\) and \(\text{CO}_2\) are strong functions of temperature. Therefore, the reaction path of oxygen reduction may change with temperature. Thus, we have studied the reaction order correlation of the Warburg coefficients as a function of temperature, and the results are shown in Figure 6.

In this figure, only case (I), i.e., the mixed diffusion of \(\text{O}_2^2\) and \(\text{CO}_2\), is shown. The other two cases did not produce a consistently linear dependence over the temperature range used in this study. Therefore, we conclude that simultaneous diffusion of \(\text{O}_2^2\) and \(\text{CO}_2\) is the dominant feature of the oxygen reduction process in bulk \((\text{Li}+\text{K})\text{CO}_3\) melt over the temperature range of 610-800°C.

CONCLUSIONS

The effect of \(\text{O}_2\) and \(\text{CO}_2\) partial pressures on \(\text{O}_2\) reduction at a Au flag electrode in \((62+38)\text{mol\%} \ (\text{Li}+\text{K})\text{CO}_3\) melt has been analyzed in the temperature range of 600-800°C. We carried out precise measurements of the Warburg coefficient of ac impedance at the rest potential, using a Randles'-Ershler equivalent circuit. Taking into account three possible diffusing species, i.e., \(\text{O}_2\), \(\text{O}_2^{2-}\) and \(\text{CO}_2\), a graphical analysis of reaction order was made, using the Warburg coefficients. We found that only the case of mixed
diffusion of $O_2^-$ and $CO_2$ results in a satisfactory linear relationship over the entire temperature range of 600-800°C. Therefore, we concluded that the simultaneous diffusion of $O_2^-$ and $CO_2$ is the dominant feature of oxygen reduction in (62+38) mol% (Li+K)CO$_3$ melt used in this study.

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Figure 1. Randles'-Ershler Equivalent Circuit for AC Impedance of Oxygen Electrode in Molten Carbonate.

Figure 2. Equivalent Circuit for Diffusion Impedance, Taking into Account Mixed Diffusion of $O_2^-$, $O_2^{2-}$ and $CO_2$. 
Figure 3. Reaction Order Analysis of Warburg Coefficients Assuming Mixed Diffusion of \( \text{O}_2 \) and \( \text{CO}_2 \) in (62+38)mol\% (Li+K)CO\(_3\) Melt at 650°C.
Figure 4. Reaction Order Analysis of Warburg Coefficients Assuming Mixed Diffusion of $O_2^{2-}$ and $CO_2$ in (62+38)mol% (Li+K)CO$_3$ Melt at 650°C.

Figure 5. Reaction Order Analysis of Warburg Coefficients Assuming Mixed Diffusion of $O_2$ and $O_2^{2-}$ in (62+38)mol% (Li+K)CO$_3$ Melt at 650°C.
Figure 6. Reaction Order Analysis of Warburg Coefficients Assuming Mixed Diffusion of \(O_2\) and \(CO_2\) in (62+38)mol% (Li+K)\(CO_3\) Melt for Various Temperature.