THE INFLUENCES OF MgO ON THE DIFFUSION OF MAGNESIUM ION IN MAGNESIUM ELECTROLYSIS

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ABSTRACT

The influences of different sorts of magnesium oxide on the diffusion rate of magnesium deposition in the MgCl$_2$-NaCl-KCl-CaCl$_2$ molten salt system have been investigated with a multiple electrochemical measuring system.

The variances of the limiting current density of the deposition of magnesium ion with the amount of MgO added have been measured with linear voltage scan methods. The diffusion coefficient and the diffusion reactivity energy of magnesium ion have been determined and the effects of MgO on them have also been studied.

It was shown that different sorts of MgO have different influences on the diffusion coefficient, and the MgO obtained from the hydrolysis of MgCl$_2$·6H$_2$O has the most obvious effects on it.

INTRODUCTION

Magnesium oxide has unfavourable effects on the electrolysis process of magnesium production. As a result of its tiny particles and strong reactivity, MgO, from the hydrolysis of the magnesium electrolyte in the electrolysis process, is prone to being absorbed by the cathode and causing the cathode to be polarized.

The present paper refers to the magnesium electrolyte system in industrial electrolysis and applies linear voltage scan electrochemical technique to study the influences of MgO on the diffusion coefficient and the limiting current density of the deposition of magnesium ion.
EXPERIMENTAL

Conditions

The chlorides used in the experiments were predried in oven, then in predried gaseous HCl until they were melted. The experiments were performed in atmosphere of argon at ambient pressure and at the temperature of 700°C.

Electrodes

The electrode system involved anode, working electrode and reference electrode. A stable Ag/AgCl reference electrode with ceramic diaphragm was used. The anode was made of spectral purity carbon and the working electrode of molybdenum.

The electrolyser was set in a quartz glass container.

RESULTS AND DISCUSSION

The Influences of MgO on the Diffusion Coefficient and the Limiting Current Density

Fig. 1 and Fig. 2 are respectively the linear voltage scan voltammograms at different scan rate with the electrolyte containing 0% (wt.) and 0.6% (wt.) MgO.

From the voltammograms we know that, at the same scan rate, the peak current density is obviously reduced after adding a small amount of MgO into the electrolyte, and the deposition voltage of Mg²⁺ is also reduced a little vs. Ag/AgCl electrode. These all show that the MgO is absorbed by the cathode. Therefore, the diffusion of Mg²⁺ to the cathode surface is impeded, the diffusion rate and the diffusion current density is lowered, and the cathodic concentration polarization is more obvious.

On the curves, it is also noticed that the peak current decreased correspondingly with the decrease of the scan rate. Based on the fundamental electrochemistry, the peak current (Ip) and the scan rate (V) satify the following electrochemical equation:

\[ Ip = 0.661(nF)^{3/2}(DoV/RT)^{1/2}A_0 \]

Where A is the area of the cathode, Do is the diffusion coefficient (cm²/sec) of reactant, and Co is the bulk
concentration \((\text{mol/cm}^3)\) of reactant.

The plots of \(I_p \text{ vs. } V^{1/2}\) are shown in Fig. 3. The slope \((\text{tg}A)\) of a plot is derived from the equation (1).

\[
\text{tg}A = 0.661(\eta F)^{3/2}(D_0/RT)^{1/2}A\text{c}_0
\]  (2)

From the equation (2), the diffusion coefficient \(D_0\) can be determined. The results are shown in Fig. 4.

Fig. 4 shows that the smaller the amount of \(\text{MgO}\) is, the more obvious the influences on the diffusion coefficient are. The similar effects on the limiting current density are shown in Fig. 5. With the adding amount of \(\text{MgO}\) increasing from 0\% (wt.) to 0.3\% (wt.), the diffusion coefficient \(D_0\) and the limiting current density \(I_d\) decrease rapidly. Then, the amount increasing further, there is only a little decrease of \(D_0\) and \(I_d\). That is, the effects of \(\text{MgO}\) become weaker and weaker.

According to the analysis above, it is assume that the increase of the absorbed \(\text{MgO}\) film on the cathode ceased when the \(\text{MgO}\) increased to a certain amount. On one hand, the film obstructs the diffusion of magnesium ion to the cathodic surface. On the other hand, it also obstructs the further absorption of the cathode.

The Diffusion Activation Energy

Generally, the diffusion coefficient \(D_0\) increases with the temperature, and they observe the following equation:

\[
\ln D_0 = A - (W/\eta T)
\]

Here \(A\) is a constant, \(W\) is the diffusion activation energy. With the electrolyte containing 0.3\% (wt.) \(\text{MgO}\), the magnesium diffusion coefficients were measured with linear voltage scan method at different temperatures. And the plot of \(\ln D_0 \text{ vs. } 1/T\) is shown in Fig. 6. From the slope of this plot, the diffusion activation energy was calculated to be \(3200 \text{ cal/mol}\).

The Influences of Different Forms of \(\text{MgO}\)

The reactivity of \(\text{MgO}\) is related to the method and process of its production. The experiments of the influences of agent \(\text{MgO}\), hydrolysis \(\text{MgO}\) and \(\text{MgOHCl}\) on the diffusion of magnesium ion have been made. The results are shown in Fig. 7.

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Like the preceding discussion, all the magnesium oxides have apparent influences on $D_0$ with the amount of MgO ranging from 0% to 0.3% (wt.). At the same amount, the influence of hydrolysis MgO on the $D_0$ is the most, the MgOHCl influence is smaller, and the agent MgO one is the smallest. The differences of the influences show that there are different reactivities with different sources of MgO.

The apparent reactivity of MgOHCl is smaller than the hydrolysis one. Actually, MgOHCl will rapidly decompose and produce MgO at the experimental temperature when it is added into the electrolyte so that the influences really are performed by MgO. The weight ratio of MgO to HCl is about 1:1. If MgOHCl is almost completely decomposed, 0.3% (wt.) MgOHCl will produce 0.15% hydrolysis MgO. Based on this hypothesis, the curve of $D_0$ (MgOHCl) vs. MgO (produced from the decomposition of MgOHCl) have been made out. As shown in Fig. 8, it is very close to the curve of hydrolysis MgO within 0.6% (wt.) MgOHCl. The similarity of the two curves shows that most of the MgOHCl decomposes into MgO instead of the MgOH$^+$ ion. The fact that there is only a small current peak of MgOH$^+$ on the wide range linear voltage scan voltammogram is one of the evidences for the hypothesis, too.

CONCLUSION

MgO, the impurity in the electrolyte, is absorbed on the cathode and cause it to be polarized. Therefore, the limiting current density and the diffusion coefficient are lowered.

At the electrolysis temperature, with the content of MgO increasing from 0% (wt.) to 0.3% (wt.), the diffusion coefficient $D_0$ and the limiting current density $I_d$ are decreased rapidly. Then, with the further increasing of the content of MgO, the decrease of $D_0$ and $I_d$ disappears gradually.

MgO from different sources possesses different reactivity. The hydrolyzed electrolyte (MgOHCl) is probably mostly decomposed into MgO, and there is very little to be dissolved into MgOH$^+$ in the molten salts.

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![Scan Voltammogram](image)

**Fig. 1** 0% MgO
Linear Voltage Scan Voltammogram

**Fig. 2** 0.6% MgO
Linear Voltage Scan Voltammogram

\[-E (E_{Ag^+/Ag} = 0), \text{Volt}\]
Fig. 3
Lines of Ip
vs. $V^{1/2}$

Fig. 4 Curve of Do vs. MgO %

Fig. 5 Curve of Id vs. MgO %
Fig. 6
Line of
\[ \ln Do \text{ vs. } \frac{1}{T} \]

\[ \begin{array}{c|c|c|c}
\text{MgO, (% wt.)} & \text{Do} \times 10^6 \text{ (cm}^2/\text{sec)} \\
1 & \text{MgO (hydro.)} & 3 \\
2 & \text{MgOHCl} & 2 \\
3 & \text{MgO (agent)} & 1 \\
\end{array} \]

Fig. 7 Curves of
Do vs. MgO% from Different Sources

Fig. 8 Curve of
Do(MgOHCl) vs. MgO %